

Chapter 6

ELEMENTS OF GROUP 6

M.G.Barker

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6.1 OXYGEN

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

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

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

Interest in the reactions of coordination compounds with oxygen continues, particularly with respect to complexes of manganese with the composition MnLX_2 where L = tertiary phosphine and X is an anion. The complexes $\text{MnBr}_2\text{PMe}_3$, $\text{MnBr}_2\text{PEt}_3$ and $\text{MnBr}_2\text{PPhMe}_2$ (prepared under anhydrous conditions with the elimination of all free phosphine) when exposed to dioxygenation/evacuation cycles in a specially designed infrared cell have been shown to interact with O_2 . However, the extent of the reversibility of the interaction with dioxygen is markedly dependent upon the nature of the tertiary phosphine ligand employed. All of the solid state

complexes also showed an irreversible decay in the presence of oxygen to a phosphine oxide complex at ambient temperature.⁵ The complex $(C_6H_5CH_2)_2Mn.C_4H_8O_2$ has been shown to react with oxygen to form an unstable deep violet compound which changes to a stable insoluble yellow peroxide with the formula $C_6H_5CH_2MnO-OMnCH_2C_6H_5$. With excess oxygen a polynuclear complex of Mn(III) is formed with the composition $Mn_4O_4(OH)_4(OCHC_6H_5)_2$.⁶

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

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

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



The primary step appears to be a nucleophilic addition of $\text{O}_2^{\cdot-}$ to CO_2 to form the anion radical $\text{CO}_4^{\cdot-}$. The apparent configuration of the $\text{C}_2\text{O}_6^{2-}$ group is $\text{OC}(\text{O})\text{OC}(\text{O})\text{OO}^{2-}$ on the basis of the vibrational spectroscopy and the hydrolysis products of the isolated reaction product $(\text{Me}_4\text{N})_2\text{C}_2\text{O}_6$.¹¹ Rate constants for the reaction of superoxide and dithionite ions with a number of oxidants have been reported.¹² The kinetics and mechanism of the reactions of aqueous superoxide ion and several $\text{Co}(\text{III})$ amine complexes and ferrocenium ion have been studied. The initial and rate-limiting step (and the only step for the ferrocenium ion reaction) is outer-sphere electron transfer from the superoxide ion to the metal complex. Dioxygen has a marked effect upon the $\text{Co}(\text{III})$ reactions, resulting in second order rate constants that are greater by a factor of 2 under anaerobic conditions than under aerobic. This effect was explained by the competing reactions of the $\text{Co}(\text{II})$ amine complexes produced in the electron transfer step with O_2 or $\text{O}_2^{\cdot-}$.¹³

Use of a Fourier transform ion cyclotron resonance spectrometer has enabled the generation of the long-lived $\text{H}_2\text{O}^{\cdot-}$ ion from the reaction of $\text{O}^{\cdot-}$ with any of the aliphatic amines, methylamine, ethylamine or dimethylamine to be observed. The generation of $\text{HDO}^{\cdot-}$ by the reaction of $\text{O}^{\cdot-}$ with CD_3NH_2 showed that one of the hydrogen atoms in $\text{H}_2\text{O}^{\cdot-}$ originate from the methyl group and the other from the amino group and that both types of hydrogen atoms in the substrate are essential for the formation of $\text{H}_2\text{O}^{\cdot-}$. Reaction of $\text{H}_2\text{O}^{\cdot-}$ with formaldehyde gave only OH^- as an observed reaction product and this reaction (equation 2) suggests that



the $\text{H}_2\text{O}^{\cdot-}$ ion can best be described as a hydroxide ion to which a hydrogen atom is attached.¹⁴

A study of the infrared spectra of Nafion membranes in twenty different cationic forms has been carried out in order to characterise the water-anion-cation interactions at low water contents. Nafion consists of a perfluorinated polyethylene backbone with pendant ether linked side chains terminating with a sulphonate group, $-\text{O}-\text{CF}_2-\text{CF}_2-\text{SO}_3-\text{M}^+$. Spectra in the OH stretching and H-O-H bending regions showed the distinction between hydrogen bonded and non-hydrogen bonded water molecules

and yielded information on the mode of attachment of water molecules to the anion-cation pairs. When there is a good match between the Lewis acid strength of the cation and the Lewis base strength of the anion, the ion pairs are relatively stable and water molecules tend to attach on the outside where the respective acid and base strengths are mismatched, as is the case for small cations of high charge or for large cations of low charge; water molecules tend to be inserted between the ion pairs even at the lowest water contents.¹⁵

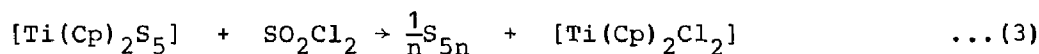
The trinuclear cluster ion $[M_3O_2(pr)_6(H_2O)_3]^{2+}$ where $M = Mo$ or W and $pr = O_2CC_2H_5$ has been shown to undergo extensive hydrolysis in aqueous solution to produce oxo species. Dimerisation and polymerisation of these clusters proceeds via formation of the hydrogen oxide bridging ligand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

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

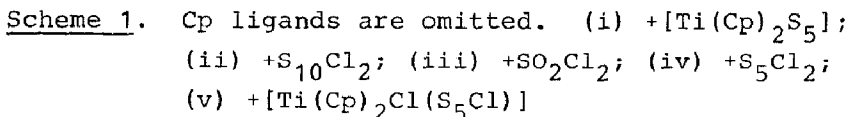
6.2 SULPHUR

6.2.1 The Element

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



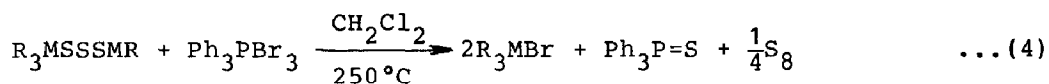
High pressure liquid chromatographic analysis of the reaction products showed the presence of S_{10} , S_{15} , S_{20} and S_{25} in order of decreasing concentration. The preferred formation of sulphur rings S_{5n} with $n = 2$ to 6 in the reaction can be understood by the series of reactions shown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



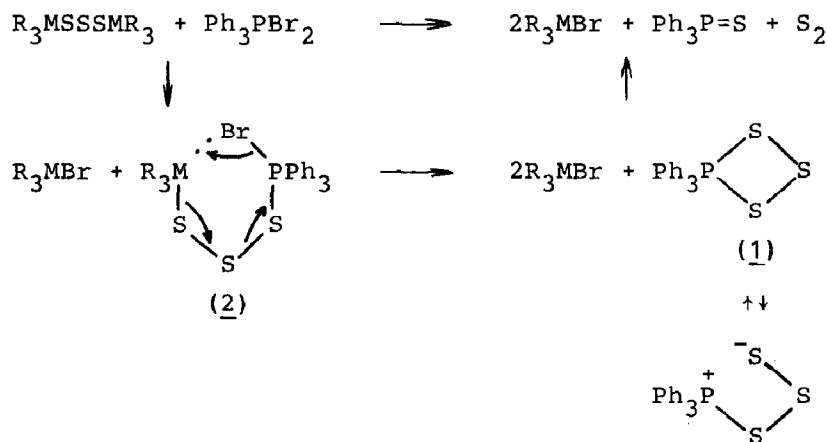
sulphur) has been investigated both theoretically and experimentally by DSC and HPLC in the temperature range 30-250°C. The polymerisation of S_8 was endothermic and endentropic, that of S_7 exothermic and endentropic and S_6 exothermic and exentropic. Thus a floor temperature exists for the polymerisation of S_8 and a hypothetical very high ceiling temperature for S_6 whilst S_7 is unstable with respect to polymerisation over the whole temperature range. With the exception of S_8 , all the allotropes

investigated, yielded polymeric sulphur on heating to 60-150°C followed by depolymerisation to the equilibrium sulphur melt consisting mainly of S_8 , some S_7 and traces of S_6 , S_9 , S_{12} and other rings. Polymeric sulphur slowly dissolves in CS_2 at 20°C to give S_8 , S_7 and traces of other rings such as S_6 , S_9 and S_{12} . On heating sealed ampoules of the S_4/CS_2 mixture to 80-100°C complete dissolution took place within several hours with the formation of S_8 and S_7 as the main products.²⁰

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



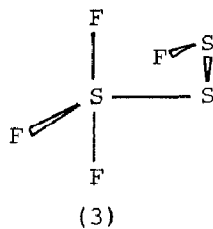
When the reaction was carried out in the presence of a conjugated diene, the formation of elemental sulphur was efficiently suppressed with the concomitant formation of the corresponding Diels-Alder adduct (eg. using Y led to Y^{S}). It was assumed that phosphine sulphide (1) or its probable precursor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



Scheme 2

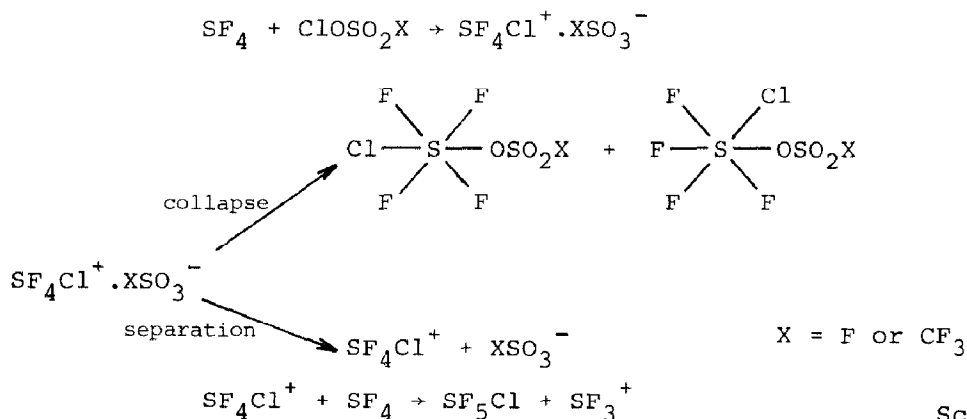
6.2.2 Bonds to Halogens

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



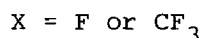
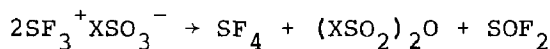
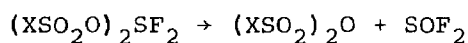
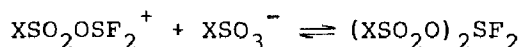
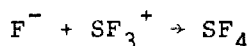
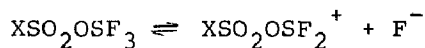
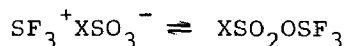
The unstable compound is a colourless, viscous liquid with an extrapolated boiling point of 94°C and a melting point of -62°C . It decomposes to SF_4 and SSF_2 in the gas phase.²² The crystal structure determination of a disordered solid phase of SF_4 has shown it to have face centred cubic space group with $a = 676\text{pm}$ and $z = 4$. During part of this study an unintentional hydrolysis in a glass capillary of the SF_4 took place to give SiF_4 and SOF_2 . The products could however be separated and grown as crystals in the glass capillary tube and structural analysis carried out. SOF_2 was found to crystallise in the monoclinic space group $\text{P}2_1/\text{c}$ and to have isolated molecules of pyramidal geometry arranged in strongly folded layers with intermolecular $\text{S}\cdots\text{O}$ contacts.²³

The reaction of ClOSO_2F , BrOSO_2F and $\text{ClOSO}_2\text{CF}_3$ with SF_4 have been studied. It was found that the reactions proceed to form either trifluorosulphonium salts or covalent adducts. In the cases where the hypochlorites were used the unusual cation SF_4Cl^+ can be postulated as a reactive intermediate (Scheme 3).



Scheme 3

Characterisations of the new compounds $\text{SF}_3^+\text{FSO}_3^-$, $\text{SF}_3^+\text{CF}_3\text{SO}_3^-$, cis- and trans- $\text{SF}_4(\text{Cl})\text{OSO}_2\text{F}$ and trans- $\text{SF}_4(\text{Cl})\text{OSO}_2\text{CF}_3$ were reported. The SF_3^+ salts are thermally unstable decomposing to SF_4 , SOF_2 and $(\text{XSO}_2)_2\text{O}$ ($\text{X} = \text{F}$ or CF_3) by the routes postulated in Scheme 4.²⁴

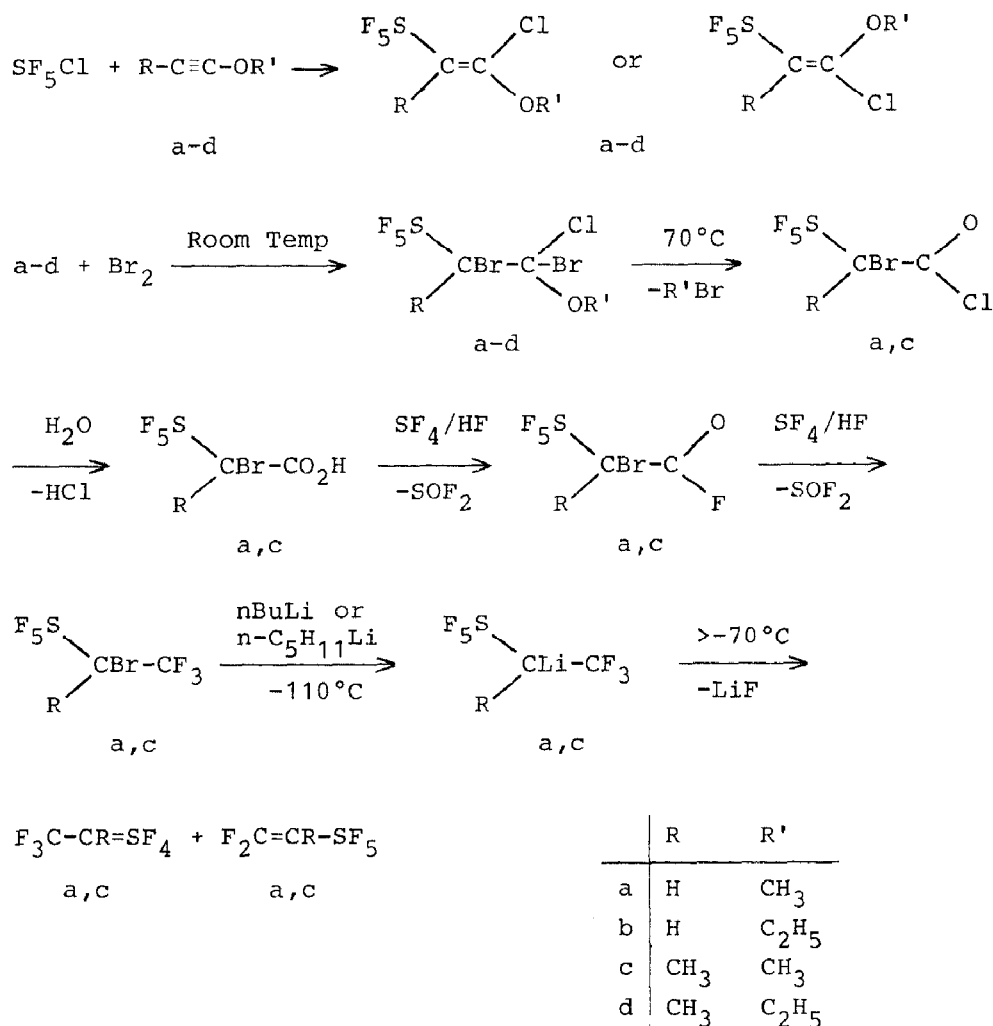


Scheme 4

The interaction of UF_5 with SF_4 , SF_4O and some Lewis-acid pentafluorides of various strengths has been studied. In anhydrous HF solutions, SF_4 was shown to yield an adduct of composition $3\text{UF}_5 \cdot \text{SF}_4$ in which both ionic and fluorine bridged species are present. The pentafluorides of As, Ta and Nb combine with UF_5 to give adducts of composition $1.5\text{UF}_5 \cdot \text{AsF}_5$, $\text{UF}_5 \cdot 2\text{TaF}_5$ and $\text{UF}_5 \cdot 2\text{NbF}_5$ respectively.²⁵

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

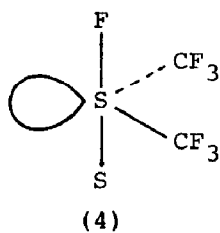
The new alkylidenesulphur tetrafluorides $\text{CF}_3\text{CH}=\text{SF}_4$ and $\text{CF}_3\text{C}(\text{CH}_3)=\text{SF}_4$ have been prepared. The former is prepared from $\text{HC}\equiv\text{C-OR}$ and SF_5Cl in a multistep preparation shown in Scheme 5. $\text{CF}_3\text{C}(\text{CH}_3)\text{SF}_4$ and $\text{F}_2\text{C}=\text{C}(\text{CH}_3)-\text{SF}_5$ are also formed in several steps from $\text{CH}_3\text{C}\equiv\text{C-OR}$ and SF_5Cl . The compounds are especially stable and have structures analogous to those of $\text{H}_2\text{C}=\text{SF}_4$ and $\text{CH}_3\text{CH}=\text{SF}_4$.²⁷



Scheme 5

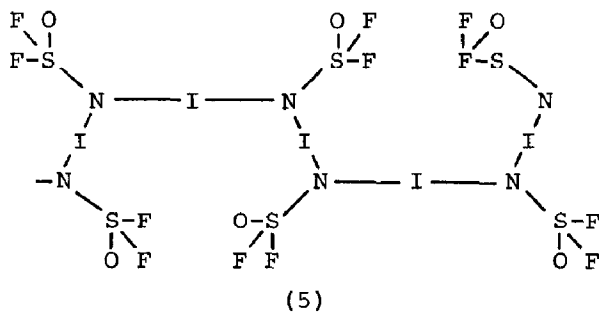
The compounds $\text{CF}_3\text{-CFCl-SF}_3$, $(\text{CF}_3\text{-CFCl})_2\text{SF}_2$ and $\text{CF}_3\text{-CFCl-SOF}$ have been prepared and the ^{19}F n.m.r. spectra fully analysed. In $\text{CF}_3\text{-CFCl-SF}_3$ the chiral carbon atom leads to a splitting of the axial fluorine atoms on sulphur. $(\text{CF}_3\text{-CFCl})_2\text{SF}_2$ exists in a dl form with equivalent (sulphur)-F atoms whilst $\text{CF}_3\text{-CFCl-SPF}$ exists in two diastereoisomeric forms.²⁸

The geometric structure of $(\text{CF}_3)_2\text{S(O)F}_2$ (4) has been studied by gas electron diffraction. Its structure obeys the VSEPR model in that the most electronegative substituents occupy the axial positions in the trigonal bipyramidal molecule. The following geometrical parameters were determined $\text{C-F} = 1.314$, $\text{S=O} = 1.422$, $\text{S-F} = 1.641$, $\text{S-C} = 1.891\text{\AA}$ and the angles $\text{CSC} = 97.8$, $\text{FSF} = 173.1$



FCF = 109.4° . Comparison was made with the structures of SF_4 , OSF_4 and $(\text{CF}_3)_2\text{SF}_2$ and an attempt made to explain the variations in the bond angles in terms of non-bonded fluorine-fluorine interactions.²⁹

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



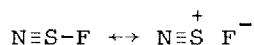
The new compound SFCl has been obtained by u.v. photolysis of FC(O)SCl in rare gas matrix and by u.v. photolysis of $\text{Cl}_2/\text{SF}_3\text{SF}$ in the gas phase. The molecular identity of the compound was confirmed by isotope substitution experiments and force constants were determined.³¹

New thermal analysis and powder diffraction data in the binary system sulphur-chlorine have been used to construct a new phase diagram for the region 50-100 atom % Cl. Sulphur chlorides with elemental ratios of 1:1, 1:2, 1:3 and 1:4 were observed with the mp's -80 , -125 , -75 and -34°C , respectively. The 1:1 compound was confirmed as S_2Cl_2 by comparison with the crystal structural data published in 1983, whilst new data was obtained for SCL_2 by growing a single crystal by zone melting in a capillary tube, which showed the crystal structure to be comprised of angular SCL_2 molecules (S-Cl bond length between 200.58 and 201.83pm) arranged

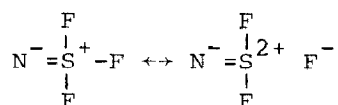
in bimolecular layers. SCl_3 is a new compound in the system and has an unknown structure, and SCl_4 is probably isotypic with $\alpha\text{-SeCl}_4$ according to powder diffraction data.³²

6.2.3 Bonds to Nitrogen

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



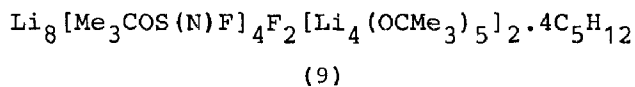
(6)



(7)

Electronic structure calculations (SCF and CEPA) have been reported for SN^+ , NSF, NSF_3 , $[\text{HNSF}]^+$, $[\text{HNSF}_3]^+$ and $[\text{CH}_3\text{NSF}]^+$. The equilibrium distance obtained for SN^+ ($1.44 \pm 0.01 \text{ \AA}$) is expected to be definitive. A marked stabilisation of SN and SF bonds arises if electrons are removed from the thiazyl group eg.

in going from NSF to NSF₃ or by complexing NSF or NSF₃ with electron acceptors. This effect appears to be correlated with the increased positive net charge on sulphur with bonding to the acceptors being most likely at the nitrogen with NSF₃ being a better donor than NSF.³⁵ Nucleophilic substitution at thiazyl fluoride has been proposed as a means of giving access to thiazyl derivatives R-S≡N but members of this class of compounds are only rarely stable since complex secondary reactions frequently take place. The addition of LiOCMe₃ to NSF is expected to be the initial step in a substitution of this type but the reaction product (8) may be converted into the more stable mixed salt (9). In the formation of (9) three moieties of (8) combine with four additional Li⁺ ions to give two Li₄(N/F)₄ eight membered rings linked by four Me₃CO-S bridges.³⁶

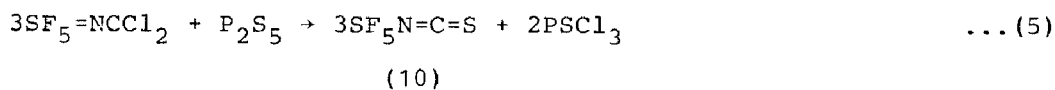


The (E,Z) and (E,E) forms of dimethylsulphurdiimine have been fully optimized by ab initio STO-3G* calculations. The (E,Z) form was predicted to be more stable than the (E,E) form by about 41 kJ/mole, in agreement with experimental data.³⁷

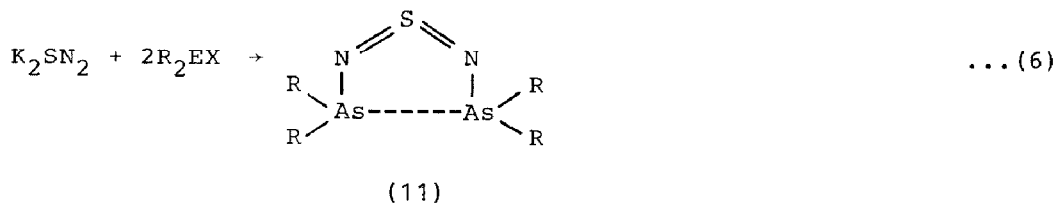
(Fluoroimido)tetrafluorosulphur has been shown to undergo a number of reactions with strong electrophiles, involving addition to the sulphur-nitrogen double bond and to react readily with fluoride ion to give the reactive nucleophile SF₅NF⁻. Chlorine(I)-, and bromine(I)fluorosulphate and peroxydisulphuryl-difluoride add to F₄S=NF to form the respective cis adducts. The ion SF₅NF⁻, generated in situ from F₄S=NF and KF, reacts readily with Br₂ forming SF₅NBrF and with acyl fluorides to give RCONFSF₅; it also reacts with F₂C=NF to form (SF₅NF)FC=NF which is isomerised to the unusual azo compound F₅SN=NCF₃ in the presence of COF. Self reaction of F₄S=NF in the presence of KF does not produce the expected dimer (SF₅NF)F₃S=NF; instead, extensive decomposition takes place and a low yield of the unusual amine

$(\text{SF}_5)_2\text{NF}$ is obtained.³⁸

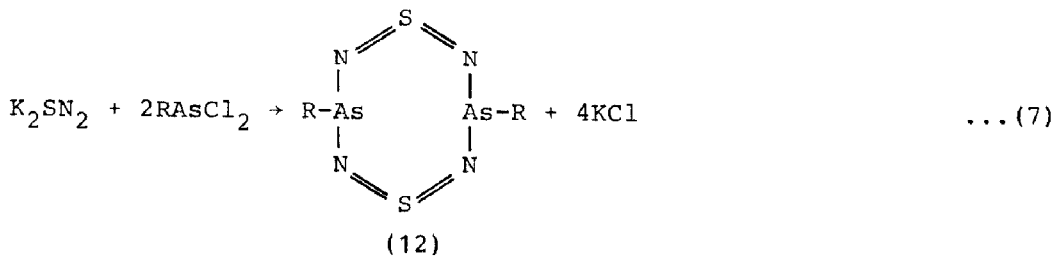
The preparations of pentafluorosulphanylisocyanate and isothiocyanate have been described and the reactions of the former with alcohols, thiols, amines, aldehydes, formamides and sulphoxides and compounds containing reactive CH groups studied. Several new synthetic routes to the isothiocyanate were described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



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



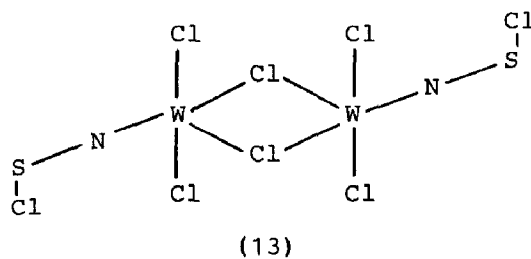
The arsino derivative is the most stable member of the series of tert-butyl compounds with the bismuth derivative decomposing under ambient conditions. Methyl, cyclohexyl and phenyl derivatives were also prepared with $\text{E} = \text{As}$.⁴⁰ Reaction of K_2SN_2 with organo arsenic chlorides (RASCl_2) leads to sulphur diimides containing organoarsino substituents at both ends (12).



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

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

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



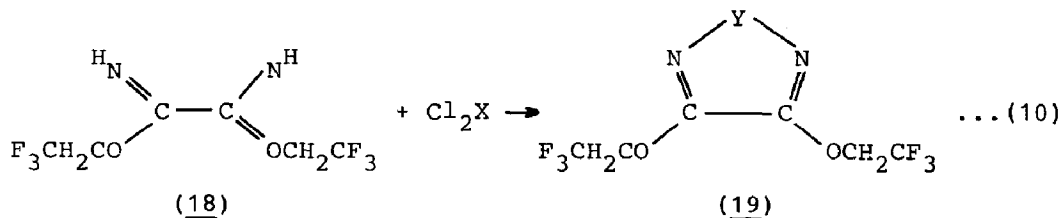
The NSCl groups are in a trans position to the longer of the terminal W-Cl bonds.⁴³

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

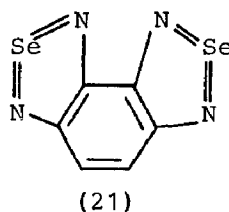
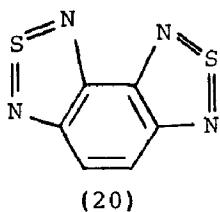
Trithiazyltrichloride reacts with $OsCl_3$ to give a product of composition $Os(NS)Cl_3$ which may be converted to $[PPh_4][(H_2O)Os(NS)Cl_4]$ in which the Os atom is octahedrally coordinated with H_2O trans to the NS group.⁴⁵

Cyclic Compounds - The reaction of the sulphur triimides $(RN=)_3S$ with $R = Me_3C$ or Me_3Si with pent-fluoroazapropene gives the

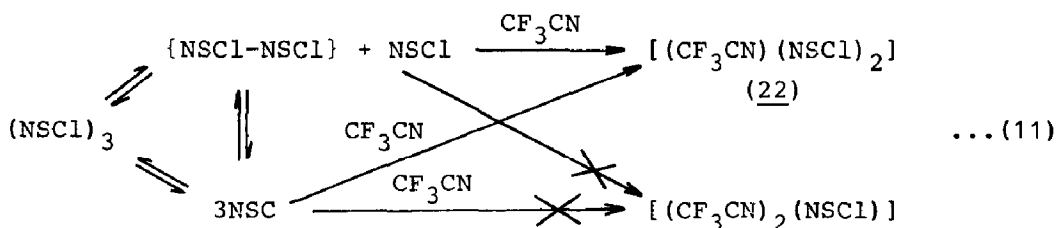
compounds (19) with Y = S or Se.⁴⁸



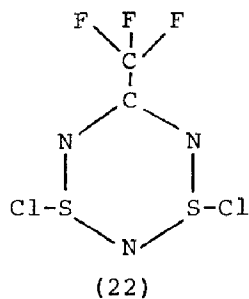
X-ray structure determinations have shown that the cyclic compounds (20) and (21) have a quasi aromatic π system in the 1,2,5-thiadiazole rings, with the aromatic character of the central benzene ring being strongly disturbed. The substitution of one sulphur by a selenium atom induces significant changes of comparable bond lengths. Quasi polymers in the form of ribbon-like structures are observed in (20) by short S---N contacts and in (21) by short Se---N contacts. In (21) (SeN₂)_x chains are also formed.⁴⁹



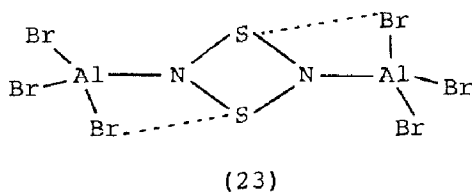
The preparation of cyclo(CF₃CN) (NSCl)₂ (22) from CF₃CN and (NSCl)₃ has been reported (equation 11). The structure of (22)



was determined by X-ray diffraction and (22) may be dechlorinated by Zn in liquid SO₂ to give either CF₃CN₃S₂ or CF₃CN₂S₂ depending on the reaction conditions.⁵⁰

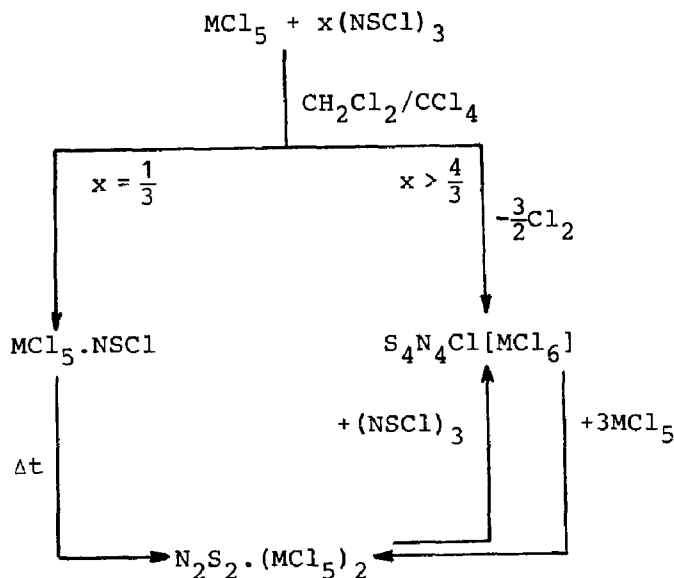
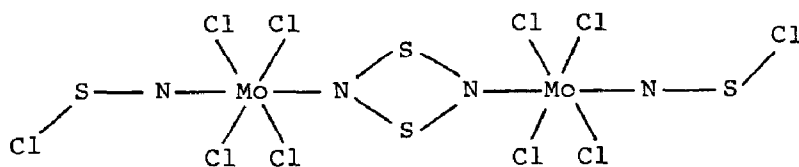


The compound $S_2N_2 \cdot 2AlBr_3$ (23) has been prepared by the reaction of S_4N_4 with $AlBr_3$ in 1,2-dibromoethane at room temperature. The S_2N_2 has S-N bond lengths of 1.629 and 1.651 Å with S-N-S and N-S-N bond angles of 95.8 and 84.2° respectively. Thus although the bond lengths agree closely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



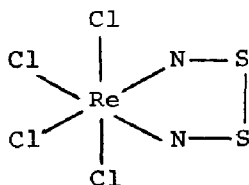
The pentachlorides of niobium and tantalum react with trithiazyl chloride in CCl_4 suspension to form the donor-acceptor complexes $MCl_5 \cdot NSCl$ and $(MCl_5)_2N_2S_2$. With excess $(NCl)_3$ the ionic compounds $S_4N_4Cl(MCl_6)$ are obtained, and another ionic species, $N(SCl)_2(MCl_6)$ was obtained from the reaction of the complexes $MCl_5 \cdot NSCl$ with SCl_2 . Further reactions in this system are shown in Scheme 6.⁵² Molybdenum pentachloride also reacts with $(NSCl)_3$ in CH_2Cl_2 suspension to give a mixture from which the complex $\mu-(S_2N_2)[MoCl_4(NSCl)]_2$ (24) was extracted. The corresponding tungsten compound was obtained by extraction of SCl_2 and chlorine from $N(SCl)_2[WCl_5(NSCl)]$ which was prepared from WCl_6 and $N_2S_3Cl_2$.⁵³

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

Scheme 6

(24)

The structure comprises PPh_3Cl cations and $\text{ReCl}_4(\text{N}_2\text{S}_2)$ anions in which the rhenium atom is six coordinated by four chlorine atoms and the nitrogen atoms of a ReN_2S_2 five membered ring in cis position. The Re-N bond lengths (181pm) and the NS bond lengths (152pm) are in the range of double bonds whilst the S-S distance is very long (253pm).⁵⁴

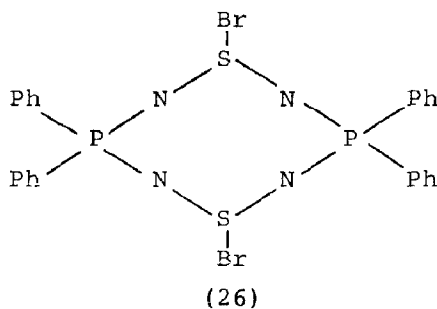


(25)

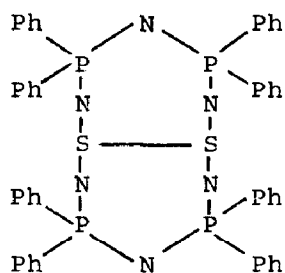
An ab initio valence bond calculation for S_2N_2 with the sulphur 3d orbitals omitted supports a conclusion obtained from a previous INDO study that the primary Lewis valence bond structure is a spin-paired diradical or long-bond structure. "Increased-valence" structures were used to provide qualitative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

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

The eight membered ring $1,5-(Ph_2PN)_2(SN)_2$ undergoes an oxidative-addition reaction with Br_2 or SO_2Cl_2 to give $1,5-(Ph_2PN)_2(NSX)_2$ where $X = Br$ or Cl . The crystal structure of the bromine compound (26) shows the ring to have the chair conformation with exocyclic bromine substituents in a trans configuration with sulphur-bromine distances of 2.454 and 2.440Å. This represents the first structural characterisation of a thiazylbromide and indicates appreciable ionic character in the S-Br bond. The average S-N and P-N bond lengths are 1.53 and 1.62Å respectively. In contrast the reaction of $1,3-(Ph_2PN)_4(SN)_2$

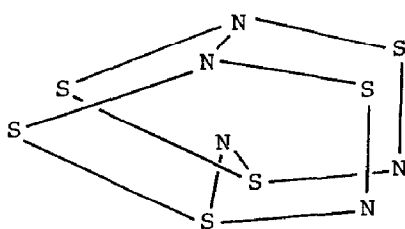


with SO_2Cl_2 results in ring contraction to give $(Ph_2PN)_2(NSCl)$ whilst the reaction with Br_2 produces $[(Ph_2PN)_4(SN)_2]^{2+}[Br_3^-]_2$ (27). The reactions of $1,3,7,9-(Ph_2PN)_4(SN)_2$ with iodine or excess Br_2 produced the six membered rings $(Ph_2PN)_2(NSI)$ and $(Ph_2PN)_2(SN)^+Br_3^-$, respectively.



(27)

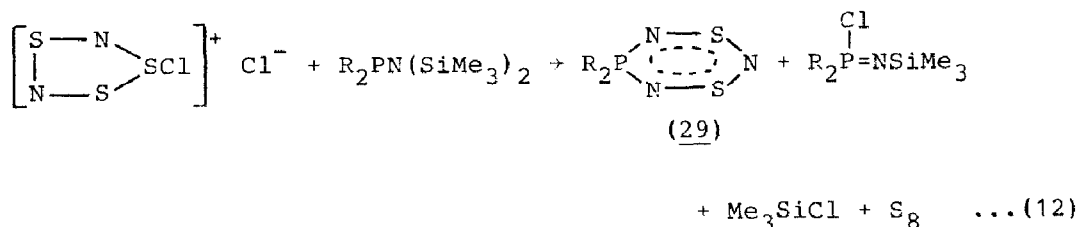
The e.p.r. spectrum of a persistent sulphur nitride radical cation, common to the oxidation of many sulphur-nitrogen compounds, has been obtained from solutions of S_4N_4/S_4N_2 mixtures highly enriched in both ^{15}N and ^{33}S . Analyses of solution and frozen spectra showed that the cation is planar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



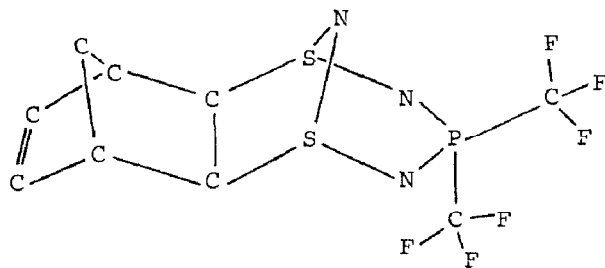
(28)

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

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



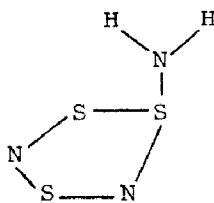
for which a crystal structure is reported. When (29) is allowed to stand for several days a crystalline compound of composition



(30)

((CF₃)₂PN₂S)₂ was formed which according to the X-ray structural data contains an eight membered ring with 1,3-P(CF₃)₂ groups.⁶⁰

Protonation of the trisulphur trinitride ion S₃N₃⁻ with HBF₄ has been shown to yield the ring contracted S-amino thiodithiazyl salt S₃N₂NH₂⁺BF₄⁻ for which an X-ray crystal structure was determined (31). The reasons for the instability of six membered rings of

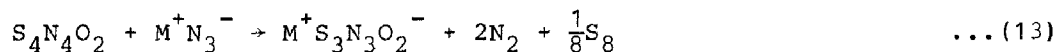


(31)

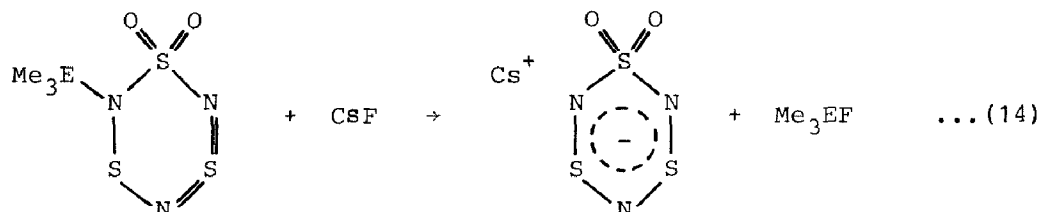
the type S₃N₃R were discussed in the light of MNDO calculations based on an S₃N₃H model.⁶¹

Two independent publication have described the preparation of the metallocycles [MCl₃(S₂N₃)]₂ where M = Mo, W. The first publication describes the preparation of the compound from quantitative reaction of MoNCl₃ with (NSCl)₃ and WOCl₄ or WSCl₄

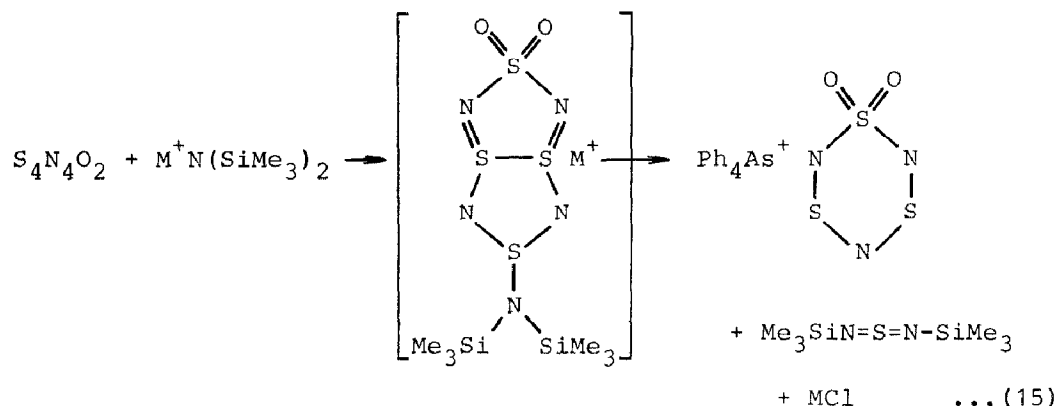
which described the following methods of synthesis 1) the reaction of $S_4N_4O_2$ with alkali azides:



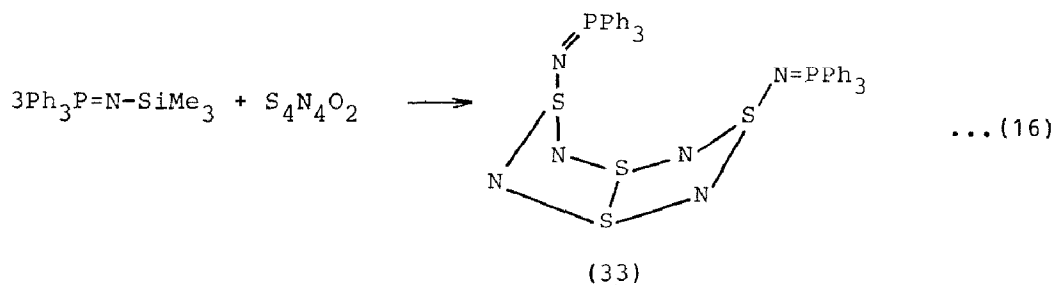
2) Metathesis of $Me_3ES_3N_3O_2$ (E = Si, Sn) with CsF:



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

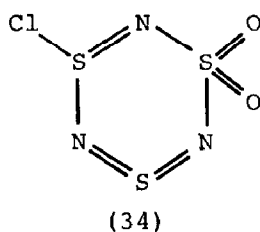


4) Reaction of $S_4N_4O_2$ with $Ph_3P=N-SiMe_3$ in a 1:1 molar ratio. Excess iminophosphorane leads to the formation of a covalent 1,5-di-substituted S_4N_4 derivative (33).⁶⁴



The second publication describes the electrochemical reduction of the anions $S_3N_3O_2^-$, $S_3N_3O^-$ and $S_4N_5O^-$ together with the neutral molecules $S_4N_4O_2$, S_3N_2O , $Ph_2CNCNCO$ and $S(NSO)_2$. The polarographic reduction of the oxygenated derivatives $S_3N_3O^-$, $S_3N_3O_2^-$, $S_4N_5O^-$ and $S_4N_4O_2$ occurred at significantly less negative potentials than the corresponding binary species, with the coulometric reduction of $S_4N_4O_2$ giving a 70% yield of $S_3N_3O_2^-$. The controlled potential electrolysis of $S_3N_3O_2^-$ or $S_4N_5O^-$ resulted in the breakdown of the ring or cage. The reduction of $Ph_2CNSNSO$ led to the quantitative formation of $Ph_2CNSNCPH_2$ and NSO^- , the latter anion reacts with S_4N_4 to give $S_3N_3O^-$ and with sulphur to give a red species tentatively identified as S_xNSO^- ($x = 1$ or 2).⁶⁵

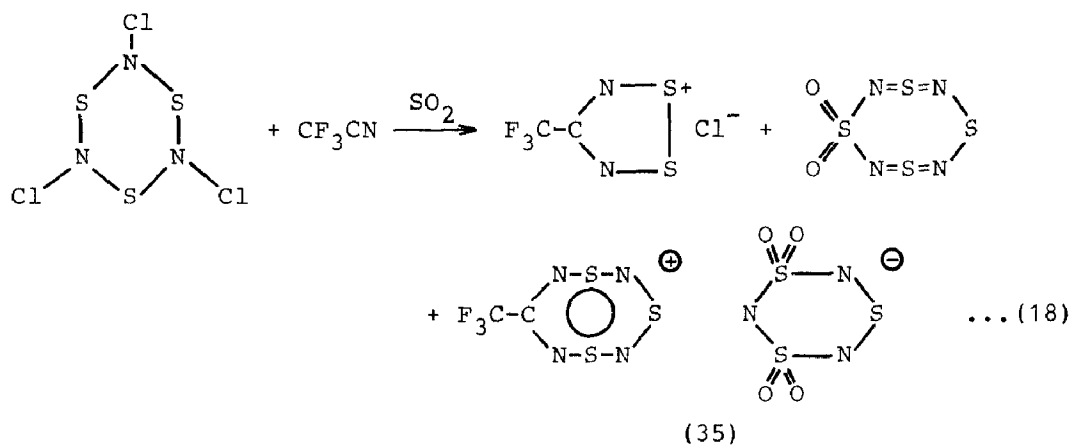
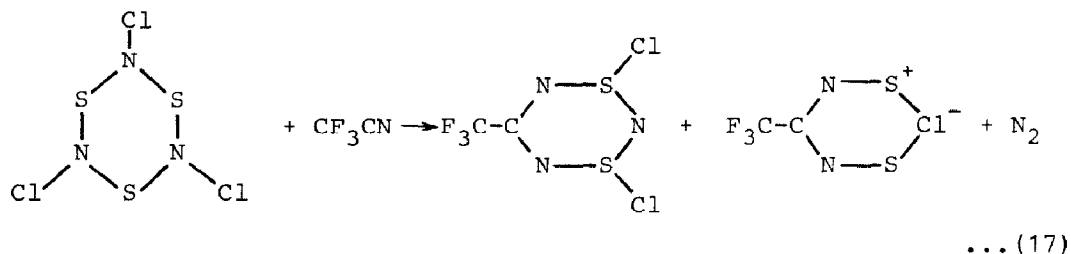
$S_3N_3O_2Cl$ has been isolated as a decomposition product of $S_3N_3O_2Cl_2$ in methylene chloride and its structure shown to contain a S_3N_3 ring with three differently coordinated sulphur atoms (34).⁶⁶



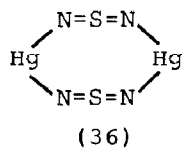
The supporting electrolyte has been shown to have a marked effect on the electrochemical reduction of the $S_3N_3^-$ ion, which in the presence of R_4N^+ accepts two electrons to give the unstable $S_3N_3^{3-}$ anion. The reduction of $S_4N_5^-$ in the presence of R_4N^+ occurs in two steps each involving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

The reaction of 1,3,5-trichloro-1,3,5,2,4,6-trithiatriazine with CF_3CN have been shown to depend on reaction conditions, solvent and even the material of the reaction vessel. In the absence of a

solvent the products are as shown in equation (17) but if SO_2 is used as a solvent the reaction follows equation (18):



The cation in (35) is the missing members of the series of isoelectronic heterocycles $\text{S}_4\text{N}_4^{2+}$, RCS_3N_4^+ and $3,7-(\text{RC})_2\text{S}_2\text{N}_4$. Crystal structure analysis of (35) showed there to be no transannular S-S interactions and the S-N distances (mean value 154.9pm) to be almost identical alternating only slightly more than in the $\text{S}_4\text{N}_4^{2+}$ ion.⁶⁹ The Hartree-Fock-Slater method has been used to elucidate the nature of the electronic spectrum of the planar S_4N_3^+ cation.⁷⁰ The crystal and molecular structures of the known compounds $\text{HgN}_2\text{S} \cdot \text{NH}_3$ and of the new inclusion compound $2\text{Hg}(\text{NH}_3)_2\text{I}_2 \cdot \text{S}_4\text{N}_4$ have been reported. $\text{Hg} \cdot \text{N}_2\text{S} \cdot \text{NH}_3$ is dimeric with two Hg atoms bridged to form eight membered rings (36) with each Hg atom also coordinated by a NH_3 molecule and by a nitrogen atom of an adjacent ring. $2\text{Hg}(\text{NH}_3)_2\text{I}_2 \cdot \text{S}_4\text{N}_4$ is an inclusion compound



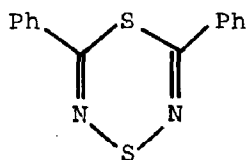
with S_4N_4 molecules in the holes of the lattice of the large $Hg(NH_3)_2I_2$ tetrahedra.⁷¹

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

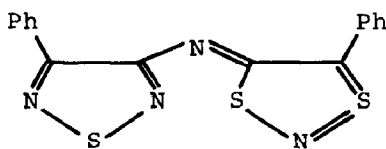
Two studies of the reactions of iron trichloride with trithiazyl chloride have been reported. The reaction yields $S_4N_4[FeCl_4]_2$, $S_3N_3Cl_2[FeCl_4]$ or $S_4N_4Cl[FeCl_4]$ depending on the reaction conditions. I.r. spectra confirmed the presence of $FeCl_4^-$ in all three compounds. A structure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

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

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

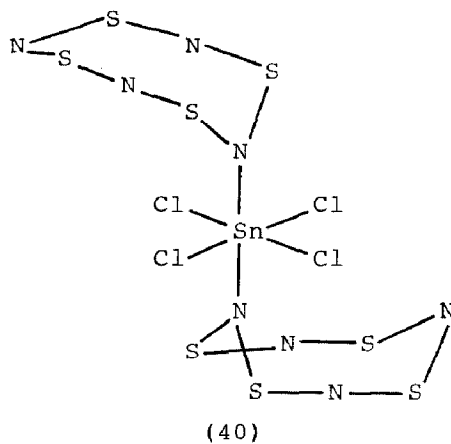
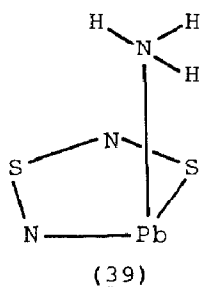


(37)



(38)

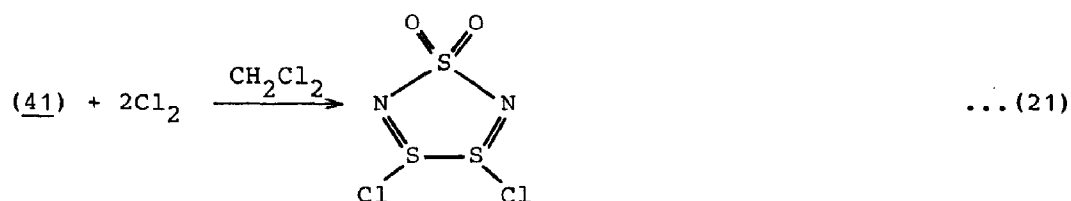
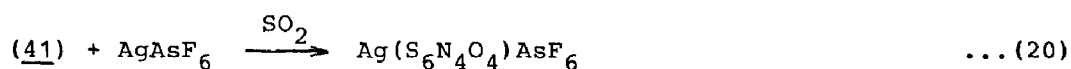
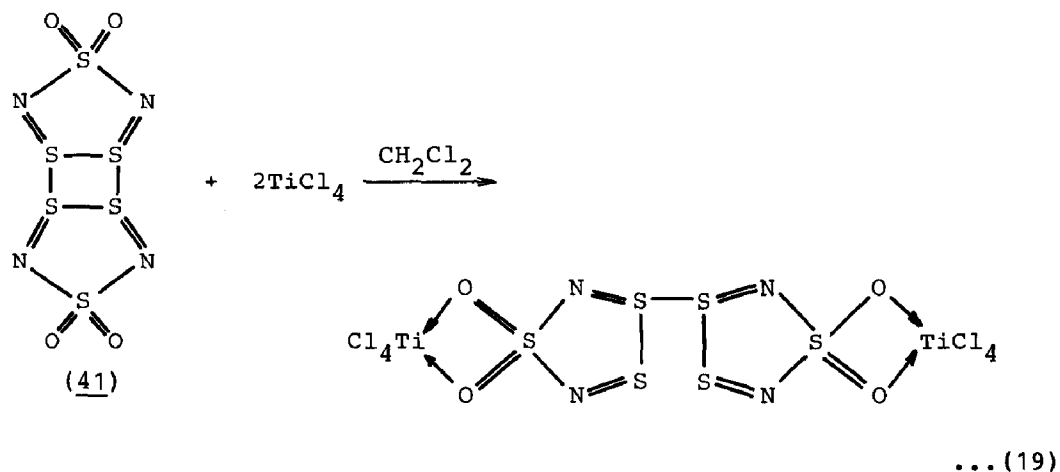
The structures of $\text{PbN}_2\text{S} \cdot \text{NH}_3$, PbN_2S_2 and $\text{SnCl}_4 \cdot 2\text{S}_4\text{N}_4$ which are the products of reactions of lead- and tin salts with S_4N_4 have been described. The first two compounds contain the same planar five membered PbN_2S_2 rings with no significant differences: in the first compound the NH_3 molecule is bound to Pb perpendicularly to the plane of the ring (39). In $\text{SnCl}_4 \cdot 2\text{S}_4\text{N}_4$ the Sn atom is in six fold coordination with the two S_4N_4 rings attached trans to each other via a nitrogen atom (40).⁷⁶



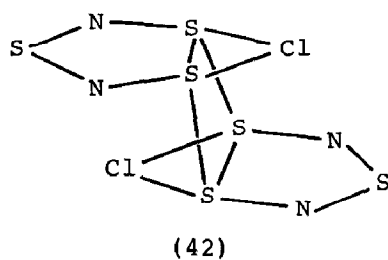
The reaction of $(\text{NSCl})_3$ with TiCl_4 leads to chlorine abstraction and the formation of the adduct $\text{TiCl}_4(\text{N}_2\text{S}_2)$. I.r. spectroscopic data suggests that the N_2S_2 ring is bonded to the titanium via the nitrogen atoms to form a polymer. A by-product of the reaction is $(\text{S}_4\text{N}_5)_2(\text{Ti}_2\text{Cl}_{10})$ which consists of S_4N_5^+ cations which are nearly the same as those found in $(\text{S}_4\text{N}_5)\text{Cl}$ and $\text{Ti}_2\text{Cl}_{10}^{2-}$ anions as observed in $(\text{PCl}_4)_2(\text{Ti}_2\text{Cl}_{10})$.⁷⁷

$\text{S}_6\text{N}_4\text{O}_4$ (41) has been prepared in high yield from $(\text{Me}_3\text{Si})_2\text{N}-\text{SO}_2-\text{N}(\text{SiMe}_3)_2$ and SCl_2 in the molar ratio of 1:2. Several reactions of (41) were investigated and are given in equations (19-21). (41) is the first compound to contain an uncharged four membered sulphur ring.⁷⁸

Crystals of $\text{S}_4\text{N}_4\text{Cl}_2$ (commonly called thiodithiazyl chloride) have been grown by three different methods based on 1) a reversible temperature dependent ring expansion-contraction ($\text{S}_6\text{N}_4\text{Cl}_2 \leftrightarrow \text{S}_4\text{N}_3\text{Cl}$) equilibrium in $\text{SO}_2-\text{SOCl}_2$ mixtures, 2) a complex chemical transport reaction in a sealed tube containing $\text{S}_3\text{N}_2\text{Cl}_2$ and liquid SO_2 and 3) a controlled slow reaction of $\text{S}_3\text{N}_2\text{Cl}_2$ with liquid SO_2 . A crystal structure determination showed the dimeric cation



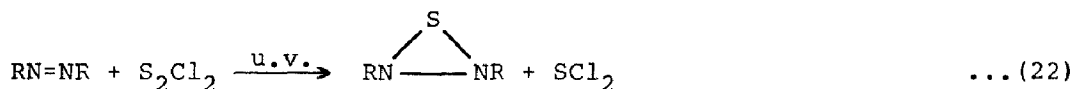
(42) to contain two centrosymmetric planar S_3N_2 rings in a chair (trans) conformation.



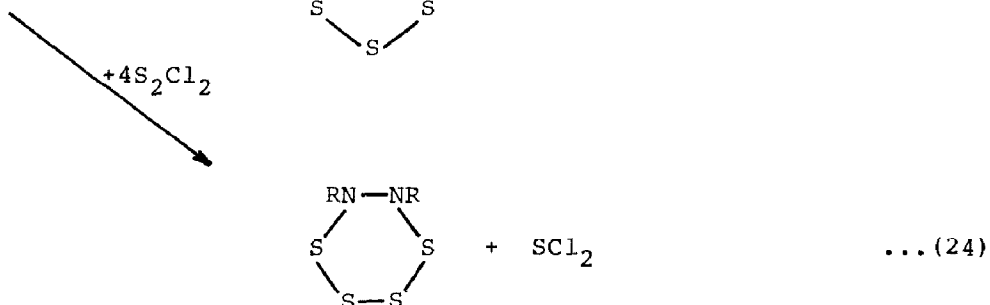
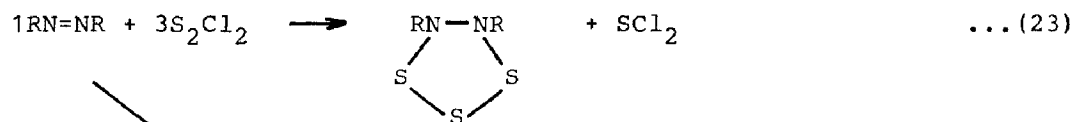
The dihedral angle between the S_3N_2 ring plane and the central S_4 ring is 110.4° . Strong, temperature independent ESR signals were obtained from solid $\text{S}_6\text{N}_4\text{Cl}_2$ suggesting the presence of some monomer.⁷⁹

The structural dichotomy exhibited by cyclic thiazenes of the type $\text{E}(\text{NSN})_2\text{E}$ where $\text{E} = \text{CR}$ or SR has been analysed in the light of MNDO molecular orbital calculations on a variety of model structures. For $\text{RS}(\text{NSN})_2\text{SR}$ molecules the activation energies for

inversion at sulphur have been estimated and the formation of exo-endo and exo-exo isomers discussed in terms of the frontier orbitals involved in the free radical and electrophilic oxidation of transannular S-S bonds.⁸⁰ A new class of S-N heterocyclic compounds with the general formula $\overline{\text{RN-S}_x\text{-NR}}$ where $\text{R} = \text{CF}_2\text{Cl}$ or C_2F_5 and $x = 1, 3$ or 4 have been shown to result from the photolysis of RN=NR and S_2Cl_2 (equation 22):

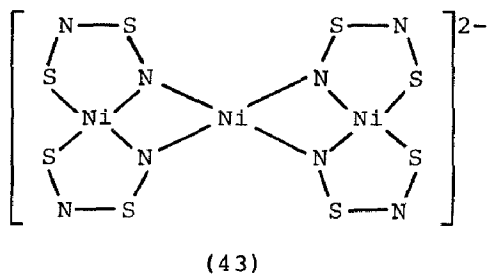


It is believed that these are the first examples of such compounds with divalent sulphur and when the reaction stoichiometries are changed, five and six membered heterocycles with vicinal nitrogen atoms are obtained in low yield. All of the new heterocycles



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

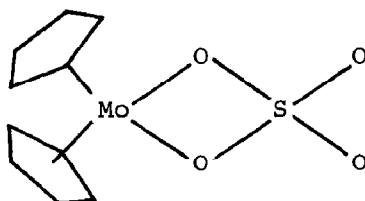
A crystal structure determination has shown that the complex $(\text{Ph}_4\text{P})_2(\text{Ni}_3\text{N}_8\text{S}_8)$ comprises two moieties of $[\text{Ni}(\text{N}_2\text{S}_2)_2]^{2-}$ linked to each other via a further nickel atom (43).⁸²



6.2.4 Bonds to Oxygen

The sulphur-33 chemical shift and ^{33}S and ^{17}O n.m.r. relaxation data have been reported for liquid sulphur dioxide. The ^{33}S nucleus in SO_2 is highly deshielded, 375±2ppm to high frequency of the sulphate ion and the temperature dependence of the ^{33}S and ^{17}O n.m.r. relaxation data can be described by an average activation energy of 6.3 kJ mole⁻¹.⁸³ Solubility and n.m.r. data have been presented for the SO_2 -pyridine system and have been analysed to determine partial vapour pressures, activity coefficients and thermodynamic functions. The results indicate that a 1:1 complex is formed in these solutions.⁸⁴ X-ray and neutron scattering measurements on liquid SO_2 have been performed at 258 and 293K respectively. The intramolecular distances within SO_2 molecules in the liquid state were found to be S-O = 1.42Å, O-O = 2.47Å which do not differ significantly from those found in the liquid and gaseous states. Experimental intensities could be satisfactorily explained by a body centred cubic cluster model in which there were fifteen SO_2 molecules with a first neighbour distance of 4.25Å.⁸⁵ The density, conductivity and electrolysis of liquid phases in the two nonaqueous systems $\text{LiCl-AlCl}_3\text{-SO}_2$ and $\text{NaCl-AlCl}_3\text{-SO}_2$ have been determined.⁸⁶

The reaction of Cp_2MH_2 (M = Mo, W) solutions with SO_2 has been found to rapidly and quantitatively give $\text{Cp}_2\text{M}(\text{S}_2\text{O}_3)$ and water. X-ray studies of the Mo product at -95°C showed bidentate coordination of thiosulphate to molybdenum (44) with Mo-O distances of 2.134 and Mo-S = 2.45Å with a dihedral angle between the Cp planes of 46.8° and a planar MoOS_2 ring.⁸⁷

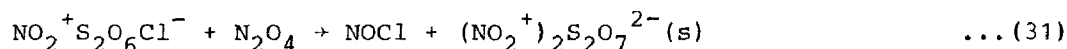
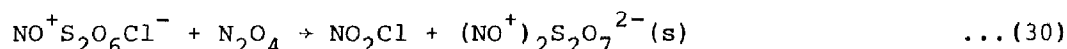
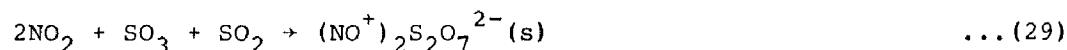
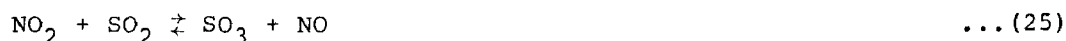


(44)

The reaction of Tl_2O with SO_2 under matrix isolation conditions gives rise to two distinct sets of product bands which were assigned to the primary reaction product being SO_3^{2-} in the $\text{Tl}_2^+\text{SO}_3^{2-}$ triple ion and the second set being assigned to the $\text{S}_2\text{O}_5^{2-}$ anion in a symmetrical oxygen-bridged form in contrast to

the asymmetric S-S linked form observed at room temperature.⁸⁸ A study of the reaction of Mn(III) with S(IV) has shown that one Mn³⁺ is consumed for each SO₂ consumed and that dithionate is produced.⁸⁹

F.T. i.r. spectroscopy has been used to study the gas phase reaction between NO₂ and SOCl₂. The initial products are NOCl, NO₂Cl and SO₂ but on standing a white solid which is a mixture of at least three different compounds is formed. Kinetic data show the initial reaction to be first order in SOCl₂ and second in NO₂. The chemistry of the reactions was partially explored and the results are shown in equations (25) to (31).⁹⁰



In agreement with recent experimental work a molecular orbital study of the formation of Na₂SO₄ and HCl from the reaction of SO₃, H₂O and NaCl shows no activation barrier. The reaction takes place by gas phase water reacting with SO₃ involving a linear O--H--O transition state giving closely associated hydroxyl and bisulphite which rearrange to become a hydrogen sulphate molecule. The latter then transfers a hydrogen atom to a surface chloride in solid NaCl and an electron and a sodium cation transfer to give sodium bisulphate and gaseous HCl.⁹¹ Solubility⁹² and compound formation⁹³ have been studied in the ZrO₂-SO₃-HCl-H₂O system. The diffusion of sulphuric acid in aqueous solution has been measured by a conductimetric technique at 25°C over a range of concentrations. At low concentrations dissociation to bisulphate and hydrogen ions produces a sharp increase in the rate

$3\text{Mg}(\text{OH})_2 \cdot \text{MgSO}_4 \cdot 8\text{H}_2\text{O}$ and $5\text{Mg}(\text{OH})_2 \cdot \text{MgSO}_4 \cdot 3\text{H}_2\text{O}$,¹⁰³ $\text{K}_6\text{R}_4(\text{SO}_4)_9$ and $\text{K}_7\text{R}_3(\text{SO}_4)_8$ (R = Lanthanide element),¹⁰⁴ and of $\text{Al}_2(\text{SO}_4)_3$ and $\text{Ga}_2(\text{SO}_4)_3$ ¹⁰⁵ have been studied. The available data for the solubility of calcium sulphate in water has been used to calculate the standard thermodynamic properties of the solution process.¹⁰⁶ The introduction of SO_4^{2-} ion onto Fe_2O_3 gives a catalyst which exhibits pronounced catalytic activity for acid catalysed reactions. An i.r. study of the catalyst showed the formation of SO_2 species after the oxidation.¹⁰⁷ Structural studies have been carried out on $\text{Cu}_4[(\text{OH})_6\text{SO}_4] \cdot 2\text{H}_2\text{O}$ ¹⁰⁸ and LiKSO_4 .¹⁰⁹

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

Table 1. Phase systems involving the sulphate ion.

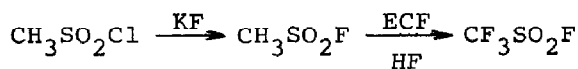
System	Ref	System	Ref
$\text{Hf}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$	110	$\text{Al}_2(\text{SO}_4)_3 \cdot \text{In}_2(\text{SO}_4)_3 \cdot \text{H}_2\text{O}$	116
$\text{UO}_2^{2+}, \text{Ti}^{4+}, \text{NO}_3^-, \text{SO}_4^{2-}, \text{H}_2\text{O}$	111	$\text{K}_2\text{SO}_4, \text{MgSO}_4, \text{ZnSO}_4, \text{H}_2\text{O}$	117
$\text{K}^+, \text{Cs}^+, \text{SO}_4^{2-}, \text{H}_2\text{O}$	112	$\text{K}_2\text{S}_2\text{O}_7 \cdot \text{V}_2\text{O}_3(\text{SO}_4)_2$	118
$\text{RbVO}_2\text{SO}_4 \cdot \text{Rb}_2\text{SO}_4 \cdot \text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$	113	$\text{K}_2\text{SO}_4, \text{MgSO}_4, \text{CuSO}_4, \text{H}_2\text{O}$	119
$\text{Li}^+, \text{Rb}^+/\text{F}^-, \text{SO}_4^{2-}$	114	$\text{K}_2\text{SO}_4, \text{MgSO}_4, \text{CoSO}_4, \text{H}_2\text{O}$	120
$\text{K}, \text{Rb}/\text{F}^-, \text{SO}_4^{2-}$	114	$\text{K}_2\text{CO}_3, \text{Rb}_2\text{SO}_4, \text{H}_2\text{O}$	121
$(\text{NH}_4)_2\text{HPO}_4 \cdot \text{K}_2\text{S}_2\text{O}_3 \cdot \text{H}_2\text{O}$	115	$(\text{NH}_4)_2\text{PO}_4, (\text{NH}_4)_2\text{H}_2\text{PO}_4, \text{K}_2\text{SO}_4, \text{H}_2\text{O}$	122
$(\text{NH}_4)_2\text{H}_2\text{PO}_4 \cdot \text{K}_2\text{S}_2\text{O}_3 \cdot \text{H}_2\text{O}$	115	$(\text{NH}_4)_2\text{HPO}_4, (\text{NH}_4)_2\text{H}_2\text{PO}_4, \text{K}_2\text{S}_2\text{O}_3$	123
		$\text{Li}, \text{Na}, \text{K}/\text{CO}_3, \text{SO}_4, \text{OH}$	124

Metal oxidation in a $\text{HSO}_3\text{F}/\text{S}_2\text{O}_6\text{F}_2$ mixture has been used to prepare the fluorosulphate derivatives of germanium, $\text{GeF}_2(\text{SO}_3\text{F})_2$, $(\text{ClO}_2)_2\text{Ge}(\text{SO}_3\text{F})_6$ and $\text{Cs}_2[\text{Ge}(\text{SO}_3\text{F})_6]$ and in the tin system a new fluorosulphate $\text{M}[\text{Sn}(\text{SO}_3\text{F})_5]$ where $\text{M} = \text{K}^+$ or Co^+ .¹²⁵ The same oxidising mixture has also been used to prepare fluorosulphates of Zn, Cd and Hg of the type $\text{M}(\text{SO}_3\text{F})_2$.¹²⁶

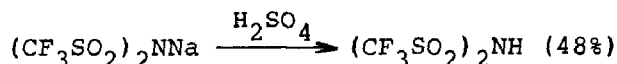
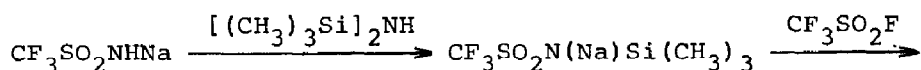
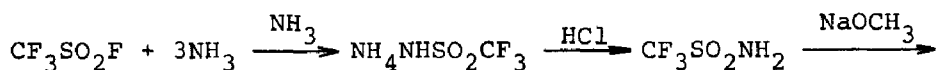
A simple synthetic route to pure $\text{Pt}(\text{SO}_3\text{F})_4$ has been described: the compound is an excellent fluorosulphate ion acceptor forming either $[\text{Pt}(\text{SO}_3\text{F})_6]^-$ or $[\text{Pt}(\text{SO}_3\text{F})_5]^-$. In a solution of HSO_3F the

novel dibasic acid, $\text{H}_2\text{Pt}(\text{SO}_3\text{F})_6$ is formed.¹²⁷

Bis[(trifluoromethyl)sulphonyl]imide, $(\text{CF}_3\text{SO}_2)_2\text{NH}$ has been prepared in 48% yield by the sequence of reactions shown in Scheme 8:

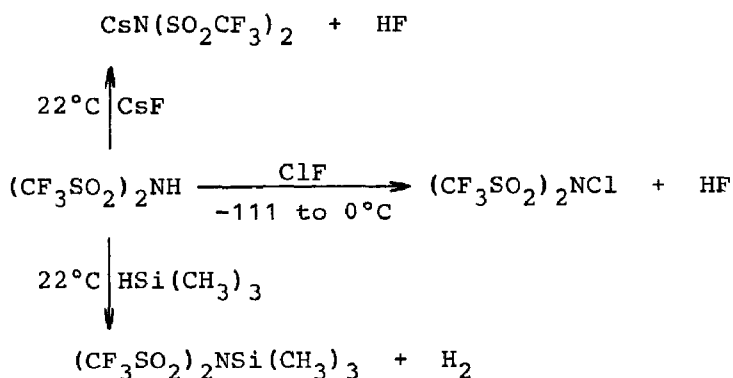


(ECF = electrochemical fluorination)



Scheme 8

The strong acidity of $(\text{CF}_3\text{SO}_2)_2\text{NH}$ allows the preparation of many derivatives to be carried out in a straightforward manner as shown in Scheme 9:¹²⁸



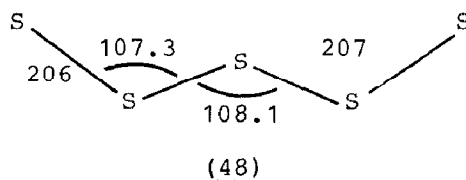
Scheme 9

The indium thiosulphates, $\text{In}_2\text{S}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$, $\text{In}_2\text{S}_2\text{O}_3 \cdot \text{InOH} \cdot 2\text{H}_2\text{O}$ and $\text{In}_2\text{S}_2\text{O}_3 \cdot 2\text{InNO}_3 \cdot 2\text{H}_2\text{O}$ have been isolated as solid products from the reaction of Indium(I) with thiosulphate ion in aqueous solution.¹²⁹ The crystal structure of $\text{Na}_2\text{S}_2\text{O}_3$ has been

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

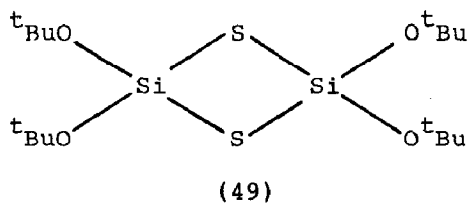
6.2.5 Sulphides

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



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

Two papers in a series of contributions to the chemistry of silicon-sulphur compounds have been published. The first deals with the ^{29}Si n.m.r. spectra of three series of compounds $(\text{RO})_3\text{SiSR}'$, $(^i\text{PrO})_{4-n}\text{Si}(\text{SEt})_n$ and cyclic Si-S compounds.¹⁴⁰ The second describes the crystal structure of $[(^t\text{BuO})_2\text{SiS}]_2$, prepared by the alcoholysis of SiS_2 by t-butanol. The molecule contains a planar Si_2S_2 ring (49) with Si-S bond distances of 214.2 and 213.1 pm and bond angles $\text{S-Si-S} = 97.8^\circ$ and $\text{Si-S-Si} = 82.2^\circ$.¹⁴¹

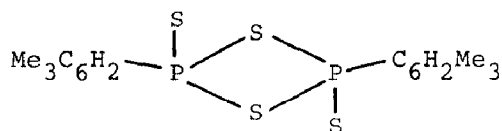


The preparation of the compounds $\text{Na}_8\text{Si}_4\text{X}_{10}$ and $\text{Na}_8\text{Ge}_4\text{X}_{10}$ where $\text{X} = \text{S}$ or Se has been described.¹⁴² The compounds Tl_4TiS_4 , Tl_4SnS_4 and Tl_4TiSe_4 have been shown to be isostructural and to contain isolated tetrahedral thioanions which are connected to each other by Tl^+ ions. The mean bond lengths are $\text{Ti-S} = 2.26$, $\text{Sn-S} = 2.40$, $\text{Ti-Se} = 2.38\text{\AA}$. $\text{Tl-S} = 2.93$ to 3.98\AA and $\text{Tl-Se} = 3.03$ to 3.96\AA .¹⁴³ The sulphide $\text{In}_5\text{Sn}_{0.5}\text{S}_7$ has been shown to have the same structure as In_6S_7 in which one indium $1+$ ion is substituted by half a tin $2+$ ion.¹⁴⁴

An alternative explanation for the stability of P_4S_3 relative to P_4S_6 and As_4S_3 has been proposed based on the concept of topological charge stabilisation.¹⁴⁵ P_4S_3 under glass-filtered u.v. irradiation is rapidly cleaved by alkyl and aryl disulphide to give tetrathiophosphate esters, $\text{SP}(\text{SR})_3$ and trithiophosphite esters, $\text{P}(\text{SR})_3$. In a competition reaction MeSSMe and PhSSPh reacted to a similar extent with P_4S_3 to give all eight possible products $\text{S}_x\text{P}(\text{SPh})_n(\text{SMe})_{3-n}$ where $x = 0$ or 1 and $n = 0$ to 3 . P_4S_3 is similarly cleaved by sulphuryl chloride under thermal conditions to give SPCl_3 and PCl_3 with no evidence for intermediates being formed.¹⁴⁶ The reaction of P_4S_{10} with P_4O_{10} in different molar ratios has led to the identification of the following oxide sulphides; $\text{P}_4\text{O}_6\text{S}_4$, $\text{P}_4\text{O}_7\text{S}_3$, $\text{P}_4\text{O}_5\text{S}_5$, $\text{P}_4\text{O}_4\text{S}_6$, $\text{P}_4\text{O}_3\text{S}_7$, $\text{P}_4\text{O}_2\text{S}_8$ and P_4OS_9 .¹⁴⁷

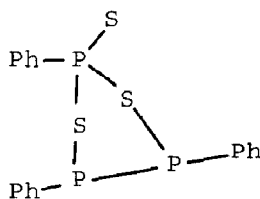
The 1:1 reaction between PRCl_2 ($\text{R} = \text{C}_6\text{H}_2\text{Me}_3\text{-2,4,6}$) and $(\text{Me}_3\text{Si})\text{S}$ in toluene yield $(\text{RPS})_4$ which slowly disproportionates to $(\text{RPS})_2$

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



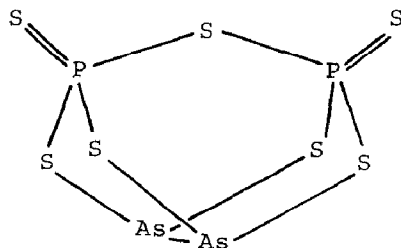
(50)

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



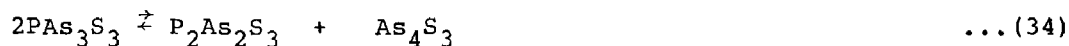
(51)

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



(52)

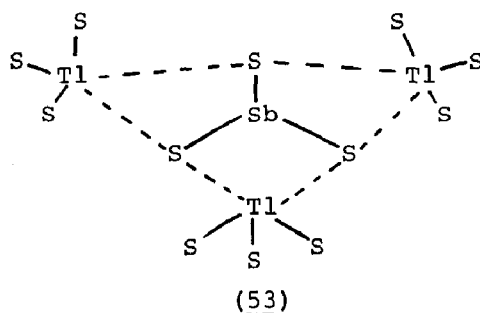
The vibrational spectrum of crystalline PAs_3S_3 and its Raman spectrum in the molten state have been measured. In the molten state a partial decomposition was observed according to equation (34).¹⁵¹



The crystal vibrational spectra of $\text{P}(\text{CH}_2\text{CH}_2\text{CN})_3$ and its sulphide, oxide and selenide have been studied. The difference between $\nu(\text{PS})$ in $\text{P}(\text{CH}_2\text{CH}_2\text{CN})_3\text{S}$ and $\nu(\text{PSe})$ in the selenide is much greater than the differences $\nu(\text{PS}) - \nu(\text{PSe})$ usually observed in related PR_3S and PR_3Se molecules.¹⁵²

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

Crystal structures of four ternary antimony sulphides have been determined. Tl_3SbS_3 contains SbS_3 groups strongly bound to three Tl atoms through Sb-S-Tl bridges to give $\text{Tl}_3\text{SbS}_{12}$ groups (53).¹⁵⁵



$\text{SrSb}_4\text{S}_7 \cdot 6\text{H}_2\text{O}$ contains anionic $(\text{Sb}_4\text{S}_7^{2-})_x$ strings which are arranged parallel in sheets separated by the hydrated Sr^{2+} ions.¹⁵⁶ $\text{Sn}_6\text{Sb}_{10}\text{S}_{21}$ was previously reported as SnSb_2S_4 and consists of bands of edge sharing half octahedra with the repeat unit consisting of two bands of composition $(\text{M}_{10}\text{S}_{12})_n$ and three of composition $(\text{M}_4\text{S}_6)_n$.¹⁵⁷ The structure of $\text{Sn}_3\text{Sb}_2\text{S}_6$ has been determined by high resolution transmission electron microscopy.¹⁵⁸ The structure of $\text{Cu}_4\text{Bi}_4\text{S}_9$ has been redetermined and refined.¹⁵⁹

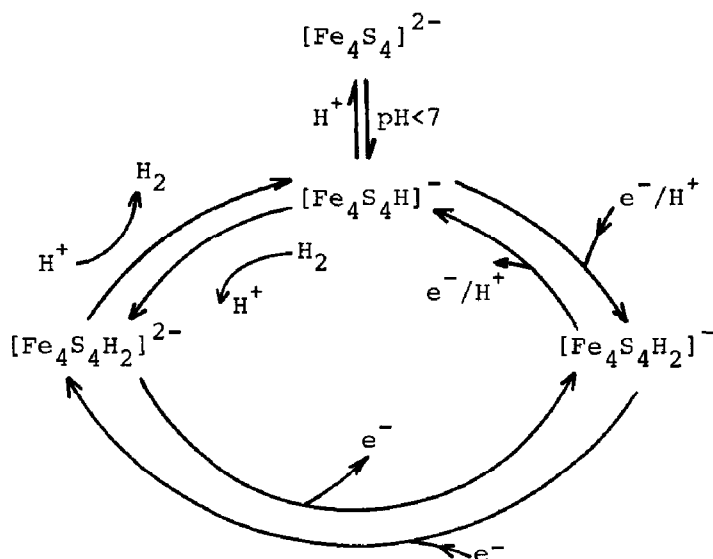
The electrochemical behaviour of sulphide ions in molten dimethylsulphone at 127°C has been carried out. The oxidation of the sulphide ion on a Pt electrode leads to sulphur through the formation of a blue polysulphide species but the oxidation of an amalgamated gold electrode in the presence of sulphide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

The photocatalytic decomposition of H_2S continues to be of interest. Three papers have given details on the improvements which can be made to the CdS catalysts. In the first paper a series of mixed semiconductor dispersions were compared with significant improvements being observed for a catalyst of composition $\text{CdS} + \text{TiO}_2\text{-RuO}_2$ (0.5wt%) in which electron transfer from the conduction band of CdS to that of TiO_2 takes place in alkaline suspensions containing SH^- ions.¹⁶¹ In the second paper an improvement by a factor of 7 is claimed for a catalyst comprising CdS loaded with 0.5wt% RuS_2 compared with CdS loaded with 0.5wt% RuO_2 .¹⁶² The third paper describes a novel system comprising CdS crystallites embedded in a polymer (Nafion) matrix that also contains a hydrogen evolution catalyst (Pt).¹⁶³

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

Scanning electron microscopy has shown that the solid state reaction of polycrystalline CdS and Cr_2S_3 starts by covering the crystallites of the reactants with a layer of the reaction product CdCr_2S_4 .¹⁶⁴ The interactions of the protein bovine insulin and bovine serum albumin with the water soluble cluster $\text{Fe}_4\text{S}_4(\text{SCH}_2\text{CH}_2\text{CO}_2)_4^{6-}$ have been described. Electrochemical studies indicate the direct involvement of protons as well as electrons in redox reactions and the mechanism shown in Scheme (10) was proposed for hydrogenase activity which was consistent with the present findings and with reports of the maximum rates of hydrogenase activity under acidic conditions.¹⁶⁵

Resonance Raman spectra have been reported for the dimeric iron chalcogen complexes $[\text{Fe}_2\text{X}_2(\text{Se})_4]^{2-}$, $[\text{Fe}_2\text{X}_2(\text{SePh})_4]^{2-}$, $[\text{Fe}_2\text{X}_2\text{Cl}_4]^{2-}$ and $[\text{Fe}_2\text{S}_2\text{Br}_4]^{2-}$ where $\text{X} = \text{S}$ or Se .¹⁶⁶ Fe_7S_8 , Co_9S_8 and Ni_3S_2 have been prepared as single phase polycrystalline materials by heating the appropriate metal sulphates in a controlled mixture of



Scheme 10

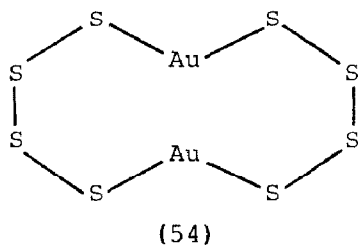
H_2 and H_2S at low temperature. The X-ray diffraction pattern and field-dependent magnetic susceptibility of Fe_7S_8 were found to be affected by the thermal history of the sample with the observed differences being related to the vacancy ordering associated with ferrimagnetic Fe_7S_8 .¹⁶⁷ The synthesis and structures of three new iron-sulphur cluster compounds, $(\text{Et}_4\text{N})_3(\text{Fe}_6\text{S}_6\text{Cl}_6)$,¹⁶⁸ $(\text{Et}_4\text{N})_2(\text{Fe}_6\text{S}_6\text{I}_6)$ ¹⁶⁹ and $(\text{Et}_4\text{N})_3\text{Fe}_8\text{S}_6\text{I}_8 \cdot 2\text{CH}_2\text{Cl}_2$ ¹⁷⁰ have been announced. Examples of the homoleptic binuclear $\text{Fe}(\text{II})$ and $\text{Co}(\text{II})$ thiolates of the type $[\text{M}_2(\text{SR})_6]^{2-}$ have also been synthesised and structurally characterised.¹⁷¹

Crystals of $\alpha\text{Ni}_3\text{S}_2$, NiS and NiS_2 together with solid solutions of $\text{Fe}_{1-y}\text{Ni}_y\text{S}_x$ have been grown by chemical transport reactions using halogens, hydrogen halides and GeI_2 as transport media.¹⁷² The reaction of H_2S and PEt_3 with $\text{Ni}(\text{C}_2\text{H}_4)(\text{PPh}_3)_2$ has been used to prepare the mercaptodithiotrinickel complex

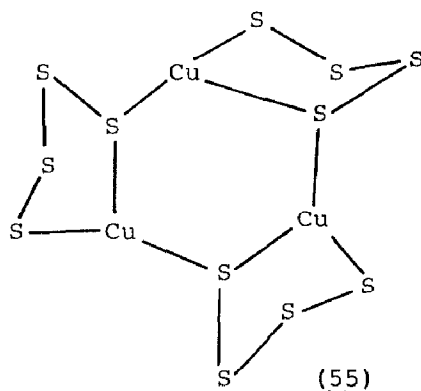
$[\text{Ni}_3(\mu_3\text{-S})_2(\text{SH})(\text{PEt}_3)_5]\text{BPh}_4$ and a structure determination carried out.¹⁷³ Several publications have dealt with the chemistry of

copper-sulphur cluster compounds. The addition of ethanolic polysulphide to a solution of $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ and PPh_4Br in CH_3CN gives the mixed crystal $\text{Cu}(\text{I})$ compound $(\text{PPh}_4)_2[\text{Cu}_4(\text{S}_4)(\text{S}_5)_2]_{0.4}[\text{Cu}_4(\text{S}_5)_3]_{0.6}$. With a comparable preparative method different monocyclic polysulphide ring species of gold such as AuS_9^- and $\text{Au}_2\text{S}_8^{2-}$ could be obtained. The reaction of $\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$ with

ethanolic polysulphide enabled the remarkable highly symmetrical $\text{Au}_2\text{S}_8^{2-}$ ring (54) compound to be isolated as a diamagnetic PPh_4^+ salt.¹⁷⁴

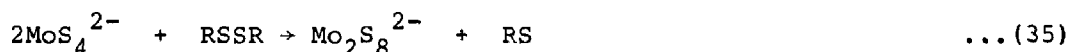


Two independent groups have described the preparation of the binary polynuclear copper complex $(\text{Cu}_3\text{S}_8)^{2-}$ from either $\text{Cu}(\text{acac})_2$ and ethanolic polysulphide solution^{175,176} or by the reaction of methanolic $\text{Cu}(\text{I})$ thiolate solution with elemental sulphur.¹⁷⁷ A good agreement for the crystal structure of the anion was found, which had an unusual arrangement of the metal atoms and novel types of ligand coordination particularly of polysulphide S_4^{2-} and S_5^{2-} ions. The use of Li_2S in place of elemental sulphur yields the $\text{Cu}_{12}\text{S}_8^{4-}$ ion which has a closed metal-sulphur cluster in the shape of a cube with sulphur atoms at each corner and copper atoms at the midpoints of each side.¹⁷⁸ Two further copper-sulphur ring systems have been characterised; $(\text{S}_6)\text{Cu}(\text{S}_8)\text{Cu}(\text{S}_6)^{4-}$ which consists of two CuS_6 seven membered rings with different conformation (C_2 and C_3 symmetry) which are linked via an S_8^{2-} ligand; and $\text{Cu}_3(\text{S}_4)_3^{3-}$ (55) which consists of three CuS_4 five membered rings with half-chair conformation and a central Cu_3S_3 six membered ring with alternating long and short Cu-S bond lengths and chair conformation.¹⁷⁹

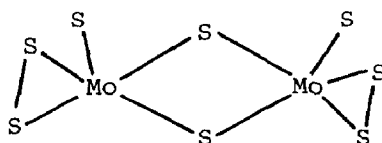


The synthesis and complete structural determination of the layered system $\text{Mn}_{0.87}\text{Cu}_{0.26}\text{PS}_3$ has been reported. The X-ray diffraction data showed the existence of disorder and led to Cu-S distances inconsistent with the data from EXAFS. This was accounted for by the fact that besides the classical S_3PPS_3 entities two distinct types of pseudooctahedra are randomly distributed between the layers - MnS_6 entities with the expected Mn-S distances of 2.61Å and $\text{S}_3\text{Cu}...\text{CuS}_3$ entities with centre to apex distances of 2.83Å.¹⁸⁰ Chemical transport methods have been used to grow single crystals of normal spinel phases in the pseudo binary system $\text{ABS}_2\text{-SnS}_2$ where A = Cu or Ag and B = Al, Cr.¹⁸¹

EXAFS studies have been carried out on the amorphous molybdenum and tungsten trisulphides and gave metal-metal distances between 2.74 and 2.79Å as well as normal, but disordered metal-chalcogen distances of Mo-S = 2.44, W-S = 2.41, Mo-Se = 2.53 and W-Se = 2.55Å. EXAFS of the triselenides gave Se-Se distances of 2.35 to 2.37Å. It is proposed that the important structural unit of these amorphous materials is a binuclear metal site with a triple bridge consisting of one chalcide ion and one dichalcide ion.¹⁸² The tetrathiomolybdate ion MoS_4^{2-} can be readily oxidised by organic disulphides to the dinuclear complex $\text{Mo}_2\text{S}_8^{2-}$ which contains reduced pentavalent molybdenum (equation 35).



X-ray structural analysis confirmed the presence of the binuclear $\text{Mo}_2(\text{S})_2(\mu\text{S})_2(\text{S}_2)_2^{2-}$ ion (56) which is isostructural with the previously reported $\text{Mo}_2\text{O}_2(\mu\text{S})(\text{S}_2)_2^{2-}$ ion.¹⁸³

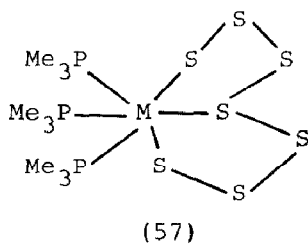


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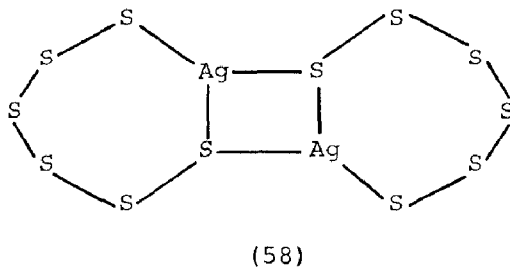
Passage of oxygen into an aqueous solution of $[(\text{Mo}^{\text{III}})_2(\text{S})_2(\text{CN})_8]^{6-}$ leads to the formation of a mixed-crystal which contains the isostructural ions $[\text{Mo}_2^{\text{III/IV}}(\text{SO}_2)(\text{S}_2)(\text{CN})_8]^{5-}$ which is paramagnetic and $[(\text{Mo}^{\text{IV}})_2(\text{SO}_2)(\text{S}_2)(\text{CN})_8]^{4-}$ which is

diamagnetic.¹⁸⁴ Cyclic voltammetry has been used to characterise electrochemical reductions of the complexes $\text{cis-[MoY(C}_5\text{H}_{10}\text{NO)}_2]$ $\text{Y} = \text{O}_2, \text{OS or S}_2$.¹⁸⁵

Attempts to prepare single crystals of $(\text{Me}_3\text{P})_3\text{MS}_6$ where $\text{M} = \text{Ru or Os}$ by slow diffusion of hexane in solutions of the compounds in acetone led to the formation of (57) which is the first example of a polysulphide metal complex with a tridentate S_n^{2-} ligand.¹⁸⁶



The novel inorganic condensed ring system $\text{Ag}_2(\text{S}_6)_2^{2-}$ (58) has been obtained as the PPh_4^+ salt from solutions of AgNO_3 and polysulphide in CH_3CN into which NH_3 and then H_2S were bubbled for a short time in the presence of PPh_4Br . The central four membered ring is exactly planar and the two seven membered rings have a distorted chair conformation.

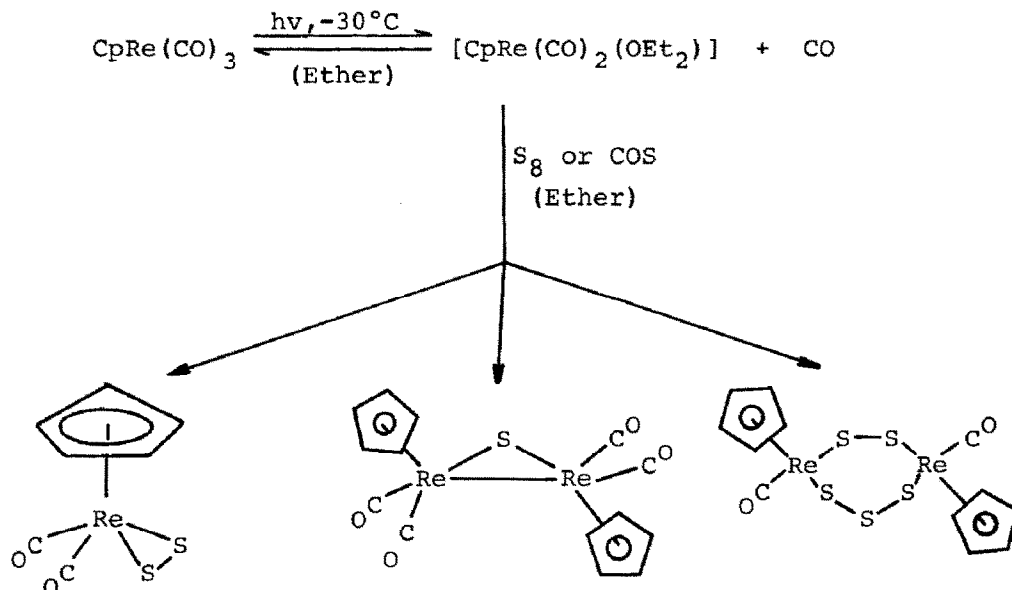


Also isolated were salts of AgS_9^- and the rather unstable heptasulphide $(\text{PPh}_4)(\text{NH}_4)\text{S}_7 \cdot \text{CH}_3\text{CN}$.¹⁸⁷

The reaction of TaX_5 ($\text{X} = \text{Br or Cl}$) with Sb_2S_3 in molar ratio 3:1 leads to the formation of TaX_3S compounds which form complexes of the type $\text{TaX}_3\text{S} \cdot 2\text{L}$ ($\text{L} = \text{dimethyl sulphide, tetrahydrothiophene or MeCN}$) and $\text{TaX}_3\text{S} \cdot \text{L}$ ($\text{L} = 1,2(\text{bis-phenylthioethane})$). Crystal structure determination of the chloride complex of the latter compound showed the metal to have a distorted octahedral coordination with a terminal $\text{Ta}=\text{S}$ bond of distance 2.204\AA , three metal-chlorine interactions and two bonds to the sulphur atoms of

the ligand.¹⁸⁸

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



Scheme 11

The synthesis and crystal structure of $(\text{Ph}_4\text{As})_4(\text{Au}_{12}\text{S}_8)$ has been described.¹⁹⁰ The compound has the same structure as reported for the $\text{Cu}_{12}\text{S}_8^{4-}$ ion mentioned earlier in this review (reference 178). The crystal structures of the mercury-sulphur compounds $[\text{Hg}(\text{S}_6)_2]^{2-}$,¹⁹¹ and complexes with the general formula $(\text{Me}_4\text{N})_4[\text{E}_4\text{M}_{10}(\text{SPh})_{16}]$ where $\text{E} = \text{S}, \text{Se}$; $\text{M} = \text{Zn}$ or Cd ¹⁹² have been reported.

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

6.2.6 Bonds to Carbon

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

Table 2.

Phase Systems

System	Ref.	System	Ref.
Tl ₂ S-GeS ₂	193	SnS ₂ -HCl-CaCl ₂ -H ₂ O	198
Hg-Tl-S	194	As ₂ S ₃ -Yb ₂ S ₃	199
Tl-Cd-S	195	Ga ₂ S ₃ -Ga ₂ O ₃	200
Nd-S	196	NbUS ₃ -TaUS ₃	201
Tl-Si-S	197	Fe ₂ As-Na ₂ S	202
		Cu ₃ As-ZnS	203

quasilinear character.²⁰⁴ The radical cation $(\text{CH}_3)_2\text{S}^+$ has been found to be formed as an intermediate in the reaction of dimethyl sulphoxide with hydrogen atoms in aqueous solutions containing high concentrations of HClO_4 . The radical cation absorbs at 285nm and is, in fact, assumed to exist as stoichiometrically defined three-electron-bonded complexes with HClO_4 or H_2O .²⁰⁵ Sulphur atoms have been shown to react with CH_3SCH_3 to generate elemental sulphur and CH_3SSCH_3 as major products along with small amounts of C_2H_6 ; and with thietane to give $\text{CH}_2(\text{CH}_2)_2\text{SS}$ and C_2H_4 in comparable yields. It is proposed that the primary adducts are vibrationally not thiosulphoxides which may then isomerise to the corresponding disulphide fragment via C-S cleavage. Bimolecular reactions between two thermalized ground state thiosulphoxide molecules and/or a thiosulphoxide molecule and an $\text{S}_2\text{-S}_7$ radical lead to regeneration of the substrate and to the formation of $\text{S}_3\text{-S}_8$ which ends up as elemental sulphur.²⁰⁶ CH_3SH and $(\text{CH}_3\text{S})_2$ as well as their mixtures have been photolysed in the presence of NO at 23°C. The identified reaction products were CH_3SNO , $(\text{CH}_3\text{S})_2$, H_2 and N_2 . Hydrogen atoms formed from the photolysis of CH_3SH reacted with both NO and CH_3SH .²⁰⁷ Ab initio calculations of the geometries of H_2CS , HFCS and F_2CS as well as their protonated cations have shown that the H or F protonation leads to molecular complexes of the form $\text{HX}\dots\text{YCS}^+$ and for H_2CS and F_2CS the S-protonation site is favoured whereas for HFCS the linear complex $\text{HF}\dots\text{HCS}^+$ is the most stable form.²⁰⁸ Calculations of the

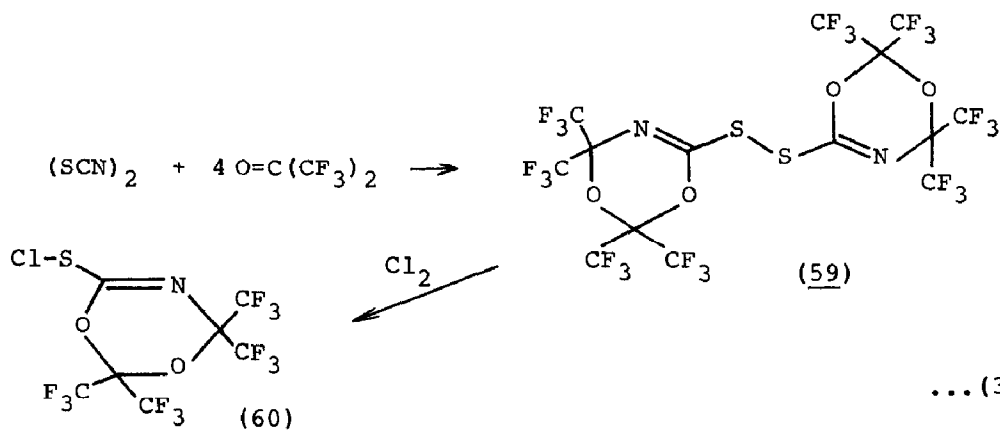
structures of $\text{SH}_3\equiv\text{CH}$, $\text{SF}_3\equiv\text{CH}$, $\text{SF}_3\equiv\text{CF}$ and the staggered and eclipsed forms of $\text{SF}_3\equiv\text{C}-\text{CF}_3$ have shown the SH_3 and SF_3 groups to have essentially octahedral configuration with XSF angles between 91 and 93° in every case. The remaining three sulphur orbitals make up the $\text{S}\equiv\text{C}$ triple bond which has a length of $1.41\text{--}1.45\text{\AA}$ compared with a $\text{S}=\text{C}$ double bond length of 1.54\AA in $\text{SF}_4=\text{CH}_2$.²⁰⁹

The compound $\text{F}_3\text{C}-\text{C}\equiv\text{SF}_3$ has been prepared by pumping $\text{F}_3\text{C}-\text{CH}=\text{SF}_4$ in the gaseous state at $50\text{--}60^\circ\text{C}$ and 10^{-1}mbar through a 40cm long quartz tube packed with dried KOH (equation 36). The product is



a colourless gas mp -122°C bp -15 to -10°C and is not as stable as $\text{F}_3\text{C}-\text{CH}=\text{SF}_4$ since it oligomerises to a product which is liquid at room temperature and crystalline at low temperature.²¹⁰

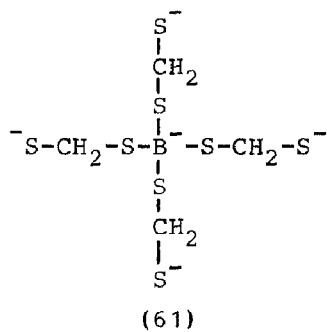
Three publications have been concerned with reactions of $(\text{SCN})_2$. The reaction of $(\text{SCN})_2$ with SnI_4 has been shown to give a compound with the formula $\text{ISn}(\text{NCS})_3\cdot\text{I}_2$ in which I_2 molecules form charge-transfer complexes with the thiocyanate groups.²¹¹ The oxidation of $[\text{OsCl}_5\text{I}]^{2-}$ with $(\text{SCN})_2$ in CH_2Cl_2 yields the bond isomers $[\text{OsCl}_5(\text{NCS})]^{2-}$ and $[\text{OsCl}_5(\text{SCN})]^{2-}$ which have been isolated as pure compounds by ion exchange chromatography.²¹² The cycloaddition of $(\text{SCN})_2$ with hexafluoroacetone has been shown to give the 4H-dioxazine (59) in 82% yield. X-ray structure analysis of (59) showed the two 4-H dioxazine rings to be coupled via the disulphide bridge so that the molecule has an almost twofold symmetry axis perpendicular to the $\text{S}-\text{S}$ bond which has a length of 202.0pm with a $\text{C}-\text{S}-\text{S}-\text{C}$ torsion angle of -86.6° (59) can be cleaved at the $\text{S}-\text{S}$ bond by chlorine to give the sulphenic acid chloride



(60) in 45% yield.²¹³

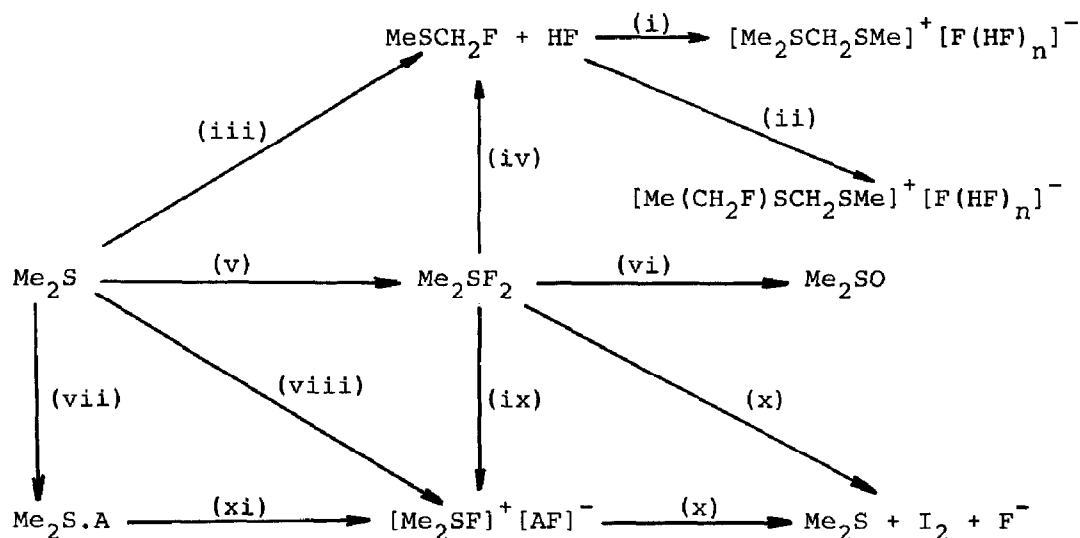
Single crystals of the trithiocyanatoargentates $\text{Rb}_2\text{Ag}(\text{SCN})_3$ and $\text{CsAg}(\text{SCN})_3$ have been obtained by crystallisation from highly concentrated aqueous solutions. Tetrahedra of $\text{Ag}(\text{SCN})_4$ are connected by common corners to give polymeric units in the Rb compounds but in the Cs compound dimeric $\text{Ag}_2(\text{SCN})_6$ anions were found.²¹⁴

Carbon disulphide reacts with NaBH_4 in THF, acetonitrile or N,N-dimethylthioformamide to give pentasodium tetrakis(dithiomethylene)borate. The reaction mechanism for the formation of this new anion $[\text{B}^-(\text{S}-\text{CH}_2-\text{S}^-)_4]$ (61) can be described by step-wise CS_2 insertion into the B-H bonds of BH_4^- and H^- transfer from BH_4^- to the intermediates.²¹⁵



The factors responsible for affecting the metal-promoted head-to-head dimerisation of CS_2 to C_2S_4 have been studied. Addition of CS_2 to a solution of $[\text{RhCl}(\text{C}_2\text{H}_4)_2]_2$ in THF and triphos in the presence of NaBPh_4 gives the diamagnetic complex $[\text{triphos-Rh}(\mu\text{C}_2\text{H}_4)\text{-Rh-triphos}](\text{BPh}_4)_2$ whilst in the presence of NaBPh_4 the complex $[\text{triphos-RhCl}(\eta^2\text{CS}_2)]$ is formed. The latter may be converted to the former complex by treatment with Lewis acids.²¹⁶

The controlled reaction of dimethylsulphide with XeF_2 in a non-acidic media gives rise via CH_2FSMe to a product best formulated as $[\text{Me}_2\text{SCH}_2\text{SMe}]^+[\text{F}(\text{HF})_n]^-$. In HF solution at -23°C the reaction gives the cation Me_2SF^+ solid derivatives of which may also be prepared by the reaction of XeF_2 with $\text{Me}_2\text{S.A}$ ($\text{A} = \text{BF}_3$ or AsF_5). The formation of dimethylsulphur difluoride are given in Scheme 13.²¹⁷

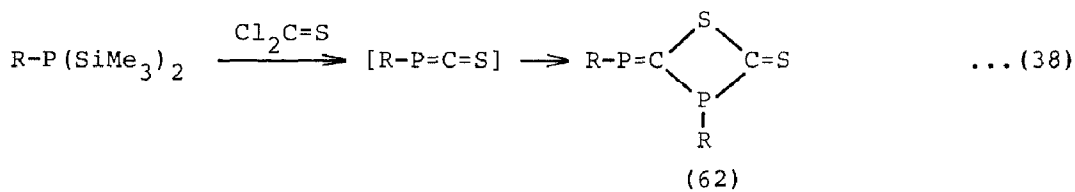


(i) Me_2S ; (ii) HF ; (iii) $\text{XeF}_2\text{-CD}_3\text{CN}$ or $\text{XeF}_2\text{-CFCl}_3 + \text{CsF}$; (iv) heat; (v) $\text{AgF}_2\text{-CDCl}_3$; (vi) Pyrex; (vii) $\text{A} = (\text{HF})_n$, BF_3 , or AsF_5 ; (viii) $\text{XeF}_2\text{-HF}$; (ix) BF_3 ; (x) $\text{I}^-(\text{aq})$; (xi) XeF_2 .

Scheme 13

The crystal structures of the lithium dithiocarbamates, $\text{Li}(\text{C}_5\text{H}_{10}\text{NS}_2) \cdot 3\text{H}_2\text{O}$,²¹⁸ $\text{Li}[\text{C}_3\text{H}_6\text{NS}_2] \cdot 4\text{H}_2\text{O}$ ²¹⁹ and $\text{Li}[\text{C}_7\text{H}_{14}\text{NS}_2] \cdot 3\text{H}_2\text{O}$ ²²⁰ have been described. In each structure pairs of distorted $\text{Li}(\text{H}_2\text{O})_4^+$ tetrahedra are formed by edge-sharing with the pairs being linked to a three dimensional network by six O-H...S hydrogen bonds.

The reactions of dithiooxamide with chloromethylsilanes have been shown to give, N,N'-silylsubstituted dithiooxamides, cyclic dithiooxamides and a dithiooximide depending on the reaction conditions used.²²¹ Neutron diffraction data at 15K has been used to refine the crystal structure of thioacetamide. The structure contains two symmetric independent molecules; one rotamer has close to m symmetry with planar S=C-C-N and C-C-NH₂ moieties, in the other the methyl group is twisted by 15.6° and the S=C-C-N and C-C-NH₂ moieties are significantly non planar.²²² The first evidence for the existence of a phosphathioketene has been published. The reaction of R-P(SiMe₃)₂ with thiophosphagene in dioxane was assumed to give the [R-P=C=S] intermediate which on addition of acetonitrile underwent an unsymmetrical [2+2] cycloaddition to form (62).²²³

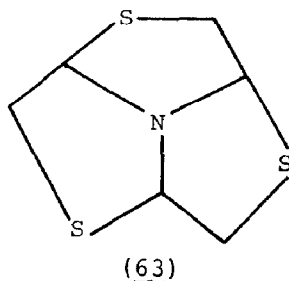


Two papers on the chemistry of trimethylsilylxanthic acid have been published: the first describes the synthesis and properties of trimethylsilylxanthates $M[S_2C-OSiMe_3]$ with $M = Li, Na, K, Rb$ and Cs ,²²⁴ and the second paper describes the preparation of the hitherto unknown S-alkyltrimethylxanthates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

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

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

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

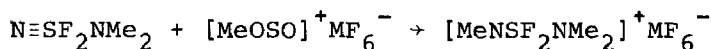


plane defined by the three sulphur atoms. Ab initio calculations and the photoelectron spectrum of the compound were used to give some insight into the electronic nature of this rather unusual molecule.²³¹

The kinetics and mechanism of the decomposition of thionitrites derived from thiourea have been determined by studying the decomposition of $(\text{NMe}_2)_2\text{CSNO}^+$ to $(\text{NMe}_2)_2\text{CSSC}(\text{NMe}_2)_2^{2+} + \text{NO}$.²³² spectrophotometrically.

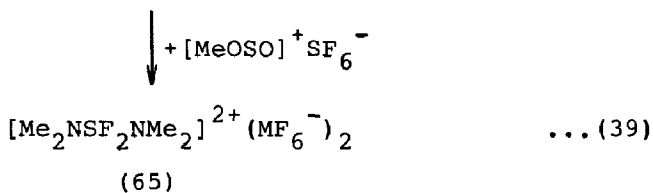
6.2.7 Other Compounds of Sulphur

The synthetic potential of the MeOSO^+ cation is convincingly demonstrated by its ability to alkylate even the monocation in (64) which leads to the salts (66) which contain the dication $[\text{Me}_2\text{N})_2\text{SF}_2]^{2+}$. When $\text{N}=\text{SF}_2-\text{NMe}_2$ and $\text{MeOSO}^+\text{MF}_6^-$ are allowed to react in 1:2 molar ratio in SO_2 (65) is formed in quantitative yield.²³³



(64)

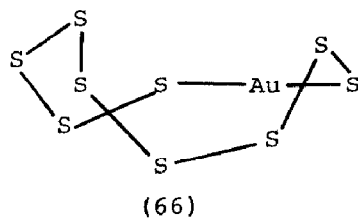
M = As or Sb.



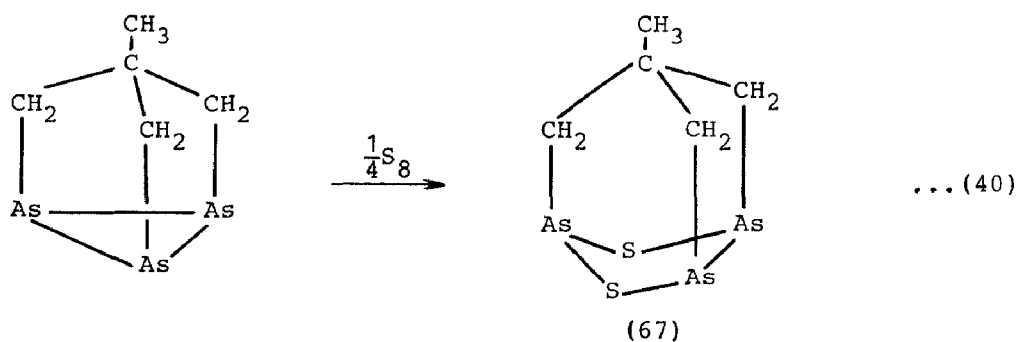
(65)

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

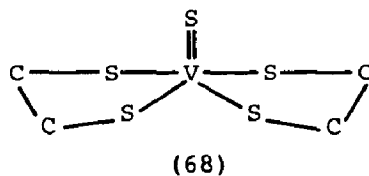
A cyclic nonasulphidoaurate(I), $[\text{Ph}_4\text{As}][\text{AuS}_9]$ is formed as the main product of the reaction of $\text{K}[\text{Au}(\text{SCN})_2]$ with tetraphenylarsonium polysulphide in absolute ethanol. X-ray structure analysis shows the anion to consist of a puckered AuS_9 ring (66) in which a chain of nine sulphur atoms is bound as a chelate ligand to the gold atom. The S-Au-S angle of 176° is consistent with linear coordination and the S-S bond lengths (average = 204.5), Au-S distance 227.1pm correspond to covalent single bonds.²³⁵



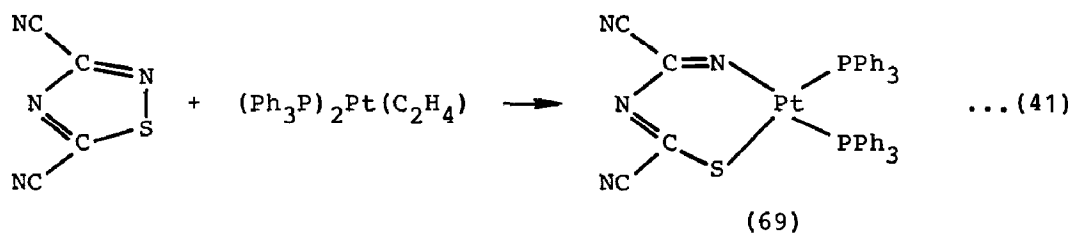
Ab initio and semi empirical CI calculations have been performed on 3,7-dihydro-1,5-dithia-2,4,6,8-tetrazocine and on the corresponding amino compound.²³⁶ The novel 1,4-dithia-2,6-diaza-3,5-diborinane ring system results from the reaction of 3,5-dialkyl (or disec amino)substituted 1,2,4-trithia-3,5-diborolanes with 1,3-disubstituted sulphur diimide by replacement of the disulphane bridge.²³⁷ The melting of $\text{CH}_3\text{C}(\text{CH}_2\text{As})_3$ with elemental sulphur or selenium in the molar ratio of 1:2 results in the formation of the noradamantanes $\text{CH}_3\text{C}(\text{CH}_2\text{As})_3\text{E}_2$ (67).²³⁸



A series of thio-chloro compounds of pentavalent niobium and tungsten have been prepared. WScCl_3 was obtained by the reaction of $(\text{WScCl}_4)_2$ with C_2Cl_4 , with PPh_4Cl in CH_2Cl_2 it yields $(\text{PPh}_4)_2(\text{WScCl}_4)_2$ which has a dimeric structure with chloro bridges. The reaction of PPh_4Cl with NbScCl_3 gives $(\text{PPh}_4)(\text{NbScCl}_4)$ which contains the quadratic pyramidal NbScCl_4^- ion with a $\text{Nb}=\text{S}$ bond length of 209pm.²³⁹ Two vanadium thiolate complexes have been prepared and their structures determined. The anion $[\text{V}(\text{SC}_2\text{H}_4\text{S})_2]^{2-}$ (68) contains vanadium with a strongly distorted square pyramidal coordination with a $\text{V}=\text{S}$ bond length of 2.098Å in the apical position and $\text{V}-\text{S}$ bond lengths to the ligand are 2.348 to 2.386Å.²⁴⁰



The reaction of a Pt(0) complex with a 1,2,4-thiadiazole has been shown to give a six membered metallaheterocycle (69) in which the Pt atom has been inserted into the S-N bond of the thiadiazole.²⁴¹



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

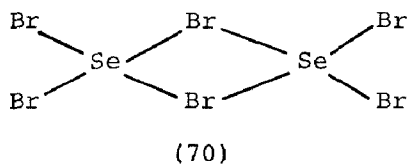
6.3 SELENIUM

6.3.1 Bonds to Halogens

The structures of crystalline SeF_4 and TeF_4 have been determined. In SeF_4 the selenium is bonded to four fluorine atoms so that including the lone pair of electrons a distorted pseudo trigonal bipyramid with longer axial S-F bonds results. In TeF_4 each tellurium atom is bonded to five fluorine atoms (distorted tetragonal pyramid) two of which (cis orientated) bridge a further neighbouring tellurium each.²⁴⁵ The compounds $F_2Se(SeF_5)_2$, $F_2Se(TeF_5)_2$ and $F_2Te(TeF_5)_2$ have been prepared and their structures investigated by n.m.r. spectroscopy. All three compounds have pseudo trigonal bipyramidal structures with axial $-SeF_5$ ($-TeF_5$) ligands with the fluorine ligands in equatorial positions in accordance with electronegativity arguments. $F_2Te(TeF_5)_2$ reacts further with $FOTeF_5$ to give $mer-F_3Te(TeF_5)_3$ but no $fac-(F_3Te(TeF_5)_3)_3$.²⁴⁶

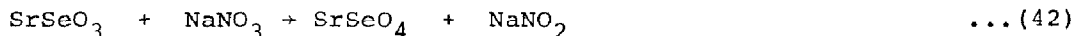
The novel anion $SeBr_4^{2-}$ has been prepared by dissociation of

SeBr_2 and subsequent reaction with bromide in acetonitrile solution. X-ray structure determination of the tetraphenyl phosphonium salt shows the salt to contain monomeric SeBr_4^{2-} anions with square planar coordination of SeII and a mean bond length Se-Br of 2.598Å. $(\text{PPh}_4)_2\text{Se}_2\text{Br}_6$ was obtained from the reaction of SeBr_4 and Br^- in acetonitrile. The compound contains a novel type of centrosymmetric $\text{Se}_2\text{Br}_6^{2-}$ ions again with square planar coordination of the selenium (70). The mean terminal and bridging Se-Br bond lengths are 2.442 and 2.799Å respectively.²⁴⁷



6.3.2 Bonds to Oxygen

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



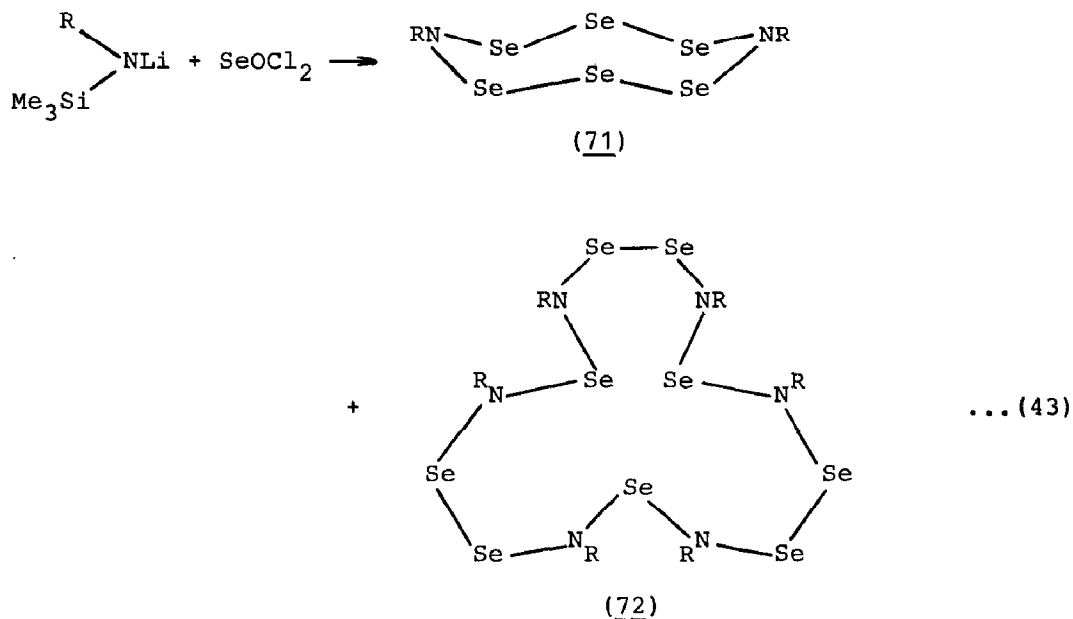
A crystal structure determination showed the compound to be ionic with SeO_4 tetrahedra with a mean Se-O distance of 1.647Å and nine coordinated Sr^{2+} ions.²⁴⁸ Solubility isotherms in the $\text{CuSeO}_4\text{-H}_2\text{SeO}_4\text{-H}_2\text{O}$ system have been studied at 25 and 100°C. The dehydration of $\text{CuSeO}_4 \cdot 5\text{H}_2\text{O}$ and the thermal dissociation of $\text{CuSeO}_4 \cdot \text{H}_2\text{O}$ were described.²⁴⁹ The following selenate phase systems have been studied; $\text{ZnSeO}_4\text{-H}_2\text{SeO}_4\text{-H}_2\text{O}$,²⁵⁰ $\text{MgSeO}_4\text{-UO}_2\text{SeO}_4\text{-H}_2\text{O}$ ²⁵¹ and $\text{Nd}_2(\text{SeO}_4)_3\text{-Sm}_2(\text{SeO}_4)_3\text{-H}_2\text{O}$.²⁵² H_2SeO_4 or H_2TeO_4 have been used to enhance the activity of ZrO_2 catalysts. $\text{Zr}(\text{OH})_4$ was exposed to 0.05M H_2SeO_4 or H_2TeO_4 followed by calcination in air at 600-800°C. The resulting dehydrogenation catalyst converted propan-2-ol into acetone with 100% selectivity.²⁵³

6.3.3 Bonds to Nitrogen

The previously unknown $\text{F}_5\text{Se-N=C=O}$ has been prepared from $\text{Xe}(\text{OSeF}_5)_2$ and HCN . Compared with that of $\text{F}_5\text{S-N=C=O}$ the isocyanate reactivity is reduced in $\text{F}_5\text{Te-N=C=O}$ and even more in $\text{F}_5\text{Se-N=C=O}$.²⁵⁴

Diselenium dichloride and seleninylchloride react with the

lithium salt of silylated tert-butylamine with the elimination of LiCl and Me₃SiCl or LiCl, Me₃SiCl and (Me₃Si)₂O respectively to form the cyclic compounds hexaselenadiazocin (71) and nonaselena-hexaazacyclopentadecane (72).



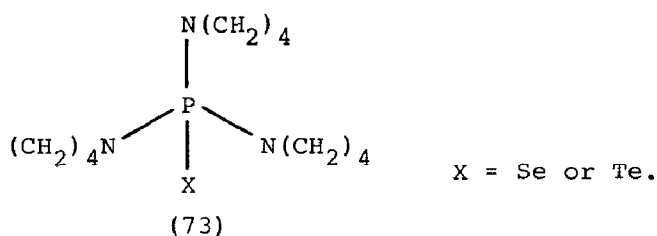
The conformation of the N₂Se₆ ring in (71) is similar to that of the eight membered ring of the sulphur molecule and has the bond lengths S-N 183.0, Se-Se 233.5pm and angles N-Se-Se 110.0°, Se-N-Se 114.8° and Se-Se-Se 108.8°. ²⁵⁵

6.3.4 Selenides

The crystal structure of (LaO)GaSe₂ has been shown to comprise alternating (LaO) and (GaSe₂) layers thus resembling the structure of (CaO)₄Ga₂S₅ and being very different from LaGaOS₂. ²⁵⁶

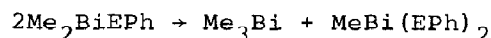
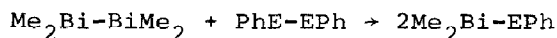
The thermal stabilities of the selenides of the elements of groups IV and V have been determined from a study of the curvature of the liquidus at the melting point. ²⁵⁷ The new compounds K₆Ge₂Se₆ and K₆Ge₂S₆ have been shown to crystallise in the monoclinic system and to be isotypic with the K₆Si₂Te₆ structure. ²⁵⁸ Na₆Ge₂Te₆ however has the K₆Sn₂Te₆ structure. The problems of the directed synthesis of solid solutions based on lead selenide and telluride which are promising opto-electronic materials have been considered by studying the P - T - x - y

diagram of the Pb-Se-Te system. The conditions required for the growth of crystals from the vapour were determined and the composition of hetero structures based on lead and tin chalcogenides were studied by Auger-electron spectroscopy.²⁵⁹ The structures of the compounds $[(CH_2)_4N]_3PSe$ and $[(CH_2)_4N]_3OTe$ have been determined. In both compounds (73) there is disorder in one or more of the five membered rings but this did not cause any ambiguity with regard to the torsion angles about the P-N bonds. The P-Se bond length was found to be 2.105 and 2.107Å for the two non equivalent molecules of the Se compound and 2.355Å for the Te compound.²⁶⁰



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

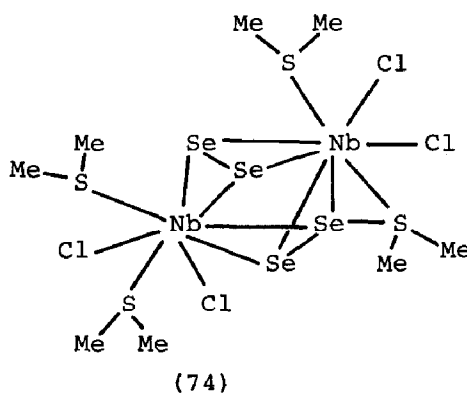
Dimethyl(phenylchalcogeno)bismuthanes with the general formula Me_2BiEPh ($E = S, Se$ and Te) have been synthesised by the reactions of tetramethyldibismuthane and diphenyldichalcogenides. These thermolabile compounds are the first molecules with a Bi-Se or Bi-Te bond and react with increasing rate in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



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

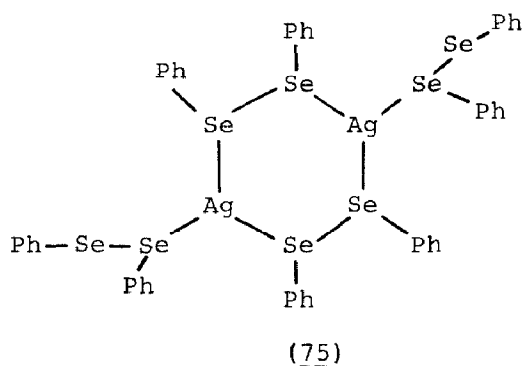
CuCrSnSe_4 have been grown by chemical transport using mixtures of AlCl_3 and I_2 as transporting agents. The compounds were both found to be normal spinels.²⁶⁵

On the basis of a crystal structure determination, the selenide V_2Se_9 can be described as a pseudo one-dimensional compound characterised by infinite $(\text{V}_2\text{Se}_9)_x$ chains. No bonding was thought to be possible between the atoms in different chains.²⁶⁶ Tight binding calculations have been performed on various MSe_4 chains (as present in $(\text{MSe}_4)\text{I}$, $\text{M} = \text{Nb}, \text{Ta}$) to probe how one-dimensional phenomena such as Peierls distortion and charge density wave formation are affected by band filling. It is found that the d_{z^2} band of an MSe_4 chain is well separated from other bands and the effect of interchain $\text{Se} \cdots \text{Se}$ interactions upon the d_{z^2} band is only appreciable for certain wave vectors.²⁶⁷ The reactions of NbCl_3Se with some sulphur donor ligands and the reaction of NbBr_3Se with tetrahydrothiophen under moisture- and oxygen-free conditions have been described. The crystal structure of the niobium compound $[(\text{dms})_2\text{Cl}_2\text{Nb}(\text{Se}_2)_2\text{NbCl}_2(\text{dms})_2]$ ($\text{dms} = \text{dimethyl sulphide}$) showed it to contain centrosymmetric dimers (74) in which each niobium atom is bonded to two chlorine atoms ($\text{Nb}-\text{Cl} = 2.527, 2.510\text{\AA}$) four selenium atoms in two bridging Se_2^{2-} groups ($\text{Nb}-\text{Se} = 2.638, 2.630, 2.640, 2.625\text{\AA}$) and two sulphur groups from the $(\text{CH}_3)_2\text{S}$ group ($\text{Nb}-\text{S} = 2.739\text{\AA}$).²⁶⁸



The reaction of Ph_2Se_2 with AgAsF_6 in liquid SO_2 leads to the formation of $[\text{Ag}_2(\text{Ph}_2\text{Se}_2)_4][\text{AsF}_6]_2$ which is isostructural with the corresponding sulphur compound. The structure of the compound (75) shows a centrosymmetric six membered ring in which two silver atoms are connected by bridging Ph_2Se_2 ligands and further

unidentate Se ligands complete the irregular three coordination at silver.²⁶⁹



Thin films of CdSe with a surface area of 1cm^2 , electrodeposited from sulphate solutions onto titanium plates have been shown to give light power conversion efficiencies between 5 and 5.5%.²⁷⁰

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

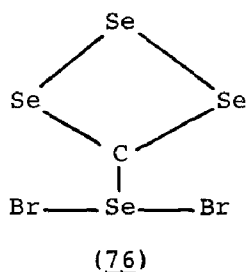
Table 3. Selenide Phase Systems.

System	Ref	System	Ref
$\text{Eu}_{1.2}\text{Mo}_6\text{S}_8\text{-Eu}_{1.2}\text{Mo}_6\text{Se}_8$	272	Yb-Sn-Se	277
$\text{LaMo}_6\text{Se}_8\text{-EuMo}_6\text{Se}_8$	272	$\text{CdSe-La}_2\text{Se}_3$	278
$\text{Ag}_2\text{Se}_{0.5}\text{Te}_{0.5}\text{-Ag}_2\text{S}$	273	$\text{As}_2\text{Se}_3\text{-CoSe, Sb}_2\text{Se}_3\text{-CoSe}$	279
$\text{Ag}_2\text{S}_{0.5}\text{Te}_{0.5}\text{-Ag}_2\text{Se}$	273	$\text{As}_2\text{Se}_3\text{-YbSe}$	280
$\text{Bi}_2\text{Se}_3\text{-FeSe}$	274	$\text{Cu}_2\text{Se-Pr}_2\text{Se}_3$	281
$\text{Cu}_2\text{GeSe}_3\text{-CdSe}$	275	$\text{GeSe}_2\text{-CoSe}$	282
$\text{SnSe-Fe (Co, Ni) Se}$	276	PbTe-TlSe	283
		PbTe-InSe	284

6.3.5 Bonds to Carbon

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

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

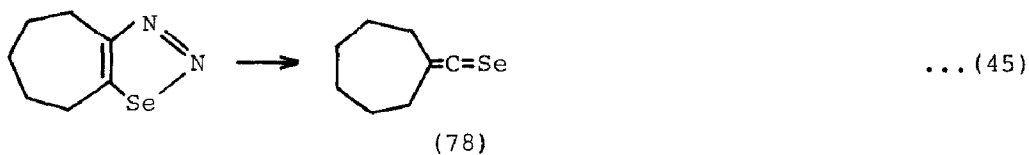
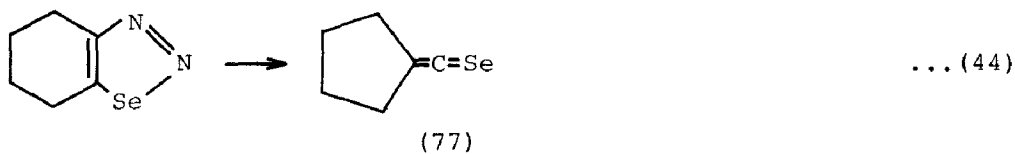


The kinetics of the formation of CBr_2Se_4 indicate that Se_2Br_2 is converted by bromide ion into a bromodiselenide ion which attacks CSe_2 in the rate determining step. The different surroundings for the two Br atoms and the preferred directions of crystal growth suggest that the crystal is formed from $\text{CBrSe}_4^+\text{Br}^-$ ion pairs.²⁸⁷

Fluorination of CF_3SeCl with AgF leads to $\text{CF}_3\text{Se}(\text{O})\text{OH}$ and

$\text{CF}_3\text{SeSeCF}_3$ after reactions of the primary products with glass. Condensation of $(\text{CF}_3\text{S})_2\text{NH}$ and $(\text{Me}_3\text{Si})_2\text{NH}$ with CF_3SeCl gave $\text{CF}_3\text{SeN}(\text{SCF}_3)_2$ and $(\text{Me}_3\text{Si})_2\text{NSeCF}_3$, $(\text{CF}_3\text{Se})_2\text{NSiMe}_3$, $\text{CF}_3\text{SeN}(\text{H})\text{SiMe}_3$ respectively. The reaction of $\text{FC}(\text{O})\text{SCl}$ with $\text{Hg}(\text{SeCF}_3)_2$ gave beside $\text{FC}(\text{O})\text{SSeCF}_3$ also $\text{CF}_3\text{SeSSeCF}_3$. When a mixture of $(\text{CF}_3\text{Se})_2\text{NH}$ with $\text{Cl}_3\text{S}_3\text{N}_3$ is heated to 500°C $\text{CF}_3\text{SeN}=\text{S}=\text{NSeCF}_3$ is formed.²⁸⁸

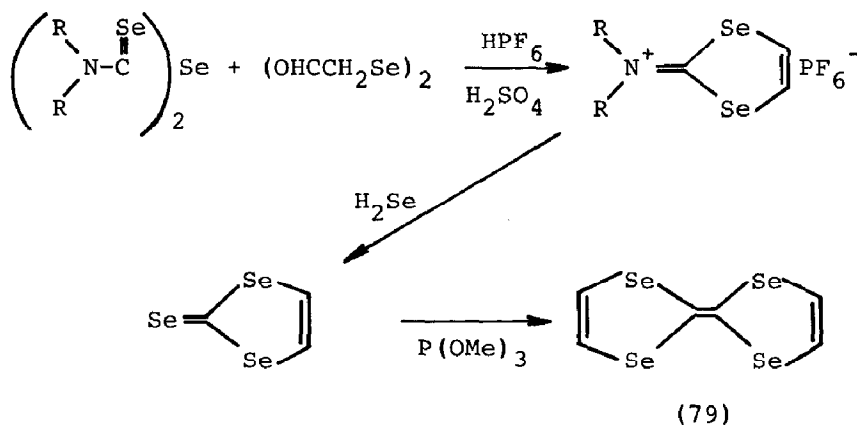
Three papers have been published describing the preparation of dialkyl esters of chalcogenocarbonic acids. The first describes the preparation of O,Se-dialkyl mono-selenocarbonates, $\text{RSe-CO-OR}'$;²⁸⁹ the second the preparation of O,Se- and S,Se-dialkyl mono-thio-mono-selenocarbonates,²⁹⁰ and the third paper the preparation of S,Se-dialkyldithio-monoselenocarbonates and evidence for the existence of alkylselenoxanthates $[\text{S}_2\text{C-SeR}]^-$.²⁹¹ The same group have also described the synthesis and properties of Se-alkyl esters of chloromonothiomonoselenoformic acid, RSe-Cs-Cl .²⁹² The gas phase pyrolysis of cyclohexeno-1,2,3-selenadiazole and cycloocteno-1,2,3-selenadiazole has been investigated by variable temperature p.e.s. and matrix i.r. spectroscopy. The ring contracted, highly reactive products, cyclopentylidenselenoketene, (77), and cycloheptylidenselenoketene, (78), which had not been found in liquid phase thermolysis experiments have been detected.²⁹³



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

while trans arrangements give rise to much smaller values (10-25Hz).²⁹⁴

A high yield synthesis of tetraselenafulvalene (79) involving a novel catalysed exchange reaction between diselenide and bis(N,N-dialkylselenocarbamoyl)selenides has been reported and is shown in Scheme 14.²⁹⁵

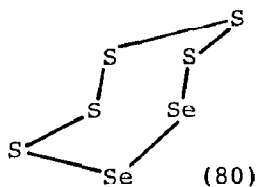


Scheme 14

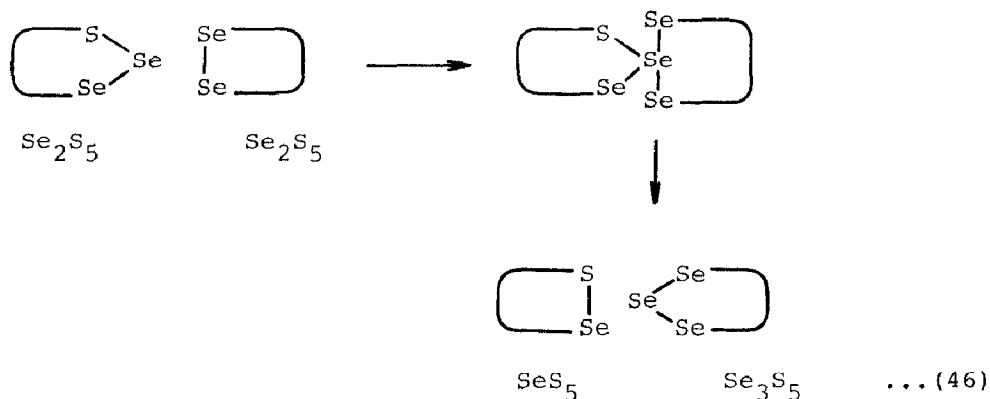
The thermal reaction of some metal(II) thioselenocarbamate complexes to form mixed ligand chelates has been studied by e.p.r. and mass spectrometric methods.²⁹⁶ Crystal structures have been published for the following compounds $C_5H_{11}NO_2Se$,²⁹⁷ $C_{12}H_{10}Cl_2O_2Se$,²⁹⁸ $C_{20}H_{24}Se_8^+ReO_4^-$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

6.3.6 Other Compounds Containing Selenium

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



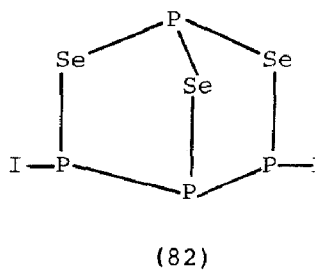
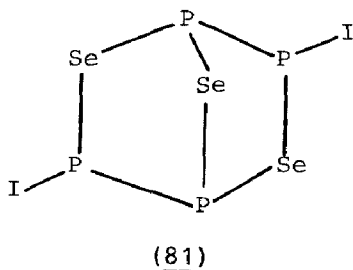
The formation of SeS_5 and $1,2,3\text{-Se}_3\text{S}_5$ from $1,2\text{-Se}_2\text{S}_5$ can be accounted for by the reaction mechanism shown in Scheme 15, in which a spirocyclic intermediate, structurally related to SeF_4 is postulated. This species forms by insertion of a Se atom into the reactive SeSe bond of a second molecule and subsequent decomposition to SeS_5 and Se_3S_5 .³⁰¹



Scheme 15

The molecular and crystal structures of the norheteroadamantanes $\text{CH}_3\text{C}(\text{CH}_2\text{As})_3[\text{C}(\text{COOCH}_2\text{CH}_3)_2]_2$ and $\text{CH}_3\text{C}(\text{CH}_2\text{As})_3\text{Se}_2$ have been determined, attempts to prepare $\text{CH}_3\text{C}(\text{CH}_2\text{As})_3\text{Te}_2$ were not successful.³⁰²

The aluminium chalcogenide halides AlSeX and AlSX ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) have been prepared and a tentative structural characterisation made on the basis of their vibrational spectra. Both compounds are thought to have a dimeric structure with planar four membered Al_2Se_2 or Al_2S_2 rings and short "terminal" Al-X bonds.³⁰³ $\alpha^1\text{-P}_4\text{Se}_3\text{I}_2$ and $\alpha^1\text{-P}_4\text{S}_3\text{I}_2$ have been prepared by the reaction of P_4Se_3 (P_4S_3) with I_2 in the molten state. The structure of the α isomer (81) of $\text{P}_4\text{Se}_3\text{I}_2$ is compared with the previously known β isomer (82) below.³⁰⁴



The crystal structures of bis(diethyldithiophosphato)-selenium(II)³⁰⁵ and tris(m-trifluoromethylphenyl)phosphine selenide³⁰⁶ have been determined.

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

6.4 TELLURIUM

6.4.1 The Element

Te₃ molecules have been made in a matrix reaction by condensing a mixture of 76% Te atoms and 24% Te₂ molecules in a nitrogen matrix at 15K followed by annealing at 25K. The Resonance Raman spectrum of Te₃ contained 8 overtones of the symmetrical stretching vibration and using a 1:1 mixture of ¹²⁶Te and ¹³⁰Te the bond shape of the envelopes of the superimposed spectra of all possible Te₃ species could only be explained by assuming a bent structure with an angle of 120°±10°. Force constant data was considered to reflect multiple bonding in the structure of the molecule.³⁰⁸ A ¹²⁵Te and ⁷⁷Se n.m.r. study has been carried out on the Te₂Se₆²⁺ cation. The solid state structure of Te₂Se₆²⁺ has been determined from the compound (Te₂Se₆)(Te₂Se₈)(AsF₆)₄(SO₂)₂ and is derived from a cube with the two tellurium atoms at opposite corners. Thus both the tellurium atoms are equivalent as are the six selenium atoms. The n.m.r. spectra confirmed that the solid state structure is retained in solution.³⁰⁹

6.4.2 Bonds to Halogens

A new and improved synthesis of TeF₅OF by means of the reaction

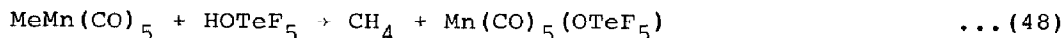


gives an 80-95% yield at 100 to 115°C after 1-3 days. Since commercial F₂ is the fluorinating agent, the need for synthesising the hazardous FOSO₂F (as required for the previous method of synthesis) is eliminated. The authors believe this preparation of TeF₅OF is the first example of the formation of a hypofluorite involving the fluorinative scission of a boron-oxygen bond.³¹⁰

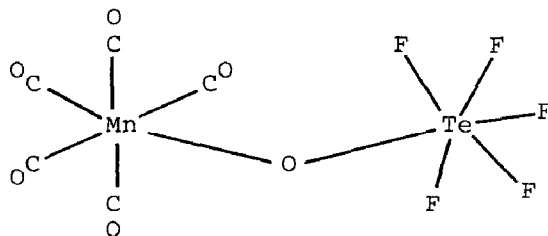
The reaction of TeClF_5 with MeOH and MeOSiMe_3 has been shown to lead to a mixture of *cis* and *trans* $(\text{MeO})\text{TeClF}_4$ in a ratio of 1:6 as well as some unidentified Te(IV) product. The vibrational spectrum of the mixture of isomers was accounted for on the basis of the predominant pseudo C_{4v} *trans* isomers. TeClF_5 is unreactive towards anhydrous HF , SbF_5 , AlCl_3 , SO_2 , F_2 and ClF at room temperature, but over the temperature range $70\text{--}250^\circ\text{C}$ it decomposes to TeF_6 , TeF_4 and Cl_2 . It slowly reacts with CsF to form CsTeF_5 , TeF_6 , Cl_2 and small amounts of ClF and with HNMe_2 it is also reduced to form $\text{TeF}_4\cdot\text{HNMe}_2$.³¹¹

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

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



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



(83)

A series of mixed fluoro/penta fluoroorthotellurate, (OTeF_5) derivative of Xe(VI) oxyfluorides, XeOF_4 and XeO_2F_2 as well as those of XeF_4 have been prepared. The compound $\text{O}_2\text{Xe}(\text{OTeF}_5)_2$ was prepared for the first time along with the previously reported $\text{Xe}(\text{OTeF}_5)_4$ and $\text{XeO}(\text{OTeF}_5)_4$.³¹⁵

6.4.3 Bonds to Oxygen

The solid state reaction between TeO_2 and SeO_2 in inert atmosphere has been shown to produce $\alpha\text{-TeSeO}_4$ at 300°C . The compound is stable at room temperature under anhydrous conditions but decomposes above 320°C . In the system $\text{TeO}_2\text{-SeO}_2\text{-H}_2\text{O}$ hydrated mixed oxides are formed with $3\text{TeO}_2\cdot\text{SeO}_2\cdot n\text{H}_2\text{O}$ being identified.³¹⁶ The crystal structures of $\text{MgTeO}_3\cdot 6\text{H}_2\text{O}$ and $\text{MgSeO}_3\cdot 6\text{H}_2\text{O}$ have been determined. Both are isomorphous with $\text{MgSO}_3\cdot 6\text{H}_2\text{O}$ and have the following bond lengths and angles; Te-O 1.859, Se-O 1.697Å; O-Te-O 98.6° and O-Se-O 101.4° .³¹⁷ The reactions of the components in the $\text{NdCl}_3\text{-TeO}_2$ and $\text{YCl}_3\text{-TeO}_2$ system have been studied. $\text{TeNd}_2\text{O}_2\text{Cl}$ which melts congruently at 720°C is formed in the $\text{NdCl}_3\text{-TeO}_2$ system.³¹⁸

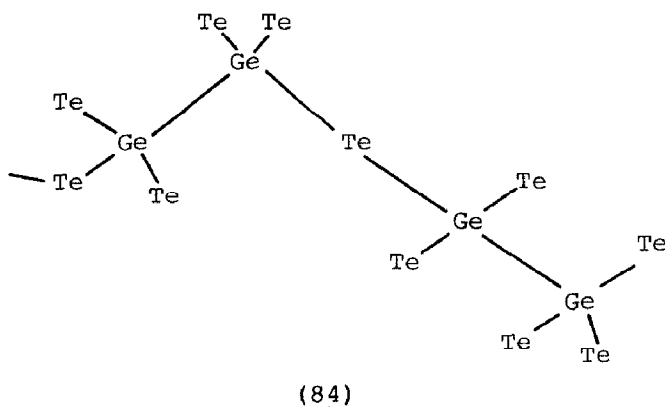
The oxygen exchange reaction between arsenate ions and water is catalysed by the addition of a small amount of tellurate ions. The catalytic process was interpreted in terms of the reversible condensation of arsenate ions with tellurate ions to form the arsenatotellurate ion.³¹⁹ In studying Li, Na and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

The structure of the adduct of orthotelluric acid and potassium iodate, $\text{Te}(\text{OH})_6\cdot\text{KIO}_3$, contains orthotelluric acid molecules and iodate anions connected by hydrogen bonds to form a three dimensional network. The orthotelluric acid is in a slightly distorted octahedral arrangement and the iodate ion is a trigonal pyramid.³²¹ Slightly distorted $\text{Te}(\text{OH})_6$ octahedra, with the Te atom placed at the centre of symmetry are also observed in the structure of telluric acid-glycine monohydrate, $\text{Te}(\text{OH})_6\cdot 2\text{C}_2\text{H}_5\text{NO}_2\cdot\text{H}_2\text{O}$. The Te-OH distances range from 1.905 to 1.929Å and in addition each glycine group is linked through hydrogen bonds such as $\text{Te-OH}\cdots\text{O-C}$ to either one or two corners of the $\text{Te}(\text{OH})_6$ octahedra.³²² The following phase systems have been studied: $\text{Li}_2\text{O-MoO}_3\text{-TeO}_2$,³²³ $\text{PbCl}_2\text{-MoO}_3\text{-TeO}_2$ ³²⁴ and $\text{Bi}_2\text{O}_3\text{-Bi}_2\text{I}_3\text{-}$

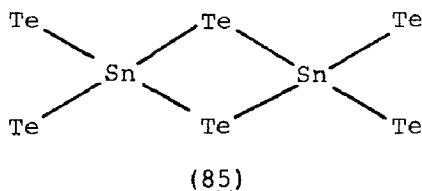
TeO₂.³²⁵

6.4.4 Tellurides

The first binary alkaline earth polytelluride, BaTe₃ which crystallises in the tetragonal system (space group P4̄2m) is isotypic with BaS₃ and BaSe₃ and contains the bent Te₃ anion.³²⁶ The new compound Ba₂Ge₂Te₅ contains distorted Ge₂Te₆ trigonal prisms connected by common corners to form infinite chains (84).



The Ge-Te-Ge bridging distances are 264.4 and 259.2 and 260.6pm.³²⁷ The reaction of KSn with Te at high temperature gives the congruently melting K₄SnTe and Sn. Depending on the cation and solvent used, a variety of products can be isolated from solutions of SnTe₄⁴⁻, including Te₄²⁻ and Sn₂Te₆⁴⁻. The compound (Me₄N)₄Sn₂Te₆ was structurally characterised and was found to be isostructural with B₂H₆ and to possess the ditinhexatelluride ion (85) with terminal Sn-Te distances of 2.700 and 2.689Å and



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

A new, potentially general method for the preparation of novel, amorphous materials based on the oxidation of main group polyanions by transition metal cations in solution, has been

described. Using this method the compounds M_2SnTe_4 ($M = Cr, Mn, Fe$ or Co) have been prepared from M^{2+} and $SnTe_4^{4-}$. When solutions of $FeBr_2$ and K_4SnTe_4 in methanol are mixed at $-20^\circ C$ a black precipitate of composition Fe_2SnTe_4 immediately forms. Fe_2SnTe_4 has a metallic appearance, with a low electrical resistivity and decomposes at $600^\circ C$ according to equation (49).



Raman spectra suggest that the $SnTe_4$ tetrahedral unit is structurally intact in amorphous Fe_2SnTe_4 .³²⁹ Transition metal tetratelluride chains MTe_4 ($M = Nb, Ta$) adopt a structure different from that of other tetrachalcogenide chains. Tight-binding calculations on $NbTe_4$ show that multidimensional character is substantially stronger in $NbTe_4$ than in $(MSe_4)_n$.¹ The band electronic structure of $NbTe_4$ is consistent with the view that in $NbTe_4$, each metal ion Nb^{4+} is surrounded by eight Te_2^{2-} dimers.³³⁰

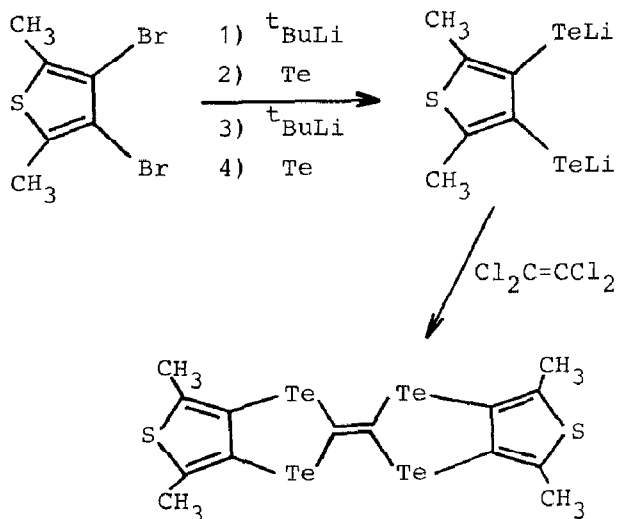
Several studies of telluride phase systems have been carried out and these are collected in Table 4.

Table 4. Telluride Phase Systems.

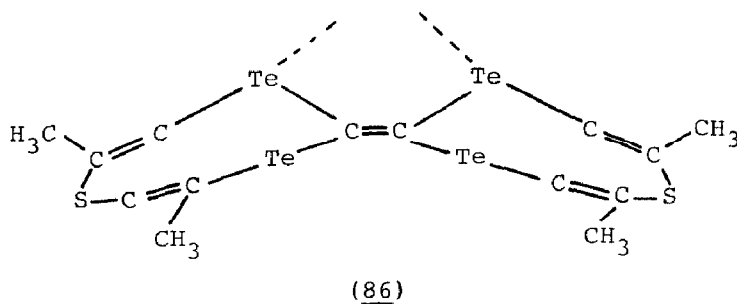
System	Ref	System	Ref
Dy-Bi-Te	331	Cd-Bi-Te	336
SnTe-FeSe	332	Ga-Fe-Te	337
Sb_2Te_3 -GdTe and Sb_2Te_3 -TbTe	333	$Hg_{1-x}Cd_xTe$ - HgI_2 -CdTe	338
Yb-Ga-Te	334	Cu-Cu ₂ Te-Ag ₂ Te-Ag	339
Zn-Bi-Te	335		

6.4.5 Bonds to Carbon

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



... (50)

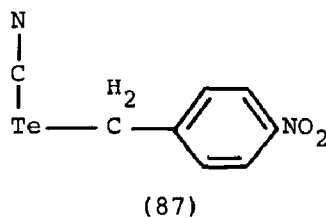


thienoditellural planes are dramatically different at 47.1 and 16.0°. Some of the deviations are thought to be due to the presence in the solid of dimers which are coupled together through short intermolecular Te...Te contacts at 3.666 and 3.758 Å, the former of which is somewhat shorter than twice the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

The crystal structure of $[\text{Te}(\text{Ph})_3]^+[\text{Hg}_2\text{Cl}_6]^{2-}$ contains trigonal pyramidal Ph_3Te^+ cations and chloro-bridged dimeric $\text{Hg}_2\text{Cl}_6^{2-}$

anions which consist of two distorted HgCl_4 tetrahedra sharing an edge; interionic $\text{Te}\dots\text{Cl}$ interactions complete a distorted octahedral geometry at Te .³⁴² A structure determination of a new form of bis(p-chlorophenyl)ditelluride, $\text{C}_{12}\text{H}_8\text{Cl}_2\text{Te}_2$, shows the $\text{Te}-\text{Te}$ bond length of 2.680 to be shorter than the values reported for diphenylditellurides in earlier investigations. The molecular geometries observed in diphenyl ditellurides appear to be dependent on the packing modes alone.³⁴³

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

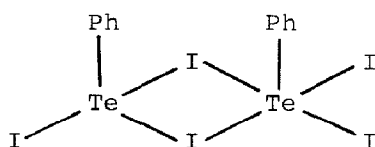


A range of organotellurium(II) compounds together with two selenium compounds have been used as donors to form donor-acceptor complexes with tcnq . Generally the stoichiometry is 1:1 but two ditellurides provide an exception in giving $\text{R}_2\text{Te}_2 \cdot 2\text{tcnq}$ ($\text{R} = \text{Ph}$ or $\text{C}_6\text{H}_4\text{OEt-p}$).³⁴⁵ The structure of the 1:1 adduct of $\text{C}_{10}\text{H}_8\text{I}_2\text{N}_2\text{Te}$ with $\text{C}_{10}\text{H}_8\text{I}_2\text{N}_2$ consists of discrete molecules with a pair of each being linked into centrosymmetric dimers by weak $\text{Te}\dots\text{I}$ linkage. The coordination about Te is a distorted octahedron with two $\text{Te}-\text{C}$ bonds (2.14Å), two axial $\text{Te}-\text{I}$ bonds (2.886, 2.911Å) and two longer equatorial $\text{Te}-\text{I}$ bonds trans to $\text{Te}-\text{C}$ (3.761, 3.788Å), the longer contact being to an iodine of the organic diiodide.³⁴⁶

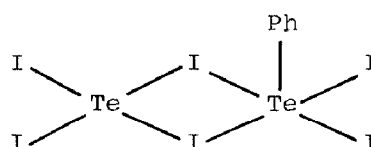
The oxidative addition of diaryl ditellurides to $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$ in toluene solution has been followed by visible spectrophotometry. An i.r. spectroscopic study of the reaction in CCl_4 shows the relatively rapid formation of an adduct before the final stages of the process occur. A mechanism is suggested which involves the initial addition of ditelluride to $\text{Ir}(\text{I})$, followed by homolytic cleavage of the $\text{Te}-\text{Te}$ bond and formation of the final trans

product.³⁴⁷ A similar mechanism involving the homolytic cleavage of a Te-Te bond to produce RTe radicals and a subsequent chain reaction involving alcohol has been proposed to account for the observation that when toluene solutions containing alcohol and R_2Te_2 ($R = p$ -ethoxyphenyl) are irradiated near the visible absorption maximum of the ditelluride, the colour of the solution gradually disappears.³⁴⁸

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



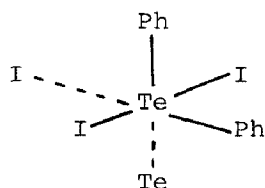
(88)



Ph

(89)

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



(90)

The crystal structures of $(p\text{-MeOC}_6\text{H}_4)_2\text{Te}(\text{O}_2\text{CMe})_2$, $[\text{Ph}_2\text{Te}(\text{O}_2\text{CCF}_3)]_2 \cdot \text{H}_2\text{O}$ and $\text{PhI}(\text{O}_2\text{CCF}_3)_2$ all have pseudo trigonal bipyramidal geometry and form secondary bonds to give pentagonal planar systems around Te and I.³⁵⁰

6.4.6 Other Compounds of Tellurium

Crystal structures have been published for the compounds bis(diethyldithiophosphato)tellurium(II) which contains a P-S-Te-S-P chain;³⁵¹ $(\text{Ph}_4\text{P})_2\text{Te}_4 \cdot 2\text{MeOH}$ which contains a tetratelluride 2-anion with MeOH molecules hydrogen bonded to each end;³⁵² $\text{C}_2\text{H}_2\text{N}_2\text{Te}$ which is a heterocycle containing N-Te-N bonds³⁵³ and $\text{C}_{20}\text{H}_{40}\text{N}_4\text{O}_8\text{S}_8\text{Te}$ which has the central tellurium atom bonded to all eight sulphur atoms in a highly distorted dodecahedral configuration.³⁵⁴

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