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Chapter 6

ELEMENTS OF GROUP 6

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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 $^{18}O_2$ 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 = 6.6897Å rather than the previously proposed monoclinic α O_2 form. The new structure of the so-called "orange" $^{18}O_2$ is very closely related to that of α O_2 and transformations from one to the other may be second order.[1]

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.[2] 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.[3] 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.[4] 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.[5] 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 α to the γ form.[6]

The reactions of O_3 with NH_3 and NH_2OH have been studied in the condensed phase. Ozone reacts with NH_3 at -170°C to give the yellow-orange ozonide $NH_3{}^+O_3{}^-$ which could be reconverted to the reactants by photolysis with near u.v. or by heating to -90°C. On warming the NH_3-O_3 system to -130°C, $NH_4NO_3.3NH_3$ was formed which starts to deamminate at about -105 to give NH_4NO_3. A second phase formed at -170°C, was tentatively identified as $NH_2O^+HO_2{}^-$ and was found to decompose at -10°C with the evolution of O_2. The reaction of NH_2OH with O_3 yielded the yellow ozonide $NH_2OH^+O_3{}^-$ at -190°C and HNO_3 which was observed immediately upon addition of O_3 to NH_2OH as the hydrogen bonded complex, $NH_2OH.HNO_3$. At -100°C the $NH_2OH^+.O_3{}^-$ started to decompose and the final product of the reaction was $NH_3OH^+NO_3{}^-$ and H_2O.[7]

The superoxide anion $O_2^{\cdot -}$ has been shown to perform the novel desulphurization of 1,3-diarylthioureas at 20°C in THF or acetonitrile to form 1,2,3-triarylguanidines in excellent yields.[8]

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, $[MnX_2(PR_3)]$ where X = Cl, Br or I and R_3 = $Bu^n{}_3$ or $PhBu^n{}_2$ in several organic solvents. Oxygen is absorbed quantitatively by the complexes to form $[MnX_2(PR_3)(O_2)]$ and repeated (more than 400 times at -20°C) cycling of oxygen absorption was shown to be possible. The solid state dioxygen binding by bis(isothiocyanato)(phosphine)manganese(II) complexes $[Mn(NCS)_2(PPh_{3-n}R_n)]$ have also been studied but only the $[Mn(NCS)_2(PR_3)]$ compounds were found to bind dioxygen reversibly.[9] Italian workers have shown that the complex NN'-4-methyl-4-azaheptane-1,7-diylbis(salicylideneiminato)cobalt(II) binds dioxygen, reversibly and a crystal structure determination of the dioxygen adducts $[Co(salmhpn)]_2.O_2.2C_6H_6$ 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 1.06Å. The non dioxygenated molecules contain high spin Co(II) atoms.[10]

The equilibrium constant for the formation of $[Co_2(en)_4(O_2)(OH)]^{3+}$ in KCl aqueous solution has been determined. Calculation of thermodynamic functions for the addition of O_2 to $[Co(en)_2]^{2+}$ to form the doubly bridged bicobalt complex

$[Co_2(en)_4(O_2)(OH)]^{3+}$ showed a large enthalpy change, but the stability of the binuclear species with respect to $[Co(en)_2]^{2+}$ is strongly reduced by a large entropy effect.[11] The reactions of oxygen with Co(II) chelates of tridentate, dianionic Schiff Base ligands[12] and orthoquinone complexes of vanadium[13] have also been reported. The application of ^{17}O n.m.r. for the study of transition metal bonded peroxidic oxygen atoms has been described. The first high resolution ^{17}O n.m.r. observations were obtained from ^{17}O enriched $\left[(CN)_4OMo\begin{array}{l}\diagup O\\ \diagdown O\end{array}\right][N(PPh_3)_2]_2$ and for non enriched alkylperoxo derivatives of platinum.[14]

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 $MgAl_2O_4$ as it does in Mg_2SiO_4 to a very hugh 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.[15] A study of the dehydration of $\alpha FeOOH$ to αFe_2O_3 has shown that the band observed in the i.r. spectrum at $1140cm^{-1}$ 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 αFe_2O_3 and assigned to adsorbed oxygen.[16]

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.[17] Several papers have been concerned with the chemistry of singlet oxygen, topics covered were the quenching of singlet oxygen by conjugated olefins[18] and with benzoquinone derivatives[19] and the mechanisms of the photooxidation of sulphides[20] and of 2,5-dimethylhexa-2,4-diene and 2-methyl-2-pentene.[21]

The ozonloysis 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.[22]

The geometries of the ions HO_3^+ and HO_3^- and of the radical HO_3 have been optimised using the gradient technique within the SCF approximation, and the calculated energies of the different isomers compared.[23] Far i.r. Fourier spectroscopic studies of H_2O and D_2O 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 40cm^{-1} and as inert gas hydrates that contribute i.r. active intermolecular vibrations between 40 and 100cm^{-1}. In solid N_2 matrices the freely rotating species are not present whilst interaction between N_2 and H_2O gives rise to intermolecular vibrations located considerably above 100cm^{-1}.[24] A short communication has dismissed the idea that the ion $H_5O_2^+$ could exist in aqueous sulphuric acid.[25]

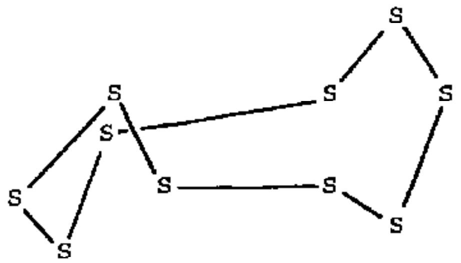
6.2 SULPHUR

6.2.1 The Element

Single crystals of S_{10} have been prepared by the reaction

$$2S_6 + 4CF_3CO_3H \rightarrow S_{10} + 2SO_2 + 4CF_3CO_2H \qquad ...(1)$$

and used for a structure determination at -110°C. The molecule (1) exhibits D_2 conformation with bond distances between 203.3 and 208.0pm, bond angles between 103 and 111° and torsional angles between 73 and 124.1°.

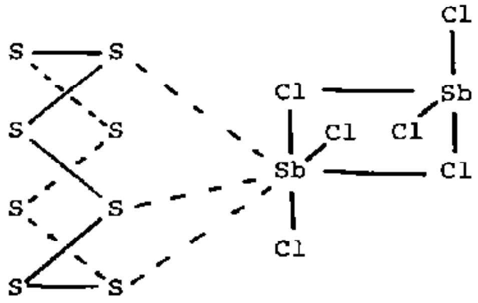


(1)

S_{10} also forms a molecular addition compound with S_6, $S_6.S_{10}$ (mp 92°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.[26]

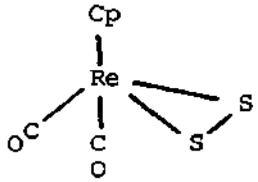
An attempt has been made to correlate the sulphur-sulphur bond distances and the torsional angles in a series of cyclic sulphur molecules. The bond distance was found to be a minimum when the torsional angle was between 90 and 100° and to be a maximum when the angle was almost zero. The bond distance 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.[27]

The reaction of $SbCl_5$ with CS_2 at 5°C has been shown to give the adduct $SbCl_3.S_8$ 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°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.[28]



(2)

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.[29] 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)



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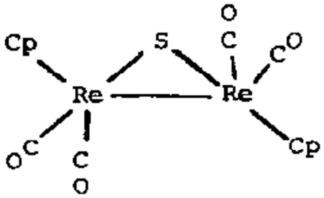

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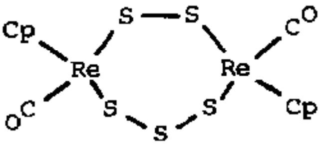
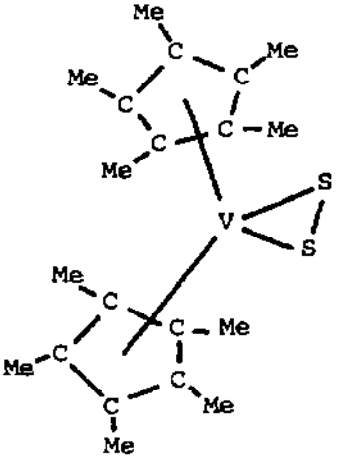


(5)

the structures of which have been determined;[30] and the formation of $(\eta^5\text{-}C_5Me_5)_2V(\eta^2\text{-}S_2)$ which maybe prepared by several methods and has the structure (6).[31]



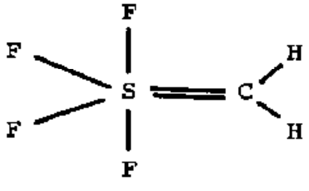
(6)

The gas phase reactions of sulphur atoms with alkynes have been studied by photolysing COS in the presence of CH≡CH, $CF_3C{\equiv}CH$ and $CF_3C{\equiv}CCF_3$. 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.[82]

6.2.2 Bonds to Halogens

The pressure dependence of axial-equatorial fluorine exchange rates of sulphur tetrafluoride obtained from exchange-broadened gas phase ^{19}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.[33] 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.[34] Reaction of 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.[35]

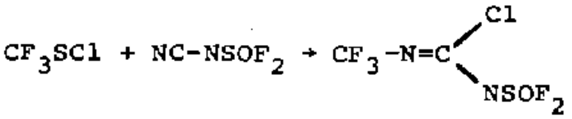
The preparation of methylene sulphur tetrafluoride, $CH_2{=}SF_4$ by bromine-lithium exchange on $Br{-}CH_2{-}SF_5$ at low temperatures and subsequent lithium fluoride elimination has been described. $CH_2{=}SF_4$, a colourless gas (bp -19°C mp -139°C) has an essentially trigonal bipyramidal structure (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 configurated $X{-}CH_2{-}SF_4{-}Y$ systems. Less often observed is the elimination of SF_4 and the formation of a carbene.[36]



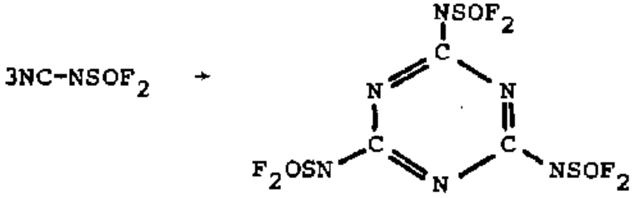
(7)

Sulphuronium ions of the type $R{-}SF_4{}^+$ may be generated from $R{-}SF_5$ by fluoride ion abstraction using SbF_5. Despite using a large variation in groups for R(Me, $CH{=}CH_2$, $C{\equiv}CH$) none of the ions were found to be stable at room temperature.[37] Characteristic i.r. fundamentals have been observed for six tungsten thio- and selenotetrahalides isolated as monomers in nitrogen matrices.[38]

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°. Three different types of molecular packing were observed; S_2Cl_2, S_2Br_2, αSe_2Br_2 and βSe_2Br_2, Se_2Cl_2.[39] 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-formylimidoylchlorides, $CF_3S\text{-}N{=}C(Cl)R$. The reaction of SCl_2 with CF_3CN and $NSOF_2CN$ gave the N-sulphenylchlorides $ClS\text{-}N{=}C(Cl)R$ (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.[40]



$$CF_3SCl + NC\text{-}NSOF_2 \rightarrow CF_3\text{-}N{=}C(Cl)(NSOF_2) \qquad \ldots(2)$$



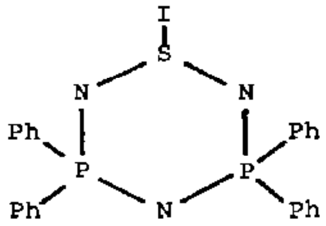
...(3)

(8)

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.[41]

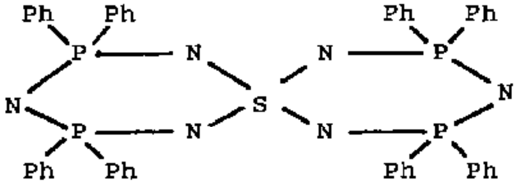
The uranium compounds UO_3, UO_2Cl_2, UCl_6 and UCl_5 have been shown to react with $SOCl_2$ to give the compounds $UCl_5.SCl_2$ and $[SCl_3]^+[UCl_6]^-$ either as single phases or as mixtures of the two, but never the adduct $UCl_5.SOCl_2$. An X-ray study of $[SCl_3]^+[UCl_6]^-$ showed it to contain isolated pyramidal SCl_3^+ and octahedral UCl_6^- ions with bond lengths S-Cl = 196.2pm, U-Cl = 251.1pm and the bond angle Cl-S-Cl = 102.34°.[42] 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^-.[43] Trifluoromethylsulphenylbromide has been obtained by a new preparative method involving the reaction between gaseous bromine and CF_3SAg or $(CF_3S)_2Hg$. Previously only bis-trifluoromethyldisulphide $(CF_3S)_2S_2$ had been obtained as the gaseous product of the same reaction with the silver compound.[44]

The reaction of $(Ph_2PN)_2NSCl$ with KI in acetonitrile produces $(Ph_2PN)_2NSI$ which has been shown by X-ray crystallography to contain a six-membered P_2SN_3 ring with an exocyclic S-I bond of length 2.713Å, (9).



(9)

The thermal decomposition of $(Ph_2PN)_2NSI$ leads to $Ph_8P_4SN_6$, a spirocyclic compound in which two, almost planar, P_2SN_3 rings share a common sulphur atom (10).



(10)

The geometry at the sulphur atom is approximately tetrahedral with bond angles in the range 105-113° and the four S-N bonds are almost equal in length with a mean value of 1.56Å.[45]

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 SO_2 in argon matrices gave rise to the SO_2F^- 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 SOF_3^- anion in C_s geometry, whereas with sulfuryl fluoride gave five product bands which were assigned to the $SO_2F_3^-$ ion isostructural with the known ClO_2F_3 species. Identification of this ion supports the claim that pentacoordinate sulphur anions play a significant role in the solution chemistry of SO_2F_3.[46] Tetramethylsilane has been shown to react with $HN(SO_2Cl)_2$ 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 CH_2Cl_2 as a diluent the product was the new compound $HN(SO_2Cl)(SO_2Me)$ (equation 4). The compound is formed in high

$$Me\text{-}SiMe_3 + Cl\text{-}SO_2NHSO_2Cl \rightarrow Cl\text{-}SiMe_3 + Me\text{-}SO_2NHSO_2Cl \qquad ...(4)$$

yield but is moisture sensitive being hydrolysed according to equation (5).[47]

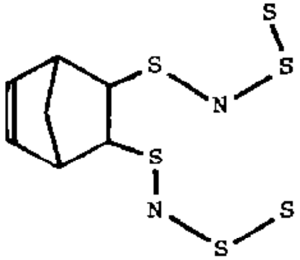
$$Me\text{-}SO_2NHSO_2Cl + 5H_2O \rightarrow MeSO_2NH_2 + SO_4{}^{2-} + Cl^- + 3H_3O^+ \qquad ...(5)$$

6.2.3 Bonds to Nitrogen

Polymeric and linear compounds - A new, direct synthesis of polymeric $(SN)_x$ films has been described. The method which avoids the use of complex chemical reactions or the dangerous pyrolysis of S_4N_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 S_4N_4 at 70-80°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 $(SN)_4$ and S_4N_4. The latter was separated by washing with CH_2Cl_2 to yield pure $(SN)_x$.[48]

The reaction of S_4N_2 with norbornadiene has been shown to give $C_7H_8(S_3N)_2$ (11). The molecule consists of a norbornenyl unit with two S_3N groups attached in an exo fashion at the 2,3 positions. Both S_3N groups possess a cis formation with the bond lengths S-S 1.903Å and CS-N 1.641Å. The molecule exhibits two strong absorptions in the visible region attributable to the excitonically coupled $\pi^*\text{-}\pi^*$ transitions of the two S_3N chromophores.[49]

The reactions of (pentafluorosulphanyl)dichloroamine, $SF_5\text{-}NCl_2$ with PCl_3, Se_2Cl_2 and Se have been shown to give the compounds



(11)

SF_5NPCl_3 and SF_5NSeCl_2 respectively (equations 6, 7 and 8).

$$SF_5\text{-}NCl_2 + PCl_3 \rightarrow SF_5\text{-}N{=}PCl_3 + PCl_5 \qquad \ldots(6)$$

$$3SF_5\text{-}NCl_2 + 2Se_2Cl_2 \rightarrow 3SF_5\text{-}N{=}SeCl_2 + SeCl_4 \qquad \ldots(7)$$

$$SF_5\text{-}NCl_2 + Se \rightarrow SF_5\text{-}N{=}SeCl_2 \qquad \ldots(8)$$

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

$$SF_5\text{-}N{=}PCl_3 \rightarrow PF_5 + Cl_2 + {}^1/n(NSCl)_n \qquad \ldots(9)$$

$$2SF_5\text{-}N{=}SeCl_2 \rightarrow 2N\ SF_3 + SeCl_4 + SeF_4 \qquad \ldots(10)$$

SF_5NCl_2 was also found to react with S_2Cl_2 or SCl_2 to give $SF_5N{=}SCl_2$ and with $SF_5N{=}SCl_2$ to give $SF_5N{=}S{=}NSF_5$, and to form an adduct with HCl.[50]

The reaction of SF_5NSF_4 with HgF_2 at 20-60°C has been shown to yield $Hg[N(SF_5)_2]_2$ (12) (equation 11):

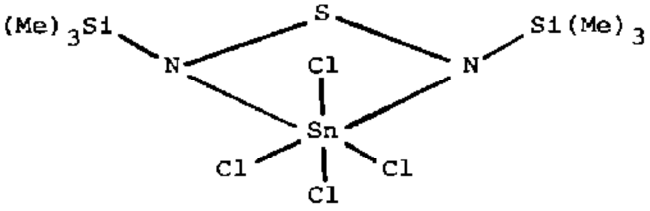
$$2SF_5NSF_4 + HgF_2 \rightarrow \underset{(12)}{Hg[N(SF_5)_2]_2} \qquad \ldots(11)$$

Reaction of (12) with Cl_2 or Br_2 gave no reaction at room temperature and raising the temperature to 60°C led to decomposition; transfer of the $N(SF_5)_2$ group was however possible with CH_3I and CF_3SCl according to equations (12) and (13).[51]

$$Hg[N(SF_5)_2]_2 + 2CH_3I \rightarrow 2CH_3N(SF_5)_2 + HgI_2 \qquad \ldots(12)$$

$$Hg[N(SF_5)_2]_2 + 2CF_3SCl \rightarrow 2CF_3S\text{-}N(SF_5)_2 + HgCl_2 \qquad \ldots(13)$$

Both Me_3SiNSO and $Me_3SiN=S=NSiMe_3$ have been shown to react with $SnCl_4$ to give the 1:1 adduct (13) in which the sulphur diimide functions as a bidentate ligand.[52]



(13)

A significant difference in the S2p binding energy has been observed between the sulphilimine (14) and its salt (15).

$Me_2\overset{+}{S}-\overset{-}{N}COC_6H_4NO_2-p$

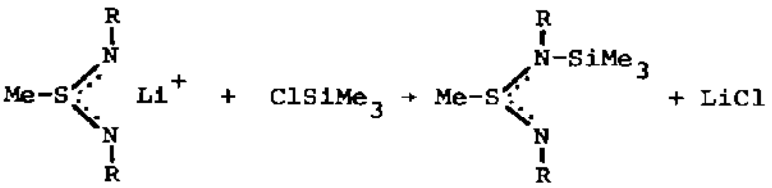
(14)

$Me_2\overset{+}{S}-NHCOC_6H_4NO_2-pCl^-$

(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 S^+ and N^- atoms.[53] Both ^{19}F and ^{13}C n.m.r. spectra of the sulphur-(IV) diimines, R-NSN-R (R = Ph, C_6F_5, C_6H_5S, C_6F_5S) and the corresponding N-sulphinylamines, R-NSO, have been measured and discussed.[54]

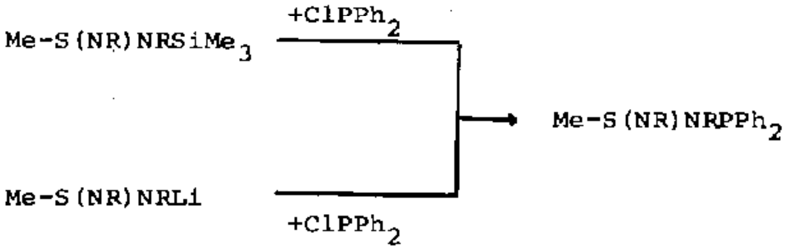
The reactions of N-lithiomethanesulphinicacidimide amides, Me-S(NR)NRLi (R = Bu^t or Me_3Si), with chlorosilanes and -phosphanes have been described. Metathetical reactions of the amides with chloromethylsilane led to the formation of sulphinic acid imide amidosilanes, Me-S(NR)NR$SiMe_3$ (equation 14):



...(1

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).[55]



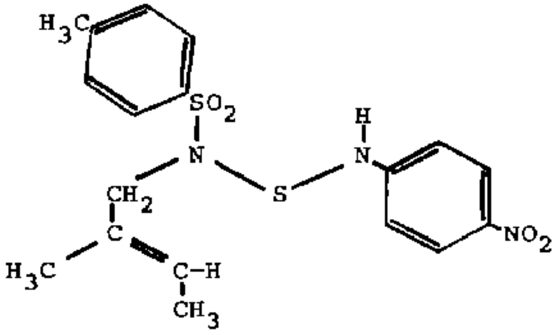
...(15)

Tetrakis(trifluoromethylthiazyl), $(CF_3SN)_4$ has been prepared from CF_3SCl and Me_3SiN_3. The compound has low stability, at -30°C it is stable for a few days, and on standing it oligomerises and after 7 days at 20°C the melting point is above 180°C (equation 16):

$$CF_3SCl + Me_3SiN_3 \xrightarrow{150\ \text{to}\ -30^{\circ}C} CF_3SN_3 \xrightarrow{-N_2} (CF_3SN)_x \xrightarrow{20^{\circ}C} (CF_3SN)_4 \qquad \ldots(16)$$

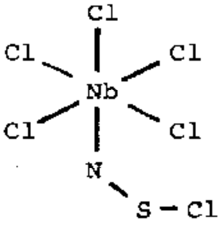
The addition of F_2 to CF_3SNCO at -78°C leads to the formation of $CF_3S(F)N{=}C(O)F$ which decomposes at 25°C in the presence of HgF_2 to $(CF_3SN)_x$.[56]

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 sp^2 with a tendency towards sp^3.[57]

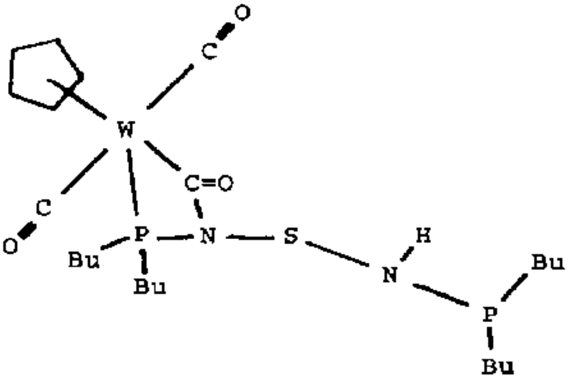


(16)

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 CCl_4 suspension to form the red, moisture sensitive compound $Cl_5NbNSCl$ (17). The compound consists of monomeric units which $NbCl_5$ is bonded to N≡S-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.[58] The new sulphur diimides, $S(NPBu^t_2)_2$ and $S(NAsBu^t_2)_2$, react with the hydrido metal complex $CpM(CO)_3H$ (M = Cr, Mo, W) to give 1:1 adducts which contain a 3 electron acyl-chelate ligand. Only one of the two PBu^t_2 or $AsBu^t_2$ 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.[59]



(17)



(18)

Thiazylfluoride complexes, which can be readily prepared from the corresponding SO_2 derivatives, have been shown to be suitable precursors for the preparation of the thionitrosyl ligand in complexes (equation 17).

$$[\mathrm{Re(CO)_5(SO_2)}]^+\mathrm{AsF_6}^- + \mathrm{NSF} \xrightarrow[-30^\circ\mathrm{C}]{\mathrm{SO_2}} [\mathrm{Re(CO)_5(NSF)}]^+\mathrm{AsF_6}^- + \mathrm{SO_2} \quad \ldots(17)$$

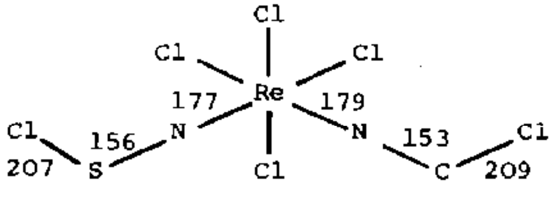
As in free NSF, a fluoride ion can be removed by fluoro Lewis acids.

$$[\mathrm{Re(CO)_5NSF}]^+\mathrm{AsF_6}^- + \mathrm{AsF_5} \rightarrow [\mathrm{Re(CO)_5NS}]^{2+}\ \mathrm{AsF_6}^-{}_2 \quad \ldots(18)$$

The corresponding hexafluoroantimonate could also be obtained from $\mathrm{Re(CO)_5Br}$ and $\mathrm{NS^+SbF_6}^-$.[60]

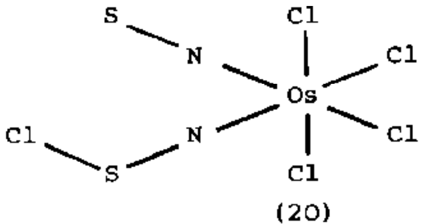
$$\mathrm{NS^+SbF_6}^- + \mathrm{Re(CO)_5Br} \rightarrow [\mathrm{Re(CO)_5NS}]^{2+}(\mathrm{SbF_6}^-)_2 \quad \ldots(19)$$

Rhenium pentachloride in $\mathrm{POCl_3}$ solution has been shown to react with $\mathrm{(NSCl)_3}$ to give the chlorothionitrene complexes $[\mathrm{(Cl_3PO)ReCl_4(NSCl)}]$ and $[\mathrm{(Cl_3PO)ReCl_3(NSCl)_2}]$. The former reacts with $\mathrm{AsPh_4Cl}$ to give $\mathrm{AsPh_4(ReNCl_4)}$ and the latter, the complex $\mathrm{AsPh_4[ReCl_4(NSCl)_2].CH_2Cl_2}$, (<u>19</u>). Crystal structure determination of (<u>19</u>) showed the two NSCl ligands to have cis arrangements with nearly linear Re=N=S groups, with interatomic distances corresponding to double bonds.[61]



(<u>19</u>)

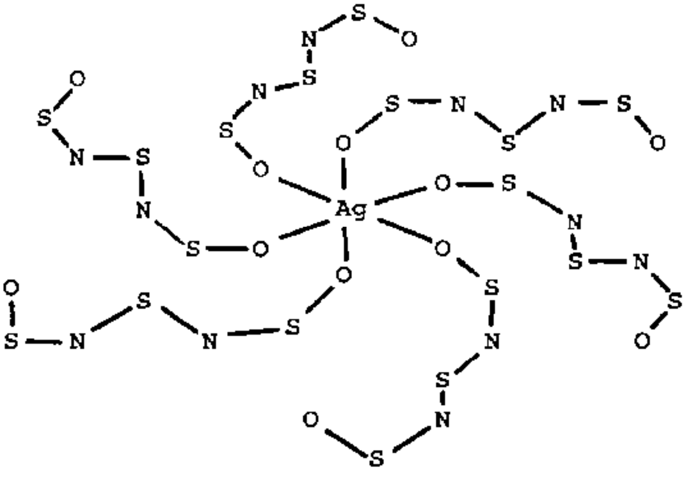
The reaction of $\mathrm{OsCl_5}$ with $\mathrm{(NSCl)_3}$ yields the thiazyl chloride complex $\mathrm{OsCl_4(NSCl)_2}$, from which the thionitrosyl complex $\mathrm{AsPh_4[OsCl_4(NS)_2Cl)]}$ (<u>20</u>) could be obtained by reaction with $\mathrm{AsPh_4Cl}$ in $\mathrm{CH_2Cl_2}$. A crystal structure determination showed the two NS groups to be in a cis configuration and to be essentially linear with the bond lengths Os=N 184pm and N=S 146pm. Loosely attached to one of the sulphur atoms is the chlorine atom (S-Cl = 228pm): in the crystal structure it statistically belongs to both



(20)

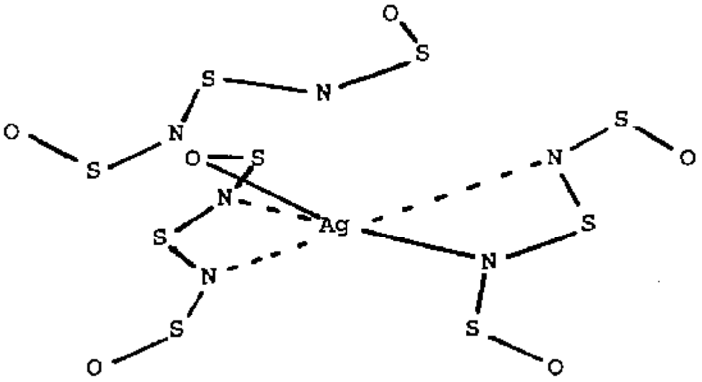
sulphur atoms and it is thought that there is a dynamical fluctuation between the sulphur atoms.[62]

The reaction of $AgAsF_6$ with $S(NSO)_2$ in liquid SO_2 has been shown to give a polymeric bis(sulphinylnitrilo)sulphur complex of silver(I), $[Ag_4(S(NSO)_2)_9][AsF_6]_4.SO_2$, containing two crystallographically independent silver atoms. One silver atom is octahedrally coordinated by the terminal oxygen atoms of six $S(NSO)_2$ ligands (21), the other is unsymmetrically coordinated by the nitrogen atoms of three $S(NSO)_2$ ligands (22). The ligands bridge the silver atoms to form a polymeric cationic network in which the AsF_6^- anions and SO_2 solvent molecules occupy holes without acting as ligands.[63]



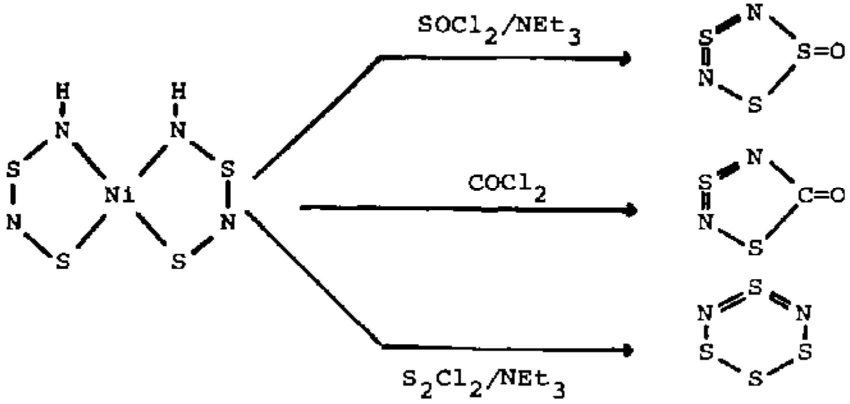
(21)

The thermochemical and spectrophotometric properties of some Ni(II) complexes of some linear tridentates with one sulphur and two nitrogen donors have been studied.[64]



(22)

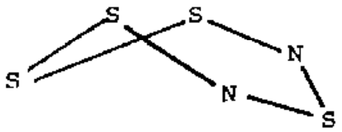
Cyclic Sulphur-nitrogen compounds - A new route to the preparation of cyclic sulphur-nitrogen compounds has been described. Facile syntheses of S_3N_2O, S_2N_2CO and S_4N_2 from $Ni(S_2N_2H)_2$ were achieved according to equation (20).[65]



...(20)

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°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° (23). Of the two types of S-N bonds, those linking the N-S-N moiety to the S_3 unit are considerably longer (1.676Å) than those within the N-S-N group (1.561Å). The

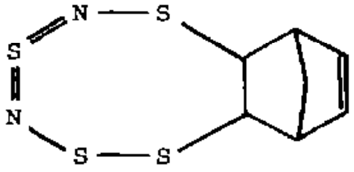
S-S bonds (2.061Å) are those expected for an S-S single bond. MNDO and ab initio Hartree-Fock-Slater SCF calculations on a variety of S_4N_2 structures showed the observed conformation to be preferred by 6-10 kcal mole^{-1} over a planar configuration.[66]



(23)

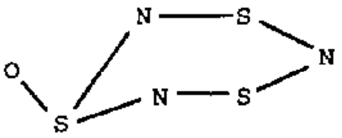
An independent study of the conformation of S_4N_2 has also concluded that the half-chair conformation is preferred to a planar model. CNDO/2 calculations had previously predicted a planar conformation but the extended Huckel calculations used in this work were in excellent agreement with the crystallographic study reported above.[67]

The reaction of S_4N_2 with norbornadiene has been shown to produce the 1:1 adduct $S_4N_2.C_7H_8$. X-ray crystallographic analysis revealed that olefin addition cleaves one of the sulphur-sulphur bonds of S_4N_2 to yield a novel eight membered $C_2S_4N_2$ ring (24). The S-S-N-S-N-S fragment of the $C_2S_4N_2$ ring is planar to within 0.15Å whilst the S-C-C-S unit is folded out of this plane to produce a dihedral angle of 74.5°.[68]

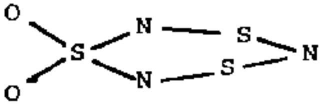


(24)

The oxidation of the $S_3N_3^-$ ion in acetonitrile solution by molecular oxygen gives rise to four major products: $S_4N_5^-$, $S_4N_5O^-$, $S_3N_3O^-$ and $S_3N_3O_2^-$. The crystal structures of the $(Ph_3P)_2N^+$ salts of two of the ions $S_3N_3O^-$ and $S_3N_3O_2^-$ were determined. The two anions both possess six membered S_3N_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 $S_3N_3^-$ poses several interesting and perplexing

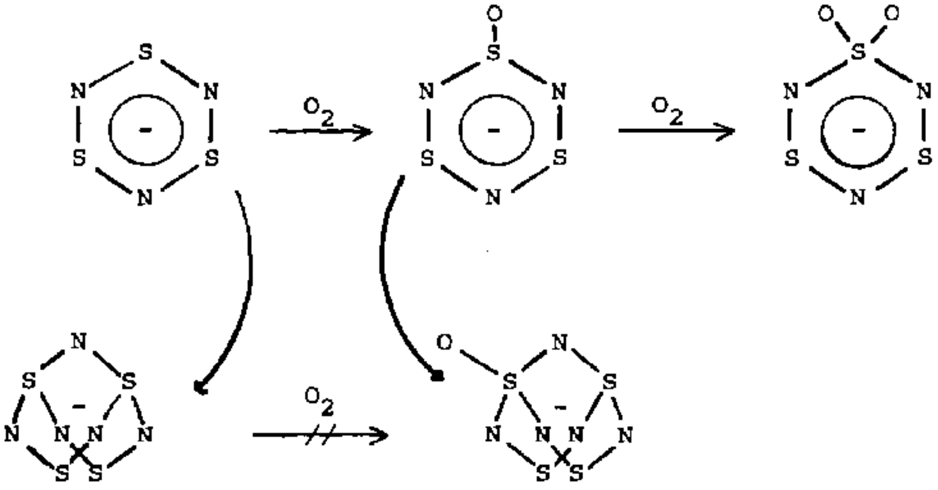


(25)



(26)

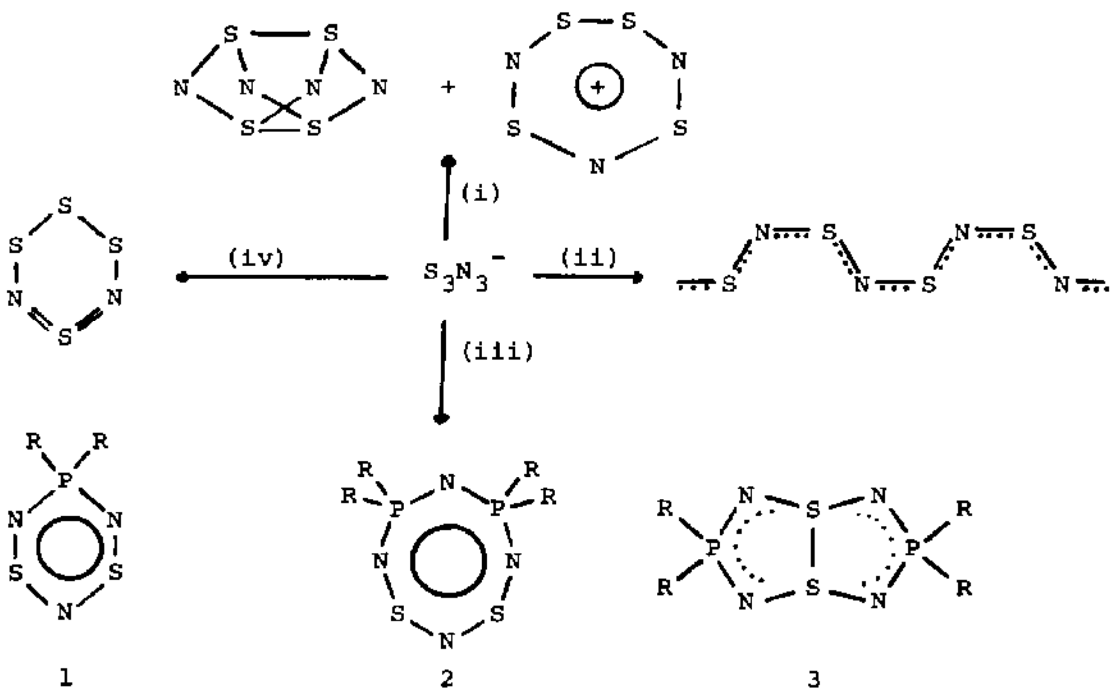
questions as to the mechanism of the reaction. Although not completely understood the authors suggest the following scheme.[69]



Scheme 1

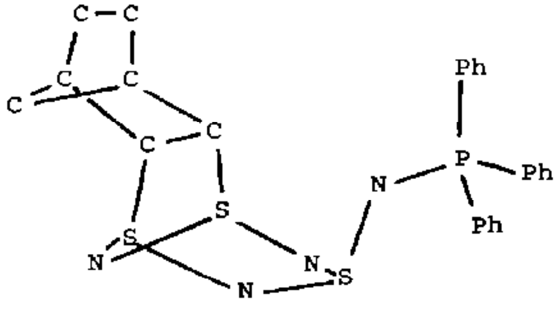
The reactions of $S_3N_3^-$ with halogens, AsF_5 and other electrophilic substrates has been shown to give mixtures of known sulphur-nitrogen compounds. The major products from reactions with halogens, $COCl_2$, Ph_2PCl and CS_2 are shown in Scheme 2. AsF_5 was found to oxidise $S_3N_3^-$ to $S_4N_4.AsF_5$, 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.[70]

The reaction of norbornadiene with (triphenylphosphoranediyl)-aminocyclotrithiatriazine produces the cycloadduct $Ph_3PN\text{-}S_3N_3.C_7H_8$. 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).[71]



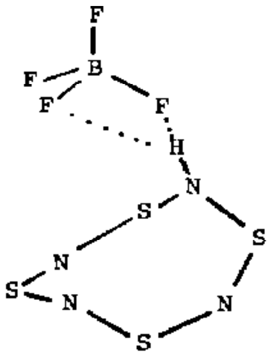
Major products from the reactions of $S_3N_3^-$ with (i) halogens, (ii) $COCl_2$, (iii) Ph_2PCl, and (iv) CS_2.

Scheme 2



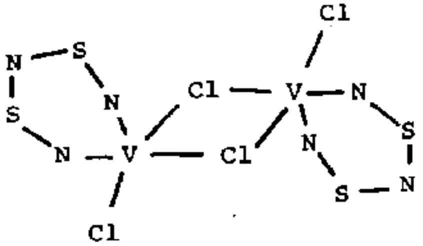
(<u>27</u>)

The reactions of S_4N_4 with a wide variety of species have been reported. With tetrafluoroboric acid diethyl etherate in methylene chloride solution, S_4N_4 reacts to give $S_4N_4H^+BF_4^-$, the first simple salt of S_4N_4. The structure of the $S_4N_4H^+$ cation consists of a boat shaped 8-membered ring with virtually coplanar sulphur atoms (<u>29</u>).[72] S_4N_4 reacts with an excess of VCl_4 in CH_2Cl_2 to give a mixture of $VCl_2(S_2N_3)$ and $S_2N_2.VCl_4$, but with



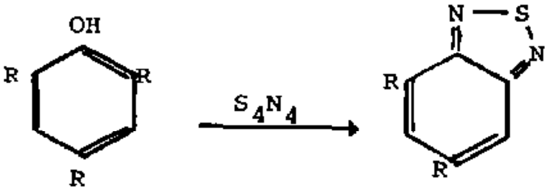
(28)

$TiCl_4$ only $S_4N_4.TiCl_4$ was obtained. A crystal structure determination showed $VCl_2(S_2N_3)$ 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.[73]



(29)

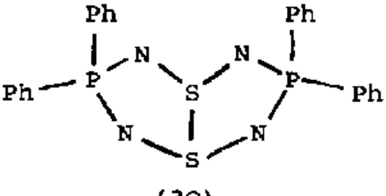
The reaction of S_4N_4 with some 4-methyl- and 4-t-butyl-phenols has been shown to give 2,1,3-benzothiadiazoles (equation 21).[74]



...(21)

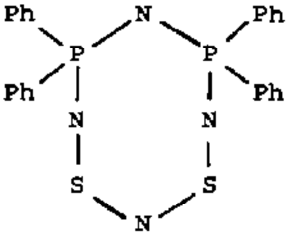
In addition to the six membered ring $R_2PS_2N_3$ reported previously and the cyclophosphazenes $(R_2PN)_{3,4}$, two structural isomers of the eight membered ring $R_4P_2S_2N_4$ are formed in the reaction of S_4N_4 with R_2PPR_2 (R = Me, Ph) and Ph_2PH in toluene under reflux. Crystal structure determinations on the phenyl derivatives

1,5-$Ph_2P(NSN)_2PPh_2$ and 1,3-$(Ph_2PNPPh_2)S_2N_3$ showed the former to consist of a folded eight membered ring with a cross ring S-S contact of 2.527Å and the angle between the two intersecting planes of the ring to be 117.3°, (30). The mean endocyclic P-N and S-N bond lengths were 1.622 and 1.590Å respectively.



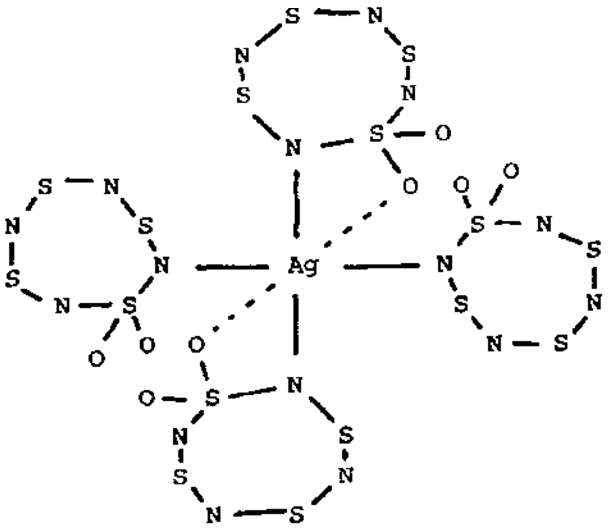
(30)

1,3-$(Ph_2PNPPh_2)S_2N_3$ 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 0.697Å. The mean endocyclic P-N and S-N bond lengths are 1.600 and 1.577Å respectively.[75]



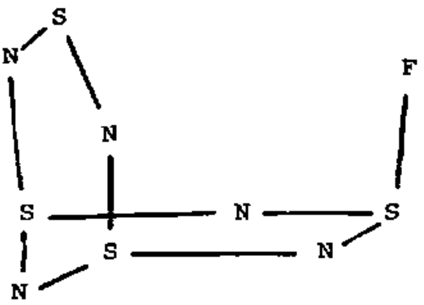
(31)

A redetermination of the structure of tetrasulphur tetranitrogen dioxide, $S_4N_4O_2$, 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 Abm2 is probably incorrect due to twinning. The space group is now considered to be $P2_1/c$.[76] The reaction of silver hexafluoroarsenate(V) with tetrasulphur tetranitrogen dioxide in SO_2 has been shown to give crystals of $[Ag(S_4N_4O_2)_4]^+[AsF_6]^-$. A structure determination showed that the silver atom lies 53pm 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 307pm, and intermolecular Ag-N and Ag-O interactions both of 273pm (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.[77]



(<u>32</u>)

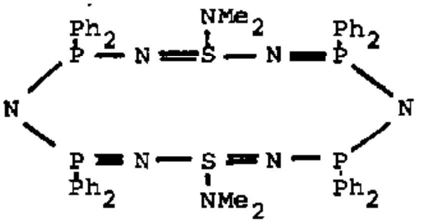
Fluoride addition to the $S_4N_5{}^+$ cation in liquid SO_2 has given S_4N_5F and a crystal structure determination showed it to have the configuration (<u>33</u>).[78]



(<u>33</u>)

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 (<u>9</u>) and (<u>10</u>)). The structure of an intermediate in the thermal decomposition of

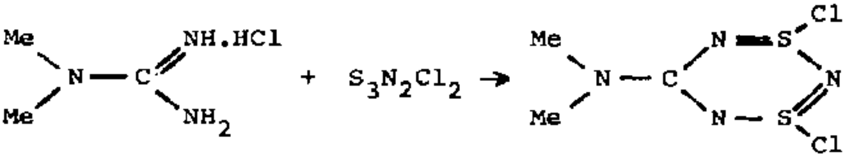
$(Ph_2PN)_2NSX$ (X = NMe_2) has also been determined. The intermediate, $Ph_8P_4N_6S_2(NMe_2)_2$ forms a twelve membered ring with a trans NMe_2 substituent on each of the two sulphur atoms (34). The endocyclic S-N bond lengths (mean 1.590Å) are considerably shorter than the exocyclic bond length of 1.703Å which is close to the value expected for a S-N single bond.[79]



(34)

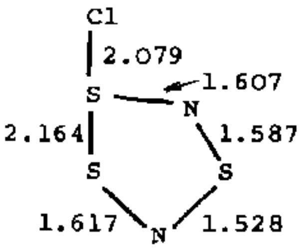
The reaction of S_4N_4 with $TlNO_3$ and NH_3 has been used to prepare $Tl_2S_7N_8$. A crystal structure determination showed the compound to be comprised of Tl^+ cations and $S_3N_3^-$ and $S_4N_5^-$ anions.[80]

The six membered ring compound, $Me_2NCN_3S_2Cl_2$, has been prepared from N,N-dimethylguanidinhydrochloride and trithiadiazindichloride.



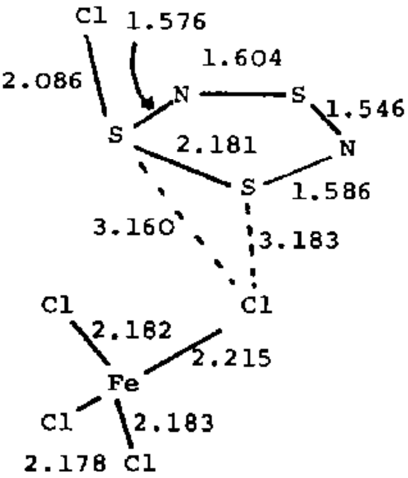
...(22)

The C_2N unit lies approximately in the plane of the CNSNSN ring with both carbon atoms on the same side of the ring.[81] The reaction of $N_4S_4SbCl_5$ and Cl_2 has been used to prepare $N_2S_3Cl^+SbCl_6^-$. The bond lengths (in Å) of the independent cation $N_2S_3Cl^+$ are shown in (35).[82]



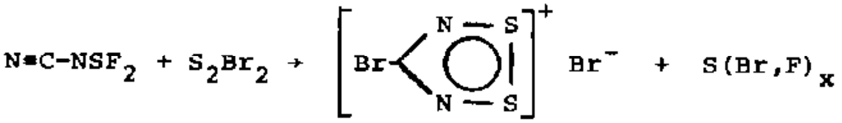
(35)

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).[83]



(36)

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:[84]



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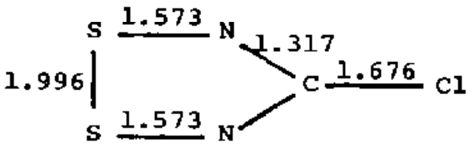
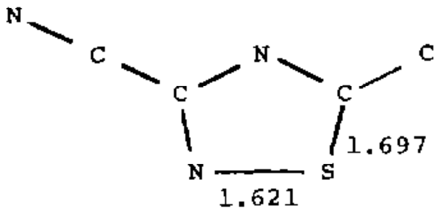


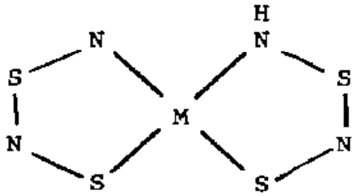
(37)

The reaction of cyanogen with elemental sulphur in dimethyl formamide at 120°C has been shown to give $(CN)_4S$. The molecule (38) is almost planar, only one carbonitrile group being slightly out of the plane of the thiadiazole ring.[85]



(38)

The compounds $[M(OS_2N_2)_6][AsF_6]_2$ where M = Zn or Cd have been prepared in which the metal atoms are coordinated by six N_2S_2O ligands. The metal atom is bonded to the heterocycle via the exocyclic oxygen atom giving a slightly distorted octahedral coordination. The S_3N_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 AsF_6^- group is slightly disordered in the Cd compound, but considerably disordered in the Zn compound.[86] The complex (39) reacts with alcoholic solutions of alkaline hydroxides by double deprotonation to the anion $[Ni(N_2S_2)_2]^{2-}$, but only one proton is removed by reaction with strong organic bases forming salts with the anion $[Ni(HN_2S_2)(N_2S_2)]^-$. The structure of the tetraphenylarsonium salt was determined.[87]



(39)

6.2.4 Bonds to Oxygen

The apparent molar heat capacities and volumes of aqueous $NaHSO_3$, $KHSO_3$ and 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 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 SO_2 and HSO_3^- were obtained from the apparent molar properties.[88] 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 SO_2 was increased by about 50% relative to unhydrolysed solute.[89] Large sensitised photocurrents in acidic media have been observed for the photosensitised oxidation of SO_2 at an optically transparent electrode coated with poly(vinylpyridine) coordinated zinc(II) tetraphenylporphine.[90] The electrochemical behaviour of SO_2 has been investigated at illuminated p-type semiconducting Si, WS_2 and InP in CH_3CN/-$Bu^n{}_4NClO_4$ solutions. SO_2 is photoreducible at each of these materials to form $S_2O_4{}^{2-}$ and preparative, controlled potential photoelectrochemical reduction at all three photoelectrodes was demonstrated to give >90% current efficiency for formation of $S_2O_4{}^{2-}$, which was precipitated and collected as $Na_2S_2O_4$.[91] SO_2 has been used as an oxidiser in the reaction of $Zn(SO_2)_n(AsF_6)_2$ and tetraphenyldiphosphane to produce $Zn(O_2P_2Ph_4)_3(AsF_6)_2$. When $Zn(SO_2)_n(AsF_6)_2$ is treated with $P[O{=}P(OMe)_2]_3$ in liquid SO_2, $Zn[P(O{=}POMe_2)_3]_2(AsF_6)_2$ is formed and its structure was determined.[92] The metals Mg, Cr, W, Fe, Ni, Cu, Zn, Hg, Al, Sn and Pb dissolve electrolytically in the mixed non-aqueous solvents, 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-SO_2 gave pure single products of metal disulphates.[93]

An ab initio study has been carried out on the complex formed between 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 1.8Å. Calculations of the electric field potential surrounding the SO_2 were also performed.[94] The thermal decomposition of $Ce_2(SO_3)_2SO_4{\cdot}4H_2O$ has been shown to take place in several stages (equations 24 to 30). A thermochemical cycle for splitting 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.[95]

400-800K

$$Ce_2(SO_3)_2SO_4.4H_2O \rightarrow Ce_2(SO_3)_2SO_4 + 4H_2O \qquad ...(24)$$

$$Ce_2(SO_3)_2SO_4 \rightarrow Ce_2O_X(SO_3)_{2-X}SO_4 + XSO_2 \qquad ...(25)$$

$$(X < 0.1)$$

800-850K

$$Ce_2(SO_3)_2SO_4 \rightarrow Ce_2O(SO_4)_2 + \tfrac{1}{4}S_2 + \tfrac{1}{2}SO_2 \qquad ...(26)$$

800-850K

$$Ce_2(SO_3)_2SO_4 \rightarrow Ce_2O_2SO_4 + 2SO_2 \qquad ...(27)$$

850-1000K

$$Ce_2O(SO_4)_2 \rightarrow CeOSO_4 + CeO_2 + SO_2 \qquad ...(28)$$

850-1000K

$$Ce_2O_2SO_4 \rightarrow 2CeO_2 + SO_2 \qquad ...(29)$$

1000-1200K

$$CeOSO_4 \rightarrow CeO_2 + SO_2 + \tfrac{1}{2}O_2 \qquad ...(30)$$

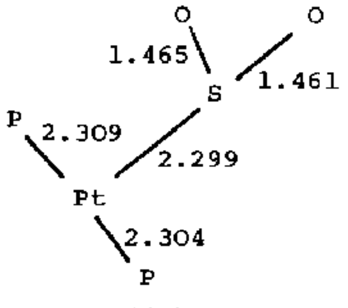
The reactive characteristics of the oxyanion radicals of sulphur, SO_2^-, SO_3^- and SO_4^- towards a number of organic substrates have been investigated by use of the rapid-mixing flow technique coupled with E.S.R. The SO_2^- was the only ion able to reduce aromatic nitro compounds to the corresponding anion radicals, but did not abstract hydrogen from saturated compounds nor add to the unsaturated compounds. SO_3^- could add to compounds having a C=C bond but did not abstract hydrogen from saturated compounds. SO_4^- abstracted hydrogen from saturated compounds and also could add to the unsaturated compounds with a C=C bond.[96] In the presence of tetraethylammonium ion, 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):

$$SO_2^- + SO_2 \rightleftarrows (SO_2^-)SO_2 \qquad ...(31)$$

$$(SO_2^-)SO_2 + SO_2^- \rightarrow {}^-O_2S\text{-}SO_2^- + SO_2 \qquad ...(32)$$

Reaction (32) could either be an electron transfer or the displacement of SO_2 by SO_2^-.[97]

Solubility and freezing point data have been presented for the system SO_2-N methyl-2-pyrrolidinone(NMP). The enthalpy and entropy of solution were found to be -33.7 kJ/mol and -94.6 kJ/-mole respectively. The freezing point diagram indicated the formation of 2:1 and 1:1 NMP: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 SO_2 with a weakening of the CO bond of NMP.[98] The chemical compounds $B_2O_3.SO_3$ and $B_2O_3.2SO_3$ have been prepared by heating boric acid in liquid sulphur trioxide at different temperatures.[99] Infrared and ^{11}B n.m.r. studies showed the molecules of both compounds to contain SO_4 and BO_3 groups together with distorted BO_4 tetrahedra.[100] The structure of pentacarbonyl(sulphur dioxide)-chromium has been determined. The sulphur dioxide is η^1-coplanar coordinated with a Cr-S distance of 219pm, the shortest bond reported so far between $Cr^{\underline{\overline{0}}}$ 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 π-acceptor capacity of SO_2.[101] The first structurally characterised three coordinate bi(phosphine)-$Pt^{\underline{\overline{0}}}$-sulphur dioxide complex, $Pt(PCy_3)_2SO_2$ (<u>40</u>), has been described.[102]

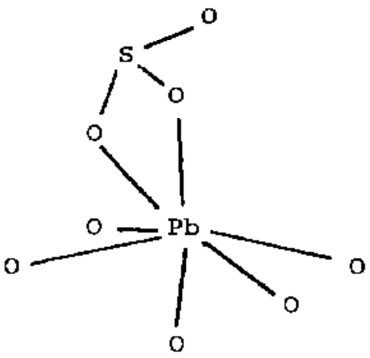


(40)

The following phase systems have been studied, ZrO_2-SO_3-HCl-H_2O;[103] K_2O-V_2O_5-SO_3,[104] $SOCl_2$-$VOCl_3$ and SO_2Cl_2-$VOCl_3$.[105]

Ab initio calculations have been performed on the sulphite and hydrogen sulphite ions, HSO_3^- and SO_2OH. The mechanism behind the shortening of the S-O bond in HSO_3^- as compared with SO_3^{2-} was confirmed to be a transformation of an antibonding into a non-bonding orbital upon protonation. The isomers HSO_3^- and SO_2OH^- were found to be of comparable energy. The very long S-OH bond (1.716Å) found, indicates the system to be assembled from comparatively weakly interacting species of SO_2 and OH^-.[106]

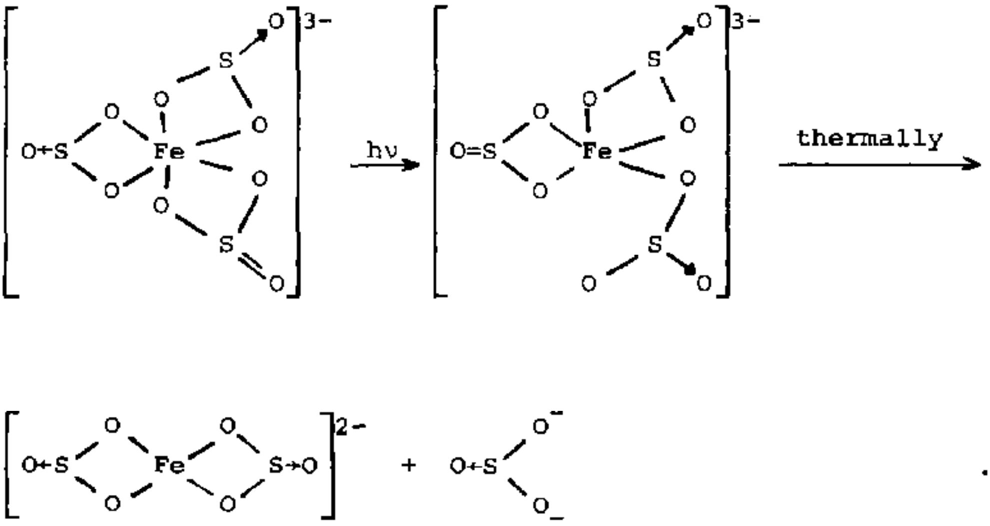
The gel crystallisation technique has been used to obtain single crystals of the hitherto unknown $Na_2Mg(SO_3)_2 2H_2O$ from $Mg(HSO_3)_2$ solutions saturated with NaCl. The crystal structure contains MgO_6 octahedra connected by sulphite bridges forming chains which are held together by strong hydrogen bonds.[107] Single cryatals of the anhydrous sulphites $BaSO_3$, $CdSO_3I$, $PbSO_3$ and $Na_2Cd_3(SO_4)_4$ and the previously unknown sulphites $CdSO_3(II)$ and $CdSO_3(III)$ have also been prepared by the gel crystallisation method.[108] The crystal structure of orthorhombic $PbSO_3$ has been determined. The sulphite ion has S-O distances of 149.4 and 153.7pm. The Pb-O distances of the edge connected PbO_7 polyhedra (distorted mono capped trigonal prism) range from 253.4 to 284.8pm (41). The structure is closely related to that of $PbSO_4$.[109]



(41)

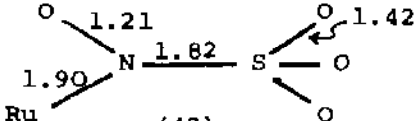
MgI_2, FeI_2 and CuI have been shown to react with tetramethylammonium disulphite to form Mg and Fe anhydrous sulphites and Cu(I) disulphite respectively. Iron(II) sulphite and copper(I) disulphite react with DMSO-SO_2 to form iron(II) disulphite and copper(II) disulphite.[110] Structural studies on $K_5(HSO_3)_3(S_2O_5)$ showed the disulphite ion to have C_s symmetry and consist of a thionite and a thionate group linked by an S-S bond of 2.226Å. The S-O distances are 1.489Å in the thionite group and 1.462Å in the thionate group. There are three crystallographically different HSO_3^- ions in the cell with average S-O distances of 1.419, 1.451 and 1.445Å respectively. The hydrogen atom is bonded to the sulphur atom in all three HSO_3^- ions with H-S distances of 1.31, 1.16 and 1.16Å respectively.[111] A new class of basic sulphites of the type $NaM_2OH(SO_3)_2H_2O$, with M = Mg, Mn, Fe, Co, Ni and Zn have been prepared by crystallisation from aqueous sulphite solutions containing Na^+ and M^{2+} ions. These hydroxide sulphites show a strongly anisotropic thermal expansion due to the presence of a layer structure and exhibit an unusually high thermal stability compared to other solid hydrates.[112]

The autoxidation of sulphite is the first well known chain reaction proceeding through free radicals in solution. It has been found that the formation of sulphite radicals in photo-initiated autoxidation of sulphite, which is a metal catalysed reaction as well as the classical thermal reaction, is due to the absorption of photons by ferrisulphite complexes rather than the sulphite itself. The reaction scheme proposed is shown in equation (33).[113]



...(33)

Convincing evidence that the red adduct which is formed in the Boedeker reaction contains the $M(N(O)SO_3)$ moiety has been obtained from a study of the reaction of $SO_3{}^{2-}$ with trans$[RuCl(py)_4(NO)]^{2+}$ or cis$[RuX(bipy)_2(NO)]^{2+}$, X = Cl or Br. The adducts formed in the reactions, $[RuCl(py)_4(N(O)SO_3)]$ and cis$[RuX(bipy)_2(N(O)SO_3)]$ both contain identical $N(O)SO_3$ ligands. This hitherto unknown ligand is coordinated to Ru(II) via the nitrogen atom and has a long N-S bond (1.82Å) (42).[114]



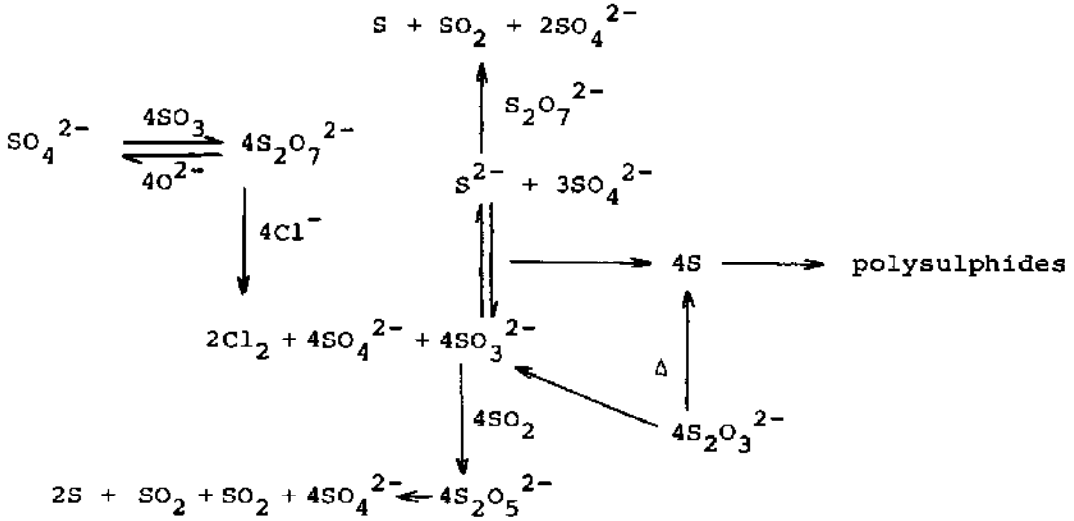
(42)

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 2.0Å. 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 $S_2O_8^{2-}$ is the more probable.[115]

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

$$MSO_4 \rightleftharpoons MO + SO_3\ (SO_2 + \tfrac{1}{2}O_2) \qquad \ldots(34)$$

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 SO_3 has to be used in preference to SO_2 and cycling was shown to decrease the reactivity of the oxides towards SO_3.[116] The reactions of sulphide and of five sulphur oxyanion salts (Na_2SO_3, $Na_2S_2O_5$, $K_2S_2O_5$, $Na_2S_2O_3$ and $K_2S_2O_7$) have been studied by themselves and in molten Li_2SO_4-Na_2SO_4-K_2SO_4 eutectic under nitrogen, with air, SO_2, SO_3 and 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).[117]



Scheme 3

A series of Raman and near infrared absorption spectra of molten $K_2S_2O_7$-$KHSO_4$ mixtures at 430°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 $S_2O_7^{2-}$

$$2HSO_4^- \rightleftharpoons S_2O_7^{2-} + H_2O \qquad \ldots(35)$$

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.[118]

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.[119] 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.[120] 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.[121] 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 supress the phase transformation in Na_2SO_4.[122] The pyroelectric properties of $LiKSO_4$ have been studied.[123] Laser interferometric galvanostatic studies have been carried out in the $Zn/ZnSO_4/Zn$ system with gelled electrolyte short-time electrolysis.[124] 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

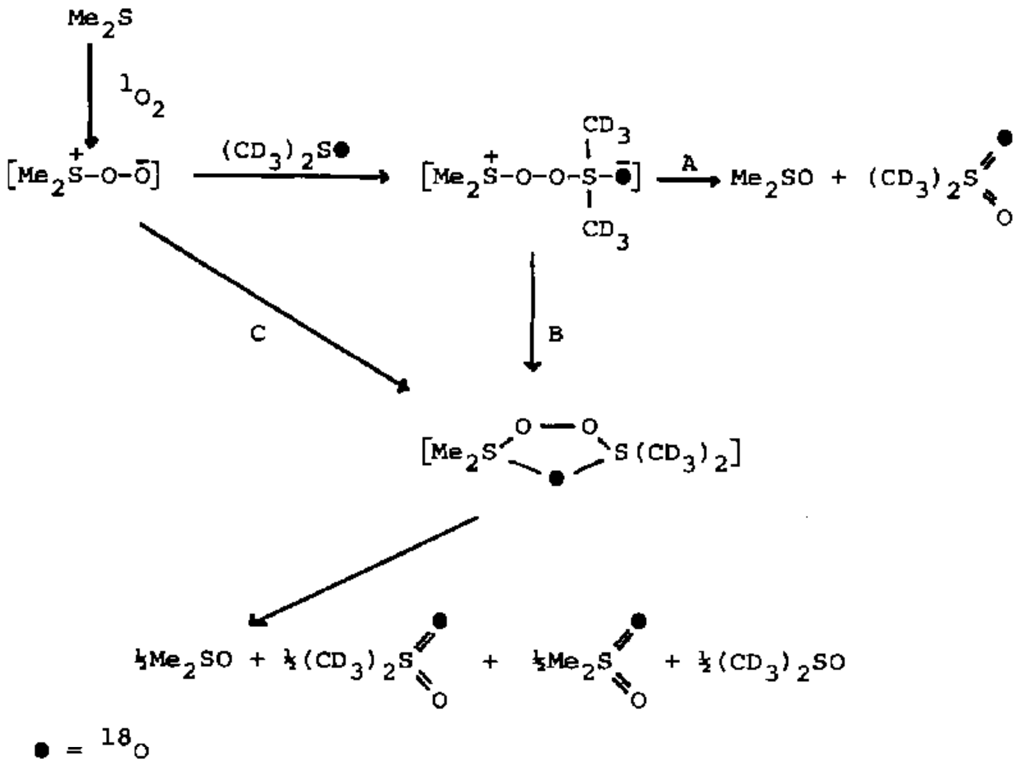
Table 1. Phase systems involving sulphates

System	ref.	System	ref.
$NaCl-Na_2SO_4-Me_2CO-H_2O$	125	$KCl-Li_2SO_4-NiCl_2$	129
$HfO_2-M_2SO_4-H_2SO_4-H_2O$	126	$Al^{3+},Ga^{3+} + H^+\Vert SO_4{}^{2-},H_2O$	130
M = Na,K,Rb,Cs or NH_4		$Ga^{3+},In^{3+} + H^+\Vert SO_4{}^{2-},H_2O$	130
$Al(NO_3)_3-Al_2(SO_4)_3-H_2O$	127	$Al^{3+},In^{3+}\Vert SO_4{}^{2-},H_2O$	130
$Gd(SO_4)_3-(NH_4)_2SO_4-Rb_2SO_4-H_2O$	128	$KVO_2SO_4-K_2SO_4-H_2SO_4-H_2O$	131
$Cs_2SO_4-Cd_2(SO_4)_3-(NH_4)_2SO_4-H_2O$	128		

ions forming complexes with sulphate or phosphate ions.[132]

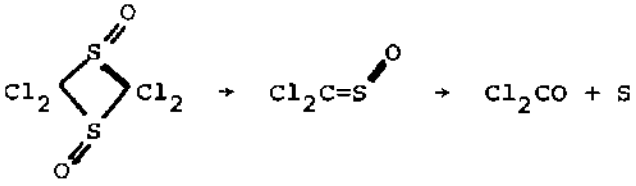
A comparative analysis of the infrared spectra and crystal structure show that the water molecules in $CaSO_4.2H_2O$ form one coordinate and two non equivalent hydrogen bonds: a stronger one with an oxygen of the SO_4 group of the layer where the Ca^{2+} ion is situated and a weak one with the oxygen atom of the next layer. In the α and β hemihydrate structures the water molecules are connected by a coordinate bond and only one hydrogen bond analogous to the stronger bond of the dihydrate.[133] A crystal structure determination of the calcium sulphate subhydrate $CaSO_4.O{\cdot}8H_2O$ showed that chains of alternating Ca^{2+} and $SO_4{}^{2-}$ ions form the framework of a tunnel structure in which four water molecules are randomly distributed over five positions and the Ca^{2+} ion is surrounded by six sulphate groups and one water molecule.[134] $(H_3O)_2Sb_2(SO_4)_4$ has a polymeric structure with sheets in which -Sb-O-S- chains are linked together by sulphate groups.[135] A study of the chemical transport reactions of anhydrous metal sulphates has shown that it is possible to prepare well formed single crystals of $CuSO_4$ and Cu_2OSO_4 by deposition from a vapour phase. Cl_2 and $HgCl_2$ were found to be suitable transporting agents for $CuSO_4$ but HCl, NH_4Cl and I_2 were less satisfactory. $HgCl_2$ proved to be a good transporting agent for Cu_2OSO_4.[136] The crystal structures of monoclinic nickel sulphate hexadeuterate[137] and $Th(SO_4)_2.8H_2O$[138] have been determined. The deformation electron density in $MgS_2O_3.6H_2O$ has been evaluated from a combination of X-ray and neutron diffraction data.[139] The conditions for the synthesis of caesium tantalum sulphates[140] and the behaviour of anhydrous lanthanide sulphates and double lithium lanthanide sulphate[141] 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.[142]

^{18}O labelling has been used to follow the reaction pathway for the nucleophilic oxidation of sulphoxide 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.[143]



Scheme 4

A complete structure-reactivity study has been carried out for both kinetics and equilibria in the transfer of the sulphate group (-SO$_3^-$) between pyridine and phenols in aqueous solution at 25°C.[144] Vibrational assignments of the polarised Raman spectra of single crystals of NaH$_2$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.[145] 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 sulphoxides of the type X_2CSO (X = Cl,F) respectively.[146]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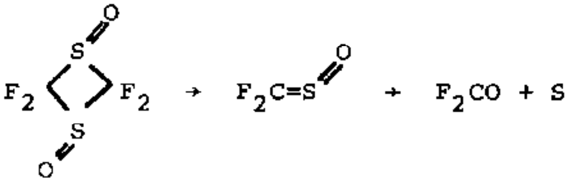
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(44)

Complexes of the type $M(NH_3)_5(OSO_2CF_3)(CF_3SO_3)_n$ have been prepared for M = Cr(III), Rh(III), Ir(III), Ru(III) and Pt(IV) and are considered to offer potential as versatile synthetic intermediates.[147] Reactions of the cyclic systems $(NPCl_2)_2NSOX$ and $NPCl_2(NSOX)_2$ (X = F,Cl,Ph) with NH_3 in diethyl ether or acetonitrile at low temperatures provide convincing evidence that the P-bonded chlorine atoms are replaced by NH_2 groups along a geminal pathway without disruption of the S-F and S-Ph groups.[148] The nitrosodisulphonate ion, $\cdot ON(SO_3)_2^{2-}$, has been found to smoothly oxidise $Fe(CN)_6^{4-}$ to $Fe(CN)_6^{3-}$ and H_2O_2 to O_2 giving $HON(SO_3)_2^{2-}$ in both reactions.[149] The reactions of perfluoroalkanesulphinates with halogen and halogen acids, and a new method for the synthesis of perfluorosulphonic acid have been described.[150] The deiodo-sulphination (the conversion of R_fI to $R_f \cdot SO_2K$ in one step) of perfluoralkyl iodides has been studied.[151]

6.2.5 Sulphides

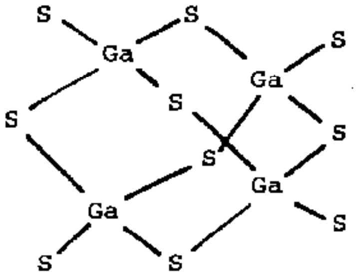
A Raman spectrometric method has been used for in situ identification of the H-S stretch in high pH solutions of H_2S and for estimating their concentrations. The observed spectrum for a 8.9N NaOH solution containing 0.6M H_2S and 0.1M $NaClO_4$ showed that virtually all sulphide was in the form of bisulphide. This data was used to determine the second dissociation constant of H_2S, the value found, 17±1 was the highest yet recorded.[152] The internal energy effects and the energetics of the ion-molecule reactions, $H_2S^+ + H_2S \rightarrow S_2^+ + 2H_2$, $HS_2^+ + H_2 + H$, $H_3S^+ + HS$, and $H_3S_2^+ + H$ have been studied by photoionisation of hydrogen-sulphide dimers synthesised by the molecular beam method.[153] 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.[155]

The equilibrium vaporisation of $CuInS_2$ has been studied by Knudsen cell mass spectrometric techniques in the temperature range 902 to 1110K. $CuInS_2$ decomposes under steady state conditions according to the reaction:

$$2CuInS_2(s) \rightarrow Cu_2S(s) + In_2S(g) + S_2(g) \qquad \ldots(38)$$

The enthalpy of formation of $CuInS_2$ was calculated to be $\Delta H^{o}_{298} = -221.7 \pm 13$ kJ/mole.[156]

Extended Hückel calculations comparing the valence electronic structures of B_8S_{16} and the isostructural but not isoelectronic porphine, and of the Cu^{2+} complexes of these two macrocycles, indicate that the B_8S_{16} complex may have a stability (relative to free ligand and metal ion) that is comparable to that of the porphine complex.[158] The crystal structure of the spinel $ZnAl_2S_4$ (obtained by chemical transport reaction at 740°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.[159] The quasibinary systems $Zn_{1-x}Cd_xAl_2S_4$, $ZnAl_{2(1-x)}Ga_{2x}S_4$ and $ZnAl_2S_{4(1-x)}Se_{4x}$ have been studied. In the spinel $ZnAl_2S_4$, up to 20% of Zn atoms can be replaced by Cd, in the other two systems; $ZnAl_2S_4$ has no detectable homogeneity range. The thiogallate phases have much broader ranges of homogeneity. At 950°C, $ZnAl_2Se_4$ undergoes a reversible phase transformation to a wurtzite type phase and this same type of transition was also observed for solid solutions, $ZnAl_2S_{4(1-x)}Se_{4x}$ with x = 1 to 0.3.[160] Structure refinement has also been carried out for the spinel $CdGa_2S_4$.[161] Crystal structure determinations of $Ga_2Sn_2S_5$ show that the structure is essentially built from alternating sheets of $(GaS_4)_n$ tetrahedra and sheets of $(Sn_2S_{11})_n$. The GaS_4 tetrahedra are linked in groups of two, sharing their opposite edges. The Sn_2S_{11} unit has the two tin atoms in different environments both of which are very asymmetric.[162] The new compound $Ba_4Ga_4S_{10}$ crystallises in the space group C2/c and has a structure in which there are adamantane-like $Ga_4S_{10}{}^{8-}$ anions (<u>45</u>) isosteric to the neutral P_4S_{10} molecule. The Ba^{2+} ion is coordinated by seven sulphur atoms.[163]

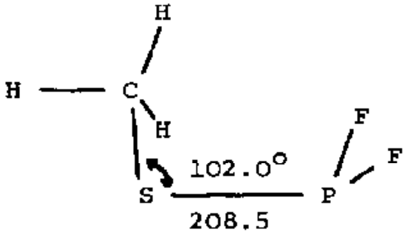


(<u>45</u>)

The crystal structure of KIn_5S_8 shows the indium atoms to have four and six-fold coordination and the potassium atoms to have six fold prismatic coordination.[164]

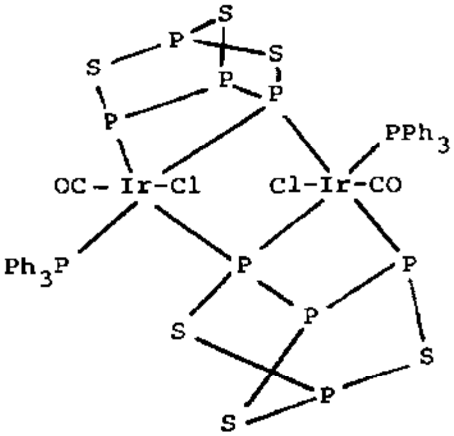
The charge distribution in some lead chalcogenides has been studied by X-ray diffraction methods. All form the NaCl structure and the results suggest a predominantly covalent bonding.[165] Potentiometric titration of 0.01M solutions of $Na_6Si_2S_6$, $Na_6Si_2Se_6$, $Na_2Ge_2S_6$ and $Na_6Ge_2Se_6$ in methanol with bromine has been used to determine thermodynamic data of reactions which take place by scission of the Si-Si or Ge-Ge bonds. The bond energies of these homonuclear bonds were estimated.[166]

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.[167] 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°.[168] 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.[169] 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) = 213.2pm, PSP = 91.3° and r(P-Se) = 227.3pm, P-Se-P = 94.6° 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° away from the position in which the C-S bond lies anti to the bisector of the FPF angle (<u>46</u>).[170]



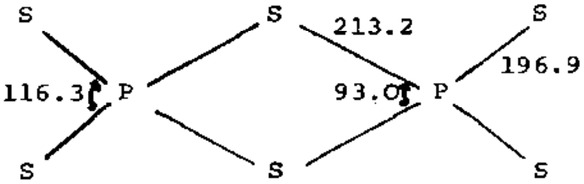
(<u>46</u>)

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).[171] The reaction P_4S_3 with $IrCl(CO)(PPh_3)$ in benzene at 60°C gives the air stable, and practically insoluble complex $[Ir)P_4S_3)(PPh_3)Cl(CO)]$. 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 (<u>47</u>). The crystal structure of α-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



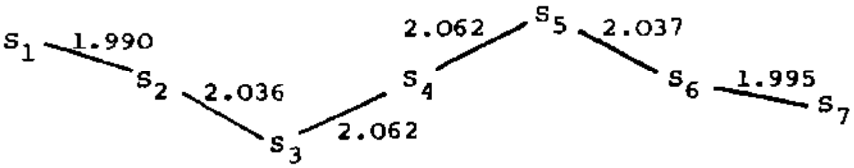
(47)

the P_4S_3 molecules are rigid.[173] 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.[174] $Tl_2P_2S_6$ 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.[175]



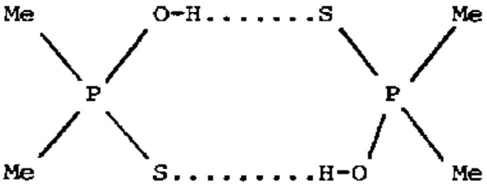
(48)

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.



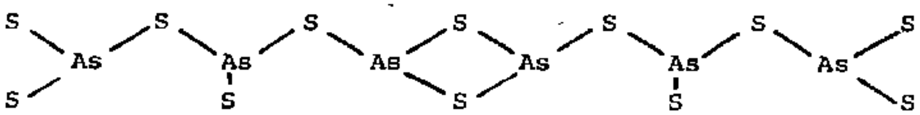
(49)

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.[176] 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.[177]



(50)

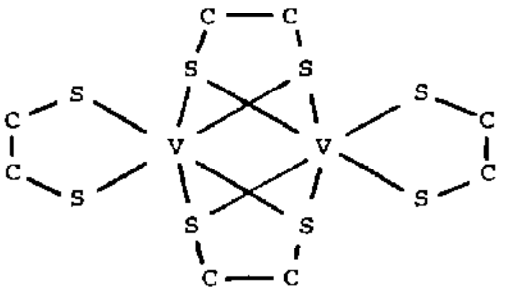
Hydrothermal synthesis in the system Tl_2S-PbS-Ag_2S_3 has been used to prepare single crystals of the new compound $PbTlAs_3S_6$. The lead atom is coordinated by seven S atoms (Pb-S = 3.074Å) to form infinite PbS_3 layers. The Tl atom is coordinated also by seven sulphur atoms (Tl-S = 2.300Å) to form infinite 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 As_6S_{12} groups (51).[178]



(51)

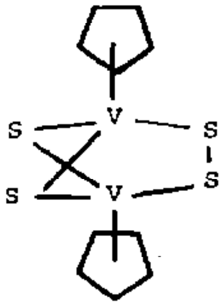
The crystal structure of $Tl_2(Sb,As)_{10}S_{16}$ contains AsS_3 and SbS_3 pyramids together with SbS_5 coordination polyhedra.[179] $TlSbS_2$ has a structure built up from sheets formed by SbS_4E trigonal bipyramids linked together. The Sb-S bond lengths lie in the range 2.41 to 2.96Å. The sheets are linked together with weak Tl...S (3.50-3.66Å), Tl...Sb (3.60-3.73Å) and Tl...Tl (3.62Å) interactions.[180] The structures of $Pb_2Sb_2S_5$ and $Sn_2Sb_2S_5$[181] and of two forms of $BaBi_2S_4$[182] have also been determined. The following Main Group element-sulphide phase systems have been studied; Ge-S-Tl,[183] GaS-PbS and GaS-Pb,[184] BiF_3-Bi_2S_3,[185] and SbF_3-Sb_2S_3.[186]

Polytypic $Ti_{1+x}S_2$ (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 $Ti_{1.32}S_2$.[187] Reaction of VCl_3 with 1,2-ethanedithiolate gives the binuclear complex $[V_2(SC_2H_4S)_4]^{2}$ 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.[188]



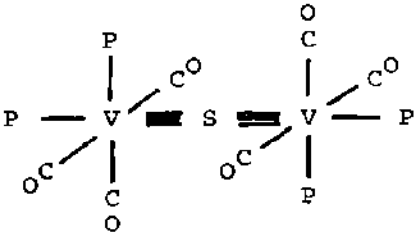
(52)

The unprecedented and unanticipated structures of $(Pr^{i}Cp)_2V_2S_4$ and the acetylene adduct of $Cp_2V_2S_4$ have been described. The two $(Pr^{i}Cp)V$ moieties (53) are bridged by an μ-η¹-S_2 and two μ-S ligands with average V-S(μ-S) and V-S(S_2) distances of 2.21 and 2.27Å respectively.[189]



(53)

The X-ray structure of the red diamagnetic complex, $[V(CO)_3diphos]_2S$ 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.[190]

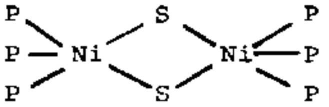


(54)

The thermal decomposition of molybdenum trisulphide has been followed using EXAFS.[191] The hetero metal sulphur aggregates $[Co(WS_4)_2]^{n-}$ 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, WS_4^{2-} like MoS_4^{2-} is a non-innocent ligand and that the additional charge upon reduction is located mainly at the sulphur atom.[192] The structure of 3c-type Fe_7S_8, grown by vapour phase transport has been reexamined.[193] The mixed valency compound $Na_3Fe_2S_4$ which is formed in iron-sodium polysulphide melts, is oxidised and hydrated in air to $NaFeS_2.xH_2O$ where x is approximately 2.[194] Salts previously reported to contain the iron-sulphur cluster nitrosyl anion $Fe_3S_2(NO)_5^-$ have now been shown to be identical with those containing the well known anion $Fe_4S_3(NO)_7^-$.[195]

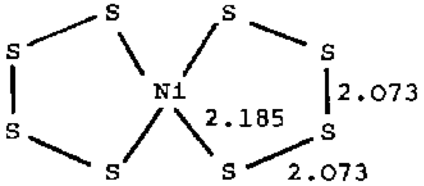
New syntheses of $Fe_2S_2Cl_4^{2-}$, and $Fe_2OCl_6^{2-}$ and terminal oxo/sulphido ligand substitution reactions have been devised using the reagents $(Me_3Si)_2S$, $NaSSiMe_3$ and $NaOSiMe_3$ in acetonitrile solutions.[196] The compound Na_6CoS_4 has been shown to be isotypic with Na_6ZnO_4 and to contain almost regular CoS_4 tetrahedra with average Co-S distances of 235pm.[197] Members of the systems $Co_{1-x}Ru_xS_2$ with x from 0 to 1 and $Rh_{1-x}Ru_xS_2$ with x from 0.5 to 1 have been prepared and their crystallographic and magnetic properties studied.[198] The nickel sulphide $Ni_{17}S_{18}$ has been shown to have a vacancy ordered superstructure of the NiAs type.[199]

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 Ni_2S_2 bridging framework is crystallographically planar with a Ni-Ni distance of 3.865Å (55). Since the S-S distance of 2.208Å indicates a weakened bond, the structure represents a rare example of a η^2 binuclear ligand that is coplanar with the two metals.[200]



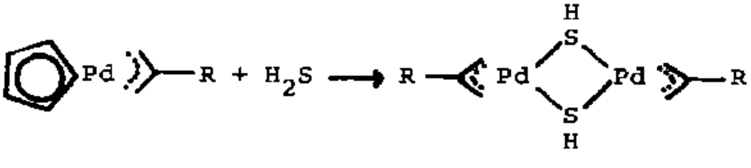
(55)

The tetraethylammonium salt of $Ni(S_4)_2^{2-}$ has been isolated and its crystal structure determined. This is the first binary nickel-sulphur complex and the first complex to contain only S_4^{2-} ligands (56).



(56)

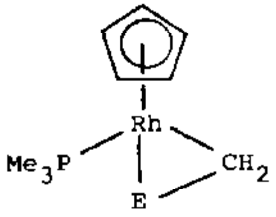
The anion has point symmetry D_2 and exists as a spirobicycle in which the central nickel atom is surrounded by an approximately square planar array of four sulphur atoms.[201] η^3-Allyl or η^3-methallyl-η^5-cyclopentadienylpalladium reacts with hydrogen sulphide at -78°C with selective cleavage of the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



(57)

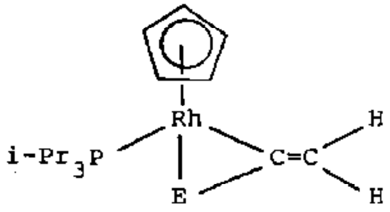
The reactions of (57) to give mono and bimetallic polynuclear η^3-allyl metal-sulphur complexes of nickel have also been studied.[203,204]

A radiochemical method for analysing the adsorption and desorption of sulphur on polycrystalline copper has been described.[205] 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.[206] 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 $RhSe_2 < IrSe_2 < RhS_2 < IrS_2$.[207] Using NaSH, NaSeH or NaTeH as substrates the rhodium complex (58) was prepared in good yield.[208]



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.[209]

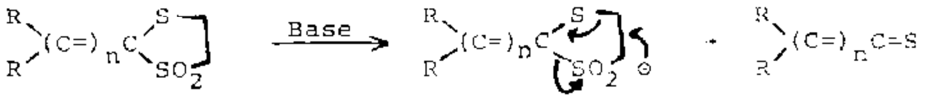
The first chalcogenide analogues of the platinum bronzes, $LaPd_3S_4$ has been prepared by heating a stoichiometric combination of the elements at 1125K in a sealed, evacuated silica tube lined with carbon.[210] The compound $Pd_3(PS_4)_2$ has been synthesised from the element at 600°C and its crystal structure derived from powder data.[211] Structural data has also been obtained for the following sulphides $Pb_{1.6}In_8Bi_4S_{19}$;[212] $Mo_6Br_6S_3$,[213] $YbS_{1.34-1.42}$,[214] $LaYbS_3$,[215] $(FeV)_3S_4$[216] and $GaLa_3OS_5$.[217]

6.2.6 Bonds to Carbon

The preparation of $CF_2(SF_3)_2$ from CS_2 and elemental fluorine has been described. In the presence of CsF, further oxidation by F_2 and ClF may be achieved with the formation of $F_2C(SF_5)_2$ and $(trans\text{-}ClSF_4)_2CF_2$ respectively.[218] The i.r. spectrum of $(CF_3S)_2CS$ 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 CF_3SCF_3 and CS_2.[219]

When the products of the reaction between fluorine atoms and CH_3SH 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 CH_3S and CH_2SH.[220] Nonempirical molecular electronic structure theory has been used to study the electronic ground state of the dimer of carbon monosulphide SCCS.[221] The influence of the ionic strength on the adsorption of thiocyanate ions on mercury has been studied.[222] A crystal structure determination of the complex formed between dibenzo-14-crown 4 and LiSCN has shown that the Li^+ cation is pentacoordinated to the four ethereal oxygens and to the nitrogen atom of the SCN^- ion, in an almost square pyramidal geometry.[223] The addition of 0.2% of OCS to a CH_4-O_2 flame has been shown to give the following sulphur containing negative ions, S^-, SH^-, SO^-, SO_2^-, S_2^-, SO_3^-, HSO_3^- and HSO_4^-. Analysis of the species along the flame showed the rapidity with which OCS is oxidised through SH and SO to SO_2.[224]

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).[225]



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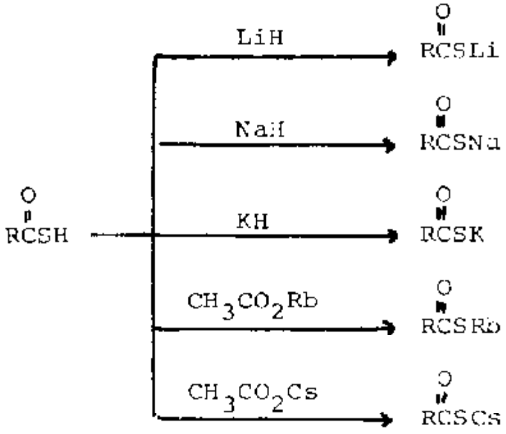
A series of alkalimetal thiocarboxylates (Scheme 5) has been found to be readily obtained in high yields by the reaction of thiocarboxylic acids with either metal hydrides or acetates.[226]



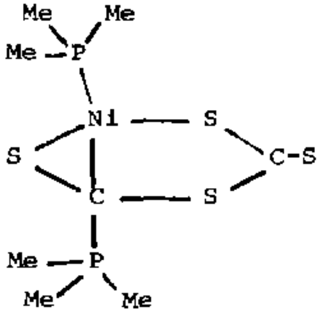
Scheme 5

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.[227] Some alkyl esters of triorganostannane dithiocarboxylic acid have also been shown to complex with metal carbonyl complexes of W, Mn and Re.[228]

A large number of papers have again been published by Cattow in the series "On Chalcogenolates". Topics covered include, the synthesis of alkali metal N-cyan-guanidino monothioformates $M[SOC-NH-C(NH_2)=N-CN]$;[229] the synthesis and reaction of alkali metal N-cyanomonothiocarbimates $M_2[SOC=N-CN].H_2O$;[230-232] the reactions of alkali metal chlorides with CS_2;[233] studies on

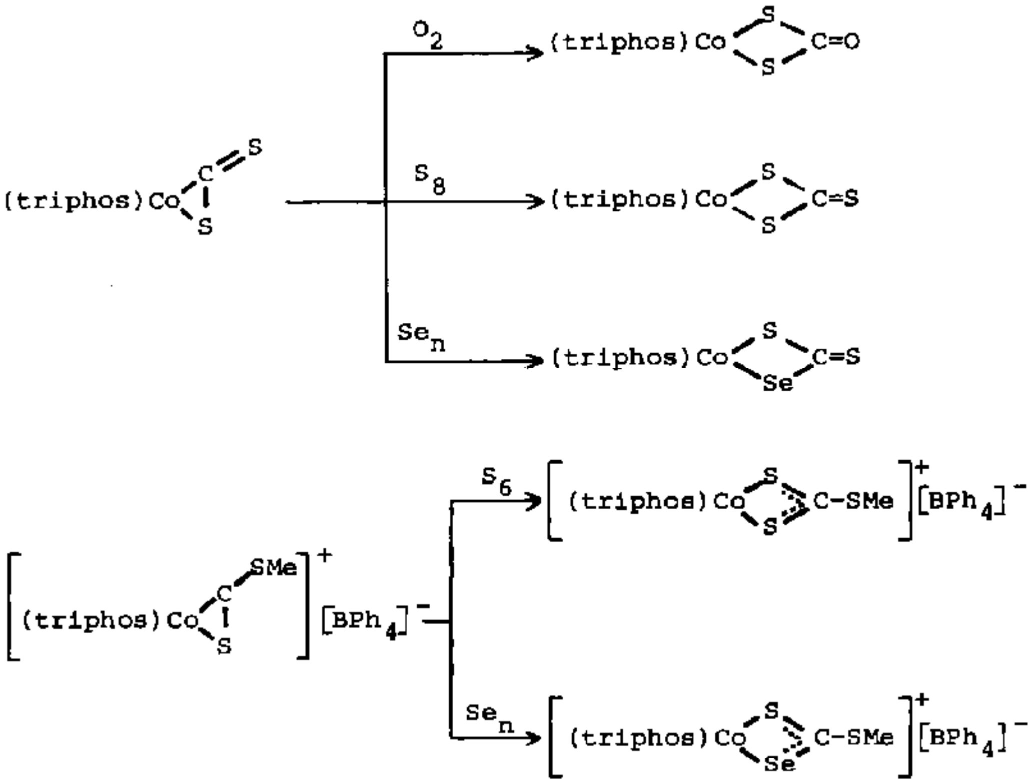
N-cyanformamidinodithiocarbamic acid,[234,235] diesters of cyaniminodiformic acid,[236] studies on Rhodanines,[237-239] and the crystal structures of guanidinodithioformic acid[240] and oxovanadium(V) ethylxanthate.[241]

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.[242] $(Ph_3P)_2Pd(N_3)_2$ 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.[243] 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.[244] 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; $P(ptol)_3$ 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 (<u>60</u>).[245]



(<u>60</u>)

$CaHg(SCN)_4.nH_2O$ where n = 2 or 3 has been isolated from an aqueous solution of $Ca(NCS)_2.4H_2O$ 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.[246] The reaction of trimeric thioformaldehyde with $AgAsF_6$ in liquid SO_2 leads to the compound $[Ag_2\{(CH_2S)_3\}_5][AsF_6]_2.SO_2$. The isolated cations, of the form $L_2AgLAgL_2$ (L = 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.[247] The reactions of oxygen, sulphur and selenium with some η^2-CS_2 and η^2-CS_2Me cobalt complexes have been shown to give the products shown in Scheme 6.[248]



Scheme 6

The reaction of $RhCl_3$ with an aqueous solution of KSCN has been shown not to yield pure $Rh(SCN)_6{}^{3-}$ as was previously thought, but a mixture of the bond isomers $[Rh(NCS)_n(SCN)_{6-n}]^{3-}$ where n = 0 to 3.[249] Similar isomeric forms were also found for the Ir complex.[250]

6.3 SELENIUM

6.3.1 The Element

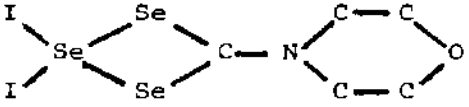
A novel application of chalcogenide esters to purify selenium and tellurium to the 99.999% purity level has been described. Crude selenium and tellurium were first converted to their respective oxides by treatment with concentrated nitric acid. The oxides were then condensed with alcohols or diols to obtain the corresponding esters which on reduction with hydrazine in organic media, provided high purity elemental selenium and tellurium.[251] 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.[252]

6.3.2 Bonds to Halogens

The electronic structures of sulphur, selenium and tellurium hexafluoride have been calculated by the discrete variation X_α method. The marked increase in the electron affinity in SeF_6 compared with SF_6 was related to the large decrease in the antibonding character of the LUMO in the case of SeF_6. The decrease in the electron affinity on going from SeF_6 to TeF_6 was attributed to the increase in 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.[253]

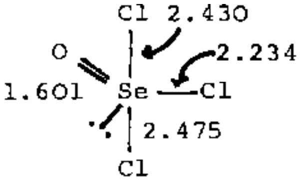
The electron diffraction patterns of the vapour from a gas jet of $SeCl_4$ with a nozzle temperature of 175°C showed the vapour to consist of $SeCl_2$(80%) and Cl_2. The bond distance in $SeCl_2$ is 2.157Å and the valence angle 99.6°.[254] Elemental selenium dissolves in solutions of SeO_2 in concentrated HCl to a small extent to give strongly yellow solutions. Gravimetric analysis and spectrophotometric studies show that the principal species in equilibrium with $SeOCl_2$ is Se_2Cl_2. A completely satisfactory interpretation of these results requires however the presence of $SeCl_2$ also.[255] The crystal structure of $Re_6Se_8Cl_2$ has been determined.[256] The compounds $Nb_2Se_2Br_6$, $Nb_2Te_2Br_6$ and $Nb_2Te_2I_6$ have been prepared from the elements in sealed quartz ampoules at 1073K. 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 $Nb_2(Y_2)X_4$ units containing single side-on bonded Nb_2 and Y_2 dumbbells forming a quasi tetrahedral Nb_2Y_2 cluster with Nb-Nb = 283.2, 287.5, 293.2pm, Se-Se = 230.5pm and Te-Te = 267.0 and 268.5pm.[257] The reaction of bis(morpholinoselenocarbonyl)triselenide, $Se_3[C(Se)NC_4H_8O]_2$ with iodine in CH_2Cl_2 leads to the formation of the compound $[OC_4H_8NCSe_3]I$. A crystal structure determination showed the compound to contain the cationic units (<u>61</u>) and to consist of polymeric

--I---Se---I---Se---I-- chains running along the c axis held together by van der Waals contacts.[258]



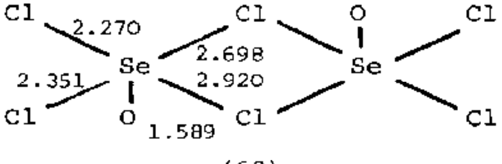
(61)

Several trifluoro- and tribromoselenate(IV) compounds, $MSeOF_3$ and $MSeOBr_3$ 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 $MSeOF_3$ with M = K, Cs but becomes significant for $MSeOCl_3$ where M = K and for $MSeOBr_3$ with M = Me_4N. Compounds with larger cations contain isolated $SeOX_3^-$ anions.[259] A crystal structure determination of the phenylarsonium salt of $SeOCl_3^-$ (prepared from $SeOCl_2$ and $As(Ph)_4Cl$ has been carried out at low temperature. The salt contains a novel type of ψ trigonal bipyramidal $SeOCl_3^-$ and shows no association to form dimers or trimers (62).



(62)

The triethylammonium salt shows the $SeOCl_3$ unit to be present as a dimer $Se_2O_2Cl_6^{2-}$, as found in the PPh_4^+ salt, with two $SeOCl_4$ pyramids linked through a Cl···Cl edge and the lone pairs trans to the axial Se-O bonds (63).[260]



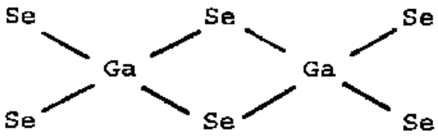
(63)

6.3.3 Bonds to Oxygen

The compound $Au_2(SeO_3)_2O$ 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.[261] The crystal structure of $Pb_2Cu_5(SeO_3)_6(UO_2)_2(OH)_6.2H_2O$ has been shown to consist of layers of $Cu(O,OH,H_2O)_6$ octahedra linked to each other by oblique chains which are formed by oxygen bridges linking uranyl and selenium ions.[262] The crystal structure of $Cu_4(UO_2)(SeO_3)_2(OH)_6$ consists of layers of $Cu(O,OH)_6$ octahedra which are linked to each other by two oblique chains of Se-U-Se which cross one another.[263] Phase equilibria in the Re_2O_7-SeO_2 system have been measured.[264]

6.3.4 Selenides

The entirely ordered monoclinic phase of Ga_2Se_3 has been shown to be a superstructure of the basic distorted sphalerite-type. Ordering of metal vacancies involved two different Se atom surroundings.[265] The moisture sensitive ternary selenide, $Cs_6Ga_2Se_6$ has been prepared from the binary selenides Cs_2Se and Ga_2Se_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 $Ga_2Se_6^{2-}$ ions (64).[266]



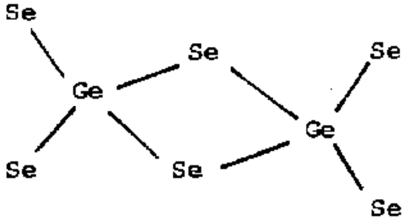
(64)

The ternary selenide $SrGa_2Se_4$ has been shown to have a structure which is a new variant of the TlSe structure.[267] The ternary chalcogenides $CuGaSe_2$ and $CuGaTe_2$ have been found to undergo a phase transition from the chalcopyrite type to the 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.[268] Quaternary compounds of the type AB_2X_3Y have been synthesised at high pressures and temperatures. $AgIn_2Se_3I$, $AgIn_2Te_3I$, $CuIn_2Se_3Br$, $CuIn_2Se_3I$, $CuIn_2Te_3Cl$, $CuIn_2Te_3Br$ and $CuInTe_3I$ were found to have the defect zinc blende structure, whilst $AgIn_2S_3Cl$, $AgIn_2S_3Br$,

$AgIn_2Se_3Cl$, $AgIn_2Se_3Br$ and $AgIn_2Se_3I$ have the spinel structure and $AgIn_2Te_3Cl$ and $AgIn_2Te_3Br$ the defect rocksalt structure. A second form of $CuIn_2Se_3I$ was found to have a structure intermediate between the ZnS and spinel structure. A survey of the different reaction pathways of AB-B_2X_3 mixtures at high pressures and temperatures was given.[269] Two new compounds, Tl_5ISe_2 and Tl_6I_4Se, have been found at the Tl_2Se corner of the TlI-T $_2$Se systems. Tl_6I_4Se was found to be isotypic with a class of compounds found in the TlX-Tl_2S systems. The compound Tl_6Cl_4S was found to have a structure based on that of TlCl in which $^1/_5$ of the Tl or Cl atoms are substituted by Tl_2S in a regular manner.[270] Experimental mass-loss data for the sublimation of SnSe has yielded the values $\Delta H^o_{298,f} = -86.4$ kJ.mol^{-1} and $S_{298} = 89.0$ JK^{-1}mol^{-1} and from the decomposition reaction:

$$SnSe_2(s) \rightarrow SnSe(s) + \frac{1}{x} Se_x(g)$$

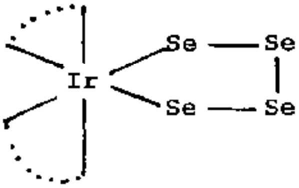
$\Delta H_{298,f} = -118.1$ kJ mol^{-1} and $S_{298} = 111.8$ JK^{-1}mol^{-1} for $SnSe_2$ were obtained.[271] The stoichiometric 1:1 reaction of sodium selenide with GeS_2 in aqueous solution has been shown to give the selenogermanate $Na_4Ge_2Se_6.16H_2O$. The compound contains the isolated $Ge_2Se_6{}^4$ anion (<u>65</u>) consisting of two edge sharing tetrahedra with Ge-Se = 2.303 - 2.419Å, which are in contact with the hydrated octahedral $Na(H_2O)_6{}^+$ ions through Se---H-O bridges within an extensive hydrogen bridge system. The 1:2 molar ratio of Na_2Se to $GaSe_2$ gives the adamantane-like $Ge_4Se_{10}{}^{4-}$.[272]



(<u>65</u>)

The vibrational spectra of solid α and β As_4S_4 and the Raman spectrum of molten As_4S_4 have been recorded. The Raman melt spectra suggest that As_4S_4 molecules (symmetry D_{2d}) are retained in the molten state. The Raman spectrum of solid As_4Se_4 was tentatively assigned on the basis of a cradle type molecule possessing D_{2d} symmetry.[273] The hitherto unknown Se_4^{2-} anion has been found in the structure of the new compound [Ba-222 Crypt]Se_4.[274] The oxidation of copper(I)selenide at temperatures above 300°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°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.[275]

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 = 2.545Å and Se-Se = 2.307Å.[276]



(66)

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.[277] 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.[278] Several studies of lanthanide uranium mixed selenides ($Ln_{0.5}U_{0.5}Se_2$;[279] $La_2U_2Se_7$;[280] $Ln_4U_5Se_{16}$[281] and

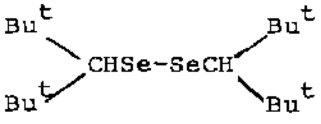
and $Yb_{2.0}U_{0.87}Se_4$[282] have been reported and the lanthanide selenides, $LnSe_{1.4}$, of the yttrium subgroup have been investigated.[283] Phase equilibria studies in selenide systems have been collected in Table 2.

Table 2. Selenide Phase Systems.

System	Ref.	System	Ref.
Ag-Se-Te	284	$FeSe-Ga_2Se_3$	288
Dy-Ge-Se	285	Hg-Se-Te	289
$GeSe_2-TeSbSe_2$	286	$GeSe_2-Sb_2Te_3$	290
$Cu_2Se-Sm_2Se_3$	287		

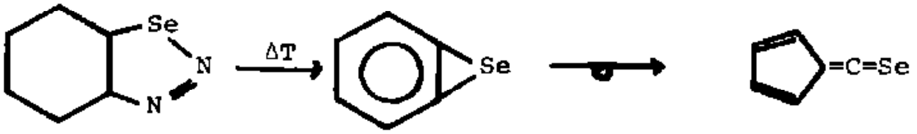
6.3.5 Bonds to Carbon

The crystal structure of 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 CS_2 and the lattice parameter c, shows the same anomalous temperature dependence.[291] 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.[292]



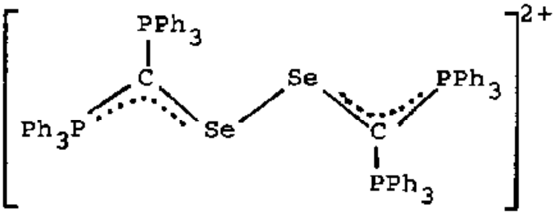
(67)

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 C_6H_4Se rearranging to the more stable final product, 6-fulveneselone (equation 40).[293]



...(40)

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 Se_nS_{8-n} (n = 1-8), prepared in a new reaction from Se_2Cl_2, SCl_2 and KI and containing all selenium atoms in neighbouring positions.[294] A crystal structure determination has shown the compound $((Ph_3P)_2CSe)_2Fe_2OCl_6.4CH_2Cl_2$ to contain the dication (68) and the dianion (69). The dianion, $Fe_2OCl_6{}^{2-}$ was found to contain a linear Fe-O-Fe axis and a staggered arrangement of the 2 x 3 chlorine atoms.[295]



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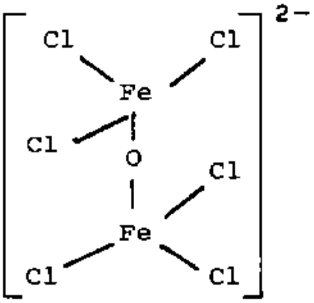
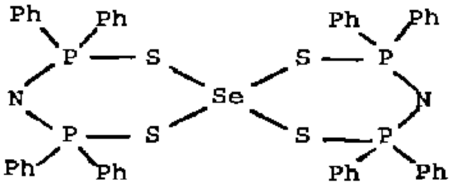


(69)

Bis(imidotetraphenyldithiodiphosphino-S,S')selenium(II) has been prepared from $NH_4{}^+N(Ph_2PS)_2{}^-$ and $Se[(EtO)_2PS_2]_2$ in methanol. Crystal structure determination shows the presence of a four coordinate Se(II) complex (70) in which the 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, 3.054Å.[296]

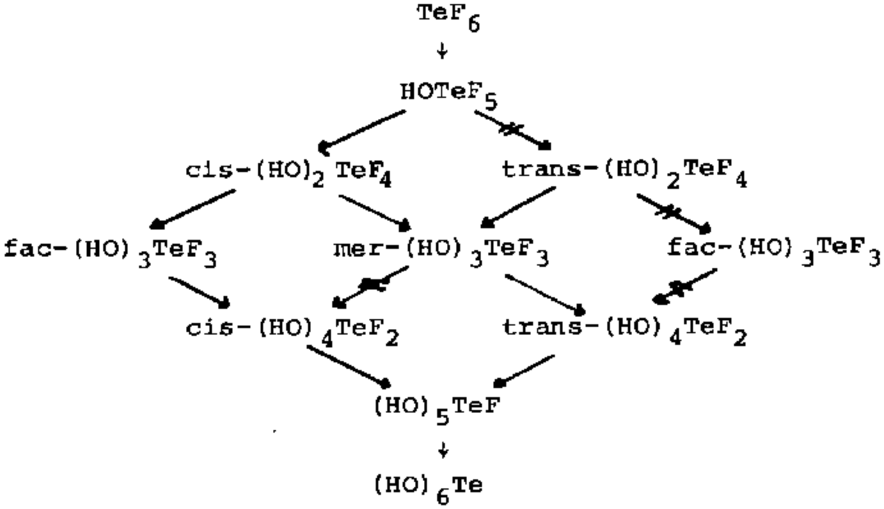


(70)

6.4 TELLURIUM

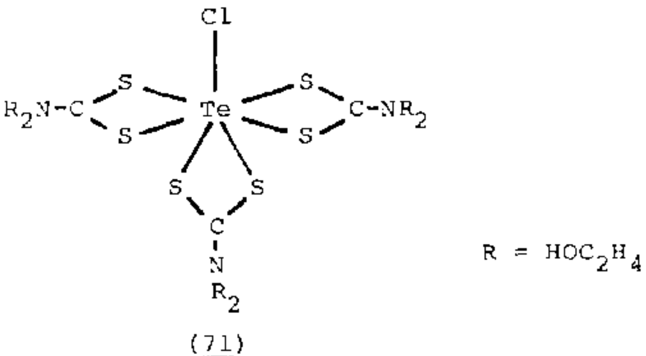
6.4.1 Bonds to Halogens

The stereochemistry of the hydrolysis of TeF_6 has been followed by ^{125}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.[297]



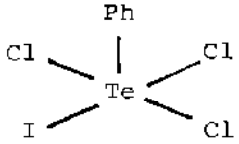
Scheme 7.

The new hypofluorite, TeF_5OF 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 TeF_5OH with a concentrated NF_4HF_2 solution. TeF_5OF is colourless both as a gas and liquid and has a boiling point of 0.6°C. Raman, ^{19}F n.m.r. and mass spectra were also reported.[298] The compounds POF_2-$OTeF_5$, $P(OTeF_5)_3$, $O=P(OTeF_5)_2$, $As(OTeF_5)_5$ and $Sb(OTeF_5)_3$ have been prepared and their properties compared with similar compounds.[299] The synthesis, properties and crystal structure of the unusual mixed-ligand complex $TeCl[(HOC_2H_4)_2NCSS]_3.2H_2O$ 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.[300] The structure of the aryl tellurium mixed halide anion, $[PhTeCl_3I]^+$ has shown it



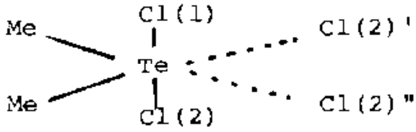
(71)

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



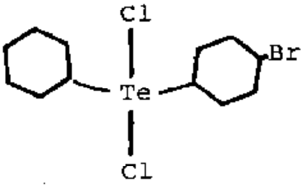
(72)

The observed bond lengths found for the $NBu^n{}_4$ salt were Te-C = 2.15, Te-Cl = 2.565 - 2.663 and Te-I = 2.837Å. Allowing for disorder the corrected values for Te-Cl and Te-I are 2.51 and 3.04Å respectively.[301] 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_2TeCl_2. 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_2TeCl_2.



(73)

The distribution supports a donor-acceptor model for the bonding that involves donation of the chlorine lone pair density to an empty tellurium orbital.[302] 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.[303]



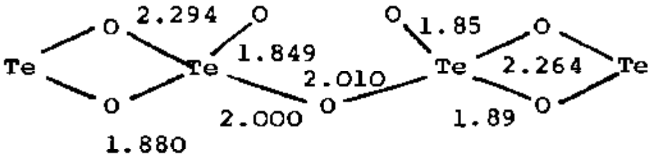
(74)

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°, the Cl-Te-C bond angle close to 90° and the C-Te-C angle 96.1° 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.[304] Phase equilibria in the CoCl-NaCl-$TeCl_4$ and NaCl-RbCl-$TeCl_4$ systems have been measured.[305]

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.[306] 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.[307] The crystal structure of SbTeI shows the Sb atom to be coordinated by three Te atoms at distances 2.831 to 2.961Å and four I atoms at distances 3.230 to 3.827Å. Although the coordination polyhedron is similar to that of the orthorhombic BiSCl and SbSeI, the structure of SbTeI is different and constitutes a new structure type.[308]

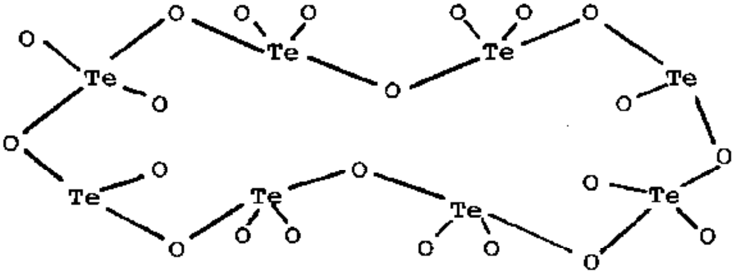
6.4.2 Bonds to Oxygen

The Nb_2O_5–TeO_2 system has been studied and the existence of three phases, $Te_3Nb_2O_{11}$ (mp. 793°C), $Te_4Nb_2O_{13}$ (mp. 795°C) and $TeNb_6O_{17}$ (mp. above 1100°C), observed.[309] The crystal structure of $K_2Te_2O_5.3H_2O$ has been investigated in order to determine whether the compound contains isolated $Te_2O_5{}^{2-}$ ions or condensed chains and to examine the coordination of the Te(IV) ion. It was shown that the Te_2O_5 units are connected by fairly strong $Te{<^{O}_{O}>}Te$ double bridges to form puckered chains (75).[310]



(75)

The structure of $Ba_3Te_4O_{11}$ consists of $TeO_3{}^{2-}$ and $Te_3O_8{}^{4-}$ ions which form $Te_8O_{22}{}^{12-}$ rings around the centre of symmetry (76). The Te–O bond distances are approximately 2.7Å with the $TeO_3{}^{2-}$ ion having the usual pyramidal symmetry but the $Te_3O_8{}^{4-}$ ion has a pseudo twofold axis instead of the twofold axis found previously in $Zn_2Te_3O_8$ and $Nb_2Te_3O_{11}$.[311]



(76)

The reduction of Te(VI) by potassium tetrahydroborate in aqueous medium has been shown to take place in stages: Te(VI) → Te(IV) → Te → Te^{2-} in acid solutions, and in alkaline or borate buffered solutions the final product is elemental tellurium.[312] The interactions of cis and trans $HOTeF_4OMe$ with BCl_3 has been shown to give B(cis and trans-$OTeF_4OMe)_3$. Transfer of the $MeOTeF_4O$ entity has also been demonstrated with AsF_3.[313]

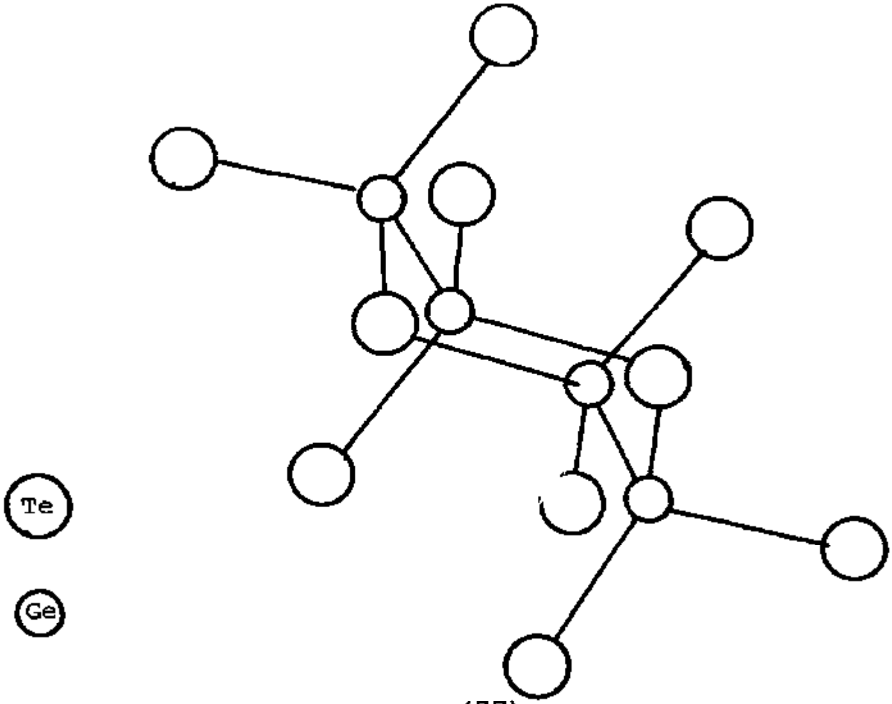
Crystal structure determinations have been carried out on the following compounds $K_3HP_2O_7.Te(OH)_6.H_2O$,[314] $Te(OH)_6 2NH_2CH_2COOH.-H_2O$,[315] $2(NH_4)_3P_3O_9Te(OH)_6$,[316] $SrTe_5O_{11}$,[317] and $Ba_3Te_2O_6Cl_2$.[318]

6.4.3 Tellurides

Rb_2Te_5, produced from stoichiometric amounts of the pure elements in supercritical 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 $^1_\infty[(Te_4Te_{2/2})^{2-}]$. The structure of Rb_2Te_5 was compared with that of Cs_2Te_5 and those of other known polychalcogenides, M_2X_n. The r(Te-Te) of 304pm, which occurs as a characteristic feature were especially discussed.[319] Electron diffraction studies of Si_2Te_3 crystals revealed a structural transformation above 673K. Deviations from stoichiometry of the form, $Si_{1+x}Te_3$ 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 Si_2Te_3 should be characterised as a non-stoichiometric compound with a considerable stoichiometry width.[320] 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 $^2_\infty[Te\text{-}Ga\text{-}Ge\text{-}Ge\text{-}Ga\text{-}Te]$.[321] The crystal structure of the second modification of $Na_8Ge_4Te_{10}$ has been determined. The structure contains $[Ge_4Te_{10}]^{8-}$ anions in the form of six membered rings (<u>77</u>) with the formulation $[(GeTe_2)_4Te_2]^{8-}$.[322]

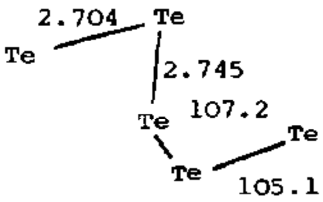
The new telluride, Na_4SnTe_4 has been found to crystallise in the orthorhombic space group $P2_12_12_1$ and to contain isolated $SnTe_4{}^{4-}$ tetrahedra.[323] D.t.a., X-ray and microprobe measurements have been used to show that the compound "Ag_8SnTe_6" seems not to be a stable argyrodite.[324]

Crystal structure determination has shown that the atomic arrangement of $Cs_7Fe_4Te_8$ corresponds to that in CsCl. The outstanding feature of the structure is the occurrence of isolated Fe_4Te_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.[325] $Cu_{0.28}LaTe_2$ has been found to have a disordered tunnel structure.[326]



(77)

The preparation and characterisation of several novel main group anions such as Sn_9^{4-}, Te_5^{2-}, Se_6^{2-}, S_6^{2-} and $SnTe_4^{4-}$, without the use of cryptates or amine solvents has been described. The polychalcogenides, $(Bu_4N)_2M_x$ (where M = Te, x = 5; M = Se, x = 6; M = S, x = 6) are prepared by the aqueous extraction of binary alkali metal/main group alloys in the presence of Bu_4NBr. The compound K_4SnTe_4 was also isolated by the aqueous extraction of ternary 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.[327]



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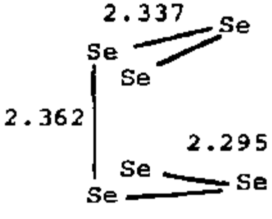

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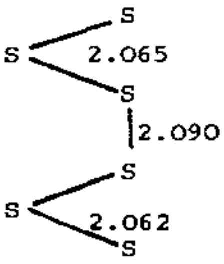


(80)

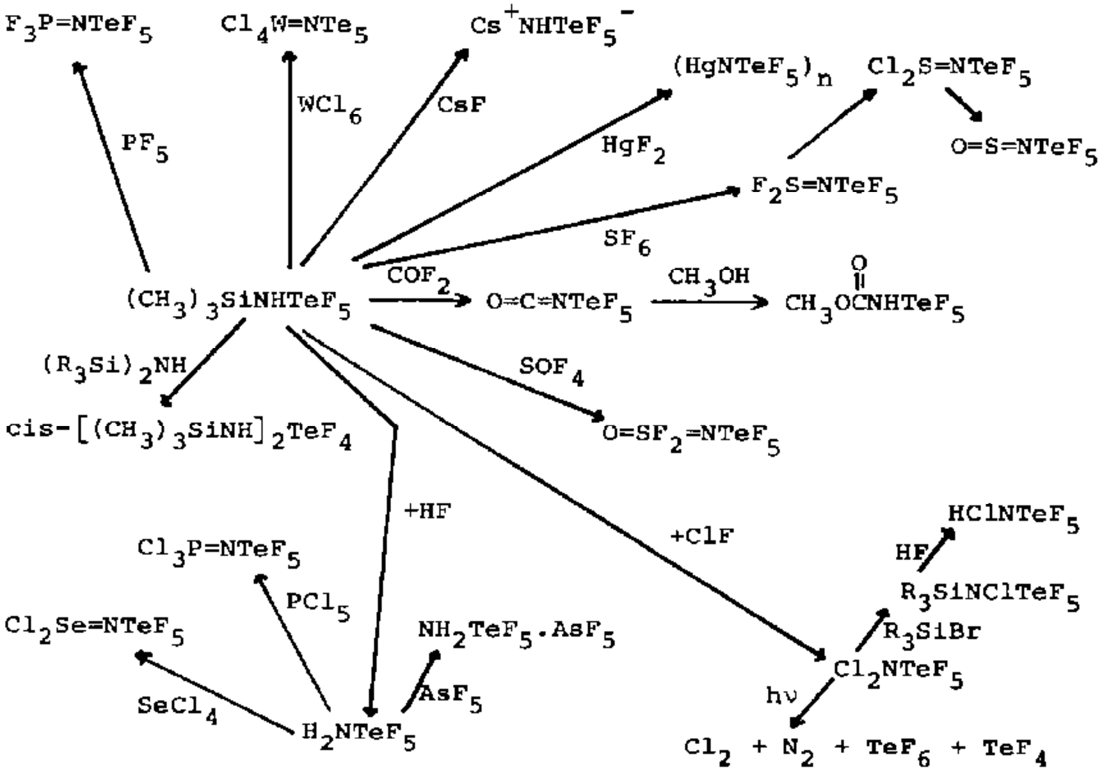
Table 3. Selected Physical Properties of the Polychalcogenides Te_5^{2-}, Se_6^{2-} and S_6^{2-}.

	Te_5^{2-}	Se_6^{2-}	S_6^{2-}
bond lengths, Å	Te(1)-Te(2) = 2.746	Se(1)-Se(1') = 2.362	S(1)-S(1') = 2.090
	Te(2)-Te(3) = 2.704	Se(1)-Se(2) = 2.337	S(1)-S(2) = 2.065
		Se(2)-Se(3) = 2.295	S(2)-S(3) = 2.062
bond angles, deg.	Te(2)-Te(1)-Te(2') = 107.2	Se(1)-Se(1')-Se(2) = 106.75	S(1)-S(1')-S(2) = 109.5
	Te(1)-Te(2)-Te(3) = 105.1	Se(1)-Se(2)-Se(3) = 108.57	S(1)-S(2)-S(3) = 110.5
visible, (nm) 25°C.	375(vbr), 530	385(sh), 440, 625(br)	605
-90°C	375(sh), 530	385(sh), 440, 615(br)	340, 462
Raman, 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: $CdTe-Gd_2Te_3$;[329] $CsSbTe_2-Sb_2Te_3$;[330] $GeTe-Te-Tl_2Te$;[331] Ag-Te-Tl;[332] and $MnTe-Sb_2Te_3$.[333]

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 H_2N-TeF_5 and $Me_3SiNHTeF_5$ as the starting materials, numerous new tellurium-nitrogen compounds have been prepared. Almost all of them contain the $\gtrdot N-TeF_5$ group, which stabilises many double-bonded systems such as $O=C=NTeF_5$ and $Cl_4W=NTeF_5$. $Cl_2Se=NTeF_5$ is a rare example of a compound containing a discrete Se=N double bond. A schematic representation of the compounds mentioned in the paper is given in Scheme 8.[334]



Scheme 8. Schematic representation of the $\gtrdot NTeF_5$ chemistry.

In a second paper, it was shown that TeF_5-Cl can add photolytically to nitriles with retention of the TeF_5 group.

$$TeF_5Cl + RC{\equiv}N \rightarrow F_5Te{-}N{=}CRCl + ClRC{=}N{-}N{=}CRCl \qquad \ldots(41)$$

$$R = Cl,\ CF_3.$$

No evidence was found for the formation of the unknown Te_2F_{10} even though S_2F_{10} is observed in the reaction of SF_5Cl with nitriles. The reaction of $F_5Te{-}N{=}CCl_2$ with excess HF gave the amine $F_5Te{-}NH{-}CF_3$ and the anion $[F_5Te{-}N{-}CF_3]^-$ could be generated directly by reaction of $F_5Te{-}N{=}CCl_2$ with CsF.[335] The crystal structure of $(TePh_2).HgI_2$ has been determined and showed the molecule to have a novel tetrameric structure involving two different iodine bridges.[336] The compound μ_3-$Te(Mn(CO)_2(\eta^5{-}C_5H_5)_3$ has been synthesised and its structure determined.[337] The reaction of organic dihalides with NaTeR (R = Ph or p-$EtOC_6H_4$) has been reported.[338] The synthesis and reactivity of $(C_5H_5)RhFe_2Te_2(CO)_x$ (x = 6,7) together with ^{125}Te n.m.r. studies have been described.[339]

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