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Chapter 6

ELEMENTS OF GROUP 6

M.G.Barker

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6.1 OXYGEN

α^1-Oxygen, first reported in 1962 and 1969, is a modification of the α-phase formed when the latter is deposited on a cold substrate at a low gas flow. Early attempts to index the electron diffraction powder patterns had proved fruitless but recent, more comprehensive and accurate data has now resulted in a solution for a monoclinic unit-cell with dimensions, $a = 9.225$, $b = 6.668$, $c = 3.414$Å and $\beta = 85.05^{\circ}$. A triangular net of O_2 molecules in an <u>ab</u> projection is predicted with centres of the molecules near the ab positions 00, $\frac{1}{2}0$, $\frac{2}{3}0$, $\frac{1}{6}\ \frac{1}{2}$, $\frac{1}{2}\ \frac{1}{2}$, and $\frac{5}{6}\ \frac{1}{2}$.[1] Electron paramagnetic resonance spectroscopy has been shown to be a very sensitive method for the detection of gaseous molecular oxygen at low temperatures (-160 to -180°C) and low pressures (<10 torr). The narrow line spectrum in the 0.5 to 1.0 Tesla field range makes identification of O_2 unequivocal.[2] The reduction of O_2 in liquid NH_3 at a platinum electrode has been investigated. Chemical and electrochemical measurements showed that the first reduction of oxygen is a one-electron process to produce $O_2^{-}\cdot$, which is a stable species in NH_3 and which can be precipitated as KO_2 on the addition of K^+. The solubility of O_2 in liquid NH_3 was determined at temperatures between -60 and -40°C and the diffusion coefficient of O_2 in liquid NH_3 was evaluated as 4.4×10^{-5} cm^2/s at -55°C.[3]

The reversible binding of oxygen by manganese and vanadium complexes has given rise to much discussion over recent years. This year the argument appears to be centred on whether Mn and V complexes of 3,5-ditert-butylcatechol may be able to reversibly bind dioxygen. Cooper claims to have shown that reversible binding by both V and Mn complexes are in error.[4] In the case of the Mn complex he proposes that the data is more reasonably ascribed to hydroxide attack on 3,5-ditert-butyl-o-benzoquinone, previously generated by air oxydation of the ligand, and direct monometric evidence for reversible oxygen uptake and release is, in his view, necessary before oxygen binding can be assumed. Sawyer, who first reported both the vanadium and Mn results, replied that the reinterpretations and conclusions of Cooper and Hartman are not supported by experimental results and quotes additional studies which support the conclusion that dioxygen is reversibly bound by dilute concentrations of $Mn^{IV}(DTBC)_3^{2-}$ in slightly alkaline acetonitrile.[6] The i.r. and resonance Raman spectra of molecular oxygen adducts of N,N'-ethylenebis(acetylacetoniminato)cobalt(II) have been reported. Its O_2 stretching frequency was much lower than that of the previously reported Co(TPP)O_2 which was interpreted as indicating that the negative charge on O_2 increases markedly with the change in the ligand.[7]

A paired Mo_2O_2 structure has been observed to be formed in the reaction between $Mo_2(\eta^3C_3H_5)_4$ and surface hydroxyl groups of SiO_2. This structure is thought to be an example of a new class of oxygen carriers.[8] An attempt has been made to rationalize, from a mechanistic point of view; the different ways in which oxygen may be transferred from inorganic and organic peroxides to nucleophilic substrates, particularly olefins. A mechanism involving dioxiranes as the reactive species was proposed in which oxygen transfer from dioxirane reagents probably involves the formation of a charge-transfer π-complex between the substrate and the C-atom of the dioxirane and the subsequent formation of a cyclic peroxide intermediate.[9] The hydroxylation of acyclic alkanes by ground state oxygen atoms $O(^3P)$ and ozone has been compared. In both cases the major products were tertiary alcohols but with ozone significant yields of ketones from C-C cleavage were observed which were not present in the $O(^3P)$ reactions.[10] The oxygenation of enolates has been shown to provide a hitherto unprecedented potential source of $^1O_2$. In view of the serious pathological effects of $^1O_2$ it seems relevant to demonstrate its involvement in enzymatic autoxidations.[11]

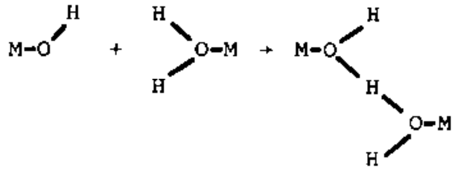
The formation of hyperstoichiometric oxides of UO_2 by the incorporation of additional oxygen atoms in the parent fluorite structure has been described in terms of oxygen clusters. The effect of a chain like ordering of oxygen clusters on structures in the oxide system UO_2-U_3O_8 was assessed and a crystal structure for U_4O_9 postulated.[12] Semiempirical calculations of iron-oxygen interactions have shown that for side bonded and linear FeO_2, as the positive charge on the Fe is increased, the linear structure is favoured. Back donation of charge from the Fe atoms into π^* orbitals on oxygen weakens the O-O bond in coordinated O_2. No activation barrier was found for rotation of the O-O group from the side-bonded to the linear position but for dissociation of the O-O bond in side-bonded FeO_2 to form O-Fe-O, an activation energy of 484 kJ/mole was calculated.[13]

A simple method for the generation and detection of superoxide in a cobalt(II) tetraphenylporphyrin-thiolate-oxygen system has been described.[14] The proton induced disproportionation of superoxide ion in dimethyl formamide and in acetonitrile has been studied. For strongly acidic substrates the disproportionation reaction is second order with respect to O_2^-, but too rapid to measure accurately. With less protic substrates the rate is first order with respect to O_2^- and with respect to substrate; proton transfer is the rate limiting step.[15] The solvation structure of O_2^- in D_2O frozen solutions has been determined at 4.2K. The analysis indicates that the first solvation shell waters have an H-O bond dipole orientated toward O_2^- and that each O_2^- is surrounded by four water molecules.[16]

A recent paper describing the anomalies,of water in the supercooled range concludes that these anomalies, such as the density maximum of the liquid phase, and the initial decrease in viscosity with pressure are confined to the pT range $T < 300K$ $p \leqslant 200MPa$. At these pressures lowering the temperature leads to an unexpected behaviour of almost all physical properties.[17] Fourier transform i.r. techniques have been used to identify the intermediates formed in the reaction of water vapour with CO over an iron catalyst.[18] It has been shown that there is practically no reaction of HO_2 radicals on walls of quartz or Pyrex glass.at ambient temperatures, whereas at lower temperatures these radicals disappear, with the rate of disappearance increasing with decreasing temperature, contrary to what occurs at high temperature (>150°C). The bimolecular recombination reaction of HO_2 radicals to produce H_2O_2 and H_2 was shown to take place by two competitive paths.[19]

$$HO_2 + HO_2 \begin{array}{l} \nearrow H_2O_2 + O_2 \\ \searrow H_2 + 2O_2 \end{array} \qquad \ldots(1)$$

The structure of the $H_3O_2^-$ ion present in the compounds $\{[M_3O_2(O_2CC_2H_5)_6(H_2O)_2]_2(H_3O_2)\}Br.6H_2O$ where M = Mo or W has been elucidated. The ion is symmetric with an O-O separation of 2.52Å and 2.50Å in the Mo and W compounds respectively and formation of the $H_3O_2^-$ bridge does not require the elimination of a water molecule.[20]



...(2)

The thermodynamics and kinetics of the gas phase reactions $H_3O^+(H_2O)_{n-1}$ + H_2O → $H_3O^+(H_2O)_n$ have been studied.[21] Two papers have been published on the decomposition of H_2O_2 in the presence of OsO_4 as a catalyst. The rate of decomposition was shown to be proportional to the first power of the OsO_4 concentration and to the power 1 - 1.2 of the H_2O_2 concentration. The pH dependence of the decomposition rate was quite characteristic with a high maximum at pH 10.6 and a much lower one at pH 8.3.[22] The second paper showed that the superoxide radical is formed in the reaction, with an initial rate of formation proportional to the 0.6 power of the concentration of H_2O_2 and the first power of the catalyst concentration. These results were interpreted in terms of a peroxo-osmic acid, the anion of which decomposes into superoxide and Os(VII) radicals.[23] Kinetic studies of the reactions of H_2O_2 with some vanadium(IV) complexes have shown the rate determining step to probably be the insertion of a hydrogen peroxide molecule into the first coordination sphere of the complex followed by rapid electron transfer and peroxo coordination to produce a vanadium(V) complex.[24] An excited state photochemical cell has been designed in which H_2O_2 and Br_2 are produced in acetonitrile solution in separate cell compartments with a high per-photon efficiency.[25] The oxidation of Ph_2S by H_2O_2 in the presence of $NaVO_3$ as a catalyst has been studied kinetically by means of iodometry of H_2O_2.[26]

6.2 SULPHUR

6.2.1 The Element

The chemistry of sulphur at ambient temperatures is usually regarded as that of S_8, however on dissolution of S_8 in polar solvents such as methanol or acetonitrile partial transformation to S_6 and S_7 has been observed. In time an equilibrium is established with approximately 1% of the sulphur being present as the smaller rings. A significant variation in the ability of solvents to promote the equilibration of S_6, S_7 and S_8 was observed. At room temperature methanol, acetonitrile and DMSO dissolve S_8 to yield solutions in which 0.2% of S_6 and S_7 may be detected within minutes to hours. In contrast, solutions of S_8 in cyclohexane, show no conversion over weeks and only on heating to above 100°C may conversion be observed in hours to days.[27] S_6 and S_7 have also been produced by heating solutions of S_8 in CS_2 at 130-155°C in sealed ampoules. The half-time of the reaction is independent of the initial S_8 concentration and decreases from 232 min. at 130° to 64 min. at 150°C. From the temperature dependence of the equilibrium constants the following reaction enthalpies were calculated $^{3}/_{4}S_8 \rightleftharpoons S_7$ $\Delta H^{o} = 24$ kJ/mole, $^{7}/_{8}\,S_8 \rightleftharpoons S_7$ $\Delta H^{o} = 21$ kJ/mole.[28]

The recent preparation of S_6Cl_2 and S_8Cl_2 by the reaction

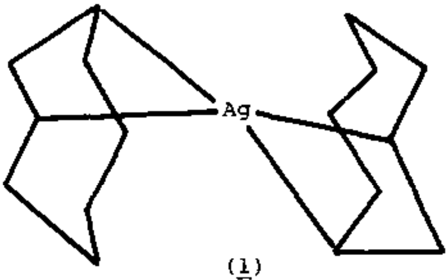
$$S_n \; + \; Cl_2 \xrightarrow[20^{o}C]{CS_2/CCl_4} S_nCl_2 \qquad n = 6,8. \qquad ...(3)$$

has led to the isolation of S_{11} and S_{13} from the reaction

$$(C_5H_5)_2TiS_5 \; + \; S_nCl_2 \xrightarrow[0^{o}C]{CS_2} (C_5H_5)_2TiCl_2 \; + \; S_{n+5} \qquad ...(4)$$

The identity and purity of the two sulphur ring compounds were determined by HPLC and Raman spectra were recorded. S_{11} (mp 74°C) and S_{13} (mp 114°C) are both readily soluble in CS_2, and moderately soluble in CCl_4, $CHCl_3$, CH_2Cl_2, and toluene, and have about the same thermal stability as S_6 which can be handled without decomposition for hours at room temperature.[29] Sulphur-selenium mixed crystals have been prepared by melting elemental mixtures in sealed glass tubes, followed by recrystallisation from benzene/CS_2. Raman spectra studies showed that molecules containing Se-Se bonds are preferably precipitated from the solutions while S_8 and molecules containing isolated Se atoms are enriched in the solvent phase.[30]

Elemental sulphur has been shown to react with Co(salophen) in THF or pyridine solution to produce tetrasulphide Co(III) complexes. When the reaction was carried out in the presence of a sodium cation bonded by Co(salophen) the isolation of a μ-persulphido dicobalt(III) complex was achieved with S-S = 1.962Å.[31] Reaction of $AgAsF_6$ with S_8 in liquid sulphur dioxide has been shown to give $(Ag(S_8)_2)AsF_6$ which contains cycloocta-sulphur ligands. Silver atoms achieve a distorted four coordination by 1,3 linkages to two S_8 rings (<u>1</u>).[32]



(1)

Two independent studies have been carried out on an analysis of the Raman and i.r. or Resonance Raman spectra of S_4^{2+}, Se_4^{2+} and Te_4^{2+}. In the first study, enrichment of sulphur to 16% in ^{34}S was used to help assign the fundamental vibrations of S_4^{2+} on the basis of a square planar structure with D_{4h} symmetry and the assignments were extended to the other cations.[33] In the second paper Raman and Resonance Raman spectra of S_4^{2+} and Se_4^{2+} in oleum at room temperature, of Te_4^{2+} in H_2SO_4 and of $Te_4[Al_2Cl_7]_2$ at ca. 80K were recorded.[34] Both studies were in good agreement for the chalcogen-chalcogen force stretching constants.

Three different cationic species have been produced either by anodic oxidation or by reaction of chlorine and elemental sulphur in a NaCl-$AlCl_3$ melt at 150°C. Two of the species were identified as the radicals S_4^{+} and S_8^{+}. No e.s.r. signals were found for the third species and its oxidation state is most likely $+^1/_6$ indicating a formula of S_{12}^{2+}.[35]

6.2.2 Bonds to Halogens

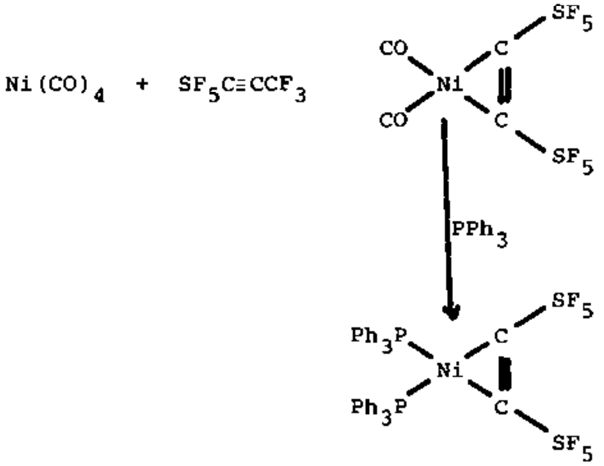
Sulphur can be directly fluorinated with UF_6 to form SF_4 but the reaction is very slow. An improved method using SCl_2 has been shown to give yields of between 69 and 78% SF_4 with the principal impurity being SOF_3 at concentrations between 3.5 to 6%.[36]

$$SCl_2 + 4UF_6 \rightarrow SF_4 + Cl_2 + 4UF_5 \qquad ...(5)$$

Electron photodetachment in the gas phase from the sulphur hexafluoride anion, SF_6^-, has been shown not to be possible. A model consistent with this behaviour is one in which SF_6^- has a geometry distorted significantly from neutral SF_6 either with an octahedral ion with weakened S-F bonds or as an ion molecule association complex $(SF_5.F)^-$.[37] Electron diffraction studies of SF_6 below 94K have shown that between 50 and 94K the lattice is hexagonal being isostructural with UCl_6. At lower temperatures the structure is distorted to a C-face centred monoclinic cell.[38]

The preparation of 1-hydropentafluorosulphur, F ethyl silver has been described. $AgCH(SF_5)CF_3$ reacts with HCl and DCl to form $HCH(SF_5)CF_3$. The reaction of 1-pentafluorosulphur F ethyl silver with HCl to form $ClCF(SF_5)CF_3$ is also described.[39] The reaction of $SClF_5$ with $CH_3C{\equiv}COR$ has been shown to give $CH_3CH{=}SF_4$, a colourless liquid which undergoes slow decomposition at room temperature. Its structure shows a trigonal bipyramidal environment of sulphur with two axial and two equatorial fluorine atoms with the ethylidene ligand also occupying an equatorial position. The methyl group lies in the same plane as the axial fluorine atoms and the sulphur atom.[40]

Pentafluoro (trifluoromethyl)acetylenyl sulphur and nickel tetracarbonyl have been found to react at room temperature, with periodic removal of CO at -196°C to produce a yellow liquid identified as $Ni(CO)_2(SF_5C_2CF_3)$ (2). Compound (2) reacts with an ether solution of triphenylphosphine at -78°C to form the bright yellow solid (3).[41]



(2)

(3)

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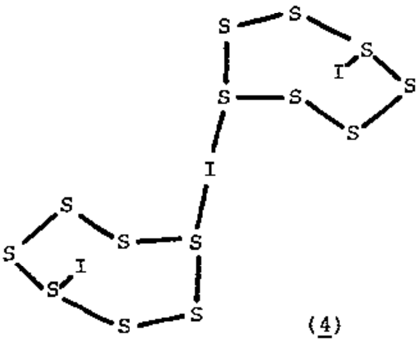
The reaction of sulphur, iodine and the corresponding pentafluoride in appropriate ratios yields the crystalline compounds $(S_7I)_4S_4(AsF_6)_6$ and $[(S_7I)_2I](SbF_6)_3.2AsF_3$. The structure of $[(S_7I)_2I]^{3+}$ (4) consists of two equivalent S_7I^+ units that have geometries similar to those observed in S_7IMF_6 (M = As, Sb) and $(S_7I)_4S_4(AsF_6)_6$. They are linked via an iodine atom, which is at a centre of symmetry, by a linear S-I-S arrangement with S-I = 2.674Å.



(4)

The square planar geometry of S_4^{2+} in $(S_7I)_4S_4(AsF_6)_6$ is similar to those in $S_4(AsF_6)_6 0.6SO_2$ and $(S_7Br)_4S_4(AsF_6)_2$.[42] ^{127}I Mössbauer spectra of some chalcogen-iodine cations have been reported.[43]

6.2.3 Bonds to Nitrogen

Linear Compounds. The ground state potential surface of thiazyl fluoride has been calculated. The relative stabilities of the isomers NSF and FNS were calculated and it was shown that NSF is more stable than FNS by 21 kcal.mol^{-1}.[44] The identity of coloured sulphur species in liquid ammonia have been investigated by Raman spectroscopy. In dilute solutions the predominant band at 535 cm^{-1} was shown to correspond with the symmetric stretching vibration of S_3^- with a weak band at 230 cm^{-1} being assigned to the symmetric bonding mode. Bands at 710 and 592 cm^{-1} could be assigned to the S_4N^- ion being the symmetrical SNS and SS stretching vibrations of the ion respectively. For more concentrated solutions the intensity of these bands increased dramatically relative to those of S_3^-. Thus it appears that the blue colour of sulphur-ammonia solutions is due both to the S_4N^- and S_3^- ions, with the reactions shown in Scheme 1 being proposed to explain their formation.[45]

$$\begin{tikzcd}
NH_2^- + S_8 \arrow[r] & H_2NS_8^- \arrow[d] & \\
S_4N^- + S^o & S_7N^- \arrow[l] & + H_2S \arrow[d, "NH_3{,}S^o"] \\
& S_3^- & (NH_4)_2S_x \arrow[l]
\end{tikzcd}$$

Scheme 1

The reaction of triphenylphosphine with $PPN^+S_4N^-$ (or $Ph_4As^+S_4N^-$) in acetonitrile has been shown to produce the corresponding salts of the S_3N^- ion. The S_3N^- ion is unstable with respect to the formation of S_4N^- in solution or in the solid state on heating or under pressure. Theoretical studies indicate that the statistical energy of the cis conformation is lower than that of the trans by 10 to 20 kcal mol^{-1}. Reaction of $PPN^+S_3N^-$ with $NiBr_2$ or $CoBr_2$ in acetonitrile produces complexes containing the $S_2N_2H^-$ ligand in addition to compounds of the type $M(S_3N)_2$.[46]

The reaction of $S_8(AsF_6)_2$ with sodium azide in SO_2, as shown in equation (7), has been found to produce S_2NAsF_6 rather than the hoped for S_xNAsF_6 with x = 7 or 8. The compound may also be

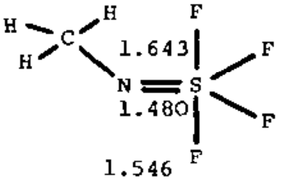
$$S_8(AsF_6)_2 + NaN_3 \rightarrow S_2NAsF_6 + NaAsF_6 + N_2 + {}^{3}/{}_{4}S_8 \qquad ...(7)$$

prepared in good yield by the reaction of sulphur with S_4N_4 and AsF_5 in the presence of traces of bromine (equation 8).[47]

$$\tfrac{1}{2}S_8 + S_4N_4 + 6AsF_5 \xrightarrow[Br_2]{SO_2} 4S_2NAsF_6 + 2AsF_3 \qquad ...(8)$$

The molecular structure of $CH_3N{=}SF_4$ in the gas phase has been determined by the joint analysis of electron diffraction and microwave spectroscopy data. A strongly distorted trigonal bipyramidal structure (5) with the double bond in an equatorial position and the methyl group pointing in an axial direction was obtained.[48]

N-(Pentafluoro-λ^6-sulphanyl)iminosulphur tetrafluoride has been shown to be produced (equation 9) in the reaction of NSF_3 with fluorine even under controlled, mild reaction conditions.



(5)

$$NSF_3 + F_2 \rightarrow F_5SNSF_4 + SF_6 + N_2 \qquad ...(9)$$

Rapid heating of the above reaction leads to the explosive-like decomposition summarised in equation (10).

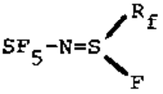
$$NSF_3 + \frac{1}{2}F_2 \rightarrow [NSF_4^{\bullet}] \rightarrow SF_4 + \frac{1}{2}N_2 \qquad ...(10)$$

In the first reaction, it was assumed that NSF_3 is oxidised by fluorine radicals via short-lived intermediates to the radical $SF_5^{\bullet}$ which reacts with F_2 to give SF_6 and with NSF_3 to give F_5SNSF_4 and another fluorine radical. The NSF_4 group in this compound can function as both a fluoride donor and as an acceptor[49] as shown in equations (11) and (12) respectively.

$$F_5SNSF_4 + AsF_5 \rightarrow F_5SNSF_3^{+}AsF_6^{-} \qquad ...(11)$$

$$F_5SNSF_4 + CsF \rightarrow Cs^{+}[N(SF_5)_2]^{-} \qquad ...(12)$$

The reaction of $TiCl_4$, $SnCl_4$ and $SbCl_5$ with $SOCl_2$ have been shown to give good yields of $SF_5N{=}SCl_2$ and to allow ready purification of the product. The reaction of $SF_5{=}NH_2$ with refluxing $SOCl_2$ for 24h and at room temperature for 2 weeks both gave $SF_5N{=}SCl_2$, SO_2, SOF_2 and the new compound $SF_5N{=}SClF$ which is believed to be the first example of a mixed halide of the type $SF_5{-}N{=}SXY$.[50] The preparation and reaction of S-perfluoroalkylsulphur monofluoride imides (6) has been described. The compounds were prepared by the reaction of NSF_3 with the appropriate sulphur trifluoride derivative. The fluorine atom bonded to S(N) may readily be substituted by reaction with PCl_5 to

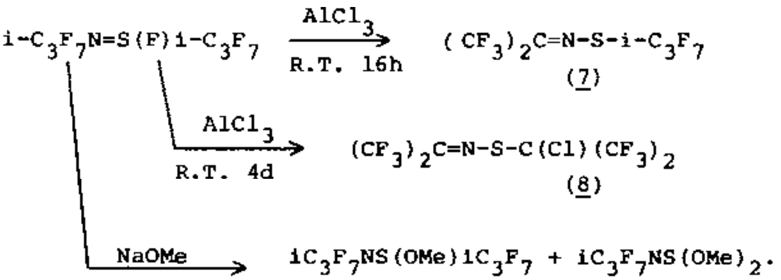


(6)

give $SF_5NS(Cl)R_f$ and the chlorine atom can likewise be substituted as shown in equation (13) by reaction with suitable Ag(I) or Hg(II) salts.[51]

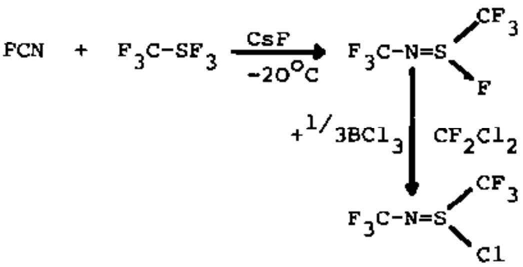
...(13)

The reaction of $i\text{-}C_3F_7SF_3$ and $(CF_3)_2CNH$ in the presence of CsF gives $i\text{-}C_3F_7N{=}S(F)i\text{-}C_3F_7$, which reacts with $AlCl_3$ to give (7) and (8); the S(11) atom in each may be oxidised by XeF_2. The sulphur bonded fluorine atom in $i\text{-}C_3F_7N{=}S(F)i\text{-}C_3F_7$ can readily be substituted by reaction with NaOMe[52] (see Scheme 2).



Scheme 2

N-trifluoromethylsulphurtrifluoromethylimidosulphurfluoride and -chloride have been obtained from the reaction of cyanogen fluoride and trifluoromethylsulphurtrifluoride and the subsequent halogen exchange reaction with BCl_3 (equation 14).[53]



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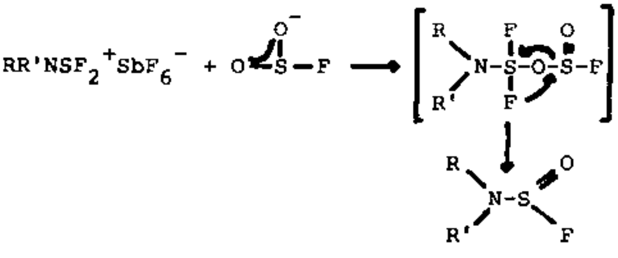
The sulphurdifluorideimides, R_1NSF_2 (R_1 = CF_3, C_2F_5, $i\text{-}C_3F_7$, C_6F_5, FSO_2 and SF_5) are alkylated in liquid SO_2 with alkoxysulphinyl salts, $R'OSO^+MF_6^-$, to give aminosulphurdifluoridehexafluoro antimonates or arsenates $RR'NSF_2^+MF_6^-$. Aminosulphinyl derivatives $RR'NSO^+MF_6^-$ were prepared by the same route or by fluoride-ion abstraction from RR'NSOF.[54]

The salts $RR'NSF_2^+SbF_6^-$ have been shown to provide a general route to [alkyl(perfluoroalkyl)amino]sulphur(IV) and -sulphur(II) compounds, and, as shown in equation (15), with NaF in liquid SO_2, aminosulphinyl fluorides (9) are obtained.



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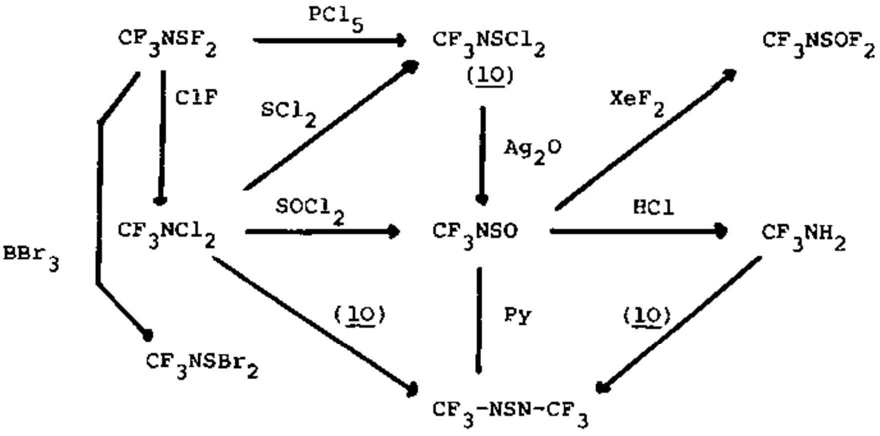
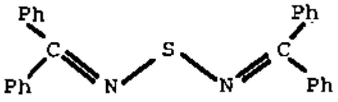
With NaF in TMSO the trifluorides $RR'NSF_3$ are produced and with NOCl or Me_3N aminosulphenyl derivatives, CF_3CH_3NSCl and sulphides $(CF_3CH_3N)_2S_x$ (x = 1 to 3) are found.[55] The preparation and reactions of CF_3NSO have been studied and the results obtained are shown in Scheme 3.[56]



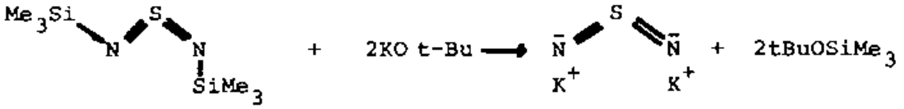
Scheme 3

The crystal structure of bis(diphenylmethyleneamino)monosulphide, $S(N{=}CPh_2)_2$ (11) has been determined. The PhCNSNCPh system is largely coplanar, with the two remaining phenyl groups twisted 62 and 49.2° respectively out of the central CNSNC plane. Bond angles at N (121.5, 122.4) and S (94.7°) and bond distances S-N (1.675, 1.676Å) and C-N (1.285, 1.288Å) indicate that the S-N bonds are essentially single with no significant delocalisation of the lone-pair charge at nitrogen.[57]



(11)

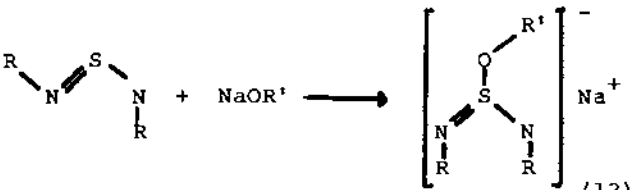
Compounds of the S(IV) diimines with the Main Group 4 elements have been prepared. Spectroscopic behaviour and the scope and limitations of the preparation of sulphurdiimines from amines and $N_3S_3Cl_3$ are discussed.[58] The electrochemical reduction and oxidation of sulphurdiimines R-NSN-R (R = Ph, C_6F_5, C_6H_5S, C_6F_5S) in organic solvents have been studied. Both reactions proceed in the sulphur-nitrogen system in a one-electron step.[59] The reaction of organosulphur diimides $S(NR)_2$ with potassium t-butoxide in boiling dimethoxyethane, equation (16), yields the pale yellow salt, K_2SN_2, in high yield. The salt is stable up to 18°C and



...(16)

above but reacts explosively with water, EtOH or halomethanes. It is insoluble in hydrocarbons, ethers and liquid ammonia.[60]

Reaction of acyclic sulphur diimides with sodium alkoxides, equation (17), has been shown to give (12) in high yield.



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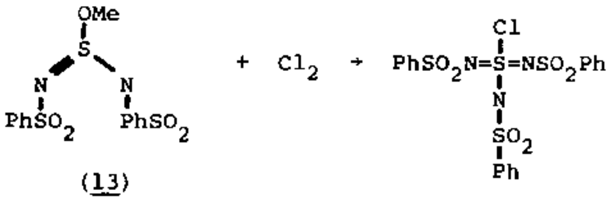
...(17)

Structural studies of the tetraphenylphosphonium salt showed that the introduction of the ethoxy group enlarged the S-N distance from ca. 1.53Å to 1.609Å (mean distance).[61]

The compound (13) reacts with elemental chlorine according to equation (18) to give the sodium salt (14) which is the aza analogue of chlorosulphonic acid. When $NaNH_2$ is used as a



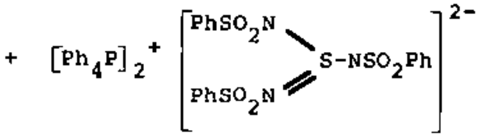
...(18)

(13)

(14)

nucleophile for the reaction in equation (19) with bis(phenylsulphonyl)sulphur diimide, tris(phenylsulphonylimido)-sulphite (15) is formed as the main product. Structural studies

$$PhSO_2N{=}S{=}NSO_2Ph + NaNH_2 \rightarrow PhSO_2NH_2 + [Ph_4P]^+[PhSO_2NSN]^-$$



...(19)

(15)

showed that (15) is analogous to the SO_3^{2-} anion having a central sulphur atom with a trigonal pyramidal configuration.[62] The reactions of CF_3SNH_2 and CF_2ClSNH_2 with a selection of aldehydes have been described.[63] The reactions of $(CF_3S)_2NCH_2OH$ with SF_4, PCl_3 and PBr_3 to form $(CF_3S)_2NCH_2X$ (X = F,Cl,Br) and with CF_3SNCO to yield $(CF_3S)_2NCH_2OC(O)N(H)SCF_3$, which can be sulphenylated at the NH functions have been reported.[64]

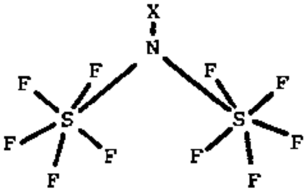
The N-(perfluoro-λ^6-sulphanyl)iminosulphurtetrafluoride mentioned earlier in this review,[49] has been shown to react, equation (20), with HF to yield $(SF_5)_2NH$ (16) in quantitative yields.

$$F_5SNSF_4 + HF \rightarrow \underset{(16)}{(SF_5)_2NH} \qquad ...(20)$$

The amine is a colourless liquid (bp. 60.4°C) and stable at room temperature; being a weak acid, salts with large cation may be precipitated. As shown in equations (21) and (22), reactions of elemental fluorine and ClF with the caesium salt give a further two amines. Electron diffraction showed (<u>16</u>) and (<u>17</u>) to have planar S_2NX (<u>18</u>) frameworks with large SNS angles (134.8 and 138.3° respectively) and with S-N distances increasing with increasing electronegativity of the substituents.[65]

$$Cs^+N(SF_5)_2^- \; + \; F_2 \; \rightarrow \; \underset{(\underline{17})}{FN(SF_5)_2} \; + \; CsF \qquad ...(21)$$

$$Cs^+N(SF_5)_2^- \; + \; ClF \; \rightarrow \; ClN(SF_5)_2 \; + \; CsF \qquad ...(22)$$



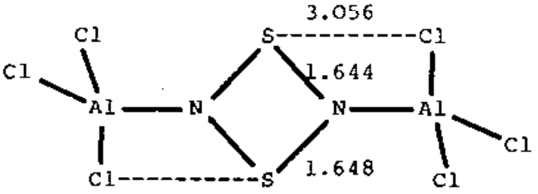
(<u>18</u>) X = H or F

The first liquid pentafluorosulphanylcarbamyl derivative $SF_5NHC(O)F$ has been prepared by reaction of equimolar quantities of NSF_3, COF_2 and anhydrous HF. The reaction of SF_5NH_2 with $ClC(O)CF_2CF_2C(O)Cl$ produced not only the expected diamide $[SF_5NHC(O)CF_2]_2$, but also the novel cyclic imide $SF_5\overline{NC(O)CF_2CF_2C}(O)$. The compound $SF_5NHC(O)NHSF_5$ was found to react with PCl_5 to produce the carbodiimide $SF_5N{=}C{=}NSF_5$.[66] The compound SF_5NFCl has been synthesised from NSF_5 by a low-temperature reaction with ClF followed by reaction with fluorine. Subsequent reduction with mercury in trifluoroacetic acid gives SF_5NHF in high yield, whilst dehydrofluorination of the latter with KF results in $FN{=}SF_4$. The imine is an unusual pentacoordinated molecule which does not undergo positional exchange of the sulphur fluorines according to ^{19}F n.m.r.[67]

<u>Polymeric and Cyclic Compounds</u>. Poly(sulphurnitride) has been prepared in 65% yield by the reaction of excess $SiMe_3N_3$ with

$S_3N_3Cl_3$, $S_3N_2Cl_2$ or S_3N_2Cl at -15°C in acetonitrile solution. The polymer was also prepared by the reaction of $S_3N_3Cl_3$ and excess of NaN_3, but reaction of S_2Cl_2 with NaN_3 in acetonitrile gave a powder containing S_3N_2Cl, S_8, NaCl and unreacted NaN_3, which when treated with an excess of $SiMe_3N_3$ yielded $(SN)_x$. Analogous reaction of Se_2Cl_2 and $SeBr_4$ gave blue-black explosive solids.[68]

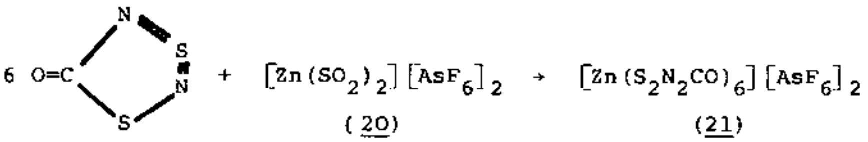
The reaction of S_4N_4 with $S_2N_2.2AlCl_3$ at 80°C in high vacuum results in the formation of S_2N_2. This method of preparation for S_2N_2 has obvious advantages on safety grounds in that cleavage of S_4N_4 takes place at 80°C instead of the normal temperature of 300°C required for pyrolysis of S_4N_4.[69] The crystal structure of $S_2N_2.2AlCl_3$ (19) shows the central S_2N_2 ring to be completely planar with S-N distances hardly different from those in free S_2N_2.



(19)

Also noteworthy are the relatively short S---Cl contacts.[70]

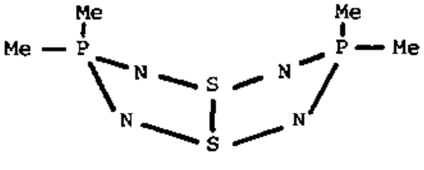
In order to clarify whether coordination of the ligand S_2N_2CO to a metal atom takes place via oxygen, sulphur or nitrogen, the reaction shown in equation (23) with the zinc complex (20) in liquid SO_2 has been investigated and the resulting product (21) examined by X-ray crystallography. The ligand was shown to be



...(23)

planar with a Zn-O-C angle of 134.2°, a C-O bond length (124.0pm) somewhat longer than in the free ligand (122.2pm) and with S-N bond lengths showing no significant change.[71] $Me_2PS_2N_3$, prepared by the reaction of Me_2PPMe_2 with S_4N_4, undergoes a ring expansion at ambient temperature to give $Me_2P(NSN)_2PMe_2$ whose crystal and molecular structure (22) has been determined by single crystal

X-ray diffraction. The structure consists of a folded eight-membered ring with a cross ring S-S contact of 2.551Å. The angle between the intersecting planes of the rings is 114.9°, with mean endocyclic P-N and S-N bond lengths of 1.636 and 1.595Å, respectively.[72]



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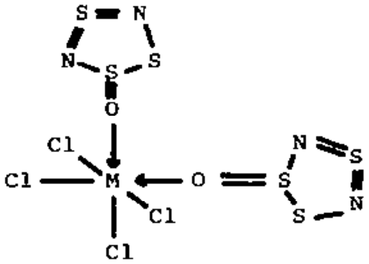
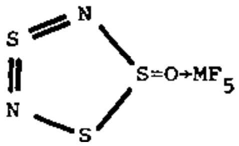


(23)

S_3N_2O has been shown to react with $SnCl_4$ and $TiCl_4$ to yield the 2:1 adducts (23), and with AsF_5 and SbF_5 to form the 1:1 adducts (24). X-ray analysis of the $SnCl_4$ adduct shows the ligands to have a cis configuration.[73].



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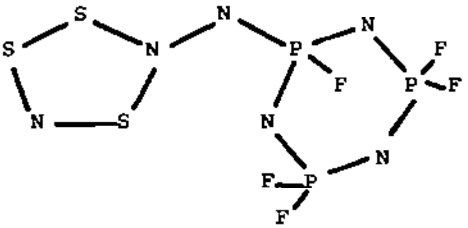
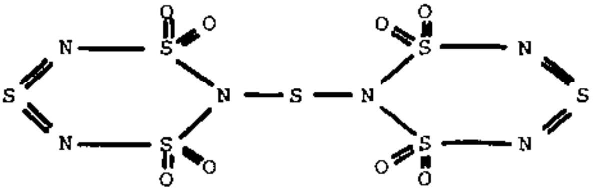


(25)

A crystal structure determination on $S_3N_2NP_3N_3F_5$, prepared from the reaction of $P_3N_3F_5N(SnMe_3)_2$ and $S_3N_2Cl_2$, shows the molecule (25) to consist of a cyclotriphosphazene ring bonded through a bridging nitrogen atom to a five membered S_3N_2 ring. The $N\text{-}S_3N_2$ part of the molecule is similar to the $S_3N_2Cl^+$ cation except that the exocyclic S-N bond involves substantial π-character with both S-N and P-N distances from the bridging nitrogen atom being considerably shorter than the corresponding single bond distance.[74] The magnetic circular dichroism spectra of the $NPPh_3$ and $NAsPh_3$ derivatives of the ten-π-electron six-atom $S_3N_3^-$ ion have been measured.[75]

The compound, $S_4N_4O_2$, reacts with SO_3 under mild conditions to yield $(S_3N_3O_4)_2S$, a new bicyclic system (26) with a skeleton comprising only of S and N atoms. The bond lengths and angles are consistent with the presence of localised sulphur-di-imide (-N=S=N-) units; the remaining sulphur-nitrogen bonds being essentially single bonds.[76]

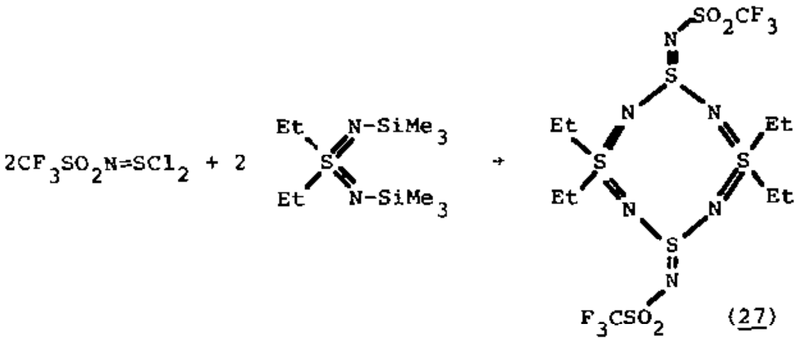


(26)

Magnetic circular dichroism of the $S_4N_3^+$ cation has revealed the presence of four low-energy electronic transitions. Their number and properties are exactly those expected for $\pi^*-\pi^*$ excitations in a ten-π-electron system with cyclic delocalisation.[77]

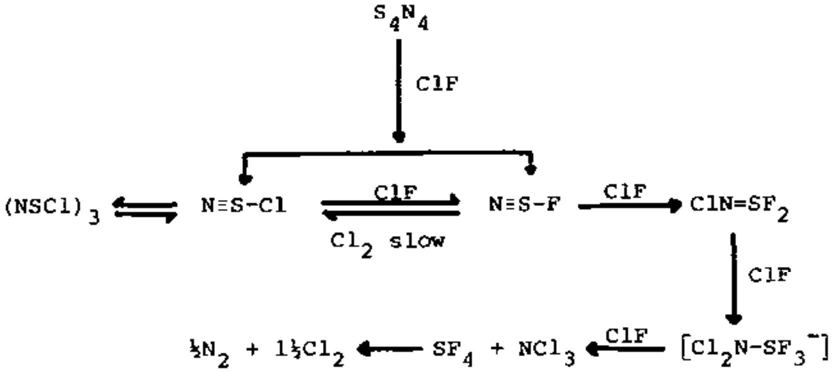
Ab initio Hartree-Fock-Slater M.O. calculation on planar $S_4N_4^{2+}$ have revealed it can be described as a fully delocalised ten-π-electron system. Overlap populations for the N-S bond suggest a bond order substantially stronger than in neutral S_4N_4. The strong u.v.-visible absorption observed for $N_4S_4^{2+}$ at 346 and 262nm are assigned to $n\pi_S \rightarrow \pi^*$ and $n\pi_N \rightarrow \pi^*$ transitions.[78] The synthesis and crystal structure of the substituted tetrasulphur tetranitride (27) has been described. The compound, which was synthesised by the reaction of $CF_3SO_2N{=}SCl_2$ with $Et_2S[NSiMe_3]_2$ shown in equation (24), possessed an eight membered S_4N_4 ring unusually in a chair conformation with C_{2h} symmetry. The bond lengths in the pyramidal $S(IV)N_3$ groups are 1.661Å for the endocyclic bonds and 1.625Å for the exocyclic bonds. The $S(VI)N_2$ groups have shorter bond lengths of 1.576Å.[79]

According to n.m.r. data the fluorination of S_4N_4 by F_2 under mild conditions gives $S_4N_4F_2$ as the primary product together with $S_4N_4F_4$ and $S_3N_3F_3$.[80] Chlorine monofluoride reacts with S_4N_4 to give thiazyl chloride (monomer and trimer) and thiazyl fluoride. With further ClF, NSCl reacts to form NSF, then $ClNSF_2$ and finally N_2, Cl_2 and SF_4; the reactions in Scheme 4 have been proposed. NSF was prepared by the new method of passing NSCl through a column of CsF at 110°C.[81]



(27)

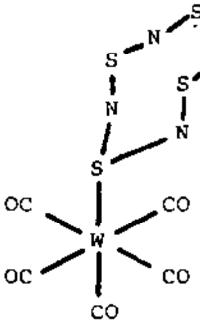
$+ 4Me_3SiCl$ ...(24)



Scheme 4

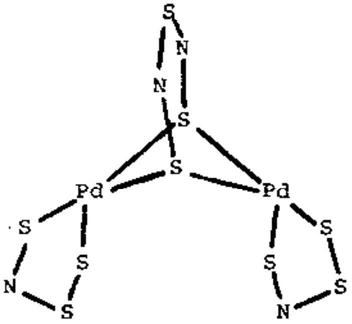
The structure of $3S_8$-$S_4(NH)_4$ has been shown to comprise of two independent eight membered ring molecules in a crown conformation, in which S and N atoms are distributed at random over all sites. This arrangement is very close to that of monoclinic γ-sulphur stabilised at room temperature by the presence of the sulphurimine ring.[82] $S_4N_4H_4$ also reacts with (THF)M(CO)$_5$, where M = Cr or W, to form isolable complexes of the type $S_4N_4H_4M(CO)_5$ and $S_4N_4H_4[M(CO)_5]_2$. In solution partial dissociation of the M(CO)$_5$ moieties is observed. Structural studies on the W complex (28) give the following bond length data: W-S 2.525, W-C 1.97 to 2.04, and S-N 1.675 to 1.705Å.[83]

The crystalline, black polymeric complex CuBr.S_4N_4 may be prepared by the reaction of $Cu(NO_3)_2.3H_2O$, NH_4Br and S_4N_4 in methanol. X-ray studies show it to be isostructural with



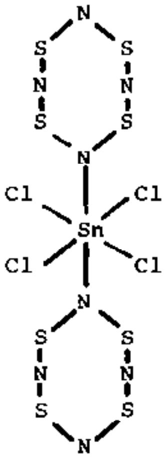
(28)

$CuCl.S_4N_4$.[84] S_4N_4 and $PdCl_2$ react in methanol to give, amongst other products, the dinuclear complex $Pd_2(S_3N)_2S_3N_2$ (29). Each Pd atom is part of an almost planar PdS_3N metallocycle with the SNSNS group acting as a bridge whereby each of its terminal S atoms is bonded to both Pd atoms. The Pd atom is in square planar coordination by four sulphur atoms with the planes forming an angle of 114.9° giving a rather short (2.921Å) Pd-Pd distance.[85]



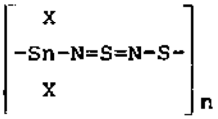
(29)

The structure of $TaCl_5.S_4N_4$ shows that the S_4N_4 group is bonded by one of its nitrogen atoms to the Ta atom to complete the octahedral coordination.[86] The reaction of S_4N_4 with a number of tin(II) and tin(IV) compounds have been studied. The tin(IV) compounds were thought to have the structure (30) by analogy with previous compounds and this conclusion was supported by the observed i.r. spectra. The tin(II) adducts have not been reported previously and analytical data gave the formulae, $SnX_2S_2N_2$, (X = Cl, Br, OMe, NMe_2). Of the various possible



(30)

structures for these compounds the authors considered that a polymeric form (31) was most probable.[87]

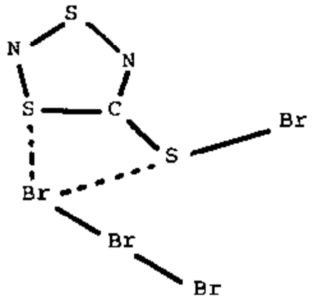


$$\left[-\overset{X}{\underset{X}{Sn}}-N=S=N-S- \right]_n$$

(31)

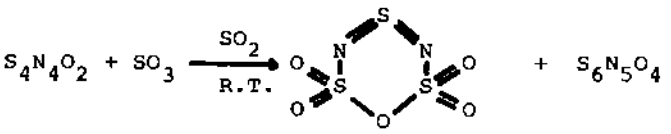
The reactions of S_4N_4 with R_2PPR_2 (R = Me,Ph) or $(PhO)_3P$ in toluene at reflux leads to the formation of $R_2PS_2N_3$ (R = Me,Ph, OPh). The crystal structure of $Ph_2PS_2N_3$ consists of a six membered PS_2N_3 ring in which the NSNSN unit is virtually coplanar, with the phosphorus atom being 0.284Å out of the plane. The S-N bond lengths are within the range 1.560-1.583Å whilst the mean P-N bond length is 1.623Å. Calculations based on the model compound H_2PS_2N show that the PS_2N_3 ring contains eight π-electrons largely delocalised over the nitrogen-sulphur atoms, the contribution from the phosphorus d-electrons have an important stabilising influence, and that the observed geometry of the PS_2N_3 ring is slightly lower in energy (ca. 15 k.cal/mole) than that of a planar PS_2N_3 ring. The crystal structure of the norbornadiene adduct confirms the ^1H and ^{13}C n.m.r. evidence that the cycloaddition of C_7H_8 occurs in a 1,3- fashion across the S atoms to give the exo-β-isomer of the adduct.[88]

S_4N_4 reacts with bromine in CCl_4 at ambient temperature to give exclusively a mixture of S_4N_3Br and $S_4N_3Br_2$. In CS_2 the additional formation of $CS_3N_2Br_2$ and $CS_3N_2Br_4$ is observed. The structure of the latter compound was confirmed by an X-ray structural study which showed an almost flat CS_2N_2 five-membered ring with an S-Br group bonded exocyclically to the carbon atom,as the cation, with Br_3^- as the anion (32).[89]



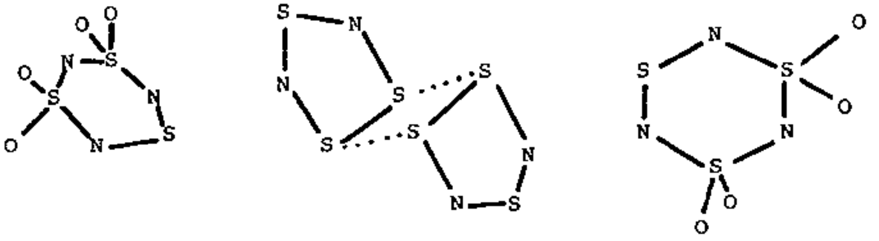
(32)

The preparation of $S_4N_5^+MF_6^-$ (M = As,Sb) from the decomposition of $S_3N_2F_2^+$ MF_6^- and by chlorine exchange in S_4N_5Cl with $AgAsF_6$ has been described. The structure of the arsenic compound was determined.[90] The reaction of S_3N_3Cl with $SbCl_5$ in a 1:2 molar ratio gives $(S_4N_4)(SbCl_6)_2$ as the major product in SO_2, CH_2Cl_2 and $SOCl_2$ as solvents. With a 1:1 molar ratio and CH_2Cl_2 as solvent, the products were $(S_5N_5)(SbCl_6)$ and $S_4N_4.SbCl_5$. This mixture reacted with additional $SbCl_5$ to give $(S_4N_4)(SbCl_6)_2$. The geometry of the planar $S_5N_5^+$ cation was found to be intermediate between the azulene and heart-shaped conformations found previously for other examples of this cation.[91] The compound $S_6N_5O_4$ (33) has been prepared by the reaction in equation (25). A crystal structure analysis shows it to be composed of



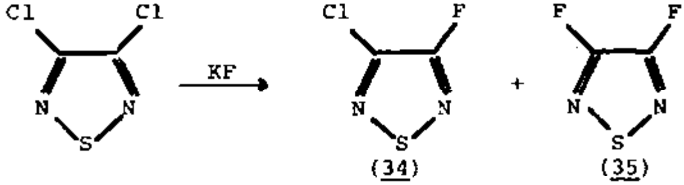
...(25)

separately stacked cyclic radical cations $S_3N_2^+$ and cyclic anions $S_3N_3O_4^-$ (33).[92]



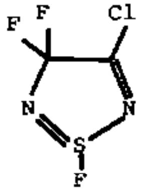
(33)

The reaction in equation (26) of 3,4-dichloro-1,2,5-thiadiazole KF in sulfolane gives (34) and (35). In the reaction with oxidising



...(26)

fluorinating agents such as XeF_2, BrF_3 or AgF_2, it is observed that (36) is the primary product whilst cleavage of the ring system at one of the S=N bonds gives bifunctional ethane derivatives.[93]

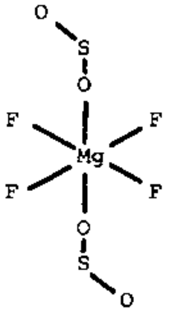


(36)

6.2.4 Bonds to Oxygen

An e.s.r. study has shown that SO_2 (with CO) on a CuO-alumina catalyst surface causes the Cu^{2+} signal to increase significantly. A new line attributed to the $SO_2^{-}\cdot$ ion appeared on heating the catalyst but it was thought that the ion did not take part in the reduction of SO_2 with CO over the catalyst.[94] The reaction of electrolytically generated $SO_2^{-}\cdot$ has been used for the synthesis of sulphur containing heterocycles such as oxathiolane, oxathiane, thiane and thiepane oxides.[95] The new reaction between SO_2 and hexamethyldisilazane which gives $(Me_3Si)_2O$, Me_3SiNSO and $NH_4(Me)_3SiOSO_2$ has been studied. In the reaction, oxygen is transferred to Si and S from SO_2 but Si-N bonding is still partially retained.[96]

The preparation of sulphur dioxide complexes $M(SO_2)_2AsF_6$, M = the top row transition metals from Mn to Zn and Mg, is possible in liquid SO_2, by oxidation of the metals with AsF_5, by metathesis of metal halides or by reaction of metal fluorides. The structure of $[Mg(SO_2)_2(AsF_6)_2]_n$, (<u>37</u>) was shown to consist of octahedrally coordinated Mg ions linked to AsF_6 ions by fluorine bridges with the SO_2 occupying trans positions.[97]



(<u>37</u>)

A series of transition metal complexes of SO_2 have been described in which both η^1 planar and η^3 coordination of SO_2 is observed.[98] The reactions of SO_2 with $RhH(CO)(PPh_3)_3$ and $IrH(CO)(PPh_3)_3$ have been reinvestigated and the products have been shown to be the complexes $MH(CO)(SO_2)(PPh_3)_2$.[99] When $Ru(NH_3)_5Me_2SO^{2+}$ is oxidised to the 3+ state, S→O isomerisation takes place but on reduction to the 2+ state, O→S isomerisation is observed.[100]

A study of the reaction of sulphuryl halides with amines has shown that, following equation (27), SO_2F_2, SO_2ClF and SO_2Cl_2 react with primary amines to form symmetrically substituted sulphamides. With secondary amines the reaction is different since the products are determined by the relative amounts of the reactants used, thus in the molar ratio 1:2 reaction proceeds

$$4RNH_2 + SO_2XY \rightarrow (RNH)_2SO_2 + RNH_2.HX + RNH_2.HY \qquad ...(27)$$

according to equation (28) while with excess amine the reaction

$$SO_2XY + 2C_5H_{10}NH \rightarrow C_5H_{10}NSO_2X + C_5H_{10}NH.HY \quad ...(28)$$

follows that in equation (29). With tertiary amines, 1:2 adducts

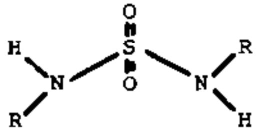
$$SO_2XY + 4C_5H_{10}NH \rightarrow (C_5H_{10})_2SO_2 + C_5H_{10}NH.HX + C_5H_{10}NH.HY \quad ...(29)$$

are formed.[101]

The vibrational spectrum of SOF_2 has been reinvestigated by means of high resolution i.r. and Raman spectroscopy. Use of ^{18}O substitution made identification of these modes to which S-O motion makes a large contribution more definitive.[102]

It has been reported that the reaction between organophosphorus compounds $\geqslant$P=X and sulphuryl chloride fluoride makes available a variety of fluorinated organophosphorus compounds including potential enzyme inhibitors.[103] Perfluoroallyl fluorosulphonate, prepared by treatment of perfluoropropene with stabilised sulphur trioxide has been shown to react with KI, KBr, NaOMe and PhMgBr to give the corresponding perfluoroallyl derivatives CF_3=$CFCF_2X$.[104] Ab initio molecular orbital studies of the rearrangement of α-disulphoxide to thiosulphonate have been carried out.[105]

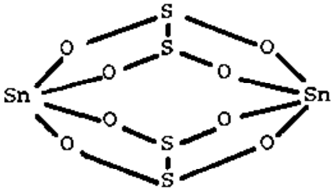
The first single crystal X-ray diffraction study of a symmetrical dialkyl-sulphamide $(t\text{-}BuNH)_2SO_2$ has shown it to have the structure (38).[106] The crystal structure of Na_5 trans-$Co(CN)_4(SO_3)_2.13H_2O$ shows the presence of two independent complex ions with CO at the centre of symmetry.[107] ^{17}O-exchange experiments have been used to show that in the reaction of $Co(NH_3)_5OH^{2+}$ with SO_2 in aqueous solution an oxygen bonded sulphato complex $(Co(NH_3)_5OSO_2{}^+$ is formed. On acidification SO_2 is released to form the corresponding aquo complex with no breakage of the Co-O bond.[108] Four new compounds of the bi- and tri-metallic imido disulphates, $HN(SO_3M)_2$ and $MN(SO_3M)_2$ where M =



(38)

Li,Cs, have been prepared.[109]

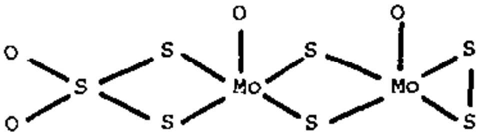
Tin(II) dithionite, $Sn_2(S_2O_4)_2$ has a cage-like structure (39) in which the Sn^{2+} ion is coordinated to four oxygens from two $S_2O_4^{2-}$ ions in a slightly distorted square pyramidal configuration. The dithionite ion has a slightly distorted C_{2v} configuration with an S-S distance of 2.350 and S-O distances from 1.503 to 1.517Å.[110]



(39)

The structures of sulphate, sulphite and disulphite ions in aqueous solution have been determined from X-ray scattering experiments at 25°C on concentrated solutions of the ammonium salts. The sulphate ion has a tetrahedral structure with an S-O distance of 1.481Å whilst the sulphite ion has a pyramidal C_{3v} structure with an S-O distance of 1.529Å. The $S_2O_5^{2-}$ ion was found to have an S-S bridge with a bond length of 2.221Å. Various hydration models were also postulated.[111] The equilibrium quotient for the dimerisation of bisulphite ions to $S_2O_5^{2-}$ has been determined from Raman and u.v. intensity measurements. In addition to the well characterised form of bisulphite ion having the hydrogen attached to sulphur, the Raman data also indicate the presence of appreciable amounts of the isomer with hydrogen bonded to one of the oxygen atoms.[112] A crystal structure determination has shown $MgS_2O_3.6H_2O$ to have an orthorhombic crystal lattice in the space group Pnma with S-S distance 2.011Å and S-O distances from 1.457 to 1.469Å.[113] $Na_3H(SO_4)_2$ crystallises in the monoclinic space group P2/c with a very short hydrogen bond linking the two parts of the $(SO_4.HSO_4)^{3-}$ dimer.[114]

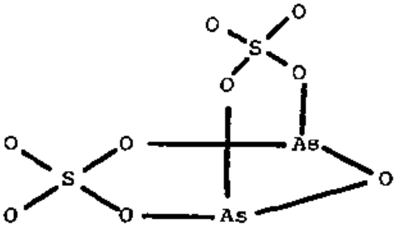
It has been found to be possible to fix, by complexation, the $S_3O_2^{2-}$ ion, formed on oxidation on S_x^{2-} ligands in a metal complex. A crystal structure determination shows the complex, $(PPh_4)_2[(S_2)OMoS_2MoO(S_3O_2)]$ to have the conformation (40). ESCA and i.r. spectra also showed the presence of $S_3O_2^{2-}$ in the molecule.[115]



(40)

Osmotic and activity coefficients for Na_2SO_4 in aqueous solution have been determined at temperatures up to 250°C and solute concentrations from 0.3M to saturation.[116] The high temperature form of Na_3PO_4 has been shown to dissolve up to 70 mol % of Na_2SO_4 whilst maintaining its crystal structure. The high temperature form of Na_3PO_4 was also found to be stabilised at room temperature by the addition of small amounts of Na_2SO_4.[117] The oxidation of graphite in both air and oxygen or inert atmospheres has been observed in sodium sulphate melts.[118] The crystal structure of $K_2SO_4.SbF_3$ has been reported.[119] The sulphate group in gypsum, $CaSO_4.2H_2O$, was found from neutron diffraction data not to be a regular tetrahedron,with S-O bond lengths of 1.474 and 1.471Å.[120] Spectroscopic studies on water-methanol solutions of magnesium sulphate have been reported.[121]

Hydrazinium(1+)hydrogen sulphate, $N_2H_5HSO_4$ has been prepared for the first time by the reaction of solid ammonium hydrogen sulphate with hydrazine monohydrate.[122] The crystal structures of $As_2(SO_4)_3$, $(As_2O_2)SO_4$ and $As_2O(SO_4)_2$ have been reported. In $As_2(SO_4)_3$ each sulphate tetrahedron bridges two AsO_3 pyramids with two S-O bridging bonds of length 1.54Å and two terminal S=O of length 1.42Å.[123] $(As_2O_2)SO_4$ contains As_2O_2 infinite chains, As-O-S bridges with As-O and S-O distances of 1.840 and 1.514Å, respectively and terminal SO_2 groups with S-O distances of 1.441Å.[124] $As_2O(SO_4)_2$ has molecular units with two hexagonal rings (41) built up from As-O-As groups linked by two SO_4 tetrahedra.[125] Crystal structures have also been determined for



(41)

Sn_2OSO_4,[126] $VOSO_4.3D_2O$,[127] $K_4(H_5O_2([Nb_3O_2(SO_4)_6(H_2O)_3].5H_2O$,[128] α-$Cd_2(OH)_2SO_4$,[129] $UO_2SO_4.H_2SO_4.5H_2O$ and $2NpO_2SO_4.H_2SO_4.4H_2O$.[130]

The oxidation of VO_3^+ by HSO_5^- has been shown to be catalysed by low concentrations of VO^{2+} in acidic solution. A mechanism is proposed in which $SO_4^{\overset{\cdot}{-}}$, formed in the rate determining step oxidises VO_3^+ to the $VO_3^{2+\cdot}$ radical cation.[131] Polycrystalline WO_3 electrodes when illuminated with visible light in acid hydrogen sulphate solutions have been shown to produce peroxodisulphate with 85% current efficiency.[132] The i.r. and Raman spectra of solid Cs and Rb fluoroxysulphates, $CsSO_4F$ and $RbSO_4F$ have been measured and shown to be consistent with a perchloric acid type structure of C_s symmetry.[133] The following phase systems have been studied: $Gd_2(SO_4)_3$-Li_2SO_4-H_2O and $Gd_2(SO_4)_3$-K_2SO_4-H_2O;[134] $Gd(SO_4)_3$-Na_2SO_4-H_2O and $Gd(SO_4)_3$-Rb_2SO_4-H_2O;[135] $Gd(SO_4)_2$-$(NH_4)_2SO_4$-H_2O and $Gd(SO_4)_3$-Cs_2SO_4-H_2O;[136] Na_2SO_4-$Al_2(SO_4)_3$;[137] Cs_2SO_4-$2NaOH$-H_2O;[138] Na_2SO_4-$Bi_2(SO_4)_3$;[139] K_2SO_4-$MgSO_4$-$CaSO_4$-H_2O;[140] $K_2S_2O_7$-K_2SO_4 and $K_2S_2O_7$-K_2SO_4-V_2O_5.[141]

6.2.5. Sulphides

The reaction of H_2S with $CrCl_3$ at 650K has been shown to produce the first chromium thiochloride $Cr_8S_{11}Cl_2$.[142] H_2S has been shown to be the first gaseous promoter of the water gas shift reaction, enhancing the formation of H_2 and CO_2 approximately 13-fold under identical experimental conditions to those of the control experiment.[143]

Parameters for calculating bond valencies from bond lengths have been given for bonds to S from 55 different cations most being reported for the first time.[144] The blue solutions produced by reaction between aluminium and sulphur in basic CsCl-$AlCl_3$ melts have been attributed to the presence of S_3^- species. An equilibrium was proposed between the S_3^- ion, S(2-) species (present in polymeric chain species of the $[AlSCl_2]_n^{n-}$ type) and molecular sulphur. No direct evidence for the formation of other sulphur species was found but there are indirect indications of a possible existence of other sulphur species.[145] The mass spectra of the cage compounds $(MeSn)_4S_6$ and $(MeSn)_4Se_6$ have been determined and compared. The ionisation potential of the Sn-X bond is lowered on changing from S to Se whereas the dissociation energy of the Sn-C bond is raised.[146] EXAFS spectra have been recorded at the manganese K edge in the layered compound $MnPS_3$.[147]

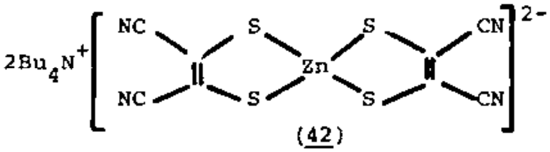
N.m.r. evidence indicates that the primary product of the desulphuration of P_4S_9 by Ph_3P is P_4S_8 - a new species of limited stability.[148] Rates of homogeneous nucleation of As_2S_3, As_2O_3 and As_2Se_3 from their undercooled melts were found to be lower than calculated, but by seeding under conditions favouring heterogeneous nucleation it was possible to grow crystalline As_2S_3 and As_2Se_3 from melts.[149]

Gaseous polysulphides of silicon and titanium have been shown to be responsible for the chemical transport of SiS_2 and TiS_2.[150] Pressure and temperature induced phase transitions in FeS have been investigated by X-ray diffraction on single crystal samples.[151]

A reaction of $FeCl_3$, Li_2S, Li(S-tBu) and LiOMe in methanol solution has been used to prepare the hexanuclear cluster $[Fe_6S_9(S\text{-}tBu)_2]^{4-}$ which may be crystallised as its $(Me_3NCH_2Ph)^+$ salt. The $[Fe_6S_9]^{2-}$ core is formed from eight non-planar Fe_2S_2 rhombs that are fused together by edge sharing to give four $Fe(\mu_2\text{-}S)(\mu_3\text{-}S)Fe$, two $Fe(\mu_2\text{-}S)(\mu_4\text{-}S)Fe$ and two $(\mu_3\text{-}S)(\mu_4\text{-}S)Fe$ subunits.[152] A series of cobalt(III) complexes containing symmetrical disulphides bonded to cobalt through one sulphur atom have been prepared via electron transfer initiated by 1-equivalent oxidation of the respective thiolato complexes with $[Co(aq)]^{3+}$. Analogous complexes containing unsymmetrical disulphides were prepared by reaction of the parent thiolato complex with $[RS]^+$ donors such as sulphenyl iodides or methoxycarbonylalkyl disulphides.[153]

Single crystals of some ternary and quaternary copper thiospinels have been grown by chemical transport using $FeCl_4$ or mixtures of $AlCl_3/I_2$ as transporting agents.[154] Electrical conductivity measurements from 15 to 300K have shown that the mixed-valence compound $Na_3Cu_4S_4$ is metallic. Measurements on single crystals revealed that the conductivity is highly anisotropic, with enhanced conductivity parallel to the crystal needle axis, corresponding to pseudo-one dimensional $[Cu_4S_4]^{3-}_{\infty}$ columns in the structure.[155]

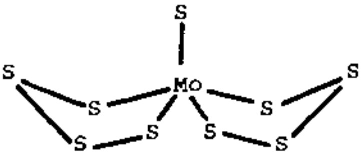
Metal dithiolanes such as (<u>42</u>) in the presence of mild reducing agents have proved to be the most effective catalytic generators of hydrogen from water with U.V. light. The actual catalysts are formed in the first reaction step from the complexes and the best system was found to be (<u>42</u>) in H_2O/2,5-dihydrofuran. Recent work on this system has elucidated the reaction mechanism and identified the catalyst to be zinc sulphide.[156]



(42)

The room temperature oxidation of r.f. sputtered molybdenum disulphide films has been investigated and their chemical states examined by XPS and AES techniques.[157]

The MoS_4^{2-} anion reacts with elemental sulphur and active sulphur agents such as organic trisulphides or ammonium sulphides to yield binary molybdenum sulphides. With Et_4N^+ as the counterion the $(S_4)_2MoS^{2-}$ anion (43) can be isolated from either MeCN or DMF solutions. The hydrolysis of (43) in DMF or MeCN gives the $(S_4)_2MoO^{2-}$ anion, while in the presence of the Ph_4P^+ cation the $Mo_2S_{10}^{2-}$ (44) and $Mo_2S_{12}^{2-}$ (45) anions can be isolated from DMF solution as mixed anion salts.[158]



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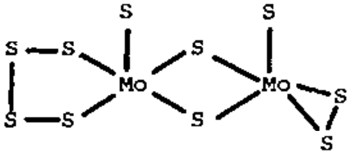

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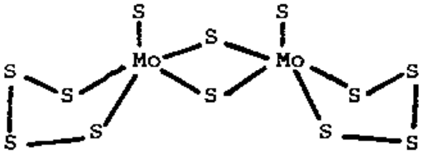


(45)

Acidification of tetrathiotungstate WS_4^{2-} produces the doubly bridged polynuclear complex $[(W_2S_4)(WS_4)_2]^{2-}$ having a central $W_2S_4^{2-}$ core, in which each W has a tetragonal sulphur environment. The apex of each pyramid is occupied by a sulphido group and the equatorial plane is formed by sulphido bridging groups and by sulphur atoms of the WS_4^{2-} ligand.[159]

The sublimation of WSF_4 at temperatures between 290 and 343 has been studied by the Knudsen effusion technique.[160] The ternary sulphides $EuZrS_3$ and $EuHfS_3$ have been prepared from the binary sulphides.[161] The standard free energy change for the semiconductor-metal transition in lanthanide monosulphides at 298.15K has been estimated.[162]

The crystal structures of a large number of sulphides have been reported, these are collected together in Table 1.

Table 1. Crystal Structure Determinations.

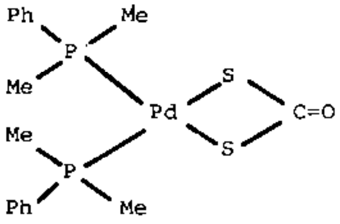
Compound	Ref	Compound	Ref	Compound	Ref
$Tl_2Sn_2S_3$	163	$Cu_5Si_2S_7$	171	$CaSc_2S_4$	180
$(NdO)_4Ga_2S_5$	164	$Tl_4Ge_2S_6$	172	$SrSe_2S_4$	180
$(CeO)_4Ga_2S_5$	165	$Eu_2Sn.S_5$	173	$PbCe_2S_4$	180
$(LaO)_4As_2S_5$	165	$Cu.Sn_{3.75}S_8$	174	$Ag_{0.37}Cr_{1.21}S_2$	181
$La_{3.33}Ga_6O_2S_{12}$	166	ZrP_2S_6	175	Th_2S_5	182
$LaGaS_3$	167	ThP_2S_6	175	$In_6La_{10}O_6S_{17}$	183
$Fe_2Ga_2S_5$	168	$Ag_7(PS_4,P_2S_7)$	176	$ZnLn_2S_4$	184
In_2S_3	169	$Na_3AsS_4.8D_2O$	177	Tl_4GeS_4	185
$Al_2In_4S_9$	170	$Bi_xSb_{2-x}Sn_2S_5$	178	Tl_4GeSe_4	185
$Ga_2In_4S_9$	170	Eu_2BiS_4	179		

The following phase systems have been reported, CdS-SnS and CdSe-SnSe,[186] Cu-S-Zn,[187] Ga_2S_3-PbS,[188] FeS-Cr_2S_3,[189] Ga_2S_3-La_2O_3 and In_2S_3-La_2O_3,[190] P_4S_3-P_4Se_3,[191] $YbMo_6S_8$-$YbMo_6Se_8$.[192]

6.2.6 Bonds to Carbon

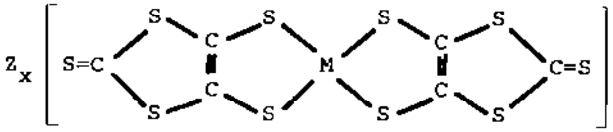
Neutron powder diffraction data taken at 90K have shown that COS has a space group $R\bar{3}m$ with the molecules aligned along the 111 crystallographic axis. Bond lengths of C-O 1.21 and C-S 1.51Å were observed.[193] COS has been found to react with some four coordinate Pd complexes to give the (dithiocarbonato-S,S')-palladium(II) compounds, $(PR_3)_2Pd(S_2CO)_3$ (<u>46</u>). X-ray structure determination shows a nearly square planar coordination of the metal and also a planar dithiocarbonate ligand.[194] COS also reacts with $Fe(CO)_2(PPh_3)_3$ in toluene to give $Fe(CO)_3(PPh_3)_2$ and $SPPh_3$. When liquified COS is used as the solvent, $Fe(S_2CO)(CO)_2(PPh_3)_2$ is also formed.[195] The reactions of several mixed ligand complexes of nickel(O) with the carbon dichalcogenides SeCS, CS_2 and SCO have been studied.[196]

The heat of formation of HCS^+ has been determined by a dissociative photoionisation study of three saturated cyclic



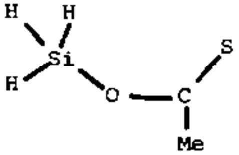
(46)

sulphur molecules, thiirane(C_2H_4S), thietane (C_3H_6S) and tetrahydrothiophene (C_4H_8S).[197] The crystal structure of solid CS_2 has been determined at six temperatures between 5.3 and 150K using a neutron diffraction powder profile refinement technique. The results confirmed the general features revealed in earlier determinations at higher temperatures. The C-S bond length was found to be shorter in the solid phase than in the gas phase being 1.546Å at 5.3K and 1.529Å at 150K.[198] Some new conducting solids with the general formula $Z_xM(C_3S_5)_2$ (47) and its Se analogues, where Z = Bu_4N, Na, Li, NH_4 and M = Ni, Pd, Pt and x = 0 to 1 have been prepared.[199]



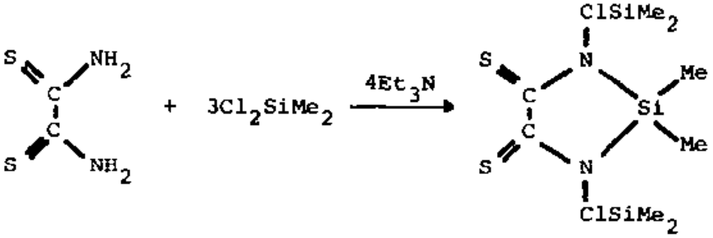
(47)

The conformation of 1,2,4,5-tetrathian has been determined by dynamic n.m.r. The barrier of the chair-twist equilibration is 14.5 kcal/mol and the chair form is the more stable in this molecule by 1.4 kcal/mol.[200] Bis(trifluoromethylthiyl)trithiocarbonate $(F_3CS)_2CS$ shows electronic transitions at 496nm ($n\pi^*$), 299nm ($\pi\pi^*$) and 259nm ($n\sigma^*$). Photolysis with 254 and 309nm light at 200 and 309K in pentane and at 371K in heptane gives mixtures of CS_2 and perfluorinated compounds. The primary photochemical prpcess is thought to be the intramolecular decomposition into CS_2 and $F_3CS^{\cdot}$ and $F_3C^{\cdot}$ radicals which dimerise in a solvent cage. No photochemical process was observed on irradiation at 496nm ($n\pi^*$).[201] The first successful isolation of the crystalline acylsulphenyl iodide RC(O)SI by the reaction of phenylmercurythiocarboxylates with iodine has been reported.[202] The thermal decomposition of the dialkylchalcogenide derivatives RSR, RSSR and RSeSeR (R = Me, CH_2Me, CH_2CH_2Me, $CHMe_2$, CMe_3) in a heated flow tube has been analysed using P.E.S. At higher temperatures (>1000K) the products are H_2, CH_4, CS_2 and HCCH but at the lowest temperatures, olefin, H_2S and S or olefin, alkane selenol, H_2Se and Se are produced respectively.[203] P.E.S. has also been used to show that the thiocarbonyl derivative $R^1R^2C{=}S$ with R^1,R^2 = H, Me, Ph can be generated thermally in the gas phase from a variety of precursors.[204] The structure of silylmonothioacetate has been determined in the solid at 130K by X-ray diffraction and in the gas phase by electron diffraction. In the structure (<u>48</u>) the Si-O and C=S bonds are eclipsed so that the intramolecular Si...S separations 3.185Å in the crystal and 3.143Å in the gas are appreciably less than the van der Waals distance.[205]



(<u>48</u>)

The first cyclic five-membered thiooxamides (<u>49</u>) and (<u>50</u>) have been synthesised by the routes shown in equations (30) and (31) from dithiooxamide and chloromethylsilanes. The compounds were obtained in small yields and are air-sensitive. Crystal structure determination showed all atoms except those of the methyl groups to be coplanar.[206]



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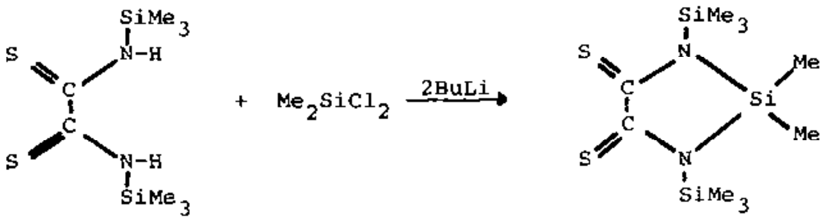
(<u>49</u>)



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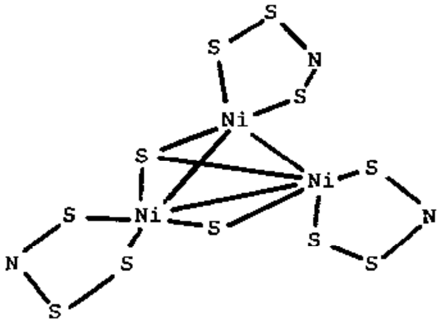
(50)

Further papers have been published in the series on chalcogenolates by Gattow and coworkers. The topics covered were the preparation and properties of metal guanidinodithioformates,[207] esters of guanidinodithioformic acid,[208] perthiocyanates,[209] esters of perthiocyanic acid,[210] methyl esters of dithiocarbamic acids;[211] the reactions of chloramine with CS_2 and with methyl esters of dithiocarbamic acids,[212] the crystal and molecular structure of dimethyl perthiocyanate[213] and the crystal structure of potassium N-cyanodithiocarbimate monohydrate, $K_2[S_2C{=}N{-}CN]H_2O$.[214] Several papers dealing with the chemistry of metal complexes with ligands containing C-S bonds have been published. Subjects covered include the use of isothiocyanates as starting materials for the synthesis of (η^2-isothiocyanate-C,S) -,(Dithiocarbamato-S,S')- and (Dithiocarbamato-S,S')bis(phosphane) palladium complexes;[215] the coordination chemistry and photochemical properties of Transition Metal(IV)-tridichalcogenocarbamates;[216] the reaction of platinum(II) and palladium(II) NN'-dialkyldithiocarbamates with diphenylphosphine chalcogenides;[217] the e.p.r. spectra of the eight coordinated complexes vanadium(IV) and niobium(IV) dithio- and diselenocarbamates;[218] and the structure of the dithiocarbonato complex (triphos)Co(S_2CO).[219] The reaction of COF_2 with $SF_5CF{=}CF_2$ has been shown to give $SF_5CF(CF_3)\underset{O}{\underset{\|}{C}}F$ in the presence of CsF. Reactions of trifluorovinylsulphurpentafluoride with NH_3, MeOH and H_2O were described.[220]

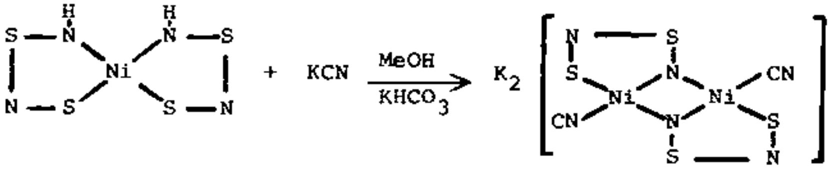
6.2.7 Other Sulphur Containing Compounds

Metal complexes with the chelate ligand S_3N^- have been prepared in alkaline media, starting from S_7NH. The trinuclear complex $[(S_3NNi)_3S_2]^-$ (51) in which the three NiS_3N moieties are bridged by two sulphur atoms was prepared from $NiCl_2$.[221]



(51)

The preparation of $K_2[Ni_2(N_2S_2)_2(CN)_2]$, a dinuclear complex with the $S_2N_2^{2-}$ chelate ligand by the reaction in equation (32), has been described and the crystal structure of the tetraphenylarsonium salt reported.[222]



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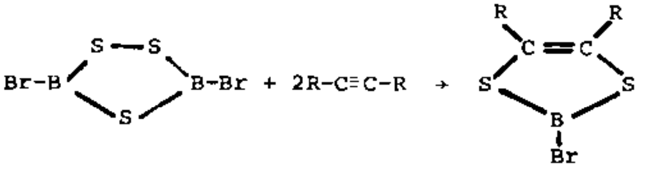
Trimethylsilylthioboranes have been obtained in high yield by the reaction of lithiotrimethylsilanthiolate with halogenoborane derivatives.[223] The reactions of several multiple bond systems with the 1,2,4-trithia-3,5-diborolane ring have been described and the results are summarised in equations (33) to (35).[224]



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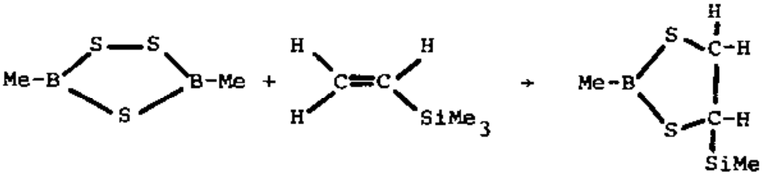

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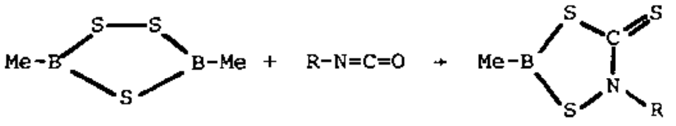
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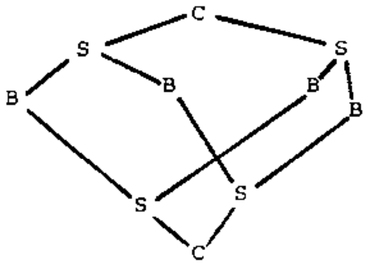
Hydroboration of CS_2 with THF-BH_3 yields the new cage compound $[CH_2(SBH_2)_2]_2$ which has the adamantane skeleton $C_2B_4S_4$ (52). The same compound could also be prepared by the action of methane dithiole on THF.BH_3 or THF.BH_2Cl.[225]


(52)

Calculations of Huckel π-electron densities have shown that the arrangement of atoms in B_8S_{16} are topologically determined, with atoms of different electronegativities being located in just the right positions to give up or accept π-electron density.[226] The emission and electronic structure of two S and Se substituted tetra phenylporphyrins, where S and/or Se replace the central NH groups have been reported.[227]

Several papers dealing with the preparation and structure of metal-sulphur cluster compounds have been published. The compounds described are: $Fe_3W_3S_{14}{}^{4-}$, a novel hexanuclear pure bimetal-sulphur cluster with $Fe_3(\mu_3\text{-}S)_2$ centre;[228] $Mo_4S_4(CN)_{12}{}^{8-}$, a cluster with high negative charge and a cubane-like Mo_4S_4 moiety;[229] Bis(pentamethylcyclopentadienyl)titana(IV)cyclotetrasulphane,[230] $[Fe_2Mo_2(\eta^5\text{-}C_5H_5)_2(\mu_3\text{-}S)_2(\mu_3\text{-}CO)_2(CO)_6]$[231] and $Fe_6S_9(SCH_2C_6H_5)_2{}^{4-}$.[232] The magnetic moments and e.s.r. spectra of some iron-sulphur molybdenum and tungsten cubane-like cluster dimers;[233] a method for the simulation of powder e.s.r. spectra of some $[Fe_4S_4(SR)_4]^{3-}$ clusters,[234] and the use of $Fe_2(\mu\text{-}E_2)(CO)_6$ compounds where E = S, Se and Te, as reagents for the preparation of mixed metal chalcogenide clusters have been described.[235]

The molecular structure of the compound $CH_2(PF_2S)_2$ and $O(PF_2S)_2$

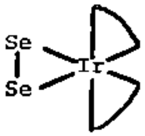
have been determined by electron diffraction. The methane derivative has two isomers gauche-gauche and anti-gauche, present in approximately equal amounts.[236] The pentachalcogenides $(C_5H_5R)_2TiE_2$ (R = H, Me; E = S, Se) have been shown to react with acetylenes $ZC{\equiv}CZ$ ($Z = CO_2Me$, CF_3) to give the alkene dichalcogenide compounds $(C_5H_4R)_2TiE_2C_2Z_2$.[237] The molecular orbital nature of the colinear M-S-M bridged linkages in dinuclear thiometal compounds[238] and the electronic structures of Cu(II) complexes with N_4 and S_4 ligand fields[239] have been described.

6.3 SELENIUM

6.3.1 The Element and Cationic Species.

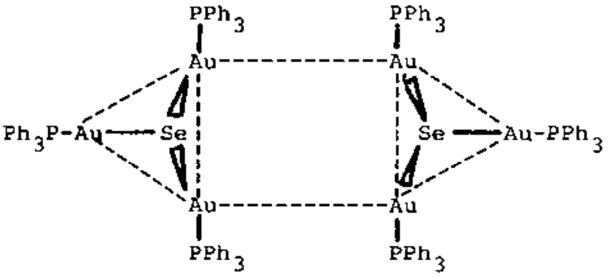
The electronic structure of selenium together with those of graphite and arsenic have been correlated with those of 'isoelectronic' molecules. The structural changes along the series were viewed in terms of simple M.O. theory arguments specifically in the response of the parent structure to the presence of extra electrons.[240] The condensation of a gaseous mixture of 90% Se_2 molecules and 10% Se atoms in an inert gas mixture at 15K followed by annealing to nearly 25K has been shown to give Se_3 molecules. Resonance Raman spectra showed the molecule to be bent.[241]

Se_8 (and S_8) rings are cleaved by coordinativley unsaturated low-valent Rh and Ir complexes to give complexes containing the Se_2 (or S_2) ligand. In the complexes $[M(Y_2)(L\text{-}L)_2]Cl$ ($Y_2 = S_2$ or Se_2, L = dppe or dmpe) the diselenium is side-on bonded to the metal at equatorial positions of a distorted octahedron (53) with a Se-Se distance of 2.313Å which is about the same as in Se_8 and 0.16Å longer than in free Se_2.[242]



(53)

Ph_3PAuPF_6 has been shown to react with $Se(SnMe_3)_2$ to form $[Se(AuPPh_3)_3]^+PF_6^-$. Crystal structure analysis showed two formula units in the asymmetric unit with short Au...Au contacts (300-340 pm)(54). The same paper describes the preparation of $[S(AuPPh_3)_2].CH_2Cl_2$ which had structure (55).[243] The compounds



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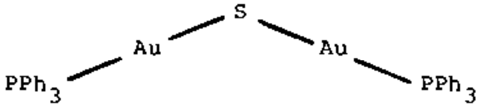
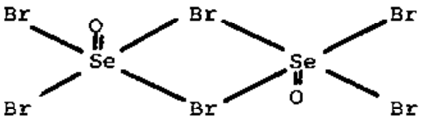


(55)

$(Se_4^{2+})(Sb_2F_4^{2+})(Sb_2F_5^{+})(Sb_2F_6^{-})_5$, $(Te_4^{2+})(SbF_6^{-})_2$ and $(Se_4^{2+})(AlCl_4^{-})_2$ have been prepared by the direct oxidation of Se and Te with SbF_5 in SO_2. All three compounds show the chalcogen cations to be approximately square-planar with average Se-Se and Te-Te distances of 2.260, 2.622 and 2.286Å respectively.[244]

6.3.2 Bonds to Halogens

Mean amplitudes of vibration and thermodynamic functions for $SeOF_4$ have been calculated over a wide temperature range from recent spectroscopic data.[245] The molecular structures of $WSeCl_4$ and $WSCl_4$ have been studied by gas-phase electron diffraction.[246] The novel oxotribromoselenate(IV) anion, $SeOBr_3^-$ has been prepared from the reaction of stoichiometric quantities of $SeOBr_2$ and bromide in acetonitrile solution. The analogous $SeOCl_3^-$ was also prepared as the tetraphenylphosphonium salt from reaction of $SeCl_4$ in the presence of a small quantity of H_2O with PPh_4Cl in acetonitrile. X-ray structure determination showed the dimeric centrosymmetric $Se_2O_2Cl_6^{2-}$ and $Se_2O_2Br_6^{2-}$ anions (56) to be present in the solid. The axial oxygen ligands, Se-O 1.597 in



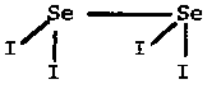
(56)

the chloride and 1.584Å in the bromide, cause a pronounced stereochemical trans-activation of the inert pairs on the selenium atoms.[247]

The reaction of selenium with $I_2Sb_2F_{11}$ in equation (36) has been shown to produce $Se_2I_2(Sb_2F_{11})_2$. The molecule was shown to

$$2I_2Sb_2F_{11} \quad + \quad 2Se \xrightarrow[R.T.]{SO_2} Se_2I_4(Sb_2F_{11})_2 \qquad \ldots(36)$$

contain the $Se_2I_4^{2+}$ cation (57) which has an eclipsed $S_2O_4^{2-}$ type of structure with two SeI_2^{+} units joined by a weak Se-Se bond (2.84Å) and very weak I-I interaction (3.756 and 3.661Å).[248]



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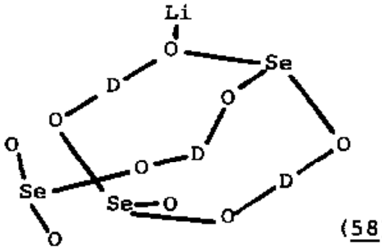
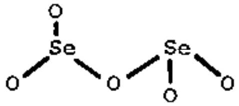
6.3.3 Bonds to Oxygen

The SeO_3-H_2SeO_4 system has been studied cryoscopically. A maximum freezing point of 18.84°C indicated the existence of diselenic acid, $H_2Se_2O_7$. Self dissociation in diselenic acid is discussed and the presence of triselenic acid predicted.[249] Double oxides of Se and Te of composition Te_3SeO_8, $Te_2Se_2O_9$ and $TeSeO_4$ have been prepared from solid state reactions between the corresponding elements and their oxides.[250] The compound $Au(SeO_3)Cl$ has been prepared from $Au_2Se_4O_{11}$, selenic acid and perchloric acid. Crystal structure determinations showed the oxygen atoms to bridge the Au and Se atoms leading to a polymeric structure.[251] Crystals of $LiD_3(SeO_3)_2$ have been prepared by the slow evaporation at room temperature of a solution of Li_2CO_3 and SeO_2 in D_2O. The molecular structure shown in (58) is built up of Li^+ and $DSeO_3^-$ ions and of D_2SeO_3 molecules.[252]



(58)

The compounds ND_4DSeO_4 and $RbDSeO_4$ have been shown to be isomorphous with SeO_4 tetrahedra connected by O-D....O bonds to form infinite chains.[254] $CaSe_2O_5$ has been synthesised by reaction of SeO_2 and CuO at 623K in a sealed tube. Structural studies show zig-zag strings of CaO_6 prisms sharing edges linked by $(Se_2O)^{6+}$ groups. The Se atoms posses 3-fold coordination with two SeO_3 groups sharing an oxygen atom to form $Se_2O_5{}^{2-}$ ions (59).[255]

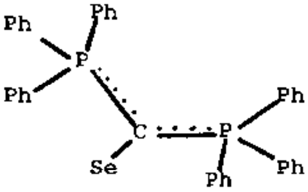


(59)

The $CuO-SeO_2-H_2O$ and $Ag_2O-SeO_2-H_2O$ systems have been studied at 100°C.[256]

6.3.4 Bonds to Carbon

The addition of selenium to the ylide $Ph_3P{:}C{:}PPh_3$ has been shown to proceed quantitatively even at -15°C to give the red crystalline product (60). The C-Se bond length (199 pm) signifies loose bonding of the selenium yet the ylide carbon atom has a planar configuration.[257] The crystal structure of polymeric $Hg(SeMe)_2$, and the tetrameric pyridinates $[HgCl(py)(SeEt)]_4$ and $[HgCl(py)_{0.5}(SeBu^t]_4$ have been determined.[258] The preparation and characterisation of pure trimeric, tetrameric and pentameric selenoformaldehyde have been described. Their separation from polymethylene selenide and oily byproducts was possible by recrystallisation, sublimation and a complexation decomposition treatment with $AgNO_3$. Using this technique S-pentaselenecane was isolated for the first time.[259] A ^{13}C n.m.r. study has established a correlation between the isotope shifts and the C-Se

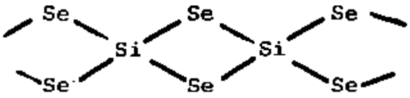


(60)

bond distance for CF_3 and CH_3 substituted selenium compounds. The isotope shift of the linear molecules SeCO, SeCS, SeCSe was inversely dependent on the force constant of the C=Se bond,[260] α-triseleno acetic aldehyde has been isolated for the first time by using a sophisticated method for the preparation of triseleno acetic aldehyde.[261] The preparation of perfluorinated hexakis-(alkylthio and -seleno)ethanes has been described.[262]

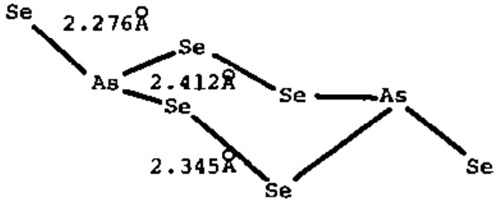
6.3.5 Selenides

A reinvestigation of the structures of SiS_2 and $SiSe_2$ has confirmed the known structure types but significant changes in cell dimension and atomic coordination were made. The structure is composed of edge sharing $SiSe_4$ tetrahedron (61) of bond length 2.275 (2.133 for Si-S). The Se-Si-Se angles are 100.1 and S-Si-S are 98.8°.[263]



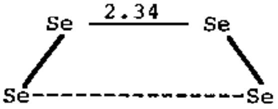
(61)

The crystal structures of SiH_3-S-SiH_3 and SiH_3-Se-SiH_3 have been determined at 120K and 125K respectively.[264] The compound $(2,22\text{-crypt Na}^+)_2As_2Se_6^{2-}$ has been prepared from the alloy $NaAs_2Se_3$. Crystal structure determination shows the hitherto unknown $As_2Se_6^{2-}$ polyanion (62) to consist of a six-membered ring in chair conformation, (As_2Se_4) bonded through the trans arsenic atoms to two exocyclic Se atoms in equatorial positions.[265]



(62)

Barium and selenium powder have been shown to react in dry ethylenediamine in the presence of (2,22-crypt) to give (Ba-4en)-Se_4.en. The structure was shown to contain Se_4^{2-} anions in the chain form (63).[266]



(63)

Solution of $Ba_4Sb_4Se_{11}$ in ethylenediamine gives $Ba(en)_4(SbSe_2)_2$ in which the characteristic elements of the structure are $[SbSe_2^-]_n$ chains which are formed by distorted trigonal $SbSe_3$ pyramids connected by common corners.[267]

Crystal structure data have also been given for the following compounds: $LaSe_2$;[268] $EuDy_2Se_4$;[269] Ta_2ISe_8;[270] $Dy_4U_5Se_{16}$;[271,272] $LaSe_{14}$;[273] $Ln_4U_5Se_{16}$;[274] $Yb_{2.0}U_{0.87}Se_4$;[275] $Ln_{0.5}U_{0.5}Se_2$;[276,277] $V_{1+x}Se_2$.[278]

The magnetic and thermoelectric properties of the nickel arsenide type $Fe_{1-x}Se$ where $x = 0.11$ have been studied.[279] Phase relationships have been studied for the following systems Ge-Se;[280] Ge-Se-$GeSe_2$-Sb_2Se_3;[281] Lu_2Se_3-PhSe;[282] $GeSe_2$-Sm_2Se_3;[283] Eu_2Se_3-$GeSe_2$;[284] ZnSe-SnSe and CdSe-SnSe[285] and ZnS-ZnSe.[286]

6.3.6 Other Compounds Containing Selenium

The reaction of di-π-cyclopentadienyltitaniumpentasulphide with dichlorodiseleno has been shown to give cyclotriseleniumpentasulphide (1,2,3-Se_3S_5). A crystal structure analysis showed the presence of an eight-membered crown shaped ring molecule with sulphur and selenium atoms statistically distributed over the atomic position.[287]

6.4 TELLURIUM

6.4.1 Cationic Species

High resolution ^{13}C n.m.r. spectra have been obtained for several tellurium complexes, $Te(S_2CNEt_2)_n$ n = 2 or 4, $Te(S_2COEt)_2$ and $AsPh_4[Te(S_2COEt)_3]$. The spectra display effects that are intermolecular in origin.[288] The extended Huckel M.O. approach and the Jahn-Teller Theorem have been applied to the structure of Te_4^{2+}, Te_6^{4+} and Te_6^{2+} and many other polyatomic cations and anions of the Main Group Elements. The stability and diamagnetism of the species have been accounted for in terms of a closed shell molecular orbital configuration for each of the observed geometries.

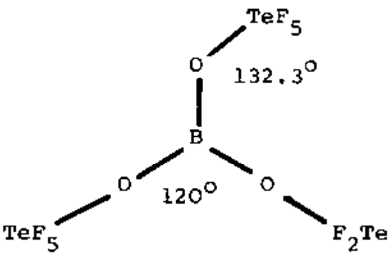
In almost every case, alternative geometries were found to be less stable.[289]

6.4.2 Bonds to Halogens

The compound Ph_3TeF has been shown to be ionic with no evidence for a covalent form in solvents of low polarity. Significant covalency has, however, been found for $Ph_2(Me)Te(OOCR)$.[290] Chlorination of pentafluoroorthotelluric acid with either chlorine fluorosulphate or chlorine monofluoride, equation (37), has been shown to give pentafluorotellurium hypochlorite in high yield.[291]

$$TeF_5OH + ClX \rightarrow TeF_5OCl + HX \qquad ...(37)$$

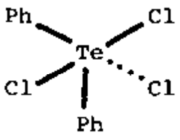
Hydrolysis of imidazolium pentafluorotellurate has been shown to give diimidazolium cis-tetrafluoroorthotellurate, whilst solvolysis of orthotelluric acid in HF/pyridine yields trans monopyridinium-trans-tetrafluoroorthotellurate. From the salts, the free acids cis- and trans-$(HO)_2TeF_4$ could be liberated with concentrated H_2SO_4. The trans form is the more stable and acidity constants could be determined in aqueous solution.[292] From an examination by n.m.r. and Mössbauer techniques of a series of $OTeF_5$ complexes of Te, I and Xe it was possible to assess the relative electronegativities of F and $OTeF_5$. In all cases examined, fluorine was found to be more electronegative than $OTeF_5$ with the latter having an estimated value of 3.87 on the Pauling Scale.[293] A review of the chemistry of compounds containing the ligands $OTeF_5$, $OSeF_5$ and OSF_5 has been published in which attention is drawn to the ability of these ligands for the stabilisation of unusual oxidation and coordination states.[294] A series of transition metal derivatives containing the $OTeF_5$ ligand have been prepared for the metals W, Mo, Os and Re, and others. Complete structures were determined for $O{=}Mo(OTeF5)_4$ and $O{=}Os(OTeF_5)_6$ and it was shown that in both species the central atoms have a square pyramidal coordination with the oxygen occupying the apical position. In the Os compound, a fluoride ion is observed close to the sixth coordination site, the F^- ion originates from cocrystallised TeF_4.[295] A structure determination has shown the compound $B(OTeF_3)_3$ (64) to possess the molecular symmetry D_{3h} in which the environment of the B and Te atoms is strictly square planar and approximately octahedral respectively. Bond lengths of B-O 1.358, Te-O 1.874 and Te-F



(64)

1.816Å were found.[296]

The reaction of $TeCl_4$ and $(CF_3)_2Hg$ at high temperature in an inert gas atmosphere leads to the formation in good yield of $(CF_3)_2Te$ together with CF_3TeCF_2Cl and $(CF_2Cl)_2Te$.[297] The compounds were isolated by low temperature distillation. Oxidation of $(CF_3)_2Te$ with Cl_2, Br_2, O_2 and ClONO leads to the formation of the new trifluoromethyl compounds $(CF_3)_2TeCl_2$, $(CF_3)_2TeBr_2$, $(CF_3)_2TeO$ and $(CF_3)_2TeONO$. By variation of reaction conditions it was also possible to prepare CF_3TeCl_3 and CF_3TeBr_3.[298] The halogen exchange reaction of $(CF_3)_2TeX_2$ where X = F, Cl, Br have also been described.[299] The crystal and molecular structures of $(Ph)_2TeCl_2$ (65) and $PhTeCl_3$ (66) have been determined. In (65) the primary coordination about Te is based on a trigonal bipyramid with a vacant equatorial position. There is also a secondary interaction with Te...Cl = 3.677Å giving a distorted octahedral arrangement about Te with the sixth position vacant.



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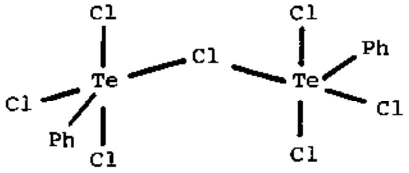
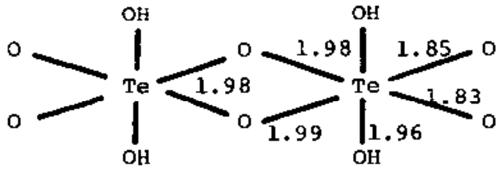


(66)

In (66) the structure shows square pyramidal geometry for its two independent Te atoms which are bridged by chlorine atoms to give a chain structure. It is thought that the secondary Te...Cl interactions are of little significance in this compound.[300] An independent study of the crystal structure of $TePhCl_3$ gives virtually identical results to that described above.[301] Structural studies have shown the compound $[NH(Me_3)][TeCl_6]$ to contain octahedral $TeCl_6^{2-}$ units with Te-Cl = 2.546 and each octahedral unit to be bonded to two $NHMe_3$ groups via weak trifurcated hydrogen bonds.[302] The crystal structure of CuTeBr has been determined.[303]

6.4.3 Bonds to Oxygen

Guanidinium tellurate (67), obtained from aqueous solution at room temperature, contains two independent anions comprised of octahedral $FeO_4(OH)_2$ units sharing an edge. The $C(NH_2)_3$ units are connected over an irregular network of bridging hydrogen atoms and terminal oxygen atoms of the anions.[304]

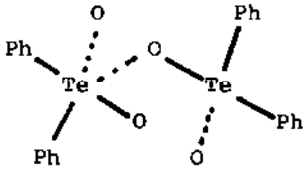


(67)

The addition of 1 wt% of TeO_2 to Co molybdates leads to Co-Mo-Te-O catalysts which are highly selective for vapour phase allylic oxidation of propene. The Te(IV) ion acts as an inhibitor for the reduction of Co(III) to Co(II) and is essential for the selectivity of the catalysts.[305] The reduction of Te(III) by potassium tetrahydroborate in aqueous media has been shown to take place in the following stages in acid solutions with pH<2.

$$Te(VI) \rightarrow Te(IV) \rightarrow Te \rightarrow Te^{2-}$$

In alkaline and borate buffer solution with pH 8-11, the final product is elemental tellurium.[306] The compound $Te(OH)_6Tl_2SO_4$ has a structure containing pure sheets of $Te(OH)_6$ octahedra and pure sheets of SO_4^{2-} tetrahedra intercalated between TeO_6 sheets and mixed sheets of both $Te(OH)_6$ and SO_4^{2-}.[307] The structure of $NaKTeO_3.3H_2O$, is built up from discrete TeO_3^{2-} groups, Na^+ and K^+ ions and water molecules linked by both electrostatic interactions and hydrogen bonds.[308] $Te_2O_3.HPO_4$ has tellurium atoms in a trigonal bipyramidal geometry with Te-O bond lengths from 1.903 to 2.183Å and with several secondary interactions from 2.730 to 3.262Å, the shortest of which completes the distorted square based pyramidal geometry at one of the tellurium atoms.[309] The molecular structure of Ph_2TeO has been shown to consist of $Ph_2Te=O$ monomers with the average bond lengths: Te-C 2.137 and Te=O 1.890Å. The monomers are linked by short Te-O secondary bonds of average length 2.554Å, to give unsymmetrical dimers. Much longer interactions of 3.771Å occupy the fifth position of octahedra (68) around each Te atom.[310]

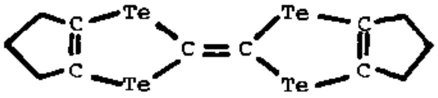


(68)

Secondary interactions are also a feature of the molecular structures of $Ph_2Te(NO_3)_2O$-$Ph_2Te(NO_3)(OH)$ (69), $[PhTeO(NO_3)]_n$ (70) and $Ph_2Te(NO_3)_2$ (71). (71) is essentially monomeric, (70) is polymeric and in (69) the component molecules are linked by bridging nitrate groups.[311] Crystal structures have also been determined for the compounds $Te(OH)_6Rb_3P_3O_9H_2O$;[312] Cd_3TeO_6 and Ca_3TeO_6.[313] Infrared spectra of the compounds $Te_2O_4.$-HNO_3,[314] and phases of the type $A(III)_{0.5}B(V)_{0.5}Te_3O_8$ where A = Fe, In, Sc; and B = Nb, Ta and UTe_3O_9[315] have been reported. The reaction of CeO_2 and ThO_2 with TeO_2 in air at 600°C gives rise to compounds of the type MTe_2O_6 with a new type of fluorite superstructure.[316]

6.3.4 Bonds to Carbon

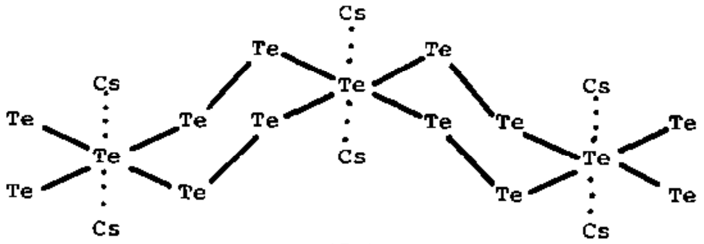
^{13}C n.m.r. data have been reported for a number of phenyl and p-methoxyphenyl tellurium compounds.[317] ^{125}Te n.m.r. spectra of a series of organo tellurium compounds and inorganic tellurium salts have been measured.[318] The reaction between cyclopentane-1,2-ditellurate and tetrachloroethylene has been shown to give (72) and not its six membered ring isomer. The compound is almost identical to its selenium analogue in intramolecular dimensions but not in its mode of packing; giving rise to the shortest (3.583Å) intermolecular Te-Te contact yet observed.[319]



(72)

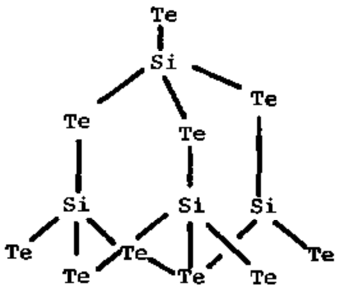
6.3.5 Tellurides

The reaction of stoichiometric quantities of Cs and Te in supercritical ammonia has been shown to lead to the formation of microcrystalline Cs_2Te_5. The Te atoms form six membered rings with chair conformation, which are connected via common vertices to form one dimensional chains (73). This is the first example of a polychalcogenide with this type of structure.[320]



(73)

The compound $K_4Si_4Te_{10}$ is the first tellurosilicate with adamantane-like $Si_4Te_{10}^{4-}$ anions (74).[321]



(74)

Single crystals of $CrTe_3$ have been grown by annealing a stoichiometric mixture of the elements at 690K for 4 months in the presence of $AlCl_3$ and HCl. The compound exhibits a layered structure with layers comprised of four edge-linked $CrTe_6$ octahedra which are connected via shared apical Te atoms to give a two dimensional infinite arrangement. Te-Te bonds link the building groups to give rise to Te_2 and Te_3 moieties.[322] Reaction of the elements under high pressure and temperature has been shown to give $AgTe_3$. The structure of $AgTe_3$ is described as an inner centred pseudocubic arrangement of the rhombohedral unit cell, with Ag atoms occupying the centre and corners and Te atoms the face and edge centres of the cube. It is best visualised as an ordered (1:3; Ag:Te) analogue of the α-polonium structure.[323] The following phase systems have been studied, Hg-Cd-Te,[324] Ag_2Te_3-AsI_3,[325] Sb_2Te_3-YSb_2 and Sb_2Te_3-YSb,[326] La_2Te_3-Sb_2Te_3,[327] Ge-Te-Te,[328] AgTe-Te[329] and MnTe-Sb_2Te_3.[330]

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