

## Chapter 6

## ELEMENTS OF GROUP 6

M.G.Barker

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## 6.1 OXYGEN

Oxygen freezes at 298K and a pressure of 5.6GPa but then at 9.6 and 9.9GPa undergoes transitions marked by dramatic colour changes. X-ray diffraction measurements on a single crystal of  $^{18}\text{O}_2$  at 9.6GPa and 297K showed that the colour change is associated with a phase transition to a new orthorhombic structure in the space group Fmmm with cell dimensions  $a = 4.2151$ ,  $b = 2.9567$  and  $c = 6.6897\text{\AA}$  rather than the previously proposed monoclinic  $\alpha \text{ O}_2$  form. The new structure of the so-called "orange"  $^{18}\text{O}_2$  is very closely related to that of  $\alpha \text{ O}_2$  and transformations from one to the other may be second order.<sup>1</sup>

Controlled-potential coulometry has been used to show that the ferrous form of iron tetrakis(N-methyl-4-pyridyl)porphyrin reduces oxygen quantitatively to water via a multi-stepped mechanism. It was assumed that the oxygen reduction proceeded through hydrogen peroxide that was either removed by disproportionation or via direct reduction by the ferrous porphyrin. This view was reinforced by tests which showed that hydrogen peroxide reacted very slowly with the Fe(III) form in acidic solutions whilst the Fe(II) porphyrin reacted rapidly.<sup>2</sup> The photochemical oxidation of tetraline by oxygen is catalysed by Fe(III) acetylacetonate. The reaction rate increased markedly with temperature and the rate determining step of the photochemical oxidation was presumed to be a catalysed thermal reaction.<sup>3</sup> Derivatives of 1,4-naphthoquinone have been synthesised and used as solution and surface bound catalysts for the electrochemical and photoelectrochemical reduction of oxygen to hydrogen peroxide.<sup>4</sup> The hydrogen - oxygen reaction has been studied in a static system over lanthanum oxide and europium oxide at different initial hydrogen pressures from 480 to 775K, both stoichiometric and non stoichiometric reactions were studied. The mechanism of the reactions involves the competitive adsorption of molecular hydrogen and oxygen with the rate-determining step involving the interaction between the adsorbed molecules or hydrogen peroxide.<sup>5</sup> The reactions of 1-butene with oxygen (and nitric oxide) have been studied in a differential flow system over manganese(III) oxide. During catalysis the oxide underwent a partial phase change from the  $\alpha$  to the  $\gamma$  form.<sup>6</sup>

The reactions of  $\text{O}_3$  with  $\text{NH}_3$  and  $\text{NH}_2\text{OH}$  have been studied in the condensed phase. Ozone reacts with  $\text{NH}_3$  at  $-170^\circ\text{C}$  to give the

yellow-orange ozonide  $\text{NH}_3^+\text{O}_3^-$  which could be reconverted to the reactants by photolysis with near u.v. or by heating to  $-90^\circ\text{C}$ . On warming the  $\text{NH}_3\text{-O}_3$  system to  $-130^\circ\text{C}$ ,  $\text{NH}_4\text{NO}_3 \cdot 3\text{NH}_3$  was formed which starts to deamminate at about  $-105$  to give  $\text{NH}_4\text{NO}_3$ . A second phase formed at  $-170^\circ\text{C}$ , was tentatively identified as  $\text{NH}_2\text{O}^+\text{HO}_2^-$  and was found to decompose at  $-10^\circ\text{C}$  with the evolution of  $\text{O}_2$ . The reaction of  $\text{NH}_2\text{OH}$  with  $\text{O}_3$  yielded the yellow ozonide  $\text{NH}_2\text{OH}^+\text{O}_3^-$  at  $-190^\circ\text{C}$  and  $\text{HNO}_3$  which was observed immediately upon addition of  $\text{O}_3$  to  $\text{NH}_2\text{OH}$  as the hydrogen bonded complex,  $\text{NH}_2\text{OH} \cdot \text{HNO}_3$ . At  $-100^\circ\text{C}$  the  $\text{NH}_2\text{OH}^+ \cdot \text{O}_3^-$  started to decompose and the final product of the reaction was  $\text{NH}_3\text{OH}^+\text{NO}_3^-$  and  $\text{H}_2\text{O}$ .<sup>7</sup>

The superoxide anion  $\text{O}_2^{\cdot -}$  has been shown to perform the novel desulphurization of 1,3-diarylthioureas at  $20^\circ\text{C}$  in THF or acetonitrile to form 1,2,3-triarylguanidines in excellent yields.<sup>8</sup>

Several publications have been concerned with the reactions of dioxygen with transition metal complexes. McAuliffe has followed his preliminary publication with a full paper describing the reversible binding of dioxygen with the novel manganese(II) phosphine complexes,  $[\text{MnX}_2(\text{PR}_3)]$  where  $\text{X} = \text{Cl}, \text{Br}$  or  $\text{I}$  and  $\text{R}_3 = \text{Bu}^n_3$  or  $\text{PhBu}^n_2$  in several organic solvents. Oxygen is absorbed quantitatively by the complexes to form  $[\text{MnX}_2(\text{PR}_3)(\text{O}_2)]$  and repeated (more than 400 times at  $-20^\circ\text{C}$ ) cycling of oxygen absorption was shown to be possible. The solid state dioxygen binding by bis(isothiocyanato)(phosphine)manganese(II) complexes  $[\text{Mn}(\text{NCS})_2(\text{PPh}_{3-n}\text{R}_n)]$  have also been studied but only the  $[\text{Mn}(\text{NCS})_2(\text{PR}_3)]$  compounds were found to bind dioxygen reversibly.<sup>9</sup> Italian workers have shown that the complex  $\text{NN}'\text{-4-methyl-4-aza-heptane-1,7-diylbis(salicylideneiminato)cobalt(II)}$  binds dioxygen, reversibly and a crystal structure determination of the dioxygen adducts  $[\text{Co}(\text{salmhpn})]_2 \cdot \text{O}_2 \cdot 2\text{C}_6\text{H}_6$  shows that the crystal lattice contains both dioxygenated and non-dioxygenated molecules in 1:1 ratio, in which the Co atoms are octahedral and five coordinated respectively. In the octahedrally coordinated low spin Co(II) moiety the sixth position is occupied by a dioxygen molecule bound in a bent, end-on manner with O-O bond distances averaging  $1.06\text{\AA}$ . The non dioxygenated molecules contain high spin Co(II) atoms.<sup>10</sup>

The equilibrium constant for the formation of  $[\text{Co}_2(\text{en})_4(\text{O}_2)(\text{OH})]^{3+}$  in KCl aqueous solution has been determined. Calculation of thermodynamic functions for the addition of  $\text{O}_2$  to  $[\text{Co}(\text{en})_2]^{2+}$  to form the doubly bridged bicobalt complex

$[\text{Co}_2(\text{en})_4(\text{O}_2)(\text{OH})]^{3+}$  showed a large enthalpy change, but the stability of the binuclear species with respect to  $[\text{Co}(\text{en})_2]^{2+}$  is strongly reduced by a large entropy effect.<sup>11</sup> The reactions of oxygen with Co(II) chelates of tridentate, dianionic Schiff Base ligands<sup>12</sup> and orthoquinone complexes of vanadium<sup>13</sup> have also been reported. The application of  $^{17}\text{O}$  n.m.r. for the study of transition metal bonded peroxidic oxygen atoms has been described. The first high resolution  $^{17}\text{O}$  n.m.r. observations were obtained from  $^{17}\text{O}$  enriched  $[(\text{CN})_4\text{OMO}(\text{O})][\text{N}(\text{PPh}_3)_2]_2$  and for non enriched alkylperoxo derivatives of platinum.<sup>14</sup>

An investigation into whether the energy of atomization of solid oxides can be divided into components, not according to the number of bonds but according to the contribution of each metal atom to the total bond strength. Using this approach it was found that magnesium, for example, contributes the same amount per equivalent to the energy of atomization in  $\text{MgAl}_2\text{O}_4$  as it does in  $\text{Mg}_2\text{SiO}_4$  to a very high degree of accuracy. The authors consider that the results of this study make a real contribution to the theories of bonding in oxides and related solids.<sup>15</sup> A study of the dehydration of  $\alpha\text{FeOOH}$  to  $\alpha\text{Fe}_2\text{O}_3$  has shown that the band observed in the i.r. spectrum at  $1140\text{cm}^{-1}$  undergoes several splittings and shifts on dehydration of the sample. It was concluded that the band was a precursor of similar bands previously observed on  $\alpha\text{Fe}_2\text{O}_3$  and assigned to adsorbed oxygen.<sup>16</sup>

A simple method for the generation of singlet oxygen for solution kinetic studies has been described. A glass plate coated with a sensitizer is placed with the sensitizer a few millimeters above the solution. Illumination of the plate generates singlet oxygen at the sensitizer, which diffuses into the solution. Electrons or hydrogen atom transfer cannot however cross the air gap.<sup>17</sup> Several papers have been concerned with the chemistry of singlet oxygen, topics covered were the quenching of singlet oxygen by conjugated olefins<sup>18</sup> and with benzoquinone derivatives<sup>19</sup> and the mechanisms of the photooxidation of sulphides<sup>20</sup> and of 2,5-dimethylhexa-2,4-diene and 2-methyl-2-pentene.<sup>21</sup>

The ozonolysis of propylene in isobutane, chlorodifluoromethane and methyl chloride has been shown to give propylene ozonide, ethylene ozonide and 2-butene ozonide (cis and trans isomers) in ratios of 82:16:2. The addition of acetaldehyde increased the amount of butene ozonide and decreased the ethylene ozonide, and

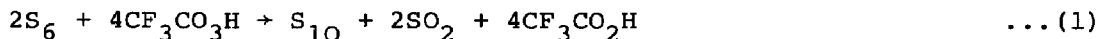
also changed the ratio of the cis and trans isomers of the former.<sup>22</sup>

The geometries of the ions  $\text{HO}_3^+$  and  $\text{HO}_3^-$  and of the radical  $\text{HO}_3$  have been optimised using the gradient technique within the SCF approximation, and the calculated energies of the different isomers compared.<sup>23</sup> Far i.r. Fourier spectroscopic studies of  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$  isolated in solid noble gas matrices (Ar, Xe, Kr) at 10K have shown that water introduced into the matrices at very low concentrations (1:1000) is present in two forms; as nearly freely rotating water molecules that have i.r. active rotational transitions below  $40\text{cm}^{-1}$  and as inert gas hydrates that contribute i.r. active intermolecular vibrations between 40 and  $100\text{cm}^{-1}$ . In solid  $\text{N}_2$  matrices the freely rotating species are not present whilst interaction between  $\text{N}_2$  and  $\text{H}_2\text{O}$  gives rise to intermolecular vibrations located considerably above  $100\text{cm}^{-1}$ .<sup>24</sup> A short communication has dismissed the idea that the ion  $\text{H}_5\text{O}_2^+$  could exist in aqueous sulphuric acid.<sup>25</sup>

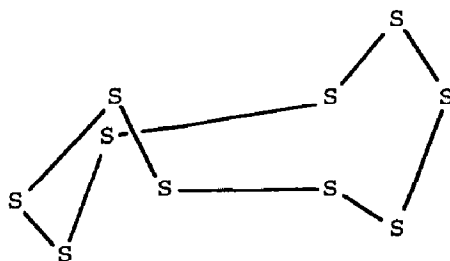
## 6.2 SULPHUR

### 6.2.1 The Element

Single crystals of  $\text{S}_{10}$  have been prepared by the reaction



and used for a structure determination at  $-110^\circ\text{C}$ . The molecule (1) exhibits  $\text{D}_2$  conformation with bond distances between 203.3 and 208.0pm, bond angles between  $103$  and  $111^\circ$  and torsional angles between  $73$  and  $124.1^\circ$ .



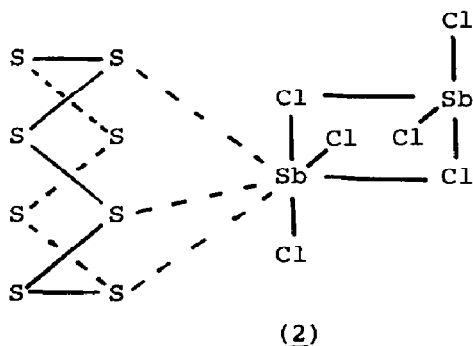
(1)

$\text{S}_{10}$  also forms a molecular addition compound with  $\text{S}_6$ ,  $\text{S}_6 \cdot \text{S}_{10}$  (mp  $92^\circ\text{C}$ ). X-ray structure determination on the addition compound

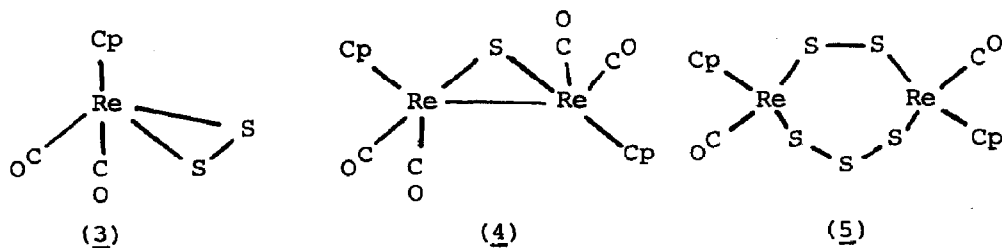
showed that  $S_{10}$  adopts an almost identical conformation to that described above for elemental  $S_{10}$  whilst that of  $S_6$  is also unchanged from the elemental form. The unit cell of the addition compound is comprised of alternating layers of  $S_6$  and  $S_{10}$  molecules and the vibrational spectrum may be explained simply as a combination of the  $S_6$  and  $S_{10}$  spectra.<sup>26</sup>

An attempt has been made to correlate the sulphur-sulphur bond distances and the torsional angles in a series of cyclic sulphur molecules. The bond distance was found to be a minimum when the torsional angle was between  $90^\circ$  and  $100^\circ$  and to be a maximum when the angle was almost zero. The bond distance variation observed amounted to 13pm or 6%. Using the enthalpy of formation of gaseous  $S_7$  the height of the torsional cis-barrier was estimated to be 24 kJ/mole or less.<sup>27</sup>

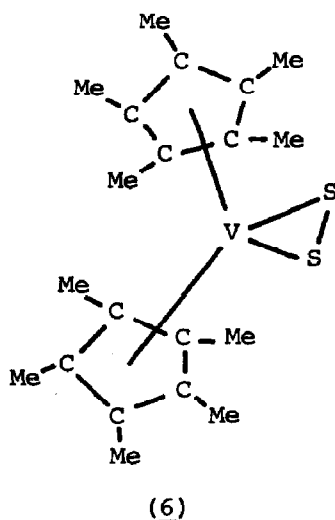
The reaction of  $SbCl_5$  with  $CS_2$  at  $5^\circ C$  has been shown to give the adduct  $SbCl_3 \cdot S_8$  and not the previously reported reaction to  $SbSCl_3$ . The adduct slowly decomposes at room temperature to  $SbCl_3$  and sulphur. Structural studies at  $-5^\circ C$  showed the compound to be built up from pyramidal  $SbCl_3$  molecules and  $S_8$  rings (2) with some relatively short Sb---S contact distances (333 to 396pm). The  $SbCl_3$  molecules form loosely associated dimeric units.<sup>28</sup>



Sodium borohydride has been shown to react with sulphur in liquid ammonia, and primary, secondary or tertiary amines, to give the corresponding amine boranes,  $R_{3-n}H_nNBH_3$  with hydrogen evolution.<sup>29</sup> The reaction of elemental sulphur with transition metals in a low oxidation state is known to give a very large number of compounds. In several instances the formation of an  $S_2$  unit is preferred for reaction of  $S_8$ . Two such examples are the reaction of  $CpRe(CO)_2(OEt)_2$  with  $S_8$  to give compounds (3) to (5)



the structures of which have been determined;<sup>30</sup> and the formation of  $(\eta^5\text{-C}_5\text{Me}_5)_2\text{V}(\eta^2\text{-S}_2)$  which maybe prepared by several methods and has the structure (6).<sup>31</sup>



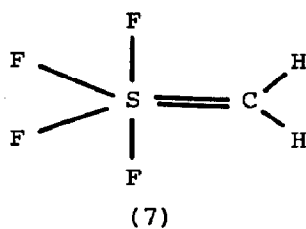
The gas phase reactions of sulphur atoms with alkynes have been studied by photolysing COS in the presence of  $\text{CH}\equiv\text{CH}$ ,  $\text{CF}_3\text{C}\equiv\text{CH}$  and  $\text{CF}_3\text{C}\equiv\text{CCF}_3$ . The formation and distribution of the reaction products could be rationalised by an overall mechanism in which the formation of highly reactive primary adducts, thiirene, and thioformylmethylene, is followed by bimolecular reactions yielding the principal end products.<sup>82</sup>

### 6.2.2 Bonds to Halogens

The pressure dependence of axial-equatorial fluorine exchange rates of sulphur tetrafluoride obtained from exchange-broadened gas phase <sup>19</sup>F n.m.r. spectra have been shown to be compatible with intramolecular vibrational redistribution rates approximately an order of magnitude slower than the statistical limit. The

temperature dependence of these exchange rates is consistent with an activation energy for axial-equatorial exchange of 12.1 kcal/mole.<sup>33</sup> The reaction of some tertiary formamides with sulphur tetrafluoride in the presence of potassium fluoride has been shown to result in the direct conversion of the formyl group to the trifluoromethyl group, to give excellent yields of the corresponding (trifluoromethyl)amines. The reaction pathway was studied and the products characterised by spectral methods, elemental analysis and hydrolysis to the corresponding N(fluoroformyl)amines.<sup>34</sup> Reaction of  $\text{SF}_4$  with 1,4-dioxan in anhydrous hydrogen fluoride in the presence of small additions of sulphur chlorides or chlorine resulted in the replacement of several hydrogen atoms in the dioxan ring by fluorine atoms. The reaction appeared to proceed via initial chlorination followed by the replacement of the chlorine atoms by fluorine atoms.<sup>35</sup>

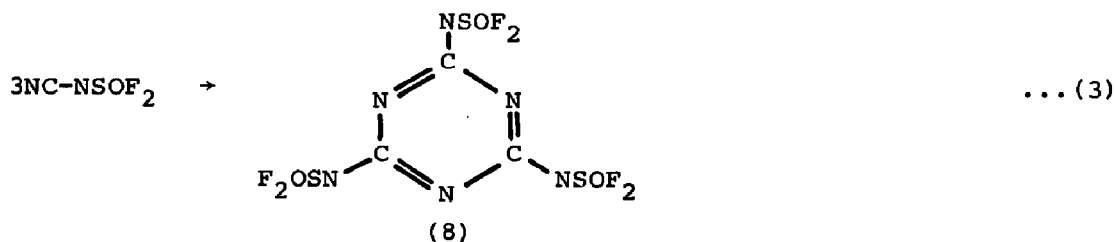
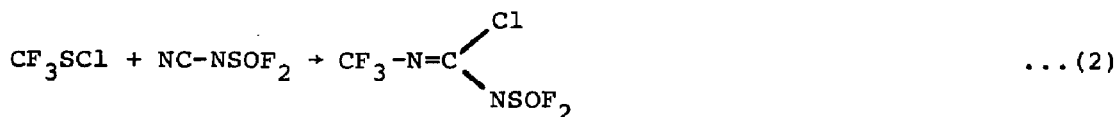
The preparation of methylene sulphur tetrafluoride,  $\text{CH}_2=\text{SF}_4$  by bromine-lithium exchange on  $\text{Br}-\text{CH}_2-\text{SF}_5$  at low temperatures and subsequent lithium fluoride elimination has been described.  $\text{CH}_2=\text{SF}_4$ , a colourless gas (bp  $-19^\circ\text{C}$  mp  $-139^\circ\text{C}$ ) has an essentially trigonal bipyramidal structure (7) with the methylene group occupying an equatorial position and the protons lying in the plane of the axial fluorine atoms. The carbon-sulphur bond, which is best described as a strong double bond with only little ylide polarity, undergoes numerous addition reactions with polar species with the formation of cis configured  $\text{X}-\text{CH}_2-\text{SF}_4-\text{Y}$  systems. Less often observed is the elimination of  $\text{SF}_4$  and the formation of a carbene.<sup>36</sup>



Sulphurionium ions of the type  $\text{R}-\text{SF}_4^+$  may be generated from  $\text{R}-\text{SF}_5$  by fluoride ion abstraction using  $\text{SbF}_5$ . Despite using a large variation in groups for  $\text{R}$  ( $\text{Me}$ ,  $\text{CH}=\text{CH}_2$ ,  $\text{C}\equiv\text{CH}$ ) none of the ions were found to be stable at room temperature.<sup>37</sup> Characteristic i.r. fundamentals have been observed for six tungsten thio- and seleno-

tetrahalides isolated as monomers in nitrogen matrices.<sup>38</sup>

The crystal structures of the chalcogen halides  $A_2X_2$  ( $A = S, Se$ ,  $X = Cl, Br$ ) have been shown to contain molecules of the type  $X-A-A-X$  with dihedral angles between  $83.9$  and  $87.4^\circ$ . Three different types of molecular packing were observed;  $S_2Cl_2$ ,  $S_2Br_2$ ,  $\alpha Se_2Br_2$  and  $\beta Se_2Br_2$ ,  $Se_2Cl_2$ .<sup>39</sup> The addition of  $CF_3SCl$  to the fluorinated nitriles  $RCN$  ( $R = CF_3$ ,  $NSF_2$ ,  $NSOF_2$ ) has been shown to lead to the formation of N-perfluoromethanesulphenyl-formylimidoyl-chlorides,  $CF_3S-N=C(Cl)R$ . The reaction of  $SCl_2$  with  $CF_3CN$  and  $NSOF_2CN$  gave the N-sulphenylchlorides  $ClS-N=C(Cl)R$  ( $R = CF_3$  or  $NSOF_2$ ) and it also proved possible to isolate the oxidation product  $CF_3CCl_2NSCl_2$  and an oligomer of the nitrile  $(NCNSOF_2)_3$  (8) the crystal structure of which was determined.<sup>40</sup>

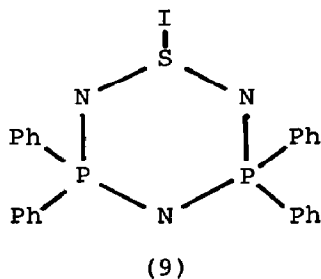


Analysis of the solid state vibrational and  $^{35}Cl$  n.q.r. spectra of the isomorphous compounds  $[SCl_3][AuCl_4]$  and  $[SeCl_3][AuCl_4]$  has shown the  $AuCl_4^-$  ion to be considerably distorted from  $D_{4h}$  symmetry.  $[TeCl_3][AuCl_4]$  was found to adopt a different crystal structure with a less severe distortion of the  $AuCl_4^-$  ion.<sup>41</sup>

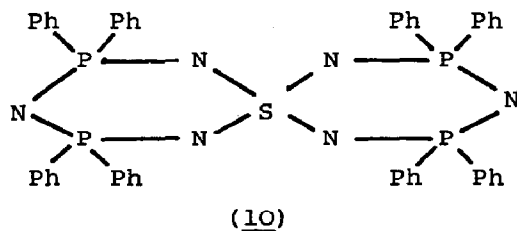
The uranium compounds  $UO_3$ ,  $UO_2Cl_2$ ,  $UCl_6$  and  $UCl_5$  have been shown to react with  $SOCl_2$  to give the compounds  $UCl_5 \cdot SCl_2$  and  $[SCl_3]^+[UCl_6]^-$  either as single phases or as mixtures of the two, but never the adduct  $UCl_5 \cdot SOCl_2$ . An X-ray study of  $[SCl_3]^+[UCl_6]^-$  showed it to contain isolated pyramidal  $SCl_3^+$  and octahedral  $UCl_6^-$  ions with bond lengths  $S-Cl = 196.2 \text{ pm}$ ,  $U-Cl = 251.1 \text{ pm}$  and the bond angle  $Cl-S-Cl = 102.34^\circ$ .<sup>42</sup> The electronic structures of sulphur, selenium and tellurium hexachlorides and their anions  $ACl_6^{2-}$  have been calculated, and compared with those of the hexafluorides and the anion  $PCl_6^-$ .<sup>43</sup> Trifluoromethylsulphenylbromide has been obtained by a new preparative method involving the reaction between

gaseous bromine and  $\text{CF}_3\text{SAg}$  or  $(\text{CF}_3\text{S})_2\text{Hg}$ . Previously only bis-trifluoromethyldisulphide  $(\text{CF}_3\text{S})_2\text{S}_2$  had been obtained as the gaseous product of the same reaction with the silver compound.<sup>44</sup>

The reaction of  $(\text{Ph}_2\text{PN})_2\text{NSCl}$  with KI in acetonitrile produces  $(\text{Ph}_2\text{PN})_2\text{NSI}$  which has been shown by X-ray crystallography to contain a six-membered  $\text{P}_2\text{SN}_3$  ring with an exocyclic S-I bond of length  $2.713\text{\AA}$ , (9).



The thermal decomposition of  $(\text{Ph}_2\text{PN})_2\text{NSI}$  leads to  $\text{Ph}_8\text{P}_4\text{SN}_6$ , a spirocyclic compound in which two, almost planar,  $\text{P}_2\text{SN}_3$  rings share a common sulphur atom (10).



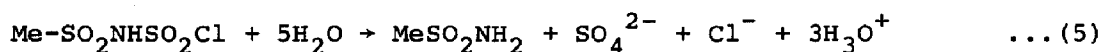
The geometry at the sulphur atom is approximately tetrahedral with bond angles in the range  $105-113^\circ$  and the four S-N bonds are almost equal in length with a mean value of  $1.56\text{\AA}$ .<sup>45</sup>

The salt-molecule reaction technique has been coupled with the matrix isolation method to synthesise a number of novel sulphur oxyfluoride anions. Reaction of COF with  $\text{SO}_2$  in argon matrices gave rise to the  $\text{SO}_2\text{F}^-$  ion and using oxygen isotopic data the equivalence of the two oxygen atoms in the ion was confirmed. Reaction of CsF with thionyl fluoride gave rise to four absorptions which were assigned to the stretching vibrations of the novel  $\text{SOF}_3^-$  anion in  $\text{C}_s$  geometry, whereas with sulfuryl fluoride gave five product bands which were assigned to the  $\text{SO}_2\text{F}_3^-$  ion isostructural

with the known  $\text{ClO}_2\text{F}_3$  species. Identification of this ion supports the claim that pentacoordinate sulphur anions play a significant role in the solution chemistry of  $\text{SO}_2\text{F}_3$ .<sup>46</sup> Tetramethylsilane has been shown to react with  $\text{HN}(\text{SO}_2\text{Cl})_2$  in a complex manner with the nature of the product depending strongly on the reaction conditions. Under reflux with the silane in excess and using  $\text{CH}_2\text{Cl}_2$  as a diluent the product was the new compound  $\text{HN}(\text{SO}_2\text{Cl})(\text{SO}_2\text{Me})$  (equation 4). The compound is formed in high



yield but is moisture sensitive being hydrolysed according to equation (5).<sup>47</sup>

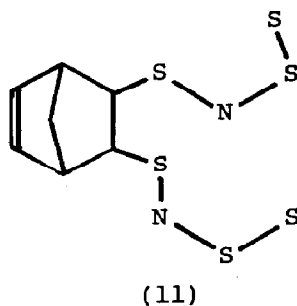


### 6.2.3 Bonds to Nitrogen

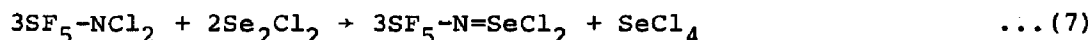
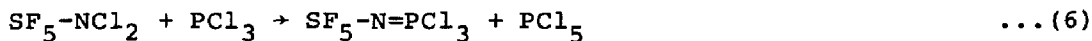
Polymeric and linear compounds - A new, direct synthesis of polymeric  $(\text{SN})_x$  films has been described. The method which avoids the use of complex chemical reactions or the dangerous pyrolysis of  $\text{S}_4\text{N}_4$ , utilises the fact that a radio frequency glow discharge is a convenient source for the generation of radicals by the homolytic cleavage of small molecules in the gas phase. The preparation involves the sublimation of  $\text{S}_4\text{N}_4$  at  $70-80^\circ\text{C}$  into a helium plasma in a pyrex reaction vessel which is cooled by liquid nitrogen so that the reaction products are rapidly condensed on the vessel walls. A 10 MHz radio frequency discharge at a power level of 40 watts gave a greenish blue film with metallic lustre which was found to be a mixture of  $(\text{SN})_4$  and  $\text{S}_4\text{N}_4$ . The latter was separated by washing with  $\text{CH}_2\text{Cl}_2$  to yield pure  $(\text{SN})_x$ .<sup>48</sup>

The reaction of  $\text{S}_4\text{N}_2$  with norbornadiene has been shown to give  $\text{C}_7\text{H}_8(\text{S}_3\text{N})_2$  (11). The molecule consists of a norbornenyl unit with two  $\text{S}_3\text{N}$  groups attached in an exo fashion at the 2,3 positions. Both  $\text{S}_3\text{N}$  groups possess a cis formation with the bond lengths S-S  $1.903\text{\AA}$  and CS-N  $1.641\text{\AA}$ . The molecule exhibits two strong absorptions in the visible region attributable to the excitonically coupled  $\pi^*-\pi^*$  transitions of the two  $\text{S}_3\text{N}$  chromophores.<sup>49</sup>

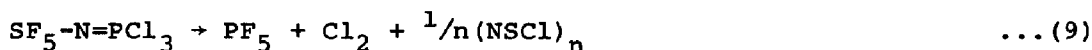
The reactions of (pentafluorosulphanyl)dichloroamine,  $\text{SF}_5\text{-NCl}_2$  with  $\text{PCl}_3$ ,  $\text{Se}_2\text{Cl}_2$  and Se have been shown to give the compounds



$\text{SF}_5\text{NPCl}_3$  and  $\text{SF}_5\text{NSeCl}_2$  respectively (equations 6, 7 and 8).



Although both compounds are produced in high yields they were found to decompose readily at room temperature.

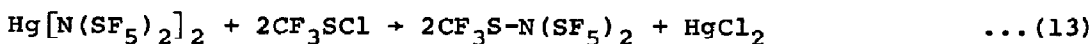
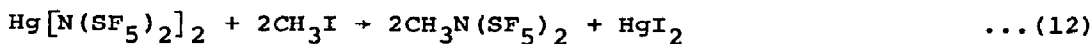


$\text{SF}_5\text{NCl}_2$  was also found to react with  $\text{S}_2\text{Cl}_2$  or  $\text{SCl}_2$  to give  $\text{SF}_5\text{N=SCl}_2$  and with  $\text{SF}_5\text{N=SCl}_2$  to give  $\text{SF}_5\text{N=S=NSF}_5$ , and to form an adduct with  $\text{HCl}$ .<sup>50</sup>

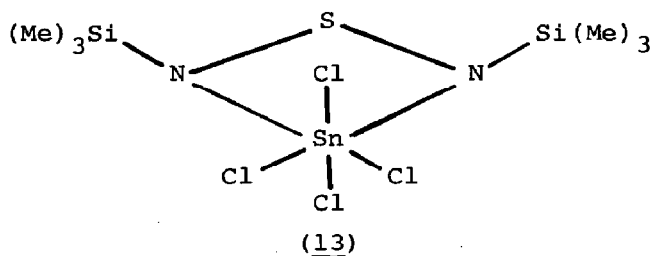
The reaction of  $\text{SF}_5\text{NSF}_4$  with  $\text{HgF}_2$  at 20-60°C has been shown to yield  $\text{Hg}[\text{N}(\text{SF}_5)_2]_2$  (12) (equation 11):



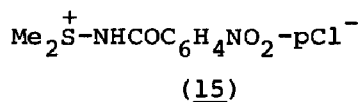
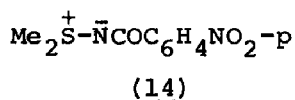
Reaction of (12) with  $\text{Cl}_2$  or  $\text{Br}_2$  gave no reaction at room temperature and raising the temperature to 60°C led to decomposition; transfer of the  $\text{N}(\text{SF}_5)_2$  group was however possible with  $\text{CH}_3\text{I}$  and  $\text{CF}_3\text{SCl}$  according to equations (12) and (13).<sup>51</sup>



Both  $\text{Me}_3\text{SiNSO}$  and  $\text{Me}_3\text{SiN}=\text{S}=\text{NSiMe}_3$  have been shown to react with  $\text{SnCl}_4$  to give the 1:1 adduct (13) in which the sulphur diimide functions as a bidentate ligand.<sup>52</sup>

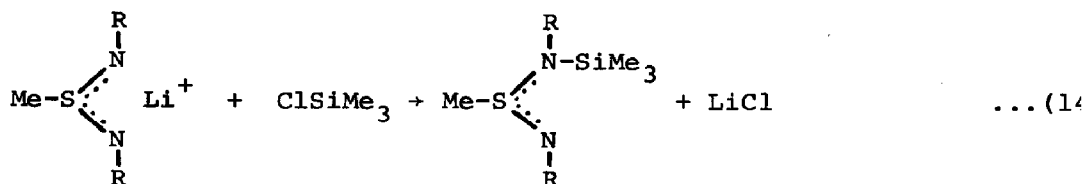


A significant difference in the  $\text{S}2\text{p}$  binding energy has been observed between the sulphilimine (14) and its salt (15).



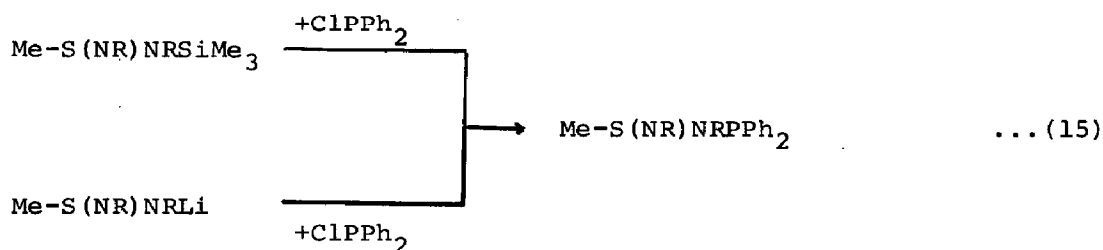
The difference was thought to be due to a higher electron density on the sulphur atom in (14) than in (15) arising from the electron displacement effect along the sigma bond between the  $\text{S}^+$  and  $\text{N}^-$  atoms.<sup>53</sup> Both  $^{19}\text{F}$  and  $^{13}\text{C}$  n.m.r. spectra of the sulphur-(IV) diimines,  $\text{R-NSN-R}$  ( $\text{R} = \text{Ph}, \text{C}_6\text{F}_5, \text{C}_6\text{H}_5\text{S}, \text{C}_6\text{F}_5\text{S}$ ) and the corresponding N-sulphinylamines,  $\text{R-NSO}$ , have been measured and discussed.<sup>54</sup>

The reactions of N-lithiomethanesulphinicacidimide amides,  $\text{Me-S(NR)NRLi}$  ( $\text{R} = \text{Bu}^t$  or  $\text{Me}_3\text{Si}$ ), with chlorosilanes and -phosphanes have been described. Metathetical reactions of the amides with chloromethylsilane led to the formation of sulphinic acid imide amidosilanes,  $\text{Me-S(NR)NRSiMe}_3$  (equation 14):

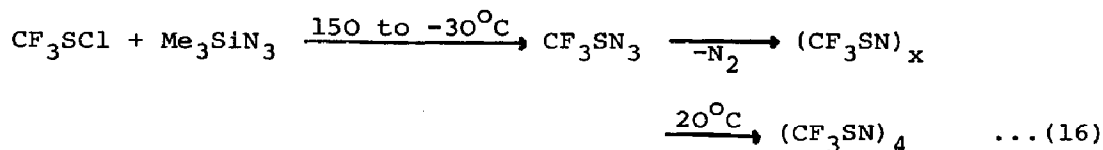


Instead of forming the corresponding phosphane derivative the amine reacted with chlorodiphenylphosphane via a sulphur to phosphorus redox-transamination to give N(iminophosphoranyl)-

sulphenic acid imides (equation 15).<sup>55</sup>

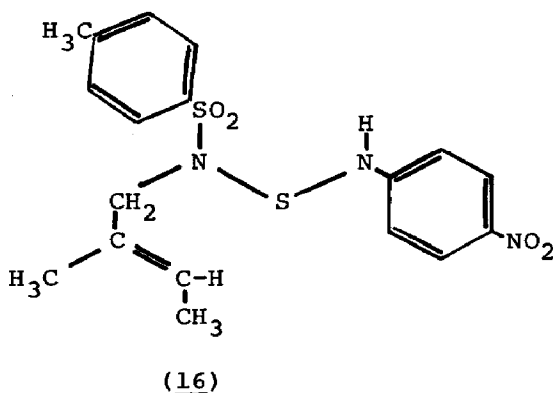


Tetrakis(trifluoromethylthiazyl),  $(\text{CF}_3\text{SN})_4$  has been prepared from  $\text{CF}_3\text{SCl}$  and  $\text{Me}_3\text{SiN}_3$ . The compound has low stability, at  $-30^\circ\text{C}$  it is stable for a few days, and on standing it oligomerises and after 7 days at  $20^\circ\text{C}$  the melting point is above  $180^\circ\text{C}$  (equation 16):

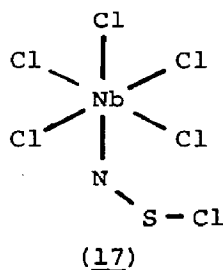


The addition of  $\text{F}_2$  to  $\text{CF}_3\text{SNCO}$  at  $-78^\circ\text{C}$  leads to the formation of  $\text{CF}_3\text{S(F)N=C(O)F}$  which decomposes at  $25^\circ\text{C}$  in the presence of  $\text{HgF}_2$  to  $(\text{CF}_3\text{SN})_x$ .<sup>56</sup>

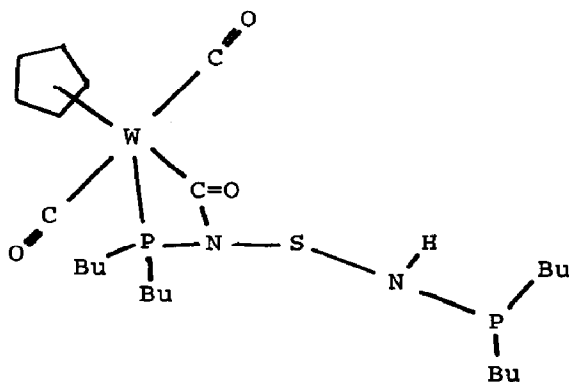
Crystal structure determination has shown that the formal S-N single bonds of the diaminosulphane moiety of (16) are shortened and differs in length (1.700 and 1.644Å). The bonds of the N-S-N group to the p-nitrophenyl and -tosyl residues are also a little shorter than single bonds. The hybridisation of the nitrogen atoms of the N-S-N moiety is  $\text{sp}^2$  with a tendency towards  $\text{sp}^3$ .<sup>57</sup>



Several papers have been published describing the formation and crystal structures of transition metal complexes with linear sulphur-nitrogen ligands. Niobium pentachloride has been shown to react with trithiazyl chloride in  $\text{CCl}_4$  suspension to form the red, moisture sensitive compound  $\text{Cl}_5\text{NbNSCl}$  (17). The compound consists of monomeric units which  $\text{NbCl}_5$  is bonded to  $\text{N}\equiv\text{S}-\text{Cl}$  in a relatively loose manner via the nitrogen atom. Bond lengths found were Nb-N



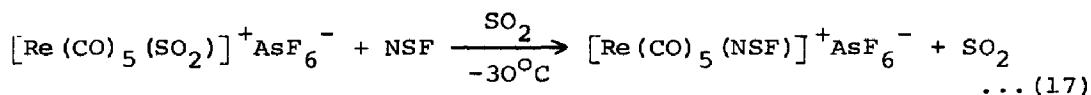
226pm, Nb-Cl 225-234pm, N-S 144pm and N-Cl 207pm.<sup>58</sup> The new sulphur diimides,  $\text{S}(\text{NPBu}^t_2)_2$  and  $\text{S}(\text{NAsBu}^t_2)_2$ , react with the hydrido metal complex  $\text{CpM}(\text{CO})_3\text{H}$  ( $\text{M} = \text{Cr}, \text{Mo}, \text{W}$ ) to give 1:1 adducts which contain a 3 electron acyl-chelate ligand. Only one of the two  $\text{PBu}^t_2$  or  $\text{AsBu}^t_2$  ligands becomes coordinated to the metal and the hydride ligand of the complex is transferred to a nitrogen atom of the sulphur diimide system. A crystal structure determination of the tungsten adduct (18) confirmed the presence of a four membered metallocycle containing W, C(acyl), N and P.<sup>59</sup>



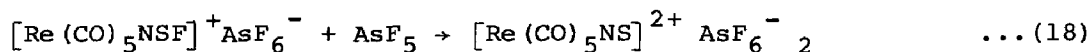
(18)

Thiazylfluoride complexes, which can be readily prepared from the corresponding  $\text{SO}_2$  derivatives, have been shown to be suitable

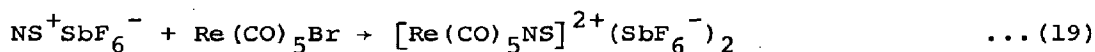
precursors for the preparation of the thionitrosyl ligand in complexes (equation 17).



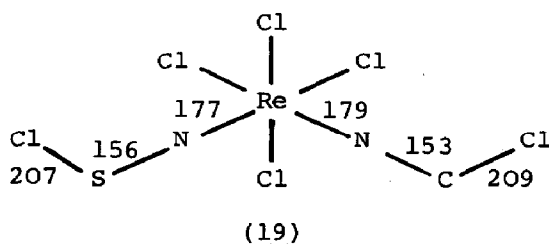
As in free NSF, a fluoride ion can be removed by fluoro Lewis acids.



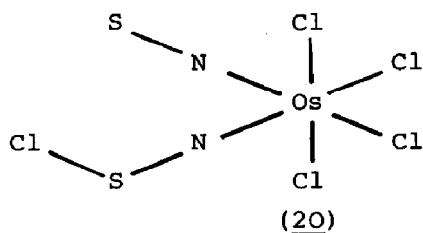
The corresponding hexafluoroantimonate could also be obtained from  $\text{Re}(\text{CO})_5\text{Br}$  and  $\text{NS}^+\text{SbF}_6^-$ .<sup>60</sup>



Rhenium pentachloride in  $\text{POCl}_3$  solution has been shown to react with  $(\text{NSCl})_3$  to give the chlorothionitrene complexes  $[(\text{Cl}_3\text{PO})\text{ReCl}_4(\text{NSCl})]$  and  $[(\text{Cl}_3\text{PO})\text{ReCl}_3(\text{NSCl})_2]$ . The former reacts with  $\text{AsPh}_4\text{Cl}$  to give  $\text{AsPh}_4[\text{ReNCl}_4]$  and the latter, the complex  $\text{AsPh}_4[\text{ReCl}_4(\text{NSCl})_2] \cdot \text{CH}_2\text{Cl}_2$ , (19). Crystal structure determination of (19) showed the two NSCl ligands to have cis arrangements with nearly linear  $\text{Re}=\text{N}=\text{S}$  groups, with interatomic distances corresponding to double bonds.<sup>61</sup>

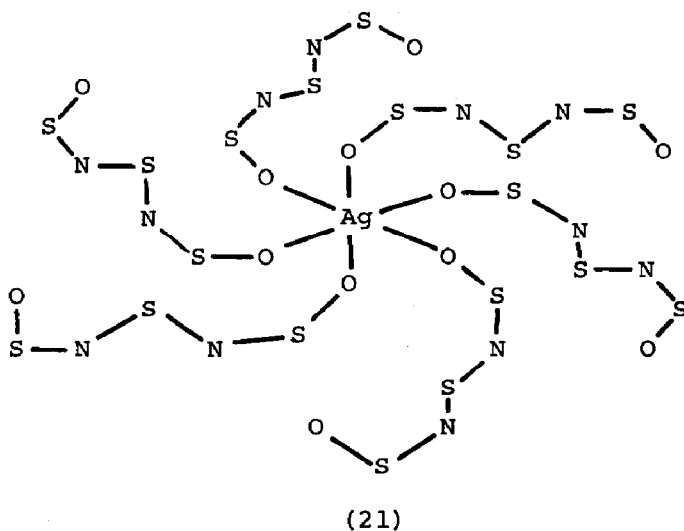


The reaction of  $\text{OsCl}_5$  with  $(\text{NSCl})_3$  yields the thiazyl chloride complex  $\text{OsCl}_4(\text{NSCl})_2$ , from which the thionitrosyl complex  $\text{AsPh}_4[\text{OsCl}_4(\text{NS})_2\text{Cl}]$  (20) could be obtained by reaction with  $\text{AsPh}_4\text{Cl}$  in  $\text{CH}_2\text{Cl}_2$ . A crystal structure determination showed the two NS groups to be in a cis configuration and to be essentially linear with the bond lengths  $\text{Os}=\text{N}$  184pm and  $\text{N}=\text{S}$  146pm. Loosely attached to one of the sulphur atoms is the chlorine atom ( $\text{S}-\text{Cl} = 228\text{pm}$ ): in the crystal structure it statistically belongs to both

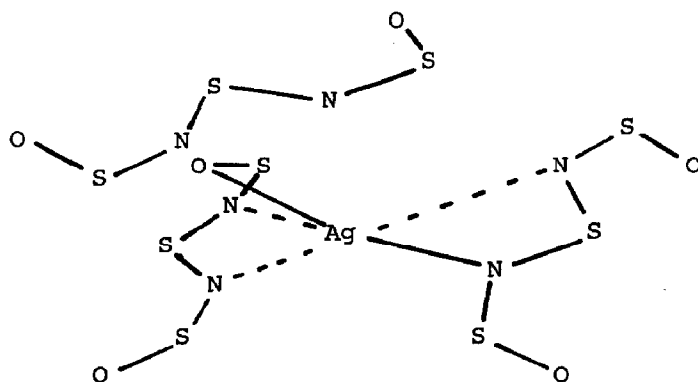


sulphur atoms and it is thought that there is a dynamical fluctuation between the sulphur atoms.<sup>62</sup>

The reaction of  $\text{AgAsF}_6$  with  $\text{S(NSO)}_2$  in liquid  $\text{SO}_2$  has been shown to give a polymeric bis(sulphinylnitrilo)sulphur complex of silver(I),  $[\text{Ag}_4(\text{S(NSO)}_2)_9][\text{AsF}_6]_4 \cdot \text{SO}_2$ , containing two crystallographically independent silver atoms. One silver atom is octahedrally coordinated by the terminal oxygen atoms of six  $\text{S(NSO)}_2$  ligands (21), the other is unsymmetrically coordinated by the nitrogen atoms of three  $\text{S(NSO)}_2$  ligands (22). The ligands bridge the silver atoms to form a polymeric cationic network in which the  $\text{AsF}_6^-$  anions and  $\text{SO}_2$  solvent molecules occupy holes without acting as ligands.<sup>63</sup>

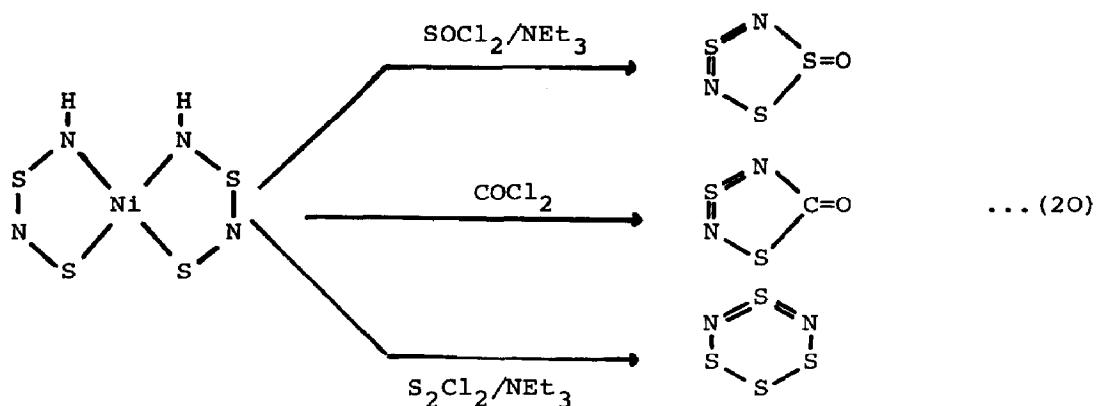


The thermochemical and spectrophotometric properties of some  $\text{Ni(II)}$  complexes of some linear tridentates with one sulphur and two nitrogen donors have been studied.<sup>64</sup>



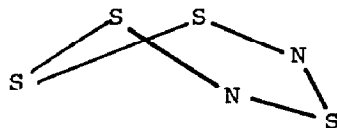
(22)

Cyclic Sulphur-nitrogen compounds - A new route to the preparation of cyclic sulphur-nitrogen compounds has been described. Facile syntheses of  $S_3N_2O$ ,  $S_2N_2CO$  and  $S_4N_2$  from  $Ni(S_2N_2H)_2$  were achieved according to equation (20).<sup>65</sup>



A simple method, the reaction of  $S_2Cl_2$  and  $NH_4OH$  in  $CS_2$  followed by crystallisation from diethyl ether, for obtaining high purity  $S_4N_2$  crystals has been described. The crystal and molecular structure of  $S_4N_2$  at  $-100^\circ C$  was described in full (a preliminary communication appeared in 1981).  $S_4N_2$  has a six membered ring with nitrogen atoms in the 1,3 positions and the molecule adopts a half chair conformation with the central sulphur of the trisulphide unit lifted out of plane of the remaining five atoms producing a dihedral angle of  $54.9^\circ$  (23). Of the two types of S-N bonds, those linking the N-S-N moiety to the  $S_3$  unit are considerably longer ( $1.676\text{\AA}$ ) than those within the N-S-N group ( $1.561\text{\AA}$ ). The

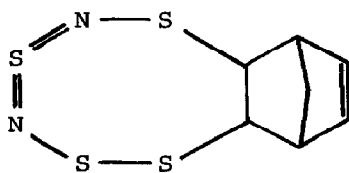
S-S bonds ( $2.061\text{\AA}$ ) are those expected for an S-S single bond. MNDO and ab initio Hartree-Fock-Slater SCF calculations on a variety of  $\text{S}_4\text{N}_2$  structures showed the observed conformation to be preferred by 6-10 kcal mole<sup>-1</sup> over a planar configuration.<sup>66</sup>



(23)

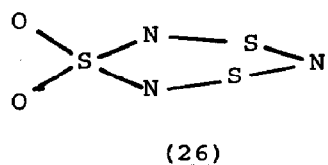
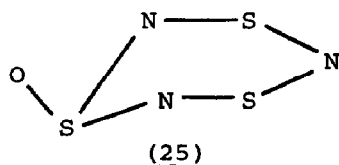
An independent study of the conformation of  $\text{S}_4\text{N}_2$  has also concluded that the half-chair conformation is preferred to a planar model. CNDO/2 calculations had previously predicted a planar conformation but the extended Huckel calculations used in this work were in excellent agreement with the crystallographic study reported above.<sup>67</sup>

The reaction of  $\text{S}_4\text{N}_2$  with norbornadiene has been shown to produce the 1:1 adduct  $\text{S}_4\text{N}_2 \cdot \text{C}_7\text{H}_8$ . X-ray crystallographic analysis revealed that olefin addition cleaves one of the sulphur-sulphur bonds of  $\text{S}_4\text{N}_2$  to yield a novel eight membered  $\text{C}_2\text{S}_4\text{N}_2$  ring (24). The S-S-N-S-N-S fragment of the  $\text{C}_2\text{S}_4\text{N}_2$  ring is planar to within  $0.15\text{\AA}$  whilst the S-C-C-S unit is folded out of this plane to produce a dihedral angle of  $74.5^\circ$ .<sup>68</sup>

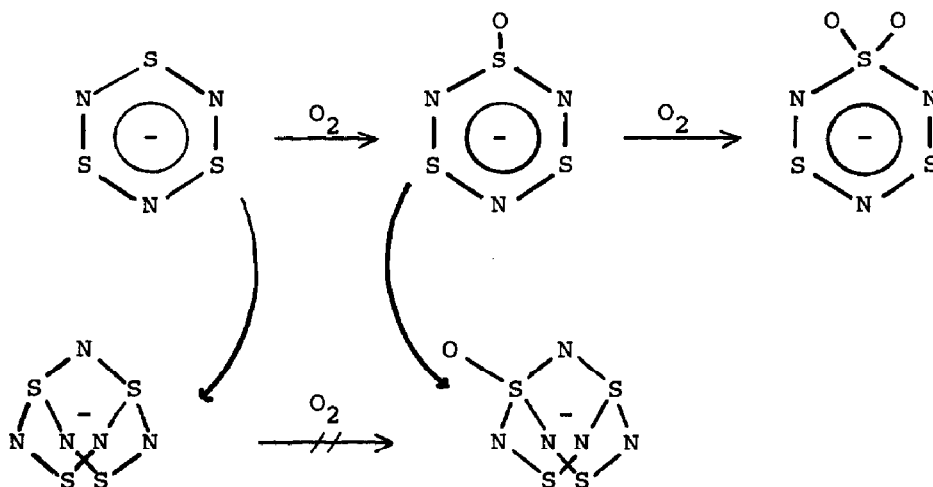


(24)

The oxidation of the  $\text{S}_3\text{N}_3^-$  ion in acetonitrile solution by molecular oxygen gives rise to four major products:  $\text{S}_4\text{N}_5^-$ ,  $\text{S}_4\text{N}_5\text{O}^-$ ,  $\text{S}_3\text{N}_3\text{O}^-$  and  $\text{S}_3\text{N}_3\text{O}_2^-$ . The crystal structures of the  $(\text{Ph}_3\text{P})_2\text{N}^+$  salts of two of the ions  $\text{S}_3\text{N}_3\text{O}^-$  and  $\text{S}_3\text{N}_3\text{O}_2^-$  were determined. The two anions both possess six membered  $\text{S}_3\text{N}_3$  ring structures with exocyclic oxygen atoms bonded to sulphur and both rings exhibit significant variations in chemically equivalent bond lengths and angles (25) and (26). The formation of four ions in the oxidation of  $\text{S}_3\text{N}_3^-$  poses several interesting and perplexing



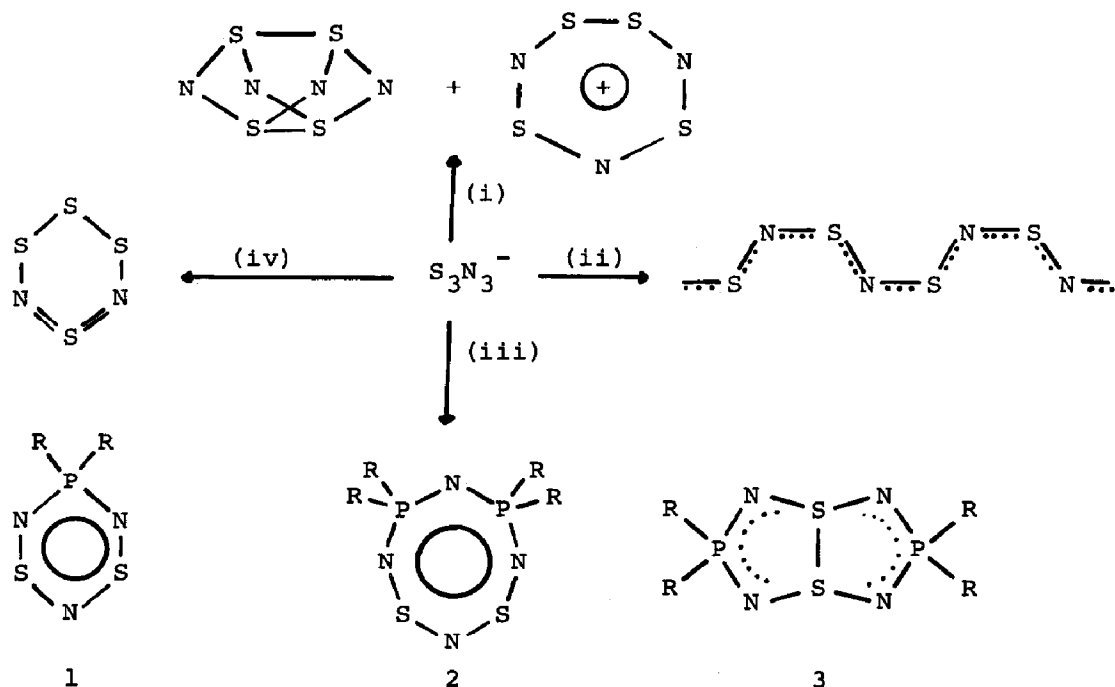
questions as to the mechanism of the reaction. Although not completely understood the authors suggest the following scheme.<sup>69</sup>



Scheme 1

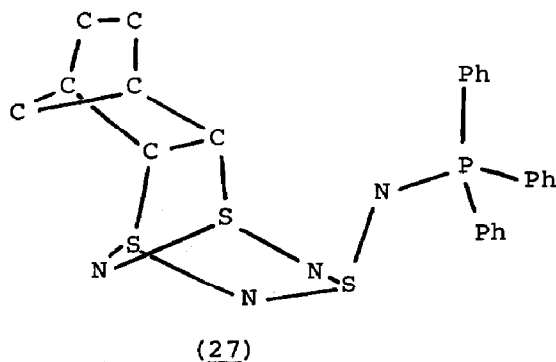
The reactions of  $S_3N_3^-$  with halogens,  $AsF_5$  and other electrophilic substrates has been shown to give mixtures of known sulphur-nitrogen compounds. The major products from reactions with halogens,  $COCl_2$ ,  $Ph_2PCl$  and  $CS_2$  are shown in Scheme 2.  $AsF_5$  was found to oxidise  $S_3N_3^-$  to  $S_4N_4 \cdot AsF_5$ , and the major products with  $SOCl_2$  or  $SO_2Cl_2$  were  $S_4N_4$ ,  $S_4N_3^+Cl^-$  and for  $SOCl_2$  only,  $S_3N_2O_2$ .  $S_2N_2Cl$  was the main reaction product with  $S_2Cl_2$ .<sup>70</sup>

The reaction of norbornadiene with (triphenylphosphorane-diyl)-aminocyclotriithiatiazine produces the cycloadduct  $Ph_3PN-S_3N_3 \cdot C_7H_8$ . The  $S_3N_3$  ring adds to  $C_7H_8$  in an exo fashion via two sulphur atoms. The  $S_3N_3$  ring adopts a chair conformation with the three ligands occupying axial positions on the same side of the ring (27).<sup>71</sup>

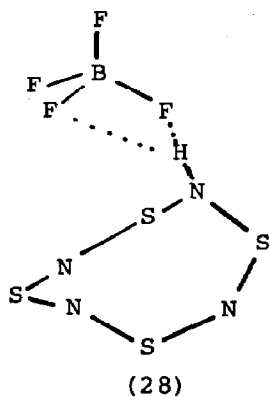


Major products from the reactions of  $\text{S}_3\text{N}_3^-$  with (i) halogens, (ii)  $\text{COCl}_2$ , (iii)  $\text{Ph}_2\text{PCl}$ , and (iv)  $\text{CS}_2$ .

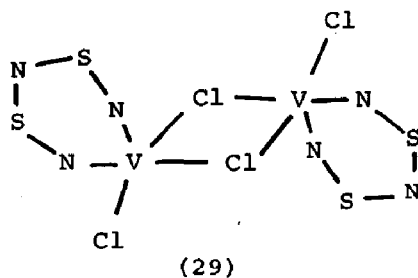
Scheme 2



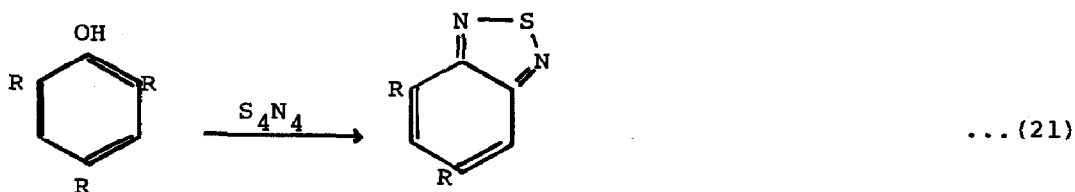
The reactions of  $\text{S}_4\text{N}_4$  with a wide variety of species have been reported. With tetrafluoroboric acid diethyl etherate in methylene chloride solution,  $\text{S}_4\text{N}_4$  reacts to give  $\text{S}_4\text{N}_4\text{H}^+\text{BF}_4^-$ , the first simple salt of  $\text{S}_4\text{N}_4$ . The structure of the  $\text{S}_4\text{N}_4\text{H}^+$  cation consists of a boat shaped 8-membered ring with virtually coplanar sulphur atoms (29).<sup>72</sup>  $\text{S}_4\text{N}_4$  reacts with an excess of  $\text{VCl}_4$  in  $\text{CH}_2\text{Cl}_2$  to give a mixture of  $\text{VCl}_2(\text{S}_2\text{N}_3)$  and  $\text{S}_2\text{N}_2 \cdot \text{VCl}_4$ , but with



$\text{TiCl}_4$  only  $\text{S}_4\text{N}_4 \cdot \text{TiCl}_4$  was obtained. A crystal structure determination showed  $\text{VCl}_2(\text{S}_2\text{N}_3)$  to consist of chlorine bridged dimers (29) linked by additional V-N interactions to form polymeric chains. The six membered V-N-S-N-S-N ring was found to be essentially planar.<sup>73</sup>

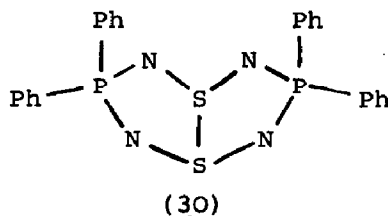


The reaction of  $\text{S}_4\text{N}_4$  with some 4-methyl- and 4-t-butyl-phenols has been shown to give 2,1,3-benzothiadiazoles (equation 21).<sup>74</sup>

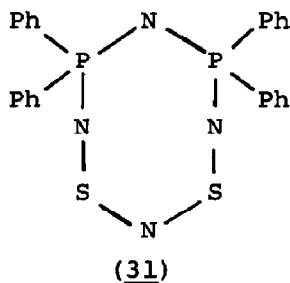


In addition to the six membered ring  $\text{R}_2\text{PS}_2\text{N}_3$  reported previously and the cyclophosphazenes  $(\text{R}_2\text{PN})_{3,4}$ , two structural isomers of the eight membered ring  $\text{R}_4\text{P}_2\text{S}_2\text{N}_4$  are formed in the reaction of  $\text{S}_4\text{N}_4$  with  $\text{R}_2\text{PPR}_2$  ( $\text{R} = \text{Me}, \text{Ph}$ ) and  $\text{Ph}_2\text{PH}$  in toluene under reflux. Crystal structure determinations on the phenyl derivatives

1,5- $\text{Ph}_2\text{P}(\text{NSN})_2\text{PPh}_2$  and 1,3- $(\text{Ph}_2\text{PNPPh}_2)\text{S}_2\text{N}_3$  showed the former to consist of a folded eight membered ring with a cross ring S-S contact of  $2.527\text{\AA}$  and the angle between the two intersecting planes of the ring to be  $117.3^\circ$ , (30). The mean endocyclic P-N and S-N bond lengths were  $1.622$  and  $1.590\text{\AA}$  respectively.

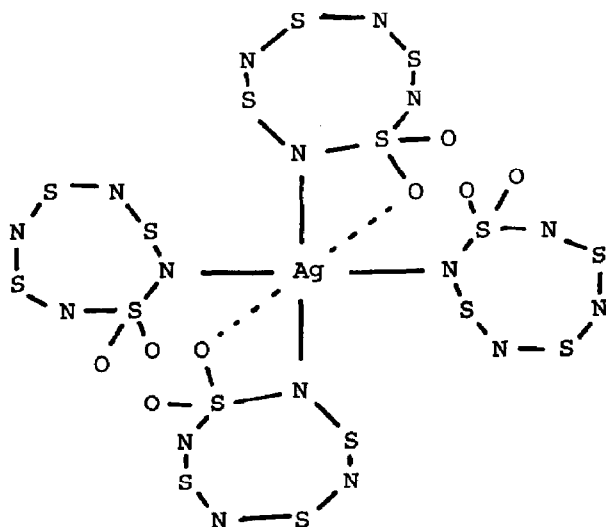


1,3- $(\text{Ph}_2\text{PNPPh}_2)\text{S}_2\text{N}_3$  consists of an eight membered ring with phosphorus atoms in the 1,3-positions (31). The NSNSN unit is essentially planar and the P atoms lie out and on opposite sides of this plane by  $0.697\text{\AA}$ . The mean endocyclic P-N and S-N bond lengths are  $1.600$  and  $1.577\text{\AA}$  respectively.<sup>75</sup>



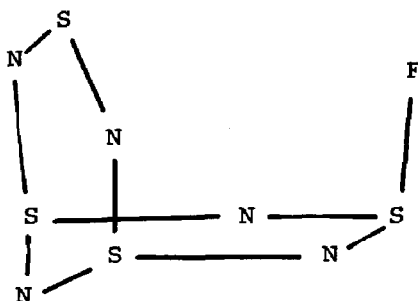
A redetermination of the structure of tetrasulphur tetranitrogen dioxide,  $\text{S}_4\text{N}_4\text{O}_2$ , has shown that the molecular structure is qualitatively identical to that reported by Roesky (Z. Naturforsch Teil B, 31(1976)680) but that the previously assigned space group  $\text{Abm}2$  is probably incorrect due to twinning. The space group is now considered to be  $\text{P}2_1/\text{c}$ .<sup>76</sup> The reaction of silver hexafluoroarsenate(V) with tetrasulphur tetranitrogen dioxide in  $\text{SO}_2$  has been shown to give crystals of  $[\text{Ag}(\text{S}_4\text{N}_4\text{O}_2)_4]^+[\text{AsF}_6]^-$ . A structure determination showed that the silver atom lies  $53\text{pm}$  below a square of four nitrogen atoms and the bisdisphenoidal (triangulated dodecahedral) coordination is completed by two intramolecular Ag-O contacts with a mean distance of  $307\text{pm}$ , and intermolecular Ag-N and Ag-O interactions both of  $273\text{pm}$  (32). The intermolecular

interactions thus give rise to a cationic dimer which is centrosymmetric. The  $S_4N_4O_2$  ligands are approximately planar except for the  $SO_2$  units. Only nitrogen and oxygen atoms attached to S(VI) interact with silver thereby causing the least disruption of the delocalised bonding in the rest of the ring.<sup>77</sup>



(32)

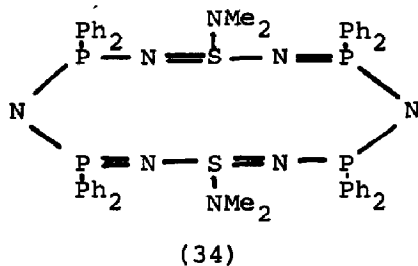
Fluoride addition to the  $S_4N_5^+$  cation in liquid  $SO_2$  has given  $S_4N_5F$  and a crystal structure determination showed it to have the configuration (33).<sup>78</sup>



(33)

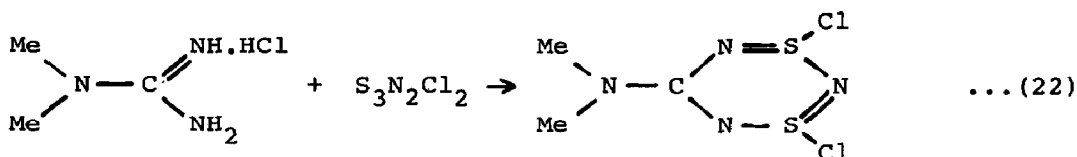
The thermal decomposition of the six membered ring compound  $(Ph_2PN)_2NSX$  ( $X = Cl, I$ ) to form a spirocyclic compound has already been discussed earlier in this review (structures (9) and (10)). The structure of an intermediate in the thermal decomposition of

$(\text{Ph}_2\text{PN})_2\text{NSX}$  ( $\text{X} = \text{NMe}_2$ ) has also been determined. The intermediate,  $\text{Ph}_8\text{P}_4\text{N}_6\text{S}_2(\text{NMe}_2)_2$  forms a twelve membered ring with a trans  $\text{NMe}_2$  substituent on each of the two sulphur atoms (34). The endocyclic S-N bond lengths (mean  $1.590\text{\AA}$ ) are considerably shorter than the exocyclic bond length of  $1.703\text{\AA}$  which is close to the value expected for a S-N single bond.<sup>79</sup>

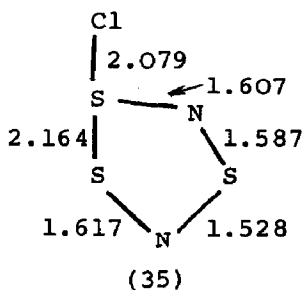


The reaction of  $\text{S}_4\text{N}_4$  with  $\text{TlNO}_3$  and  $\text{NH}_3$  has been used to prepare  $\text{Tl}_2\text{S}_7\text{N}_8$ . A crystal structure determination showed the compound to be comprised of  $\text{Tl}^+$  cations and  $\text{S}_3\text{N}_3^-$  and  $\text{S}_4\text{N}_5^-$  anions.<sup>80</sup>

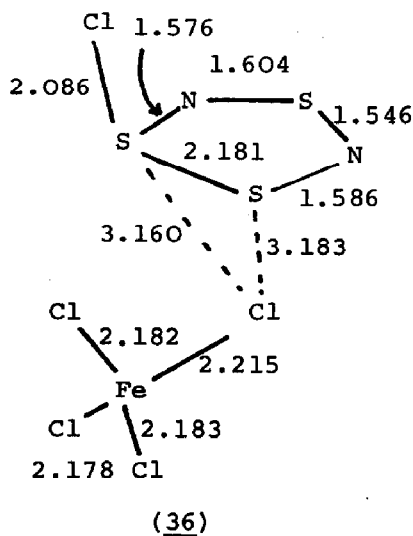
The six membered ring compound,  $\text{Me}_2\text{NCN}_3\text{S}_2\text{Cl}_2$ , has been prepared from N,N-dimethylguanidindihydrochloride and trithiadiazindichloride.



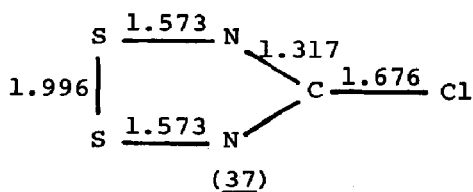
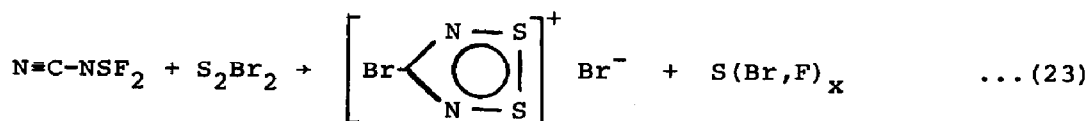
The  $\text{C}_2\text{N}$  unit lies approximately in the plane of the  $\text{CNSNSN}$  ring with both carbon atoms on the same side of the ring.<sup>81</sup> The reaction of  $\text{N}_4\text{S}_4\text{SbCl}_5$  and  $\text{Cl}_2$  has been used to prepare  $\text{N}_2\text{S}_3\text{Cl}^+\text{SbCl}_6^-$ . The bond lengths (in  $\text{\AA}$ ) of the independent cation  $\text{N}_2\text{S}_3\text{Cl}^+$  are shown in (35).<sup>82</sup>



The same cation has been found in the reaction product of  $S_4N_4$  with  $FeCl_3$  in thionyl chloride solution. The product  $[S_3N_2Cl]^+[FeCl_4]^-$  shows an interaction between one of the chlorine atoms of the  $FeCl_4$  unit and two sulphur atoms of the  $S_3N_2$  ring, this interaction distorts the tetrahedral coordination about the iron atom by lengthening the Fe-Cl bond. The bond lengths found in this study are given in (36).<sup>83</sup>

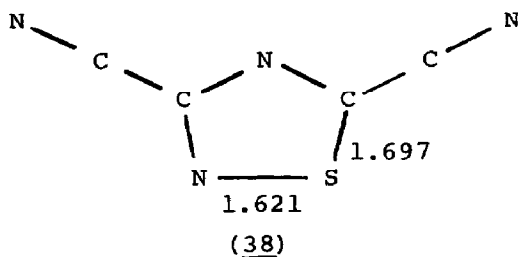


The synthesis of 4-chloro-1,2,3,5-dithiadiazolium chloride (37) from  $SCl_2$  and either N-cyanosulphur difluoride imide or  $R_3Si-N=C=N-SiR_3$  has been described, and the structure of the hexafluoroarsenate salt determined. The analogous dibromide was also prepared by the reaction:<sup>84</sup>

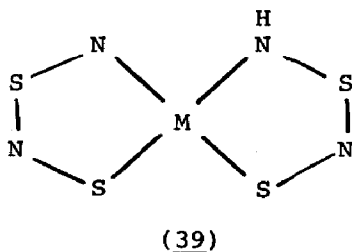


The reaction of cyanogen with elemental sulphur in dimethyl

formamide at 120°C has been shown to give  $(\text{CN})_4\text{S}$ . The molecule (38) is almost planar, only one carbonitrile group being slightly out of the plane of the thiadiazole ring.<sup>85</sup>



The compounds  $[\text{M}(\text{OS}_2\text{N}_2)_6][\text{AsF}_6]_2$  where  $\text{M} = \text{Zn}$  or  $\text{Cd}$  have been prepared in which the metal atoms are coordinated by six  $\text{N}_2\text{S}_2\text{O}$  ligands. The metal atom is bonded to the heterocycle via the exocyclic oxygen atom giving a slightly distorted octahedral coordination. The  $\text{S}_3\text{N}_2$  rings have an envelope conformation where the sulphur atom connected to the oxygen is out of a plane formed by the other four atoms. The  $\text{AsF}_6^-$  group is slightly disordered in the  $\text{Cd}$  compound, but considerably disordered in the  $\text{Zn}$  compound.<sup>86</sup> The complex (39) reacts with alcoholic solutions of alkaline hydroxides by double deprotonation to the anion  $[\text{Ni}(\text{N}_2\text{S}_2)_2]^{2-}$ , but only one proton is removed by reaction with strong organic bases forming salts with the anion  $[\text{Ni}(\text{HN}_2\text{S}_2)(\text{N}_2\text{S}_2)]^-$ . The structure of the tetraphenylarsonium salt was determined.<sup>87</sup>



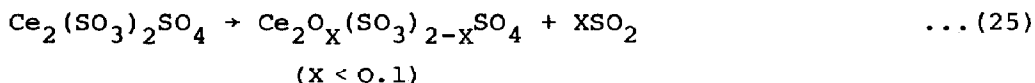
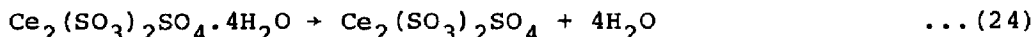
#### 6.2.4 Bonds to Oxygen

The apparent molar heat capacities and volumes of aqueous  $\text{NaHSO}_3$ ,  $\text{KHSO}_3$  and  $\text{SO}_2$  have been obtained. The contribution of "chemical relaxation" (changes in equilibrium state and enthalpy due to change in temperature) to the experimental heat capacities of aqueous  $\text{SO}_2$  required special attention, leading to the

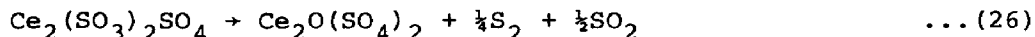
derivation of a new equation for calculating this effect. Standard state values for the heat capacities and volumes of aqueous  $\text{SO}_2$  and  $\text{HSO}_3^-$  were obtained from the apparent molar properties.<sup>88</sup> Practical equations have been derived for estimating diffusion coefficients and Onsager transport coefficients of several aqueous solutes subject to hydrolysis. In dilute solutions where hydrolysis is extensive it was found that the rate of diffusion of  $\text{SO}_2$  was increased by about 50% relative to unhydrolysed solute.<sup>89</sup> Large sensitised photocurrents in acidic media have been observed for the photosensitised oxidation of  $\text{SO}_2$  at an optically transparent electrode coated with poly(vinylpyridine) coordinated zinc(II) tetraphenylporphine.<sup>90</sup> The electrochemical behaviour of  $\text{SO}_2$  has been investigated at illuminated p-type semiconducting Si,  $\text{WS}_2$  and InP in  $\text{CH}_3\text{CN}/\text{Bu}^n_4\text{NClO}_4$  solutions.  $\text{SO}_2$  is photoreducible at each of these materials to form  $\text{S}_2\text{O}_4^{2-}$  and preparative, controlled potential photoelectrochemical reduction at all three photoelectrodes was demonstrated to give >90% current efficiency for formation of  $\text{S}_2\text{O}_4^{2-}$ , which was precipitated and collected as  $\text{Na}_2\text{S}_2\text{O}_4$ .<sup>91</sup>  $\text{SO}_2$  has been used as an oxidiser in the reaction of  $\text{Zn}(\text{SO}_2)_n(\text{AsF}_6)_2$  and tetraphenyldiphosphane to produce  $\text{Zn}(\text{O}_2\text{P}_2\text{Ph}_4)_3(\text{AsF}_6)_2$ . When  $\text{Zn}(\text{SO}_2)_n(\text{AsF}_6)_2$  is treated with  $\text{P}[\text{O}=\text{P}(\text{OMe})_2]_3$  in liquid  $\text{SO}_2$ ,  $\text{Zn}[\text{P}(\text{O}=\text{POMe}_2)_3]_2(\text{AsF}_6)_2$  is formed and its structure was determined.<sup>92</sup> The metals Mg, Cr, W, Fe, Ni, Cu, Zn, Hg, Al, Sn and Pb dissolve electrolytically in the mixed non-aqueous solvents,  $\text{SO}_2$ -DMSO, -DMF, -acetonitrile, -acetone, or -nitrobenzene to form solutions containing several sulphur anions. Reactions of Mg, Cr, Fe, Cu and Zn with DMSO- $\text{SO}_2$  gave pure single products of metal disulphates.<sup>93</sup>

An ab initio study has been carried out on the complex formed between  $\text{SO}_2$  and HF. The most stable geometry (-5.2 kcal/mol relative to the non-interacting molecules) was found, as expected, to be with the HF linear to the S-O bond with a separation of 1.8 Å. Calculations of the electric field potential surrounding the  $\text{SO}_2$  were also performed.<sup>94</sup> The thermal decomposition of  $\text{Ce}_2(\text{SO}_3)_2\text{SO}_4 \cdot 4\text{H}_2\text{O}$  has been shown to take place in several stages (equations 24 to 30). A thermochemical cycle for splitting  $\text{SO}_2$  into sulphur and oxygen was described in which sulphur and/or oxygen and/or cerium all change oxidation state in four different reactions.<sup>95</sup>

400-800K



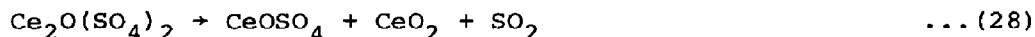
800-850K



800-850K



850-1000K



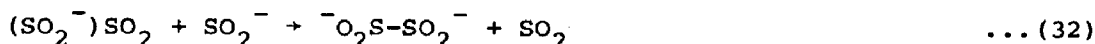
850-1000K



1000-1200K

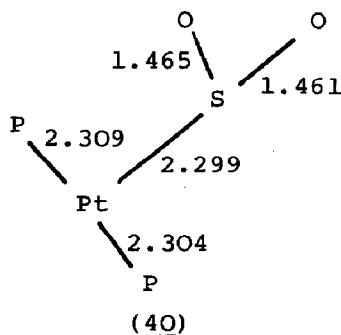


The reactive characteristics of the oxyanion radicals of sulphur,  $\text{SO}_2^-$ ,  $\text{SO}_3^-$  and  $\text{SO}_4^-$  towards a number of organic substrates have been investigated by use of the rapid-mixing flow technique coupled with E.S.R. The  $\text{SO}_2^-$  was the only ion able to reduce aromatic nitro compounds to the corresponding anion radicals, but did not abstract hydrogen from saturated compounds nor add to the unsaturated compounds.  $\text{SO}_3^-$  could add to compounds having a C=C bond but did not abstract hydrogen from saturated compounds.  $\text{SO}_4^-$  abstracted hydrogen from saturated compounds and also could add to the unsaturated compounds with a C=C bond.<sup>96</sup> In the presence of tetraethylammonium ion,  $\text{SO}_2^-$  undergoes reversible dimerisation. When the counterion is the tetrabutylammonium ion a different mechanism was observed consisting of the reversible association (equation 31) followed by reaction (32):



Reaction (32) could either be an electron transfer or the displacement of  $\text{SO}_2$  by  $\text{SO}_2^-$ .<sup>97</sup>

Solubility and freezing point data have been presented for the system  $\text{SO}_2$ -N methyl-2-pyrrolidinone (NMP). The enthalpy and entropy of solution were found to be  $-33.7 \text{ kJ/mol}$  and  $-94.6 \text{ kJ/-mole}$  respectively. The freezing point diagram indicated the formation of 2:1 and 1:1 NMP: $\text{SO}_2$  complexes. N.m.r. and Raman spectroscopic data suggest an overall shift of electron density from the nitrogen and carbonyl carbon of NMP to the oxygen of  $\text{SO}_2$  with a weakening of the CO bond of NMP.<sup>98</sup> The chemical compounds  $\text{B}_2\text{O}_3 \cdot \text{SO}_3$  and  $\text{B}_2\text{O}_3 \cdot 2\text{SO}_3$  have been prepared by heating boric acid in liquid sulphur trioxide at different temperatures.<sup>99</sup> Infrared and  $^{11}\text{B}$  n.m.r. studies showed the molecules of both compounds to contain  $\text{SO}_4$  and  $\text{BO}_3$  groups together with distorted  $\text{BO}_4$  tetrahedra.<sup>100</sup> The structure of pentacarbonyl(sulphur dioxide)-chromium has been determined. The sulphur dioxide is  $\eta^1$ -coplanar coordinated with a Cr-S distance of 219pm, the shortest bond reported so far between  $\text{Cr}^0$  and sulphur. The Cr-C axial bond was found to be only marginally shorter than the Cr-C equatorial bonds providing proof of the high  $\pi$ -acceptor capacity of  $\text{SO}_2$ .<sup>101</sup> The first structurally characterised three coordinate bi(phosphine)- $\text{Pt}^0$ -sulphur dioxide complex,  $\text{Pt}(\text{PCy}_3)_2\text{SO}_2$  (40), has been described.<sup>102</sup>

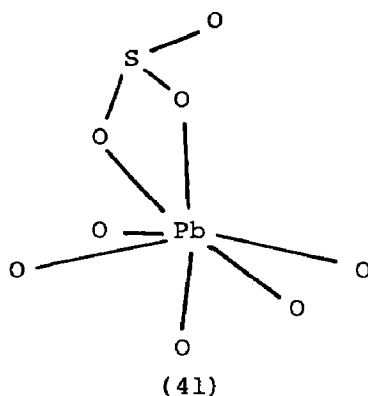


The following phase systems have been studied,  $\text{ZrO}_2$ - $\text{SO}_3$ - $\text{HCl}$ - $\text{H}_2\text{O}$ ;<sup>103</sup>  $\text{K}_2\text{O}$ - $\text{V}_2\text{O}_5$ - $\text{SO}_3$ ,<sup>104</sup>  $\text{SOCl}_2$ - $\text{VOCl}_3$  and  $\text{SO}_2\text{Cl}_2$ - $\text{VOCl}_3$ .<sup>105</sup>

Ab initio calculations have been performed on the sulphite and hydrogen sulphite ions,  $\text{HSO}_3^-$  and  $\text{SO}_2\text{OH}$ . The mechanism behind the shortening of the S-O bond in  $\text{HSO}_3^-$  as compared with  $\text{SO}_3^{2-}$  was confirmed to be a transformation of an antibonding into a non-bonding orbital upon protonation. The isomers  $\text{HSO}_3^-$  and  $\text{SO}_2\text{OH}^-$  were found to be of comparable energy. The very long S-OH bond ( $1.716\text{\AA}$ ) found, indicates the system to be assembled from

comparatively weakly interacting species of  $\text{SO}_2$  and  $\text{OH}^-$ .<sup>106</sup>

The gel crystallisation technique has been used to obtain single crystals of the hitherto unknown  $\text{Na}_2\text{Mg}(\text{SO}_3)_2 \cdot 2\text{H}_2\text{O}$  from  $\text{Mg}(\text{HSO}_3)_2$  solutions saturated with  $\text{NaCl}$ . The crystal structure contains  $\text{MgO}_6$  octahedra connected by sulphite bridges forming chains which are held together by strong hydrogen bonds.<sup>107</sup> Single crystals of the anhydrous sulphites  $\text{BaSO}_3$ ,  $\text{CdSO}_3$ ,  $\text{PbSO}_3$  and  $\text{Na}_2\text{Cd}_3(\text{SO}_4)_4$  and the previously unknown sulphites  $\text{CdSO}_3(\text{II})$  and  $\text{CdSO}_3(\text{III})$  have also been prepared by the gel crystallisation method.<sup>108</sup> The crystal structure of orthorhombic  $\text{PbSO}_3$  has been determined. The sulphite ion has S-O distances of 149.4 and 153.7 pm. The Pb-O distances of the edge connected  $\text{PbO}_7$  polyhedra (distorted monocapped trigonal prism) range from 253.4 to 284.8 pm (41). The structure is closely related to that of  $\text{PbSO}_4$ .<sup>109</sup>



$\text{MgI}_2$ ,  $\text{FeI}_2$  and  $\text{CuI}$  have been shown to react with tetramethylammonium disulphite to form Mg and Fe anhydrous sulphites and  $\text{Cu(I)}$  disulphite respectively. Iron(II) sulphite and copper(I) disulphite react with  $\text{DMSO-SO}_2$  to form iron(II) disulphite and copper(II) disulphite.<sup>110</sup> Structural studies on  $\text{K}_5(\text{HSO}_3)_3(\text{S}_2\text{O}_5)$  showed the disulphite ion to have  $\text{C}_s$  symmetry and consist of a thionite and a thionate group linked by an S-S bond of 2.226 Å. The S-O distances are 1.489 Å in the thionite group and 1.462 Å in the thionate group. There are three crystallographically different  $\text{HSO}_3^-$  ions in the cell with average S-O distances of 1.419, 1.451 and 1.445 Å respectively. The hydrogen atom is bonded to the sulphur atom in all three  $\text{HSO}_3^-$  ions with H-S distances of 1.31, 1.16 and 1.16 Å respectively.<sup>111</sup> A new class of basic sulphites of the type  $\text{NaM}_2\text{OH}(\text{SO}_3)_2 \cdot \text{H}_2\text{O}$ , with  $\text{M} = \text{Mg}, \text{Mn}, \text{Fe}, \text{Co}, \text{Ni}$  and  $\text{Zn}$  have

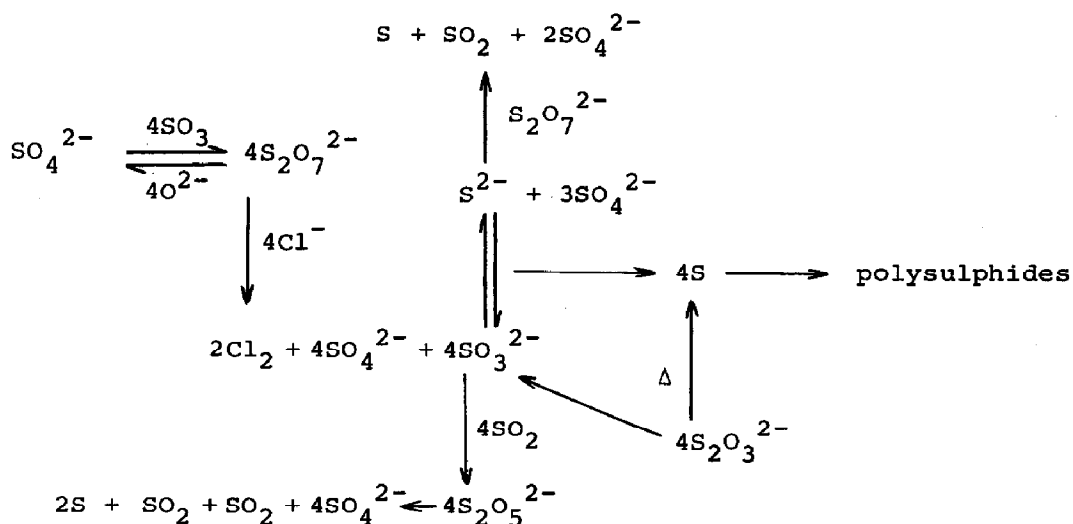


Electron density distributions have been calculated using the IND/2 method for S-O and O-O bonds in the persulphate ion for the two different O-O bond lengths of 1.5 and 2.0 Å. The results of the calculations show that the electron density is lowest on the -O-O- bond which is in accordance with experimental data, leading to the conclusion that the homolytic cleavage of the -O-O- bond in  $\text{S}_2\text{O}_8^{2-}$  is the more probable.<sup>115</sup>

Interest in energy storage systems has led to a study of the reversible reaction (34) where M is Mg, Zn or Ni. The aim of the



study was to determine the experimental conditions for the backward reaction and to know the effect of cycling on the overall performance of the cycle. Experiments carried out in a fixed bed reactor showed that  $\text{SO}_3$  has to be used in preference to  $\text{SO}_2$  and cycling was shown to decrease the reactivity of the oxides towards  $\text{SO}_3$ .<sup>116</sup> The reactions of sulphide and of five sulphur oxyanion salts ( $\text{Na}_2\text{SO}_3$ ,  $\text{Na}_2\text{S}_2\text{O}_5$ ,  $\text{K}_2\text{S}_2\text{O}_5$ ,  $\text{Na}_2\text{S}_2\text{O}_3$  and  $\text{K}_2\text{S}_2\text{O}_7$ ) have been studied by themselves and in molten  $\text{Li}_2\text{SO}_4$ - $\text{Na}_2\text{SO}_4$ - $\text{K}_2\text{SO}_4$  eutectic under nitrogen, with air,  $\text{SO}_2$ ,  $\text{SO}_3$  and  $\text{CO}_2$  and with acidic, basic and reducing solutes. The sulphur containing products were elemental sulphur and sulphate, although sulphur oxides were sometimes evolved and a number of intermediates formed (Scheme 3).<sup>117</sup>



Scheme 3

A series of Raman and near infrared absorption spectra of molten  $K_2S_2O_7$ - $KHSO_4$  mixtures at  $430^\circ\text{C}$  under an equilibrium vapour pressure of water have been measured. The spectra could best be interpreted by the presence of the three species involved in the temperature-sensitive equilibrium (35). The structure of  $S_2O_7^{2-}$



in the melts was found to be most probably  $C_{2v}$  whilst  $HSO_4^-$  was presumed to have  $C_s$  symmetry. No intermediate compounds were observed and the presence of hydrogen bonding between the species was thought to account for the previously observed low vapour pressure of water.<sup>118</sup>

Several papers have been published concerned with physico-chemical aspects of sulphate systems. The order-disorder phase transitions occurring in the  $Na_2SO_4$ - $K_2SO_4$  system have been investigated and kinetic and structural studies on the compounds  $KNaSO_4$  and  $K_3Na(SO_4)_2$  reported.<sup>119</sup> The electrical conductivities of the latter two compounds in the pure state and doped with  $Cd^{2+}$  and  $Gd^{3+}$  have been measured. High ionic conductivity values were observed in the high temperature phase.<sup>120</sup> Studies of the order-disorder phase transitions and electrical conductivity of the  $Na_2SO_4$ - $Ag_2SO_4$  system showed that the lower conductivity of  $Ag_2SO_4$  with  $Na^+$  present relative to pure  $Ag_2SO_4$  could be attributed to lattice contraction.<sup>121</sup> With the aim of developing useful solid electrolytes for  $SO_2$  detectors, a study has been made of the electrical and thermal properties of  $Na_2SO_4$  doped with  $NaVO_3$ ,  $Eu_2(SO_4)_3$  and  $Pr_2(SO_4)_3$ . Europium sulphate was found to enhance the electrical conductivity of  $Na_2SO_4$  and the other two sulphates were found to suppress the phase transformation in  $Na_2SO_4$ .<sup>122</sup> The pyroelectric properties of  $LiKSO_4$  have been studied.<sup>123</sup> Laser interferometric galvanostatic studies have been carried out in the  $Zn/ZnSO_4/Zn$  system with gelled electrolyte short-time electrolysis.<sup>124</sup> Phase systems involving sulphates which have been investigated are collected together in Table 1.

An infrared spectroscopic study has shown that  $AgBr$  and  $AgCl$  crystals take up small concentrations (up to 0.01 mole%) of sulphate or phosphate ions if prepared from melts of  $Ag_2SO_4$  or  $Ag_3PO_4$ . Spectroscopic evidence showed that the excess charges of the tetrahedral guest ions are compensated by interstitial silver

Table 1. Phase systems involving sulphates

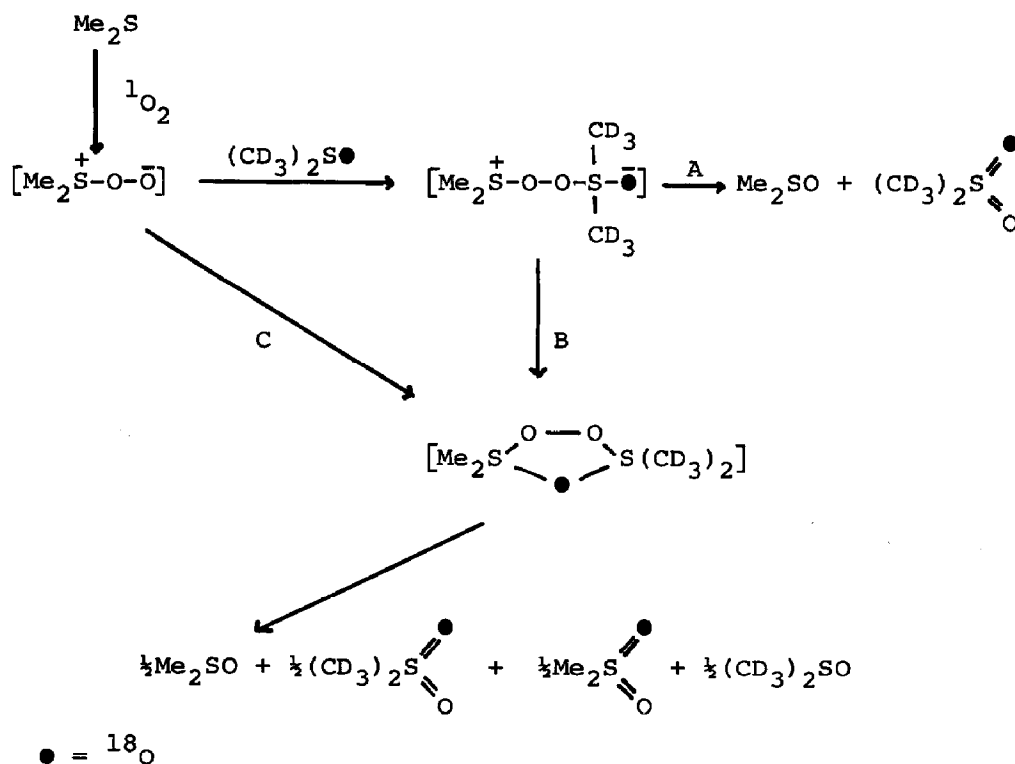
System	ref.	System	ref.
$\text{NaCl}-\text{Na}_2\text{SO}_4-\text{Me}_2\text{CO}-\text{H}_2\text{O}$	125	$\text{KCl}-\text{Li}_2\text{SO}_4-\text{NiCl}_2$	129
$\text{HfO}_2-\text{M}_2\text{SO}_4-\text{H}_2\text{SO}_4-\text{H}_2\text{O}$	126	$\text{Al}^{3+}, \text{Ga}^{3+} + \text{H}^+    \text{SO}_4^{2-}, \text{H}_2\text{O}$	130
$\text{M} = \text{Na}, \text{K}, \text{Rb}, \text{Cs} \text{ or } \text{NH}_4$		$\text{Ga}^{3+}, \text{In}^{3+} + \text{H}^+    \text{SO}_4^{2-}, \text{H}_2\text{O}$	130
$\text{Al}(\text{NO}_3)_3-\text{Al}_2(\text{SO}_4)_3-\text{H}_2\text{O}$	127	$\text{Al}^{3+}, \text{In}^{3+}    \text{SO}_4^{2-}, \text{H}_2\text{O}$	130
$\text{Gd}(\text{SO}_4)_3-(\text{NH}_4)_2\text{SO}_4-\text{Rb}_2\text{SO}_4-\text{H}_2\text{O}$	128	$\text{KVO}_2\text{SO}_4-\text{K}_2\text{SO}_4-\text{H}_2\text{SO}_4-\text{H}_2\text{O}$	131
$\text{Cs}_2\text{SO}_4-\text{Cd}_2(\text{SO}_4)_3-(\text{NH}_4)_2\text{SO}_4-\text{H}_2\text{O}$	128		

ions forming complexes with sulphate or phosphate ions.<sup>132</sup>

A comparative analysis of the infrared spectra and crystal structure show that the water molecules in  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  form one coordinate and two non equivalent hydrogen bonds: a stronger one with an oxygen of the  $\text{SO}_4$  group of the layer where the  $\text{Ca}^{2+}$  ion is situated and a weak one with the oxygen atom of the next layer. In the  $\alpha$  and  $\beta$  hemihydrate structures the water molecules are connected by a coordinate bond and only one hydrogen bond analogous to the stronger bond of the dihydrate.<sup>133</sup> A crystal structure determination of the calcium sulphate subhydrate  $\text{CaSO}_4 \cdot 0.8\text{H}_2\text{O}$  showed that chains of alternating  $\text{Ca}^{2+}$  and  $\text{SO}_4^{2-}$  ions form the framework of a tunnel structure in which four water molecules are randomly distributed over five positions and the  $\text{Ca}^{2+}$  ion is surrounded by six sulphate groups and one water molecule.<sup>134</sup>  $(\text{H}_3\text{O})_2\text{Sb}_2(\text{SO}_4)_4$  has a polymeric structure with sheets in which  $-\text{Sb}-\text{O}-\text{S}-$  chains are linked together by sulphate groups.<sup>135</sup> A study of the chemical transport reactions of anhydrous metal sulphates has shown that it is possible to prepare well formed single crystals of  $\text{CuSO}_4$  and  $\text{Cu}_2\text{OSO}_4$  by deposition from a vapour phase.  $\text{Cl}_2$  and  $\text{HgCl}_2$  were found to be suitable transporting agents for  $\text{CuSO}_4$  but  $\text{HCl}$ ,  $\text{NH}_4\text{Cl}$  and  $\text{I}_2$  were less satisfactory.  $\text{HgCl}_2$  proved to be a good transporting agent for  $\text{Cu}_2\text{OSO}_4$ .<sup>136</sup> The crystal structures of monoclinic nickel sulphate hexadeuterate<sup>137</sup> and  $\text{Th}(\text{SO}_4)_2 \cdot 8\text{H}_2\text{O}$ <sup>138</sup> have been determined. The deformation electron density in  $\text{MgS}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$  has been evaluated from a combination of X-ray and neutron diffraction data.<sup>139</sup> The

conditions for the synthesis of caesium tantalum sulphates<sup>140</sup> and the behaviour of anhydrous lanthanide sulphates and double lithium lanthanide sulphate<sup>141</sup> at high pressures have been described. The thermal dehydration of sodium thiosulphate pentahydrate when heated in air to 300°C has been studied. Dehydration is accompanied by fusion of the compound at 65°C and takes place in the temperature range 30-185°C.<sup>142</sup>

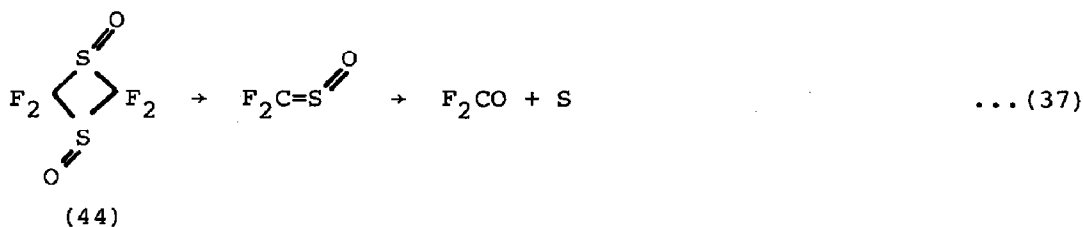
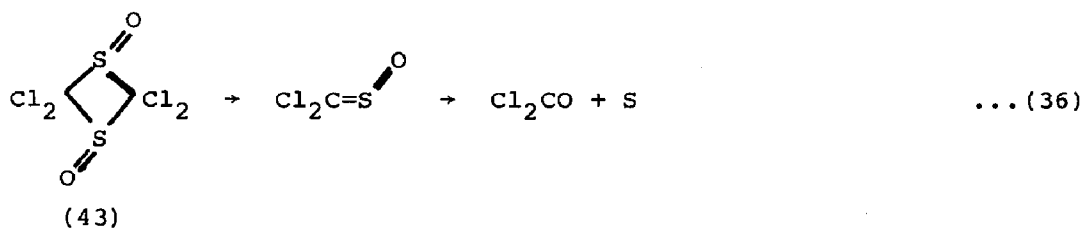
<sup>18</sup>O labelling has been used to follow the reaction pathway for the nucleophilic oxidation of sulfoxide by a persulphoxide intermediate. The possible pathways are shown in Scheme 4 and the labelling experiments clearly showed that route A was the pathway followed.<sup>143</sup>



Scheme 4

A complete structure-reactivity study has been carried out for both kinetics and equilibria in the transfer of the sulphate group ( $-\text{SO}_3^-$ ) between pyridine and phenols in aqueous solution at 25°C.<sup>144</sup> Vibrational assignments of the polarised Raman spectra of single crystals of  $\text{NaH}_2\text{SO}_3$  have indicated that there is no water of crystallisation, the hydrogen bonding is extremely weak

and the strength of the N-S bond is stronger than in sulphamic acid.<sup>145</sup> Two new oxidising agents, trifluoromethane and nonafluorobutanepersulphonic acid have been used to prepare several new perchlorinated and perfluorinated 1,3-dithietanes which are partially oxidised at the sulphur atoms, pyrolysis of the 1,3-dioxides (43 and 44) leads to the formation of sulfoxides of the type  $X_2CSO$  ( $X = Cl, F$ ) respectively.<sup>146</sup>



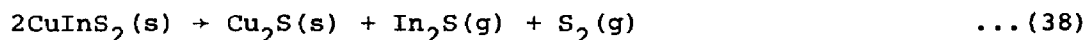
Complexes of the type  $M(\text{NH}_3)_5(\text{OSO}_2\text{CF}_3)(\text{CF}_3\text{SO}_3)_n$  have been prepared for  $M = \text{Cr(III)}, \text{Rh(III)}, \text{Ir(III)}, \text{Ru(III)}$  and  $\text{Pt(IV)}$  and are considered to offer potential as versatile synthetic intermediates.<sup>147</sup> Reactions of the cyclic systems  $(\text{NPCl}_2)_2\text{NSOX}$  and  $\text{NPCl}_2(\text{NSOX})_2$  ( $X = \text{F}, \text{Cl}, \text{Ph}$ ) with  $\text{NH}_3$  in diethyl ether or acetonitrile at low temperatures provide convincing evidence that the P-bonded chlorine atoms are replaced by  $\text{NH}_2$  groups along a geminal pathway without disruption of the S-F and S-Ph groups.<sup>148</sup> The nitrosodisulphonate ion,  $\cdot\text{ON}(\text{SO}_3)_2^{2-}$ , has been found to smoothly oxidise  $\text{Fe}(\text{CN})_6^{4-}$  to  $\text{Fe}(\text{CN})_6^{3-}$  and  $\text{H}_2\text{O}_2$  to  $\text{O}_2$  giving  $\text{HON}(\text{SO}_3)_2^{2-}$  in both reactions.<sup>149</sup> The reactions of perfluoroalkanesulphinates with halogen and halogen acids, and a new method for the synthesis of perfluorosulphonic acid have been described.<sup>150</sup> The deiido-sulphination (the conversion of  $\text{R}_f\text{I}$  to  $\text{R}_f\cdot\text{SO}_2\text{K}$  in one step) of perfluoroalkyl iodides has been studied.<sup>151</sup>

#### 6.2.5 Sulphides

A Raman spectrometric method has been used for in situ identifi-

cation of the H-S stretch in high pH solutions of  $\text{H}_2\text{S}$  and for estimating their concentrations. The observed spectrum for a 8.9N NaOH solution containing 0.6M  $\text{H}_2\text{S}$  and 0.1M  $\text{NaClO}_4$  showed that virtually all sulphide was in the form of bisulphide. This data was used to determine the second dissociation constant of  $\text{H}_2\text{S}$ , the value found,  $17 \pm 1$  was the highest yet recorded.<sup>152</sup> The internal energy effects and the energetics of the ion-molecule reactions,  $\text{H}_2\text{S}^+ + \text{H}_2\text{S} \rightarrow \text{S}_2^+ + 2\text{H}_2$ ,  $\text{HS}_2^+ + \text{H}_2 + \text{H}$ ,  $\text{H}_3\text{S}^+ + \text{HS}$ , and  $\text{H}_3\text{S}_2^+ + \text{H}$  have been studied by photoionisation of hydrogen-sulphide dimers synthesised by the molecular beam method.<sup>153</sup> Tritium isotope fractionation in the exchange reaction between methanol and hydrogen sulphide has been studied in the gaseous phase over the temperature range 283-373K. Investigations of the ionic transport properties of solid CaS have been carried out. The observed dependence of the conductivity with the sulphur partial pressure is explained in terms of a Schottky type defect model for CaS.<sup>155</sup>

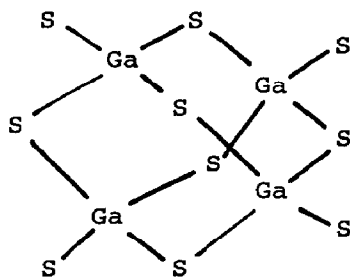
The equilibrium vaporisation of  $\text{CuInS}_2$  has been studied by Knudsen cell mass spectrometric techniques in the temperature range 902 to 1110K.  $\text{CuInS}_2$  decomposes under steady state conditions according to the reaction:



The enthalpy of formation of  $\text{CuInS}_2$  was calculated to be  $\Delta H_{298}^\circ = -221.7 \pm 13$  kJ/mole.<sup>156</sup>

Extended Hückel calculations comparing the valence electronic structures of  $\text{B}_8\text{S}_{16}$  and the isostructural but not isoelectronic porphine, and of the  $\text{Cu}^{2+}$  complexes of these two macrocycles, indicate that the  $\text{B}_8\text{S}_{16}$  complex may have a stability (relative to free ligand and metal ion) that is comparable to that of the porphine complex.<sup>158</sup> The crystal structure of the spinel  $\text{ZnAl}_2\text{S}_4$  (obtained by chemical transport reaction at  $740^\circ\text{C}$ ) has been refined. The cation distribution corresponds to the normal spinel structure, the fraction of tetrahedral sites occupied by aluminium ions being smaller than 0.02.<sup>159</sup> The quasibinary systems  $\text{Zn}_{1-x}\text{Cd}_x\text{Al}_2\text{S}_4$ ,  $\text{ZnAl}_2(1-x)\text{Ga}_{2x}\text{S}_4$  and  $\text{ZnAl}_2\text{S}_4(1-x)\text{Se}_{4x}$  have been studied. In the spinel  $\text{ZnAl}_2\text{S}_4$ , up to 20% of Zn atoms can be replaced by Cd, in the other two systems;  $\text{ZnAl}_2\text{S}_4$  has no detectable homogeneity range. The thiogallate phases have much

broader ranges of homogeneity. At  $950^{\circ}\text{C}$ ,  $\text{ZnAl}_2\text{Se}_4$  undergoes a reversible phase transformation to a wurtzite type phase and this same type of transition was also observed for solid solutions,  $\text{ZnAl}_2\text{S}_4(1-x)\text{Se}_{4x}$  with  $x = 1$  to  $0.3$ .<sup>160</sup> Structure refinement has also been carried out for the spinel  $\text{CdGa}_2\text{S}_4$ .<sup>161</sup> Crystal structure determinations of  $\text{Ga}_2\text{Sn}_2\text{S}_5$  show that the structure is essentially built from alternating sheets of  $(\text{GaS}_4)_n$  tetrahedra and sheets of  $(\text{Sn}_2\text{S}_{11})_n$ . The  $\text{GaS}_4$  tetrahedra are linked in groups of two, sharing their opposite edges. The  $\text{Sn}_2\text{S}_{11}$  unit has the two tin atoms in different environments both of which are very asymmetric.<sup>162</sup> The new compound  $\text{Ba}_4\text{Ga}_4\text{S}_{10}$  crystallises in the space group  $\text{C2/c}$  and has a structure in which there are adamantane-like  $\text{Ga}_4\text{S}_{10}^{8-}$  anions (45) isosteric to the neutral  $\text{P}_4\text{S}_{10}$  molecule. The  $\text{Ba}^{2+}$  ion is coordinated by seven sulphur atoms.<sup>163</sup>



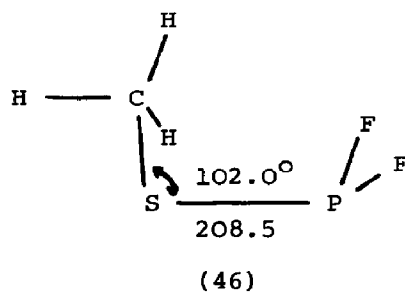
(45)

The crystal structure of  $\text{KIn}_5\text{S}_8$  shows the indium atoms to have four and six-fold coordination and the potassium atoms to have six foldprismatic coordination.<sup>164</sup>

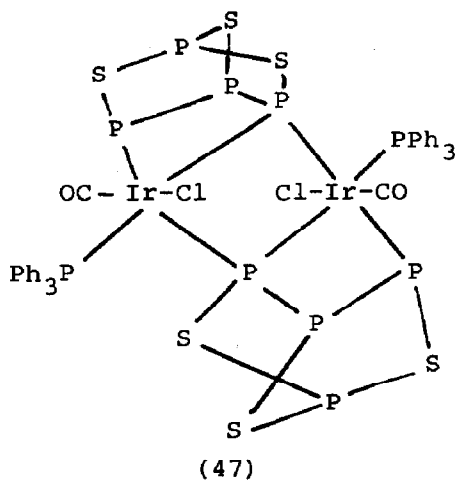
The charge distribution in some lead chalcogenides has been studied by X-ray diffraction methods. All form the  $\text{NaCl}$  structure and the results suggest a predominantly covalent bonding.<sup>165</sup> Potentiometric titration of  $0.01\text{M}$  solutions of  $\text{Na}_6\text{Si}_2\text{S}_6$ ,  $\text{Na}_6\text{Si}_2\text{Se}_6$ ,  $\text{Na}_2\text{Ge}_2\text{S}_6$  and  $\text{Na}_6\text{Ge}_2\text{Se}_6$  in methanol with bromine has been used to determine thermodynamic data of reactions which take place by scission of the  $\text{Si-Si}$  or  $\text{Ge-Ge}$  bonds. The bond energies of these homonuclear bonds were estimated.<sup>166</sup>

Red and white phosphorus are oxidised by aqueous solutions of alkalipolysulphides to give mixtures of thiophosphates containing phosphorus in different oxidation states. Some novel thiophosphates were isolated from these mixtures and possessed chains or

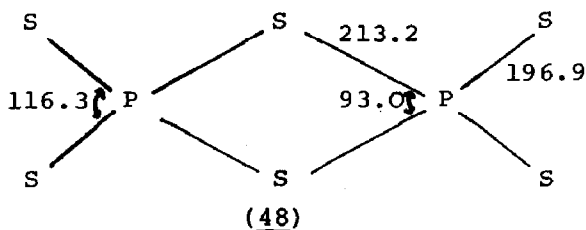
rings of directly connected phosphorus atoms. The reaction of  $P_4S_3$  under the same conditions also led to the formation of thiopolyphosphates with P-P bonds.<sup>167</sup> Gaseous  $PSCl$  has been prepared by the reaction of silver with  $PSCl_3$  at about 1100K, and isolated in an argon matrix at 15K. The use of  $^{34}S$  enriched samples showed that phosphorus is the central atom in this molecule which has an S-P-Cl angle of approximately  $110^\circ$ .<sup>168</sup> A mass spectrometric study of the above reaction gave the heat of formation and entropy of  $PSCl$  to be -11.9 kJ/mole and 285.93 J/K.mol. respectively.<sup>169</sup> The molecular structures of  $S(PF_2)_2$  and  $Se(PF_2)_2$  in the gas phase have been determined by electron diffraction. The parameters  $r(P-S) = 213.2\text{pm}$ ,  $PSP = 91.3^\circ$  and  $r(P-Se) = 227.3\text{pm}$ ,  $P-Se-P = 94.6^\circ$  were obtained. The structure of  $PF_2(SMe)$  was also determined; three conformations fitted the observed data almost equally well but the most favoured structure has the  $PF_2$  group twisted  $106^\circ$  away from the position in which the C-S bond lies anti to the bisector of the FPF angle (46).<sup>170</sup>



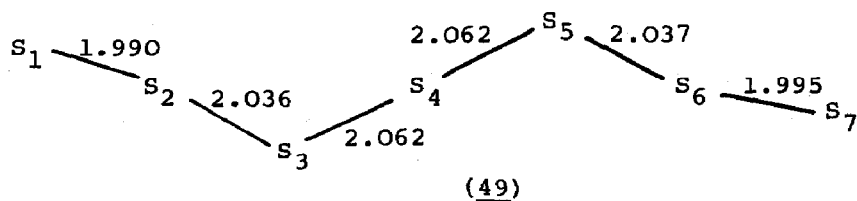
Pure forms of the  $A_4B_3$  molecules with the compositions  $P_xAs_{4-x}S_3$  and  $P_4S_xSe_{3-x}$  ( $x = 1, 2, 3$  and  $1, 2$  respectively) have been isolated by high performance liquid chromatography on an RP-18 column (solvent CS; eluent methanol/water).<sup>171</sup> The reaction  $P_4S_3$  with  $IrCl(CO)(PPh_3)_3$  in benzene at  $60^\circ C$  gives the air stable, and practically insoluble complex  $[Ir(P_4S_3)(PPh_3)_2Cl(CO)]$ . X-ray structure analysis showed the compound to be a dimeric iridium(III) derivative, the  $P_3$  ring of the  $P_4S_3$  molecule having opened and one  $PPh_3$  group per metal centre being displaced (47). The crystal structure of  $\alpha-P_4S_3$  has been investigated as a function of temperature from 4K to 309K by X-ray and neutron diffraction. No phase transitions were observed below 314K and the temperature variation of the intramolecular distances is negligible, although the intermolecular distances change significantly indicating that



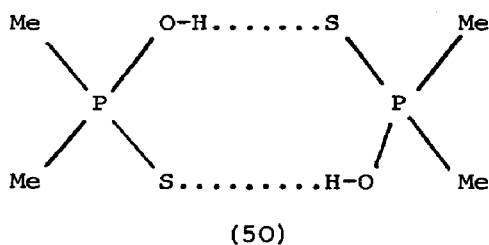
the  $P_4S_3$  molecules are rigid.<sup>173</sup> The structure of a second form of  $Ag_4P_2S_6$  is the same as that of  $Ag_4P_2Se_6$ , with the sulphur atoms adopting an approximately hexagonal close-packed arrangement and the  $P_2S_6^{4-}$  groups forming almost planar layers which alternate with double layers of  $Ag^+$  ions.<sup>174</sup>  $Tl_2P_2S_6$  has been shown to consist of discrete  $P_2S_6^{2-}$  anions (48) in the form of a hexathiometadiphosphate group where the two P atoms are linked by two sulphur bridges.<sup>175</sup>



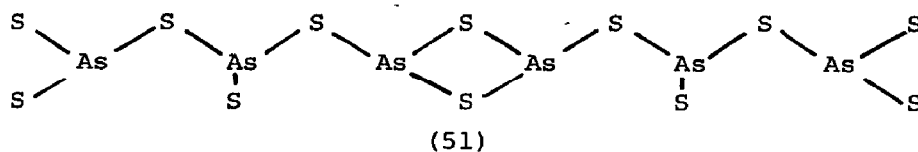
The  $S_7^{2-}$  anion has been obtained by the reaction of  $MoS_9^{2-}$  with an excess of the sodium salt of the diethyldithiocarbamate ion in acetonitrile solution. A structure determination of the tetraphenylphosphonium salt of  $S_7^{2-}$  showed the ion to be a right-handed non-branched helix (49) with very short terminal S-S bonds.



The torsional angles in the chain are S(2)-S(3) 73.28, S(3)-S(4) 74.41, S(4)-S(5) 65.22, S(5)-S(6) 79.86°. The salt dissolves in polar solvents to give blue solutions with absorption bands at 610, 470, 345 and 304nm.<sup>176</sup> The structures of dimethylthiophosphinic acid (50) and of dicyclohexylthiophosphinic acid have been determined at 140K. Both compounds have unit cells containing two molecules which form centrosymmetric dimers by nearly linear O-H...S hydrogen bonds. The O...S bond distances are 3.121 and 3.148Å respectively.<sup>177</sup>



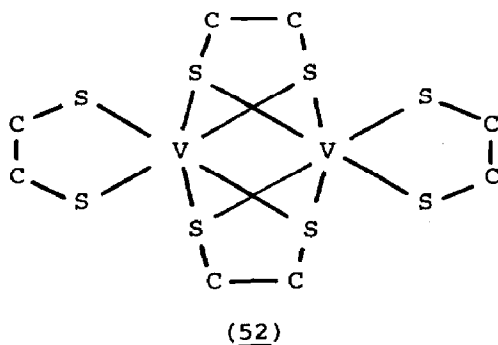
Hydrothermal synthesis in the system  $\text{Tl}_2\text{S}-\text{PbS}-\text{Ag}_2\text{S}_3$  has been used to prepare single crystals of the new compound  $\text{PbTlAs}_3\text{S}_6$ . The lead atom is coordinated by seven S atoms ( $\text{Pb-S} = 3.074\text{\AA}$ ) to form infinite  $\text{PbS}_3$  layers. The Tl atom is coordinated also by seven sulphur atoms ( $\text{Tl-S} = 2.300\text{\AA}$ ) to form infinite  $\text{TlS}_5$  double chains. The As atoms are bonded to three sulphur atoms forming a trigonal bipyramid with the arsenic atom at the apex. The pyramids are connected to form  $\text{As}_6\text{S}_{12}$  groups (51).<sup>178</sup>



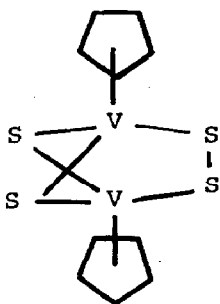
The crystal structure of  $\text{Tl}_2(\text{Sb,As})_{10}\text{S}_{16}$  contains  $\text{AsS}_3$  and  $\text{SbS}_3$  pyramids together with  $\text{SbS}_5$  coordination polyhedra.<sup>179</sup>  $\text{TlSbS}_2$  has a structure built up from sheets formed by  $\text{SbS}_4\text{E}$  trigonal bipyramids linked together. The Sb-S bond lengths lie in the range 2.41 to 2.96Å. The sheets are linked together with weak  $\text{Tl}\cdots\text{S}$  (3.50-3.66Å),  $\text{Tl}\cdots\text{Sb}$  (3.60-3.73Å) and  $\text{Tl}\cdots\text{Tl}$  (3.62Å) interactions.<sup>180</sup> The structures of  $\text{Pb}_2\text{Sb}_2\text{S}_5$  and  $\text{Sn}_2\text{Sb}_2\text{S}_5$ <sup>181</sup> and of two forms of  $\text{BaBi}_2\text{S}_4$ <sup>182</sup> have also been determined. The following Main Group element-sulphide phase systems have been

studied; Ge-S-Tl,<sup>183</sup> GaS-PbS and GaS-Pb,<sup>184</sup> BiF<sub>3</sub>-Bi<sub>2</sub>S<sub>3</sub>,<sup>185</sup> and SbF<sub>3</sub>-Sb<sub>2</sub>S<sub>3</sub>.<sup>186</sup>

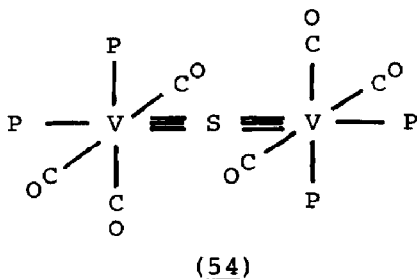
Polytypic Ti<sub>1+x</sub>S<sub>2</sub> (x = 0.25 to 0.33) has been studied by electron- and X-ray diffraction. Ordered titanium atoms and vacancies were observed with superstructures resulting from infra- and inter-layer order found for the composition Ti<sub>1.32</sub>S<sub>2</sub>.<sup>187</sup> Reaction of VCl<sub>3</sub> with 1,2-ethanedithiolate gives the binuclear complex [V<sub>2</sub>(SC<sub>2</sub>H<sub>4</sub>S)<sub>4</sub>]<sup>2-</sup> which is the first vanadium-sulphur compound in which the ligands have "pure thiolate character". The metal atoms in the dinuclear anion (52) are symmetrically bridged by the sulphur atoms of two 1,2-ethanedithiolate ligands in such a way that an almost square arrangement of sulphur atoms results.<sup>188</sup>



The unprecedented and unanticipated structures of (Pr<sup>i</sup>Cp)<sub>2</sub>V<sub>2</sub>S<sub>4</sub> and the acetylene adduct of Cp<sub>2</sub>V<sub>2</sub>S<sub>4</sub> have been described. The two (Pr<sup>i</sup>Cp)V moieties (53) are bridged by an  $\mu$ - $\eta^1$ -S<sub>2</sub> and two  $\mu$ -S ligands with average V-S( $\mu$ -S) and V-S(S<sub>2</sub>) distances of 2.21 and 2.27 Å respectively.<sup>189</sup>



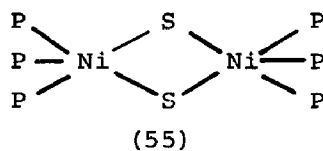
The X-ray structure of the red diamagnetic complex,  $[\text{V}(\text{CO})_3\text{diphos}]_2\text{S}$  reveals a centrosymmetric molecule (54) with very short V-S distances (217.2pm). Values for comparison are not available since this is the first carbonyl vanadium compound containing sulphido ligands but in other sulphur containing compounds V-S distances are always greater than 230pm.<sup>190</sup>



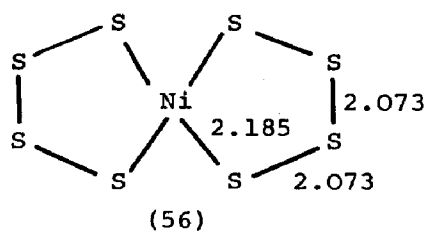
The thermal decomposition of molybdenum trisulphide has been followed using EXAFS.<sup>191</sup> The hetero metal sulphur aggregates  $[\text{Co}(\text{WS}_4)_2]^{n-}$  with variable electron population  $n = 2, 3$ , have been isolated as salts and characterised by various physical methods including X-ray structure analysis. Experimental and theoretical investigations show that due to a strong metal-ligand electron delocalisation,  $\text{WS}_4^{2-}$  like  $\text{MoS}_4^{2-}$  is a non-innocent ligand and that the additional charge upon reduction is located mainly at the sulphur atom.<sup>192</sup> The structure of 3c-type  $\text{Fe}_7\text{S}_8$ , grown by vapour phase transport has been reexamined.<sup>193</sup> The mixed valency compound  $\text{Na}_3\text{Fe}_2\text{S}_4$  which is formed in iron-sodium polysulphide melts, is oxidised and hydrated in air to  $\text{NaFeS}_2 \cdot x\text{H}_2\text{O}$  where  $x$  is approximately 2.<sup>194</sup> Salts previously reported to contain the iron-sulphur cluster nitrosyl anion  $\text{Fe}_3\text{S}_2(\text{NO})_5^-$  have now been shown to be identical with those containing the well known anion  $\text{Fe}_4\text{S}_3(\text{NO})_7^-$ .<sup>195</sup>

New syntheses of  $\text{Fe}_2\text{S}_2\text{Cl}_4^{2-}$ , and  $\text{Fe}_2\text{OCl}_6^{2-}$  and terminal oxo/sulphido ligand substitution reactions have been devised using the reagents  $(\text{Me}_3\text{Si})_2\text{S}$ ,  $\text{NaSSiMe}_3$  and  $\text{NaOSiMe}_3$  in acetonitrile solutions.<sup>196</sup> The compound  $\text{Na}_6\text{CoS}_4$  has been shown to be isotypic with  $\text{Na}_6\text{ZnO}_4$  and to contain almost regular  $\text{CoS}_4$  tetrahedra with average Co-S distances of 235pm.<sup>197</sup> Members of the systems  $\text{Co}_{1-x}\text{Ru}_x\text{S}_2$  with  $x$  from 0 to 1 and  $\text{Rh}_{1-x}\text{Ru}_x\text{S}_2$  with  $x$  from 0.5 to 1 have been prepared and their crystallographic and magnetic properties studied.<sup>198</sup> The nickel sulphide  $\text{Ni}_{17}\text{S}_{18}$  has been shown to have a vacancy ordered superstructure of the  $\text{NiAs}$  type.<sup>199</sup>

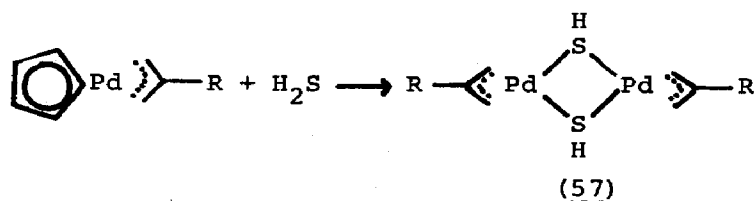
The compound  $[(\text{triphos})\text{Ni}(\mu\text{-S}_2)\text{Ni}(\text{triphos})]\text{ClO}_4$  has been shown to be a novel nickel dimer bridged by two sulphur atoms in which the  $\text{Ni}_2\text{S}_2$  bridging framework is crystallographically planar with a Ni-Ni distance of  $3.865\text{\AA}$  (55). Since the S-S distance of  $2.208\text{\AA}$  indicates a weakened bond, the structure represents a rare example of a  $\eta^2$  binuclear ligand that is coplanar with the two metals.<sup>200</sup>



The tetraethylammonium salt of  $\text{Ni}(\text{S}_4)_2^{2-}$  has been isolated and its crystal structure determined. This is the first binary nickel-sulphur complex and the first complex to contain only  $\text{S}_4^{2-}$  ligands (56).

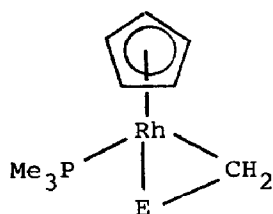


The anion has point symmetry  $D_2$  and exists as a spirobicycle in which the central nickel atom is surrounded by an approximately square planar array of four sulphur atoms.<sup>201</sup>  $\eta^3$ -Allyl or  $\eta^3$ -methallyl- $\eta^5$ -cyclopentadienylpalladium reacts with hydrogen sulphide at  $-78^\circ\text{C}$  with selective cleavage of the cyclopentadienyl group to give the dimeric thermolabile  $\eta^3$ -allyl or  $\eta^3$ -methallyl hydrogensulphidopalladium compound (57) which decomposes at temperatures above  $-60^\circ\text{C}$  to palladium sulphide and propene or isobutene.<sup>202</sup>



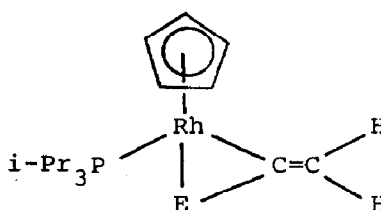
The reactions of (57) to give mono and bimetallic polynuclear  $\eta^3$ -allyl metal-sulphur complexes of nickel have also been studied.<sup>203,204</sup>

A radiochemical method for analysing the adsorption and desorption of sulphur on polycrystalline copper has been described.<sup>205</sup> Crystalline (3-methylpentane-3-thiolato)silver has been shown to be one dimensionally nonmolecular. Silver and sulphur atoms constitute the cores of chains which are approximately linear and well separated from each other by the alkyl substituents that radiate from the chains. Each chain contains two separate strands comprising approximately planar zig-zag S-Ag-S-Ag-S-Ag-S segments which are connected at their ends by single Ag atoms linking segments on one side of the chain to parallel segments on the opposite side of the chain.<sup>206</sup> SCF- $X_\alpha$ -SW calculations have been carried out on the model compounds  $[M(X_2)(PH_3)_4]^+$  ( $M = Rh, Ir, X = S, Se$ ) in order to investigate the electronic structure and bonding in complexes of side-on-bonded disulphur and diselenium. In agreement with experiment the calculations predict a bond order of about 1 for the X-X bond and reveal that the M- $X_2$  covalent interaction increases along the sequence  $RhSe_2 < IrSe_2 < RhS_2 < IrS_2$ .<sup>207</sup> Using NaSH, NaSeH or NaTeH as substrates the rhodium complex (58) was prepared in good yield.<sup>208</sup>



E = S, Se or Te

(58)



E = S, Se or Te

(59)

The chalcogenoketenerhodium compounds (59) have been prepared by reaction of the corresponding vinylidene complex with sulphur (in hexane), selenium and tellurium (in benzene). The reactivity of the chalcogenes decreases markedly from sulphur via selenium to tellurium and red selenium was found to be more reactive than the grey allotrope. The sulphur and selenium complexes were found to be air stable but the tellurium compound oxidised readily.<sup>209</sup>

The first chalcogenide analogues of the platinum bronzes,  $LaPd_3S_4$  has been prepared by heating a stoichiometric combination

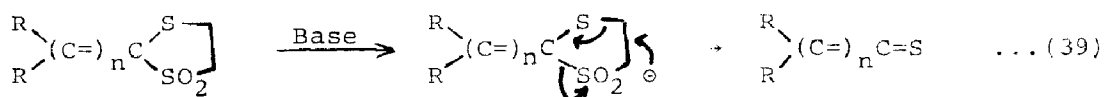
of the elements at 1125K in a sealed, evacuated silica tube lined with carbon.<sup>210</sup> The compound  $\text{Pd}_3(\text{PS}_4)_2$  has been synthesised from the element at 600°C and its crystal structure derived from powder data.<sup>211</sup> Structural data has also been obtained for the following sulphides  $\text{Pb}_{1.6}\text{In}_8\text{Bi}_4\text{S}_{19}$ ,<sup>212</sup>  $\text{Mo}_6\text{Br}_6\text{S}_3$ ,<sup>213</sup>  $\text{YbS}_{1.34-1.42}$ ,<sup>214</sup>  $\text{LaYbS}_3$ ,<sup>215</sup>  $(\text{FeV})_3\text{S}_4$ <sup>216</sup> and  $\text{GaLa}_3\text{OS}_5$ .<sup>217</sup>

#### 6.2.6 Bonds to Carbon

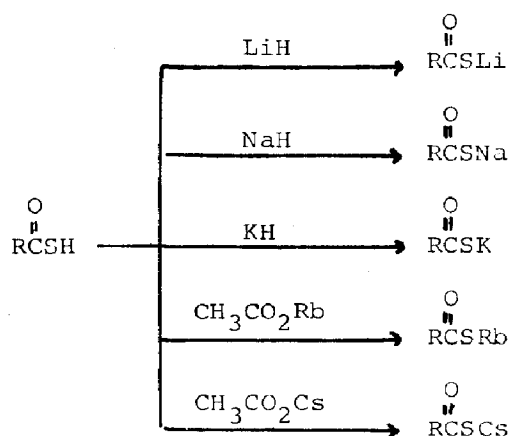
The preparation of  $\text{CF}_2(\text{SF}_3)_2$  from  $\text{CS}_2$  and elemental fluorine has been described. In the presence of  $\text{CsF}$ , further oxidation by  $\text{F}_2$  and  $\text{ClF}$  may be achieved with the formation of  $\text{F}_2\text{C}(\text{SF}_5)_2$  and  $(\text{trans-ClSF}_4)_2\text{CF}_2$  respectively.<sup>218</sup> The i.r. spectrum of  $(\text{CF}_3\text{S})_2\text{CS}$  in gas and solid phase and isolated in noble gas matrix together with the Raman spectrum in the liquid phase have been recorded. Analysis of the spectrum shows the compound to consist of a complex mixture of conformers, the distribution of which could be changed by photolysis of the matrix. Photochemical decomposition could be induced at a threshold of 300nm the products being an equimolar mixture of  $\text{CF}_3\text{SCF}_3$  and  $\text{CS}_2$ .<sup>219</sup>

When the products of the reaction between fluorine atoms and  $\text{CH}_3\text{SH}$  are frozen in a large excess of Ar at 14K, the absorptions of isolated and hydrogen bonded HF are observed. Using deuterium substituted methanethiols it was shown that the reaction products were HF hydrogen bonded to  $\text{CH}_3\text{S}$  and  $\text{CH}_2\text{SH}$ .<sup>220</sup> Nonempirical molecular electronic structure theory has been used to study the electronic ground state of the dimer of carbon monosulphide  $\text{SCCS}$ .<sup>221</sup> The influence of the ionic strength on the adsorption of thiocyanate ions on mercury has been studied.<sup>222</sup> A crystal structure determination of the complex formed between dibenzo-14-crown 4 and  $\text{LiSCN}$  has shown that the  $\text{Li}^+$  cation is pentacoordinated to the four ethereal oxygens and to the nitrogen atom of the  $\text{SCN}^-$  ion, in an almost square pyramidal geometry.<sup>223</sup> The addition of 0.2% of  $\text{OCS}$  to a  $\text{CH}_4\text{-O}_2$  flame has been shown to give the following sulphur containing negative ions,  $\text{S}^-$ ,  $\text{SH}^-$ ,  $\text{SO}^-$ ,  $\text{SO}_2^-$ ,  $\text{S}_2^-$ ,  $\text{SO}_3^-$ ,  $\text{HSO}_3^-$  and  $\text{HSO}_4^-$ . Analysis of the species along the flame showed the rapidity with which  $\text{OCS}$  is oxidised through  $\text{SH}$  and  $\text{SO}$  to  $\text{SO}_2$ .<sup>224</sup>

A novel route to thiocarbonyl compounds has been reported in which the carbonyl function is initially protected as the dithiolane S,S-dioxide and is released by treatment with base

(equation 39).<sup>225</sup>

A series of alkalimetal thiocarboxylates (Scheme 5) has been found to be readily obtained in high yields by the reaction of thiocarboxylic acids with either metal hydrides or acetates.<sup>226</sup>



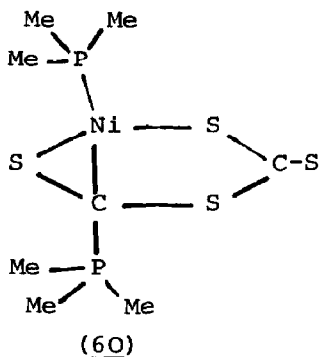
Scheme 5

The reaction of lithium triphenylstannanedithiocarboxylate with 1,n-dibromoalkanes in THF solution yields for n from 3 to 6, stable 1,n-bis(triphenylstannanedithiocarboxylic)alkylene esters, whereas for n = 1 or 2 elimination takes place. The propylene and butylene esters have been shown to form neutral dinuclear complexes of the type M-L-M with monodentate coordination of the thiocarbonyl group on each side where M is a tungsten or manganese carbonyl.<sup>227</sup> Some alkyl esters of triorganostannane dithiocarboxylic acid have also been shown to complex with metal carbonyl complexes of W, Mn and Re.<sup>228</sup>

A large number of papers have again been published by Gattow in the series "On Chalcogenolates". Topics covered include, the synthesis of alkali metal N-cyan-guanidino monothioformates  $\text{M}[\text{SOC}=\text{NH}-\text{C}(\text{NH}_2)=\text{N}-\text{CN}]$ ;<sup>229</sup> the synthesis and reaction of alkali metal N-cyanomonothiocarbimides  $\text{M}_2[\text{SOC}=\text{N}-\text{CN}]\cdot\text{H}_2\text{O}$ ;<sup>230-232</sup> the reactions of alkali metal chlorides with  $\text{CS}_2$ ;<sup>233</sup> studies on

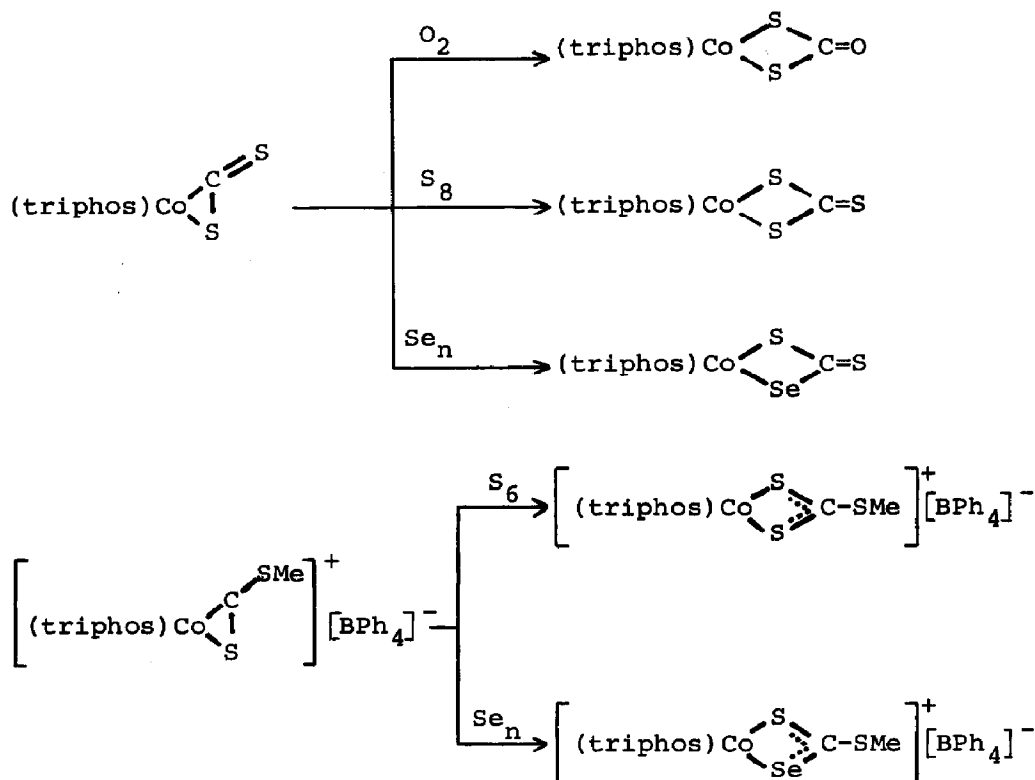
N-cyanformamidinodithiocarbamic acid,<sup>234,235</sup> diesters of cyanimino-diformic acid,<sup>236</sup> studies on Rhodanines,<sup>237-239</sup> and the crystal structures of guanidinodithioformic acid<sup>240</sup> and oxovanadium(V) ethylxanthate.<sup>241</sup>

Alkylisocyanides have been shown to react with  $B_9H_{11}E$  ( $E = S$  or  $Se$ ) to initially form two isomeric  $B_9H_{11}E \cdot CNR$  compounds.<sup>242</sup>  $(Ph_3P)_2Pd(N_3)_2$  reacts with  $CS_2$  by 1,3-cycloaddition to give the thiatriazoline,5 thionate complex  $(Ph_3P)_2Pd(N_3CS_2)_2$ . The reaction of  $(Ph_4As)_2(Co(N_3)_4)$  with  $CS_2$  gave the complex  $[Ph_4As]_2[Co(NCS)_4]$  and the intermediate  $[Ph_4As]_2[Co(N_2CS_2)_4]$  was detected by its electronic spectrum.<sup>243</sup> The reaction of  $CS_2$  with some Cu(I) phosphine complexes have also been investigated and the crystal structure of  $[(PPh_3)_2Cu(S_2CPEt_3)]BPh_4$  determined.<sup>244</sup> The reactions of  $CS_2$  with a number of Ni(O) phosphine complexes have been shown to give two classes of Ni- $CS_2$  coordination compounds,  $[Ni(CS_2)L]_2$  when  $L = PPh_3$ ;  $P(p\text{-tol})_3$  and  $PCy_3$  and  $Ni(C_2S_4PR_3)(PR_3)$  when  $R = Me$  or  $Et$ . A crystal structure determination shows the complex  $Ni(SC(S)SC(PMe_3)S)(PMe_3)$  to have the structure (60).<sup>245</sup>



$CaHg(SCN)_4 \cdot nH_2O$  where  $n = 2$  or  $3$  has been isolated from an aqueous solution of  $Ca(NCS)_2 \cdot 4H_2O$  and  $Hg(SCN)_2$ . The dihydrate contains nearly tetrahedral  $Hg(SCN)_4$  and octahedral  $Ca(OH_2)_2(NCS)_4$  groups which are joined by  $Hg-SCN-Ca$  bridges, in contrast the trihydrate structure is based on the diamond net.<sup>246</sup> The reaction of trimeric thioformaldehyde with  $AgAsF_6$  in liquid  $SO_2$  leads to the compound  $[Ag_2\{(CH_2S)_3\}_5][AsF_6]_2 \cdot SO_2$ . The isolated cations, of the form  $L_2AgLA_gL_2$  ( $L = \text{ligand}$ ) display irregular coordination geometry at silver with one silver atom coordinated by four sulphur atoms from three ligands and the other by five sulphur atoms from three ligands.<sup>247</sup> The reactions of oxygen, sulphur and

selenium with some  $\eta^2$ -CS<sub>2</sub> and  $\eta^2$ -CS<sub>2</sub>Me cobalt complexes have been shown to give the products shown in Scheme 6.<sup>248</sup>



Scheme 6

The reaction of  $\text{RhCl}_3$  with an aqueous solution of  $\text{KSCN}$  has been shown not to yield pure  $\text{Rh}(\text{SCN})_6^{3-}$  as was previously thought, but a mixture of the bond isomers  $[\text{Rh}(\text{NCS})_n(\text{SCN})_{6-n}]^{3-}$  where  $n = 0$  to 3.<sup>249</sup> Similar isomeric forms were also found for the Ir complex.<sup>250</sup>

### 6.3 SELENIUM

#### 6.3.1 The Element

A novel application of chalcogenide esters to purify selenium and tellurium to the 99.999% purity level has been described. Crude selenium and tellurium were first converted to their respective oxides by treatment with concentrated nitric acid. The oxides were then condensed with alcohols or diols to obtain the corresponding esters which on reduction with hydrazine in organic

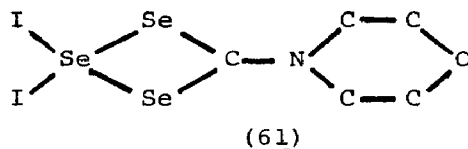
media, provided high purity elemental selenium and tellurium.<sup>251</sup> The extraction of selenium(IV) from hydrogen halide solutions by tetrasubstituted alkyldiamines has been studied. The compositions of the complexes extracted were determined and an extraction method developed for the separation of selenium from tellurium, tin and lead and determining it in semiconducting materials.<sup>252</sup>

### 6.3.2 Bonds to Halogens

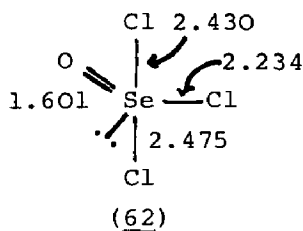
The electronic structures of sulphur, selenium and tellurium hexafluoride have been calculated by the discrete variation  $X_\alpha$  method. The marked increase in the electron affinity in  $\text{SeF}_6$  compared with  $\text{SF}_6$  was related to the large decrease in the antibonding character of the LUMO in the case of  $\text{SeF}_6$ . The decrease in the electron affinity on going from  $\text{SeF}_6$  to  $\text{TeF}_6$  was attributed to the increase in  $\text{TeF}_6$ , in the energy of all the valence molecular orbitals ( $a_{1g}$ ) due to the higher energy of the 5s atomic orbitals of the Te atom compared with the 4s of Se.<sup>253</sup>

The electron diffraction patterns of the vapour from a gas jet of  $\text{SeCl}_4$  with a nozzle temperature of  $175^\circ\text{C}$  showed the vapour to consist of  $\text{SeCl}_2$  (80%) and  $\text{Cl}_2$ . The bond distance in  $\text{SeCl}_2$  is  $2.157\text{\AA}$  and the valence angle  $99.6^\circ$ .<sup>254</sup> Elemental selenium dissolves in solutions of  $\text{SeO}_2$  in concentrated  $\text{HCl}$  to a small extent to give strongly yellow solutions. Gravimetric analysis and spectrophotometric studies show that the principal species in equilibrium with  $\text{SeOCl}_2$  is  $\text{Se}_2\text{Cl}_2$ . A completely satisfactory interpretation of these results requires however the presence of  $\text{SeCl}_2$  also.<sup>255</sup> The crystal structure of  $\text{Re}_6\text{Se}_8\text{Cl}_2$  has been determined.<sup>256</sup> The compounds  $\text{Nb}_2\text{Se}_2\text{Br}_6$ ,  $\text{Nb}_2\text{Te}_2\text{Br}_6$  and  $\text{Nb}_2\text{Te}_2\text{I}_6$  have been prepared from the elements in sealed quartz ampoules at  $1073\text{K}$ . These stable, crystalline solids, exhibiting metallic lustre, undergo several reversible phase transitions with temperature. The structures consist of one-dimensional infinite chains of halogen bridged  $\text{Nb}_2(\text{Y}_2)\text{X}_4$  units containing single side-on bonded  $\text{Nb}_2$  and  $\text{Y}_2$  dumbbells forming a quasi tetrahedral  $\text{Nb}_2\text{Y}_2$  cluster with  $\text{Nb-Nb} = 283.2, 287.5, 293.2\text{pm}$ ,  $\text{Se-Se} = 230.5\text{pm}$  and  $\text{Te-Te} = 267.0$  and  $268.5\text{pm}$ .<sup>257</sup> The reaction of bis(morpholino-selenocarbonyl)triselenide,  $\text{Se}_3[\text{C}(\text{Se})\text{NC}_4\text{H}_8\text{O}]_2$  with iodine in  $\text{CH}_2\text{Cl}_2$  leads to the formation of the compound  $[\text{OC}_4\text{H}_8\text{NCSe}_3]\text{I}$ . A crystal structure determination showed the compound to contain the cationic units (61) and to consist of polymeric

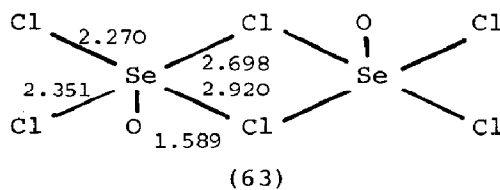
--I---Se---I---Se---I--- chains running along the c axis held together by van der Waals contacts.<sup>258</sup>



Several trifluoro- and tribromoselenate(IV) compounds,  $\text{MSeOF}_3$  and  $\text{MSeOBr}_3$  have been prepared. I.r. and Raman spectroscopic data are consistent with the trigonal-bipyramidal stereochemistry predicted by VSEPR theory with the oxygen and lone electron pair equatorial. Anion polymerisation via oxygen or halogen bridging is very weak for  $\text{MSeOF}_3$  with  $\text{M} = \text{K}, \text{Cs}$  but becomes significant for  $\text{MSeOCl}_3$  where  $\text{M} = \text{K}$  and for  $\text{MSeOBr}_3$  with  $\text{M} = \text{Me}_4\text{N}$ . Compounds with larger cations contain isolated  $\text{SeOX}_3^-$  anions.<sup>259</sup> A crystal structure determination of the phenylarsonium salt of  $\text{SeOCl}_3^-$  (prepared from  $\text{SeOCl}_2$  and  $\text{As}(\text{Ph})_4\text{Cl}$  has been carried out at low temperature. The salt contains a novel type of  $\psi$  trigonal bipyramidal  $\text{SeOCl}_3^-$  and shows no association to form dimers or trimers (62).



The triethylammonium salt shows the  $\text{SeOCl}_3$  unit to be present as a dimer  $\text{Se}_2\text{O}_2\text{Cl}_6^{2-}$ , as found in the  $\text{PPh}_4^+$  salt, with two  $\text{SeOCl}_4$  pyramids linked through a  $\text{Cl}\cdots\text{Cl}$  edge and the lone pairs trans to the axial Se-O bonds (63).<sup>260</sup>

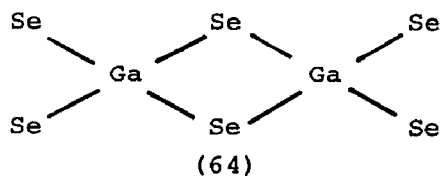


### 6.3.3 Bonds to Oxygen

The compound  $\text{Au}_2(\text{SeO}_3)_2\text{O}$  has been prepared by the reaction of gold and excess selenic acid in a sealed tube at 533K. A crystal structure determination shows the gold atoms to be bridged by oxygen and selenite ions.<sup>261</sup> The crystal structure of  $\text{Pb}_2\text{Cu}_5(\text{SeO}_3)_6(\text{UO}_2)_2(\text{OH})_6 \cdot 2\text{H}_2\text{O}$  has been shown to consist of layers of  $\text{Cu}(\text{O},\text{OH},\text{H}_2\text{O})_6$  octahedra linked to each other by oblique chains which are formed by oxygen bridges linking uranyl and selenium ions.<sup>262</sup> The crystal structure of  $\text{Cu}_4(\text{UO}_2)(\text{SeO}_3)_2(\text{OH})_6$  consists of layers of  $\text{Cu}(\text{O},\text{OH})_6$  octahedra which are linked to each other by two oblique chains of Se-U-Se which cross one another.<sup>263</sup> Phase equilibria in the  $\text{Re}_2\text{O}_7$ - $\text{SeO}_2$  system have been measured.<sup>264</sup>

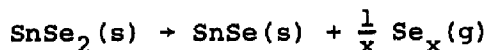
### 6.3.4 Selenides

The entirely ordered monoclinic phase of  $\text{Ga}_2\text{Se}_3$  has been shown to be a superstructure of the basic distorted sphalerite-type. Ordering of metal vacancies involved two different Se atom surroundings.<sup>265</sup> The moisture sensitive ternary selenide,  $\text{Cs}_6\text{Ga}_2\text{Se}_6$  has been prepared from the binary selenides  $\text{Cs}_2\text{Se}$  and  $\text{Ga}_2\text{Se}_3$ , its structure comprises gallium atoms occupying tetrahedral holes in pairs between layers formed by Cs and Se ions leading to the formation of double tetrahedral isolated  $\text{Ga}_2\text{Se}_6^{2-}$  ions (64).<sup>266</sup>

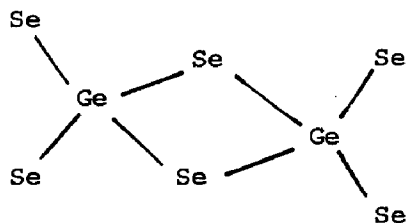


The ternary selenide  $\text{SrGa}_2\text{Se}_4$  has been shown to have a structure which is a new variant of the  $\text{TlSe}$  structure.<sup>267</sup> The ternary chalcogenides  $\text{CuGaSe}_2$  and  $\text{CuGaTe}_2$  have been found to undergo a phase transition from the chalcopyrite type to the  $\text{NaCl}$  structure at 300K and pressures of 12.5 GPa and 8 GPa respectively. The phase transition is accompanied by a volume change of 8.6 and 3.8% for the selenide and telluride respectively.<sup>268</sup> Quaternary compounds of the type  $\text{AB}_2\text{X}_3\text{Y}$  have been synthesised at high pressures and temperatures.  $\text{AgIn}_2\text{Se}_3\text{I}$ ,  $\text{AgIn}_2\text{Te}_3\text{I}$ ,  $\text{CuIn}_2\text{Se}_3\text{Br}$ ,  $\text{CuIn}_2\text{Se}_3\text{I}$ ,  $\text{CuIn}_2\text{Te}_3\text{Cl}$ ,  $\text{CuIn}_2\text{Te}_3\text{Br}$  and  $\text{CuInTe}_3\text{I}$  were found to have the defect zinc blende structure, whilst  $\text{AgIn}_2\text{S}_3\text{Cl}$ ,  $\text{AgIn}_2\text{S}_3\text{Br}$ ,

$\text{AgIn}_2\text{Se}_3\text{Cl}$ ,  $\text{AgIn}_2\text{Se}_3\text{Br}$  and  $\text{AgIn}_2\text{Se}_3\text{I}$  have the spinel structure and  $\text{AgIn}_2\text{Te}_3\text{Cl}$  and  $\text{AgIn}_2\text{Te}_3\text{Br}$  the defect rocksalt structure. A second form of  $\text{CuIn}_2\text{Se}_3\text{I}$  was found to have a structure intermediate between the ZnS and spinel structure. A survey of the different reaction pathways of  $\text{AB-B}_2\text{X}_3$  mixtures at high pressures and temperatures was given.<sup>269</sup> Two new compounds,  $\text{Tl}_5\text{ISe}_2$  and  $\text{Tl}_6\text{I}_4\text{Se}$ , have been found at the  $\text{Tl}_2\text{Se}$  corner of the  $\text{TlI-T}_2\text{Se}$  systems.  $\text{Tl}_6\text{I}_4\text{Se}$  was found to be isotypic with a class of compounds found in the  $\text{TlX-Tl}_2\text{S}$  systems. The compound  $\text{Tl}_6\text{Cl}_4\text{S}$  was found to have a structure based on that of  $\text{TlCl}$  in which  $1/5$  of the Tl or Cl atoms are substituted by  $\text{Tl}_2\text{S}$  in a regular manner.<sup>270</sup> Experimental mass-loss data for the sublimation of  $\text{SnSe}$  has yielded the values  $\Delta H_{298,f}^\circ = -86.4 \text{ kJ}\cdot\text{mol}^{-1}$  and  $S_{298} = 89.0 \text{ JK}^{-1}\text{mol}^{-1}$  and from the decomposition reaction:



$\Delta H_{298,f}^\circ = -118.1 \text{ kJ mol}^{-1}$  and  $S_{298} = 111.8 \text{ JK}^{-1}\text{mol}^{-1}$  for  $\text{SnSe}_2$  were obtained.<sup>271</sup> The stoichiometric 1:1 reaction of sodium selenide with  $\text{GeS}_2$  in aqueous solution has been shown to give the selenogermanate  $\text{Na}_4\text{Ge}_2\text{Se}_6 \cdot 16\text{H}_2\text{O}$ . The compound contains the isolated  $\text{Ge}_2\text{Se}_6^{4-}$  anion (65) consisting of two edge sharing tetrahedra with  $\text{Ge-Se} = 2.303 - 2.419 \text{ \AA}$ , which are in contact with the hydrated octahedral  $\text{Na}(\text{H}_2\text{O})_6^+$  ions through  $\text{Se} \cdots \text{H-O}$  bridges within an extensive hydrogen bridge system. The 1:2 molar ratio of  $\text{Na}_2\text{Se}$  to  $\text{GaSe}_2$  gives the adamantane-like  $\text{Ge}_4\text{Se}_{10}^{4-}$ .<sup>272</sup>

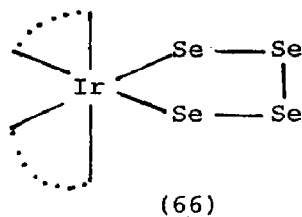


(65)

The vibrational spectra of solid  $\alpha$  and  $\beta$   $\text{As}_4\text{S}_4$  and the Raman spectrum of molten  $\text{As}_4\text{S}_4$  have been recorded. The Raman melt spectra suggest that  $\text{As}_4\text{S}_4$  molecules (symmetry  $\text{D}_{2d}$ ) are retained in the molten state. The Raman spectrum of solid  $\text{As}_4\text{Se}_4$  was tentatively assigned on the basis of a cradle type molecule

possessing  $D_{2d}$  symmetry.<sup>273</sup> The hitherto unknown  $Se_4^{2-}$  anion has been found in the structure of the new compound [Ba-222 Crypt] $Se_4$ .<sup>274</sup> The oxidation of copper(I)selenide at temperatures above  $300^\circ C$  at an oxygen pressure of 130-140 mmHg, has been shown to take place by a complex kinetic law changing with time from parabolic to cubic. Below  $300^\circ C$  the oxidation does not affect the non-metallic component the reaction products being  $Cu_{2-x}Se$  and  $CuO$ , but at high temperatures the oxidation product is copper oxide selenite.<sup>275</sup>

The square planar complex  $[Ir(dmpe)_2]Cl$  has been shown to react with  $Se_8$  to form two highly coloured products. Purple  $[Ir(Se_2)(dmpe)_2]Cl$  contains side-on-bonded diselenium and is analogous to the known dppe complex. The deep-red,  $[Ir(Se_4)(dmpe)_2]Cl$ , contains a cation with cis octahedral geometries with the  $Se_4$  group symmetrically chelated to the iridium at equatorial position and each dmpe group chelating axial and equatorial positions (66). The  $IrSe_4$  ring has a half chair conformation with the two central selenium atoms equidistant from and on opposite sides of, the plane of the iridium atoms and the two coordinated Se atoms. Bond distances are  $Ir-Se = 2.545\text{\AA}$  and  $Se-Se = 2.307\text{\AA}$ .<sup>276</sup>



The effect on crystallographic parameters of replacing sulphur by selenium in several series of ternary molybdenum chalcogenides has been studied. In all the systems studied,  $MMo_6(S_{1-x}Se_x)_8$  with  $M = La, Sm, Eu, Yb, Pb$  or  $Ag$ , the hexagonal  $c/a$  ratio showed a minimum when plotted against the percentage sulphur replaced.<sup>277</sup> The pseudo binary systems  $YbMo_6S_8-LaMo_6S_8$  and  $YbMo_6Se_8-LaMo_6Se_8$  have been investigated to trace out the effects of replacing a two-electron donor,  $Yb$ , by a three-electron donor,  $La$ , on the crystal structure parameters and on the superconducting critical temperatures.<sup>278</sup> Several studies of lanthanide uranium mixed selenides ( $Ln_{0.5}U_{0.5}Se_2$ ;<sup>279</sup>  $La_2U_2Se_7$ ;<sup>280</sup>  $Ln_4U_5Se_{16}$ <sup>281</sup> and

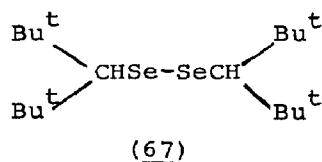
and  $\text{Yb}_{2.0}\text{U}_{0.87}\text{Se}_4$ <sup>282</sup> have been reported and the lanthanide selenides,  $\text{LnSe}_{1.4}$ , of the yttrium subgroup have been investigated.<sup>283</sup> Phase equilibria studies in selenide systems have been collected in Table 2.

Table 2. Selenide Phase Systems.

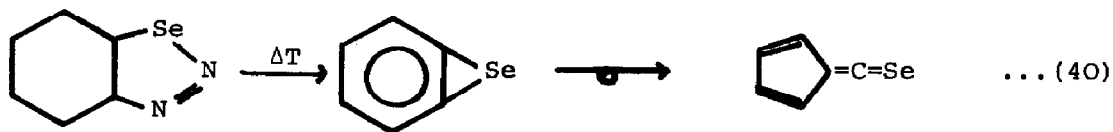
System	Ref.	System	Ref.
Ag-Se-Te	284	FeSe-Ga <sub>2</sub> Se <sub>3</sub>	288
Dy-Ge-Se	285	Hg-Se-Te	289
GeSe <sub>2</sub> -TeSbSe <sub>2</sub>	286	GeSe <sub>2</sub> -Sb <sub>2</sub> Te <sub>3</sub>	290
Cu <sub>2</sub> Se-Sm <sub>2</sub> Se <sub>3</sub>	287		

#### 6.3.5 Bonds to Carbon

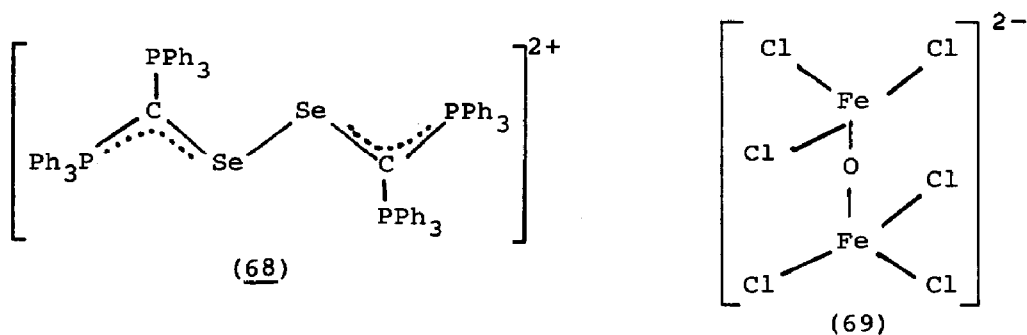
The crystal structure of  $\text{CSe}_2$  has been determined at 17.5, 50 and 200K using neutron powder profile refinement with a wavelength of 1.9887Å. The C-Se bond (1.689Å) is orientated at 41.6° to the b axis in the bc plane. The structure is similar to that of  $\text{CS}_2$  and the lattice parameter c, shows the same anomalous temperature dependence.<sup>291</sup> Bis(di-tert-butylmethyl)diselenide (67) has been shown to be the first example of a diselenide with an abnormal obtuse dihedral angle resulting from steric crowding. Its value was determined as 112.1° by X-ray crystallography, as compared with typical dihedral angles of 74-87° for other diselenides.<sup>292</sup>



Photoelectron spectroscopy has been used to detect a short lived intermediate in the pyrolysis of 1,2,3-benzoselenodiazole. Mass spectra recorded under similar conditions suggest an isomer  $\text{C}_6\text{H}_4\text{Se}$  rearranging to the more stable final product, 6-fulveneselone (equation 40).<sup>293</sup>

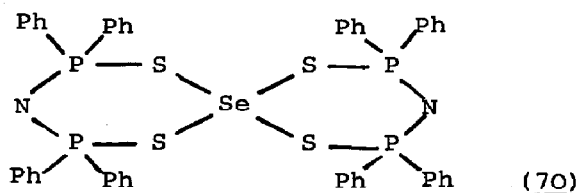


The separation of a number of cyclic methylene selenides and sulphides by reverse phase HPLC has been reported. The retention times as well as the capacity factors were shown to depend in a systematic way on the ring size, the number and kind of chalcogen atoms, and the number of heteronuclear bonds within the ring. These relationships were then used to assign the chromatograms of cyclic selenium sulphides of the type  $\text{Se}_n\text{S}_{8-n}$  ( $n = 1-8$ ), prepared in a new reaction from  $\text{Se}_2\text{Cl}_2$ ,  $\text{SCl}_2$  and  $\text{KI}$  and containing all selenium atoms in neighbouring positions.<sup>294</sup> A crystal structure determination has shown the compound  $(\text{Ph}_3\text{P})_2\text{CSe})_2\text{Fe}_2\text{OCl}_6 \cdot 4\text{CH}_2\text{Cl}_2$  to contain the dication (68) and the dianion (69). The dianion,



$\text{Fe}_2\text{OCl}_6^{2-}$  was found to contain a linear Fe-O-Fe axis and a staggered arrangement of the 2 x 3 chlorine atoms.<sup>295</sup>

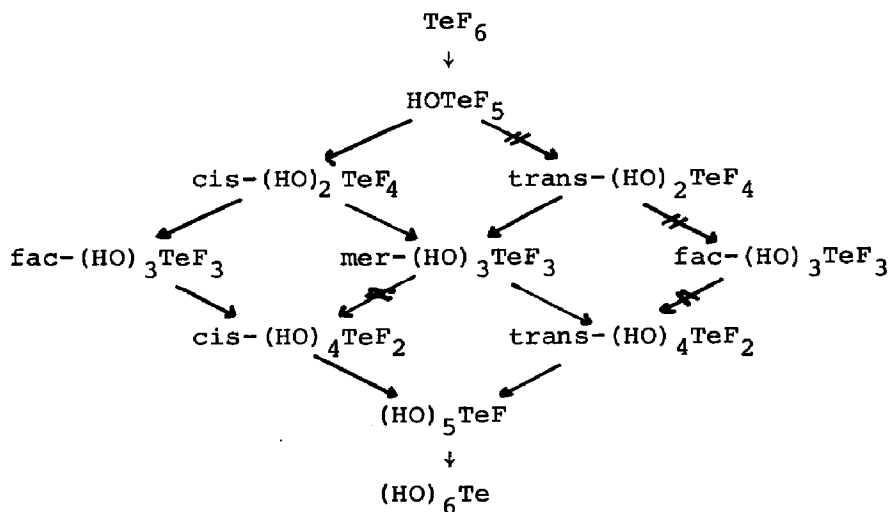
Bis(imidotetraphenyldithiodiphosphino-S,S')selenium(II) has been prepared from  $\text{NH}_4^+\text{N}(\text{Ph}_2\text{PS})_2^-$  and  $\text{Se}[(\text{EtO})_2\text{PS}_2]_2$  in methanol. Crystal structure determination shows the presence of a four coordinate Se(II) complex (70) in which the  $\text{SeS}_4$  coordination sphere is roughly trapezoid planar with selenium forming a long and a short bond to each bidentate ligand. Se-S bond lengths were 2.264, 2.948 and 2.270, 3.054 Å.<sup>296</sup>



## 6.4 TELLURIUM

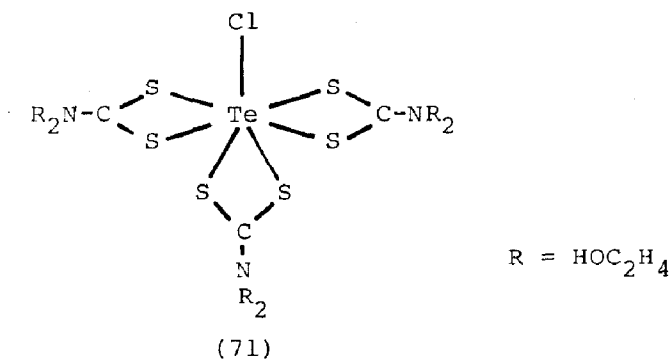
## 6.4.1 Bonds to Halogens

The stereochemistry of the hydrolysis of  $\text{TeF}_6$  has been followed by  $^{125}\text{Te}$  n.m.r. spectroscopy for each individual step of the replacement of fluorine by a hydroxy group. The hydrolysis may be described by Scheme 7.<sup>297</sup>

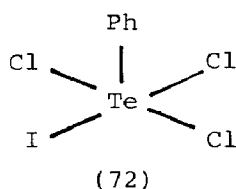


Scheme 7.

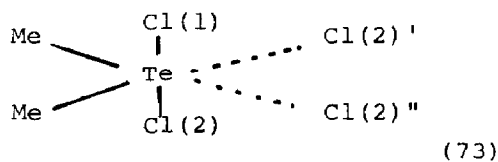
The new hypofluorite,  $\text{TeF}_5\text{OF}$  has been prepared by a novel method using fluorine fluorosulphate as the fluorinating agent. The compound was also prepared, but in poor yield, by the fluorination of  $\text{TeF}_5\text{OH}$  with a concentrated  $\text{NF}_4\text{HF}_2$  solution.  $\text{TeF}_5\text{OF}$  is colourless both as a gas and liquid and has a boiling point of  $0.6^\circ\text{C}$ . Raman,  $^{19}\text{F}$  n.m.r. and mass spectra were also reported.<sup>298</sup> The compounds  $\text{POF}_2\text{-OTeF}_5$ ,  $\text{P(OTeF}_5)_3$ ,  $\text{O=P(OTeF}_5)_2$ ,  $\text{As(OTeF}_5)_5$  and  $\text{Sb(OTeF}_5)_3$  have been prepared and their properties compared with similar compounds.<sup>299</sup> The synthesis, properties and crystal structure of the unusual mixed-ligand complex  $\text{TeCl}[(\text{HOC}_2\text{H}_4)_2\text{NCSS}]_3 \cdot 2\text{H}_2\text{O}$  have been described. The complex is monomeric with a highly distorted pentagonal bipyramidal coordination around Te with both strong and weak Te-S bonds in the equatorial plane and a strong Te-S bond and a rather weak Te-Cl bond in the axial positions (71). The chlorine atom and all the oxygen atoms participate in hydrogen bonding.<sup>300</sup> The structure of the aryl tellurium mixed halide anion,  $[\text{PhTeCl}_3\text{I}]^+$  has shown it



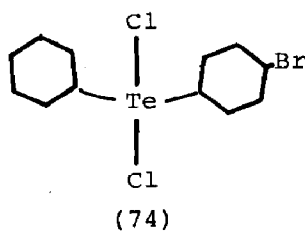
to be a square based pyramid with a lone pair in the sixth position of an octahedron (72).



The observed bond lengths found for the NBU<sub>4</sub><sup>n</sup> salt were Te-C = 2.15, Te-Cl = 2.565 - 2.663 and Te-I = 2.837 Å. Allowing for disorder the corrected values for Te-Cl and Te-I are 2.51 and 3.04 Å respectively.<sup>301</sup> Direct experimental evidence to support the Alcock thesis on secondary bonding to non-metallic elements has been provided by a detailed experimental electron density deformation density for Me<sub>2</sub>TeCl<sub>2</sub>. Deformation density maps clearly showed that the asymmetric Te(IV) lone-pair density is predominantly localised and occupies the third equatorial site of a distorted pseudo trigonal bipyramid (73). The electron density in the elongated Te-Cl bonds is polarised towards Cl and has a distribution consistent with the interpretation that the covalent radius of the central atom in a trigonal bipyramidal molecule is expanded in the axial direction. A trans arrangement of electron density was found in the C-Te...Cl(2) segments of the crystal and was taken as evidence for the existence of intermolecular bonding in Me<sub>2</sub>TeCl<sub>2</sub>.



The distribution supports a donor-acceptor model for the bonding that involves donation of the chlorine lone pair density to an empty tellurium orbital.<sup>302</sup> The crystal structure of (p-bromophenyl)dichloro(phenyl)tellurium(IV) consists of discrete tetramers in which individual molecules are linked through weak secondary Te...Cl interactions (74). The phenyl and bromophenyl rings are in propeller rather than the butterfly arrangement.<sup>303</sup>

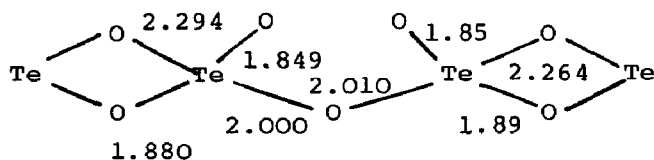


Bis(p-bromophenyl)tellurium(IV) dichloride has a distorted trigonal bipyramidal arrangement with the chlorine atoms in axial positions and the two bromophenyl rings in equatorial positions. The Cl-Te-Cl bond angle is close to  $180^\circ$ , the Cl-Te-C bond angle close to  $90^\circ$  and the C-Te-C angle  $96.1^\circ$  typical of  $R_2TeCl_2$  compounds. An interesting aspect of this compound is the apparent absence of Te...Cl secondary bonding, however, it is possible that Te...Br secondary interactions may be present.<sup>304</sup> Phase equilibria in the  $CoCl-NaCl-TeCl_4$  and  $NaCl-RbCl-TeCl_4$  systems have been measured.<sup>305</sup>

The crystal structures of the tetraphenylarsonium salts of  $PhTeI_2$  and  $PhTeBrI$  have been determined. In each compound the tellurium atom is three coordinated being bonded to a phenyl carbon and in direction nearly normal to the Te-C bond to two iodine atoms or to an iodine or bromine atom. The three centre systems I-Te-I and I-Te-Br are nearly linear and the Te-C bond nearly bisects the angle of the three centre system.<sup>306</sup> The crystal structure of  $[Na(H_2O)_3]_2TeBr_6$  has been determined, and shows face sharing  $Na(H_2O)_6$  octahedra forming infinite chains with isolated  $TeBr_6^{2-}$  octahedra between the chains.<sup>307</sup> The crystal structure of  $SbTeI$  shows the Sb atom to be coordinated by three Te atoms at distances 2.831 to 2.961 Å and four I atoms at distances 3.230 to 3.827 Å. Although the coordination polyhedron is similar to that of the orthorhombic  $BiSbCl$  and  $SbSeI$ , the structure of  $SbTeI$  is different and constitutes a new structure type.<sup>308</sup>

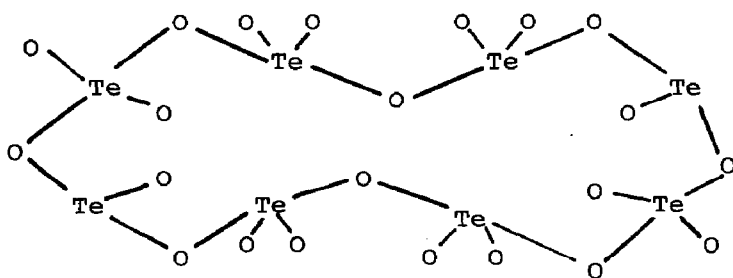
#### 6.4.2 Bonds to Oxygen

The  $\text{Nb}_2\text{O}_5\text{-TeO}_2$  system has been studied and the existence of three phases,  $\text{Te}_3\text{Nb}_2\text{O}_{11}$  (mp.  $793^\circ\text{C}$ ),  $\text{Te}_4\text{Nb}_2\text{O}_{13}$  (mp.  $795^\circ\text{C}$ ) and  $\text{TeNb}_6\text{O}_{17}$  (mp. above  $1100^\circ\text{C}$ ), observed.<sup>309</sup> The crystal structure of  $\text{K}_2\text{Te}_2\text{O}_5 \cdot 3\text{H}_2\text{O}$  has been investigated in order to determine whether the compound contains isolated  $\text{Te}_2\text{O}_5^{2-}$  ions or condensed chains and to examine the coordination of the  $\text{Te}(\text{IV})$  ion. It was shown that the  $\text{Te}_2\text{O}_5$  units are connected by fairly strong  $\text{Te}-\text{O}-\text{Te}$  double bridges to form puckered chains (75).<sup>310</sup>



(75)

The structure of  $\text{Ba}_3\text{Te}_4\text{O}_{11}$  consists of  $\text{TeO}_3^{2-}$  and  $\text{Te}_3\text{O}_8^{4-}$  ions which form  $\text{Te}_8\text{O}_{22}^{12-}$  rings around the centre of symmetry (76). The  $\text{Te-O}$  bond distances are approximately  $2.7\text{\AA}$  with the  $\text{TeO}_3^{2-}$  ion having the usual pyramidal symmetry but the  $\text{Te}_3\text{O}_8^{4-}$  ion has a pseudo twofold axis instead of the twofold axis found previously in  $\text{Zn}_2\text{Te}_3\text{O}_8$  and  $\text{Nb}_2\text{Te}_3\text{O}_{11}$ .<sup>311</sup>



(76)

The reduction of  $\text{Te}(\text{VI})$  by potassium tetrahydroborate in aqueous medium has been shown to take place in stages:  $\text{Te}(\text{VI}) \rightarrow \text{Te}(\text{IV}) \rightarrow \text{Te} \rightarrow \text{Te}^{2-}$  in acid solutions, and in alkaline or borate buffered solutions the final product is elemental tellurium.<sup>312</sup> The interactions of cis and trans  $\text{HOTeF}_4\text{OMe}$  with  $\text{BCl}_3$  has been shown to give  $\text{B}(\text{cis and trans-OTeF}_4\text{OMe})_3$ . Transfer of the  $\text{MeOTeF}_4\text{O}$  entity has also been demonstrated with  $\text{AsF}_3$ .<sup>313</sup>

Crystal structure determinations have been carried out on the following compounds  $\text{K}_3\text{HP}_2\text{O}_7 \cdot \text{Te}(\text{OH})_6 \cdot \text{H}_2\text{O}$ ,<sup>314</sup>  $\text{Te}(\text{OH})_6 \cdot 2\text{NH}_2\text{CH}_2\text{COOH} \cdot \text{H}_2\text{O}$ ,<sup>315</sup>  $2(\text{NH}_4)_3\text{P}_3\text{O}_9\text{Te}(\text{OH})_6$ ,<sup>316</sup>  $\text{SrTe}_5\text{O}_{11}$ ,<sup>317</sup> and  $\text{Ba}_3\text{Te}_2\text{O}_6\text{Cl}_2$ .<sup>318</sup>

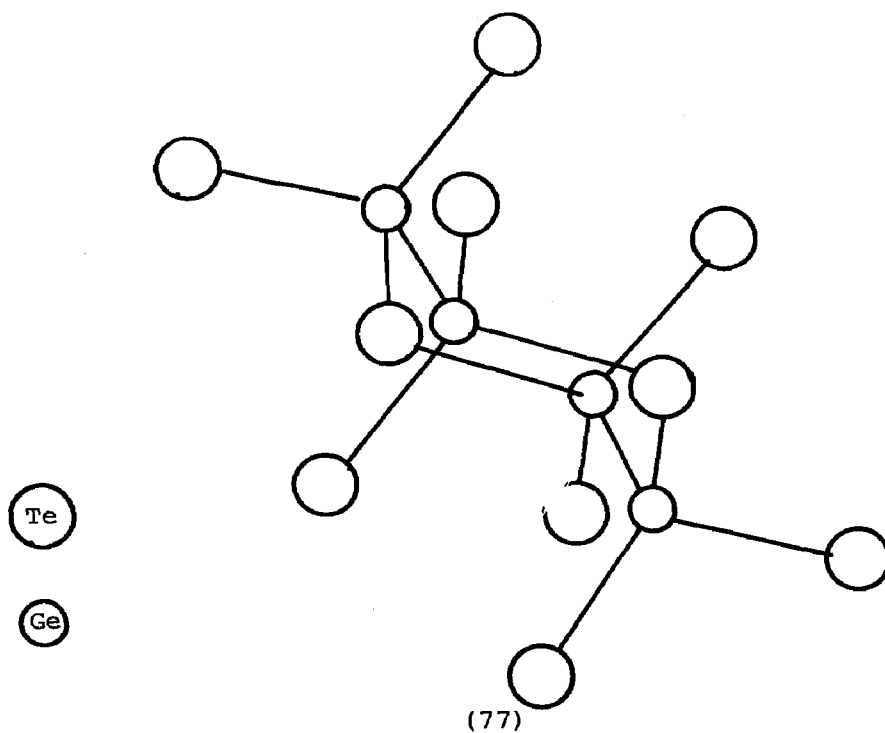
#### 6.4.3 Tellurides

$\text{Rb}_2\text{Te}_5$ , produced from stoichiometric amounts of the pure elements in supercritical  $\text{NH}_3$ , has a structure in which the Te atoms form a six membered rings which are connected via common vertices to form infinite one dimensional chains of  ${}^\infty[(\text{Te}_4\text{Te}_2)_2]^{2-}$ . The structure of  $\text{Rb}_2\text{Te}_5$  was compared with that of  $\text{Cs}_2\text{Te}_5$  and those of other known polychalcogenides,  $\text{M}_2\text{X}_n$ . The  $r(\text{Te}-\text{Te})$  of 304pm, which occurs as a characteristic feature were especially discussed.<sup>319</sup> Electron diffraction studies of  $\text{Si}_2\text{Te}_3$  crystals revealed a structural transformation above 673K. Deviations from stoichiometry of the form,  $\text{Si}_{1+x}\text{Te}_3$  where  $x = 0.5$  to 1.0 did not affect the structure and this was explained by the statistical occupancy of silicon atoms in a tellurium sub-lattice. Thus  $\text{Si}_2\text{Te}_3$  should be characterised as a non-stoichiometric compound with a considerable stoichiometry width.<sup>320</sup>  $\text{GaGeTe}$ , which crystallises from a melt of the elements in the form of dull-grey hexagonal crystals, cleaves like graphite parallel to the hexagonal 001 plane. The compound represents a novel structure type characterised by two dimensional infinite block layers of the  ${}^\infty[\text{Te}-\text{Ga}-\text{Ge}-\text{Ge}-\text{Ga}-\text{Te}]$ .<sup>321</sup> The crystal structure of the second modification of  $\text{Na}_8\text{Ge}_4\text{Te}_{10}$  has been determined. The structure contains  $[\text{Ge}_4\text{Te}_{10}]^{8-}$  anions in the form of six membered rings (77) with the formulation  $[(\text{GeTe}_2)_4\text{Te}_2]^{8-}$ .<sup>322</sup>

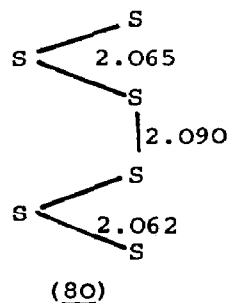
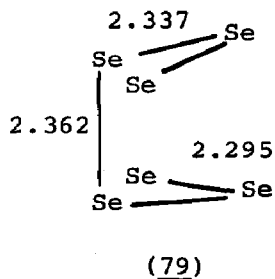
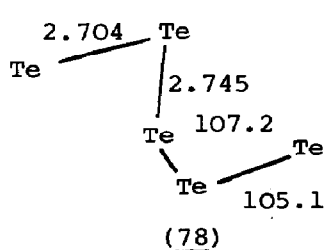
The new telluride,  $\text{Na}_4\text{SnTe}_4$  has been found to crystallise in the orthorhombic space group  $\text{P}2_12_12_1$  and to contain isolated  $\text{SnTe}_4^{4-}$  tetrahedra.<sup>323</sup> D.t.a., X-ray and microprobe measurements have been used to show that the compound " $\text{Ag}_8\text{SnTe}_6$ " seems not to be a stable argyrodite.<sup>324</sup>

Crystal structure determination has shown that the atomic arrangement of  $\text{Cs}_7\text{Fe}_4\text{Te}_8$  corresponds to that in  $\text{CsCl}$ . The outstanding feature of the structure is the occurrence of isolated  $\text{Fe}_4\text{Te}_8$  clusters in which the iron atoms are tetrahedrally surrounded by Te atoms and four tetrahedra are mutually linked such that each is joined to the others via three edges.<sup>325</sup>

$\text{Cu}_{0.28}\text{LaTe}_2$  has been found to have a disordered tunnel structure.<sup>326</sup>



The preparation and characterisation of several novel main group anions such as  $\text{Sn}_9^{4-}$ ,  $\text{Te}_5^{2-}$ ,  $\text{Se}_6^{2-}$ ,  $\text{S}_6^{2-}$  and  $\text{SnTe}_4^{4-}$ , without the use of cryptates or amine solvents has been described. The polychalcogenides,  $(\text{Bu}_4\text{N})_2\text{M}_x$  (where  $\text{M} = \text{Te}$ ,  $x = 5$ ;  $\text{M} = \text{Se}$ ,  $x = 6$ ;  $\text{M} = \text{S}$ ,  $x = 6$ ) are prepared by the aqueous extraction of binary alkali metal/main group alloys in the presence of  $\text{Bu}_4\text{NBr}$ . The compound  $\text{K}_4\text{SnTe}_4$  was also isolated by the aqueous extraction of ternary  $\text{K/Sn/Te}$  alloys. The polychalcogenides are isomorphous and have been structurally characterised by X-ray crystallography, (78)-(80), selected properties are compared in Table 3.<sup>327</sup>



**Table 3.** Selected Physical Properties of the Polychalcogenides  $\text{Te}_5^{2-}$ ,  $\text{Se}_6^{2-}$  and  $\text{S}_6^{2-}$ .

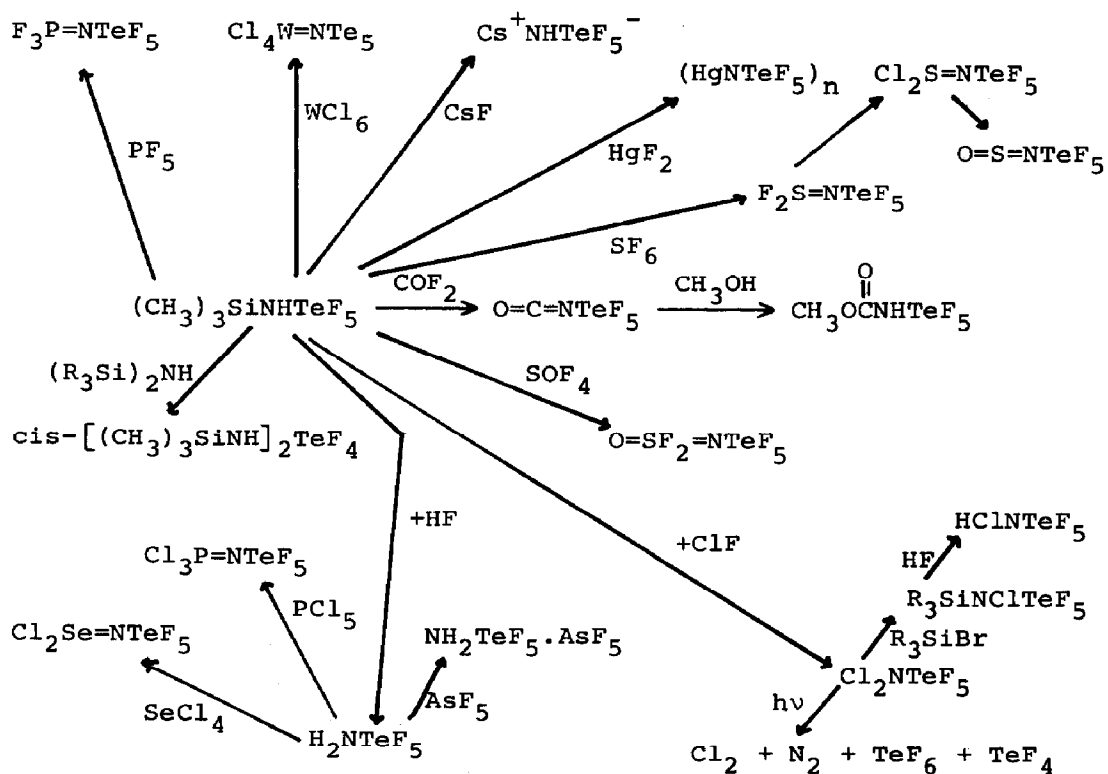
	$\text{Te}_5^{2-}$	$\text{Se}_6^{2-}$	$\text{S}_6^{2-}$
bond lengths, Å	<p><math>\text{Te}(1)-\text{Te}(2) = 2.746</math></p> <p><math>\text{Te}(2)-\text{Te}(3) = 2.704</math></p>	<p><math>\text{Se}(1)-\text{Se}(1') = 2.362</math></p> <p><math>\text{Se}(1)-\text{Se}(2) = 2.337</math></p> <p><math>\text{Se}(2)-\text{Se}(3) = 2.295</math></p>	<p><math>\text{S}(1)-\text{S}(1') = 2.090</math></p> <p><math>\text{S}(1)-\text{S}(2) = 2.065</math></p> <p><math>\text{S}(2)-\text{S}(3) = 2.062</math></p>
bond angles, deg.	<p><math>\text{Te}(2)-\text{Te}(1)-\text{Te}(2') = 107.2</math></p> <p><math>\text{Te}(1)-\text{Te}(2)-\text{Te}(3) = 105.1</math></p>	<p><math>\text{Se}(1)-\text{Se}(1')-\text{Se}(2) = 106.75</math></p> <p><math>\text{Se}(1)-\text{Se}(2)-\text{Se}(3) = 108.57</math></p>	<p><math>\text{S}(1)-\text{S}(1')-\text{S}(2) = 109.5</math></p> <p><math>\text{S}(1)-\text{S}(2)-\text{S}(3) = 110.5</math></p>
visible, (nm) $25^\circ\text{C}$ .	$375(\text{vbr}), 530$	$385(\text{sh}), 440, 625(\text{br})$	605
$-90^\circ\text{C}$	$375(\text{sh}), 530$	$385(\text{sh}), 440, 615(\text{br})$	340, 462
Raman, $\text{cm}^{-1}$			
solid	195, 170	285, 255(sh), 240	440, 395
solution	195, 170	405, 285, 235	538

The following telluride phase systems have been studied:

$\text{CdTe-Gd}_2\text{Te}_3$ ; <sup>329</sup>  $\text{CsSbTe}_2\text{-Sb}_2\text{Te}_3$ ; <sup>330</sup>  $\text{GeTe-Te-Tl}_2\text{Te}$ ; <sup>331</sup>  
 $\text{Ag-Te-Tl}$ ; <sup>332</sup> and  $\text{MnTe-Sb}_2\text{Te}_3$ . <sup>333</sup>

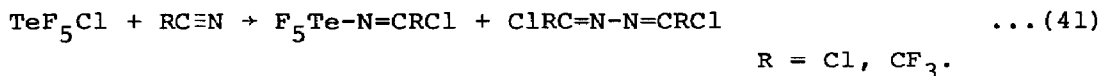
#### 6.4.4 Other Compounds of Tellurium

Although there is an extensive chemistry of sulphur-nitrogen compounds, very little is known about the corresponding tellurium-nitrogen system. Two recent publications have, however, described the preparation of several new, such compounds. With  $\text{H}_2\text{N-TeF}_5$  and  $\text{Me}_3\text{SiNHTeF}_5$  as the starting materials, numerous new tellurium-nitrogen compounds have been prepared. Almost all of them contain the  $>\text{N-TeF}_5$  group, which stabilises many double-bonded systems such as  $\text{O=C=NTeF}_5$  and  $\text{Cl}_4\text{W=NTeF}_5$ .  $\text{Cl}_2\text{Se=NTeF}_5$  is a rare example of a compound containing a discrete  $\text{Se=N}$  double bond. A schematic representation of the compounds mentioned in the paper is given in Scheme 8. <sup>334</sup>



Scheme 8. Schematic representation of the  $>\text{N-TeF}_5$  chemistry.

In a second paper, it was shown that  $\text{TeF}_5\text{-Cl}$  can add photolytically to nitriles with retention of the  $\text{TeF}_5$  group.



No evidence was found for the formation of the unknown  $\text{Te}_2\text{F}_{10}$  even though  $\text{S}_2\text{F}_{10}$  is observed in the reaction of  $\text{SF}_5\text{Cl}$  with nitriles. The reaction of  $\text{F}_5\text{Te-N=CCl}_2$  with excess HF gave the amine  $\text{F}_5\text{Te-NH-CF}_3$  and the anion  $[\text{F}_5\text{Te-N-CF}_3]^-$  could be generated directly by reaction of  $\text{F}_5\text{Te-N=CCl}_2$  with  $\text{CsF}$ .<sup>335</sup> The crystal structure of  $(\text{TePh}_2)\cdot\text{HgI}_2$  has been determined and showed the molecule to have a novel tetrameric structure involving two different iodine bridges.<sup>336</sup> The compound  $\mu_3\text{-Te}(\text{Mn}(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5))_3$  has been synthesised and its structure determined.<sup>337</sup> The reaction of organic dihalides with  $\text{NaTeR}$  ( $\text{R} = \text{Ph}$  or  $p\text{-EtOC}_6\text{H}_4$ ) has been reported.<sup>338</sup> The synthesis and reactivity of  $(\text{C}_5\text{H}_5)\text{RhFe}_2\text{Te}_2(\text{CO})_x$  ( $x = 6, 7$ ) together with  $^{125}\text{Te}$  n.m.r. studies have been described.<sup>339</sup>

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