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Chapter 6

ELEMENTS OF GROUP 6

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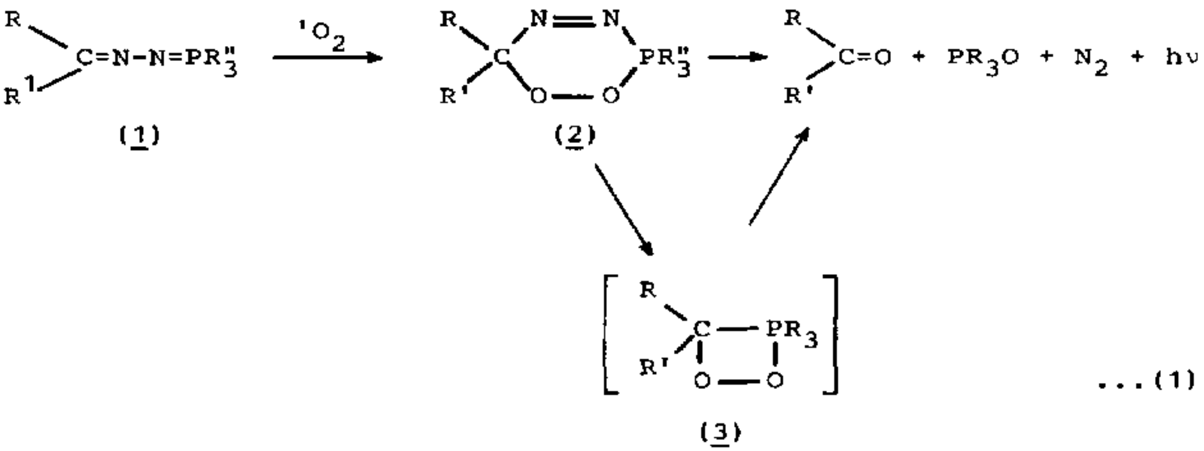
6.1 OXYGEN

The 1.27μm emission of O_2 ($^1\Delta_g$) has been used to gain evidence for the formation of singlet oxygen in the gas phase reactions of ozone with a variety of organic substrates. These reactions are characterized by the transfer of one oxygen atom from ozone to the oxidised substrate concurrent with singlet oxygen production.[1] Kinetic parameters have been reported for the trapping of singlet oxygen by anthracene-9,10-bis(ethanesulphonate) (aes) in water and deuterium oxide solutions, and the formation of singlet oxygen from hydrogen peroxide with a variety of two-electron donors. Using aes as a trap it was shown that both chloramine-T and N-chlorosuccinamide react with H_2O_2 to produce singlet oxygen in essentially quantitative yields. Iodylbenzene reacts with H_2O_2 to give, in the rate determining step, iodosylbenzene and oxygen and then iodobenzene and oxygen; 47% of the oxygen produced being in the singlet state. Periodate and H_2O_2 however give lower yields of singlet oxygen, and it was thought two concomitant processes are involved.[2] The decomposition of H_2O_2 in alkaline solution in the presence of the chelating agent N,N,N',N",N"-penta(methylphosphonic acid) was found to have the slowest rate yet reported but it was thought that this still represents a catalyzed reaction. When the reaction was carried out with aes as a trapping agent, small but significant amounts of singlet oxygen were observed. The decomposition of H_2O_2 in the presence of halide ions was also studied.[3] The possibility of singlet oxygen being produced in the decomposition of H_2O_2 by mineral compounds in aqueous basic solutions has been examined and several compounds have been shown to lead to its production.[4] The decomposition of the peroxyacids peroxyacetic acid, peroxy monosulphuric acid and monoperoxy phthalic acid in aqueous solution at pH values close to the pK_a of the acids has been shown to yield singlet oxygen in essentially quantitative yields when precautions are taken to eliminate metal ion catalysis. It was concluded that the reactions of H_2O_2 with peroxy-acid anions are extremely sensitive to catalysis, probably by transition-metal ions.[5] Three water-soluble square-planar nickel complexes have been investigated as quenchers of singlet oxygen in aqueous solution using aes as a trap. Disodium[NN'-ethylenebis(5-sulphosalicylideneiminato)]nickelate(II) and its propylene analogue were found to be efficient quenchers but the efficiency of the phenylene analogue was much less and seems to be concentration dependent.[6] A series of methyl substituted poly(vinylnaphthalenes), prepared by radical polymerization of the corresponding vinylnaphthalenes have been shown to bind and release singlet oxygen reversibly at temperatures between 0 and 35°C.[7]

Singlet oxygen has been found to degrade vitamin B_{12} to form a secocobamide. This reaction is of interest because of the medicinal and biological role played by singlet oxygen and provides a simple entry to secocorrinoid cleavage products of vitamin B_{12}.[8] High field ^{31}P n.m.r. spectroscopy has been used for the first time to detect 3-phospha-1,2-dioxa-4,5-diazine (2) and its thermal decomposition product (3) which are formed in the reaction of singlet oxygen with the phosphazine (1).[9]



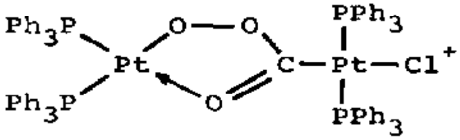
...(1)

The quantitative generation of singlet dioxygen by the reaction of tris(bipyridine)ruthenium(III) with superoxide ion in aqueous solution has been reported. Also described were a useful photochemical method for the aqueous generation of superoxide ion and the kinetics of its oxidation by $Ru(bpy)_3^{3+}$ as a function of pH.[10]

A series of polytungstate anions $[XW_{12}O_{40}]^{n-}$ with X = P, Si, Fe, Co, or H_2 and n = 3, 4, 5, 6 and 6 respectively, spanning a range of reduction potentials, have been studied as sensitizers for the photoreduction of water and oxygen. The silicon tungstate anion was found to be the most efficient sensitizer for hydrogen evolution in the presence of colloidal platinum. The maximum rate was found to depend on competition between the natural decay of the excited polyanion and quenching by alcohol.[11]

The reaction of dioxygen and carbon monoxide is slow in the absence of catalysts, studies of the reaction of CO and O_2 on Pt/SiO_2 led to a proposal of a multimetal atom mechanism involving the dissociative adsorption of O_2 and subsequent reaction with coordinated CO. A new study has now provided evidence for a bimetallic-modulated pathway for the reaction of CO and O_2: dioxygen complexes such as $Pt(PPh_3)_2O_2$ have been shown to react with metal carbonyl complexes which are susceptible to nucleophilic attack to form a cyclo peroxy carbonyl (4) which subsequently decomposes to form CO_2.[12]

$(PPh_3)_2PtO_2$ + $[PtCO(PPh_3)_2Cl]^+$ →



(4)

...(2)

The gas phase equilibrium involving the reaction of methyl radicals with molecular oxygen to form methylperoxy radicals has been studied at seven temperatures between 421 and 538°C. The enthalpy change for the reaction

$$CH_3 + O_2 \rightarrow CH_3O_2 \qquad ...(3)$$

was obtained from the measured equilibrium constant by both Second and Third Law methods, the values being -30.9 and -32.4 kcal mol^{-1} respectively.[13] The gas phase ion-molecule reactions of dioxygen anion radical, $O_2^{\overline{\cdot}}$, with a variety of neutral organic substrates have shown that the anion radical is intrinsically and kinetically an excellent nucleophile in gas phase S_N2 displacement reactions with CH_3X molecules. The anion radical was also shown to react with $(CF_3)_2C{=}O$ to give $(CF_3)_2CO^{\overline{\cdot}}$ and with $H_2C{=}CHCN$ in a stepwise manner to form monomeric and dimeric species.[14] Photochromism in dioxygen, disulphur and diselenium complexes of Rh and Ir has been observed at liquid nitrogen temperature both in solid state and in dilute EPA glass solutions.[15]

The kinetics of the decomposition of ozone have been studied in aqueous solution. In slightly basic solution the reaction can be described by a rate law involving first and second order terms in ozone but the second order term is not observed if a radical scavenger (Na_2CO_3) is present in the solution. In solutions of high OH^-, the rate law changes markedly. The addition of Na_2CO_3 retards the reaction only in the latter stages and the rate becomes nearly first order in ozone as the concentration of Na_2CO_3 is increased. These results provide evidence for the initiation step

$$O_3 + OH^- \rightarrow HO_2^- + O_2 \qquad \text{...(4)}$$

which corresponds to a two electron transfer process or an oxygen atom transfer from ozone to hydroxide ion.[16] The reaction of ozone with silane at low pressure produces visible chemiluminescence and a portion of the emission corresponds to a transition of the OH radical. The dominant feature of the visible portion of the spectrum is thought to be due to emission from H_2SiO.[17] Infrared spectra recorded after irradiation of argon matrices containing SiH_4 and ozone have provided the first direct evidence for silanone H_2SiO as well as silanoic (HO)HSiO and silicic $(HO)_2SiO$ acid molecules which contain a silicon-oxygen double bond.[18] The absolute second order rate constant for the reaction

$$Na + O_3 \rightarrow NaO + O_2 \qquad \text{...(5)}$$

has been determined, thus resolving large differences for various estimates of this important quantity used in modelling the sodium layer in the mesosphere approximately 90km above the earth's surface.[19]

Bond systems with uneven numbers of electrons - such as the ozonide ion - being an exception to the rule for main group elements have always attracted the interest of experimental and theoretical chemists. However, the exact structural data for O_3^- in KO_3 and RbO_3 have only now been determined. The average bond lengths 135.7 and 134.1 and bond angles 113.48 and 114.6 respectively of the two ozonides agree within the standard deviations.[20]

The production of hydrogen peroxide from dioxygen and hydroxylamine catalyzed by manganese(II) complexes has been reported. The Mn(II)/4,5-dihydroxybenzen-1,3-disulphonate (Tiron) system is a efficient catalyst in the pH range 7.5-8.6.[21] The reaction of hydrogen peroxide with the aquocopper(I) ion in aqueous solution has been shown to result in the formation of a copper(II) species rather than the hydroxyl free radical as had been previously assumed.[22] The structures of two, so-called hydroxoaqua complex ions of chromium(III) and cobalt(III) have been shown not to be mononuclear hydroxoaqua ions, with distinct OH and H_2O ligands, but binuclear or polynuclear ions with symmetrical hydrogen oxide bridges (H_3O_2) between metal atoms. In cis$[Cr(bpy)_2(H_3O_2)]_2I_4.2H_2O$ there are two H_3O_2 units that are symmetry related with an O-O distance of 2.446Å. In trans$[Co(en)_2(H_3O_2)](ClO_4)_2$ the cobalt atom and the central hydrogen atom of the H_3O_2 group reside on crystallographic inversion centres thus forming infinite chains of ---Co-H_3O_2-Co--- with an O---O distance of 2.441Å. The authors concluded that hydroxoaqua ions do not exist as such in the crystalline state, the cis hydroxoaqua ions being dimers bridged by two H_3O_2 bridges and the trans, polynuclear chains of metal atoms bridged by single H_3O_2 ligands.[23] A series of ab initio SCF calculations have been made for water molecules in various model complexes e.g., $(H_2O)_2$ $H_2O.OH^-$ $Li^+.H_2O$ in which the water molecule is in different geometries, with the object of pinpointing specific electron rearrangement features for the different water environments. Different types of neighbour were found to give essentially the same electron redistribution namely an enhancement of the molecular dipole moment, with electron depletion at hydrogen and in the lone pair region close to the oxygen nucleus and an extended region of slight electron excess between oxygen and the neighbouring cation or hydrogen donor.[24] The crystal and molecular structure of the water oxidation catalyst, $[(bpy)_2(OH_2)RuORu(OH_2)(bpy)_2](ClO_4)_4.2H_2O$ has been determined.[25]

6.2 SULPHUR

6.2.1 The Element

The quantitative composition of quenched sulphur melts which had been equilibrated at 116-387°C has been determined by HPLC.

The melts contained the ring molecules from S_8 to S_{23} and from the temperature dependence of the equilibrium constants, $K = [S_n]/[S_8]^{n/8}$, the enthalpies of the 18 equilibrium reactions

$$n/_8 \quad S_8 \rightleftharpoons S_n (n \neq 8) \qquad \ldots(6)$$

were calculated. These are the first thermodynamic data for sulphur molecules containing more than ten atoms and are given in Table 1.[26]

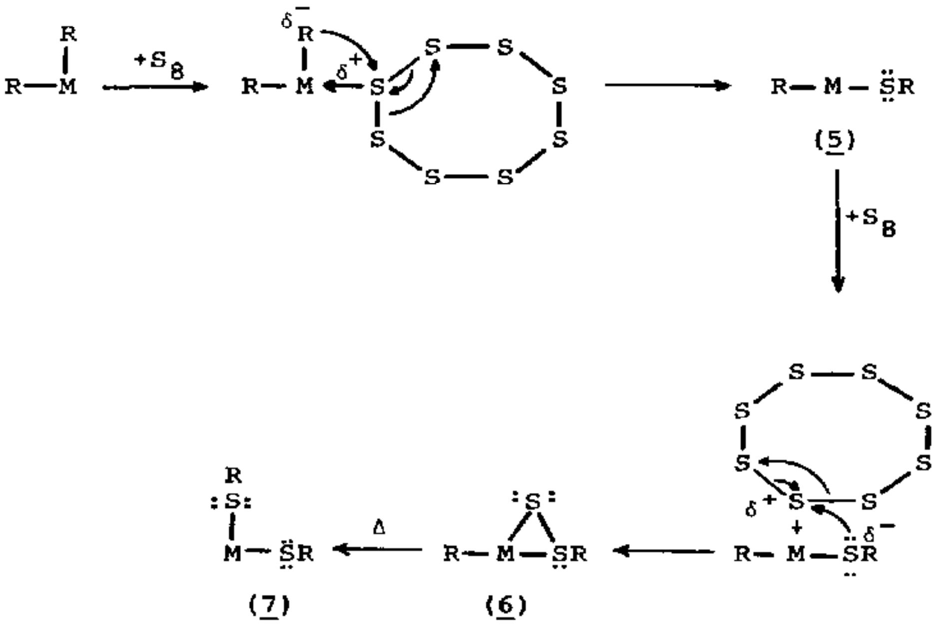
Table 1. Reaction enthalpies ΔH(1) for reaction (6) at 116-159°C (1.013 bar).

n	ΔH(1) [kJ.mol^{-1}]	n	ΔH(1) [kJ.mol^{-1}]
6	22.4±0.5	16	30±3
7	21.2±0.6	17	34±1
9	28±2	18	22±1
10	30±3	19	25.3±0.4
11	33±3	20	28±3
12	12±1	21	24±2
13	31±3	22	21±3
14	30±2	23	27±2
15	26±1		

The Raman spectrum of solid S_9 has been recorded for the first time and shows that S_9 crystallises in two allotropes, both consisting of cyclic molecules of either C_1 or C_2 symmetry with bond distances between 203 and 209pm. The homocyclic oxides S_9O (mp. 33°C) and $S_{10}O$ (mp. 51°C) were prepared by the oxidation of the corresponding sulphur rings with trifluoroperoxy acetic acid in a CS_2 methylene chloride mixture. According to i.r. and Raman spectra they both contain an exocyclic oxygen atom and both decompose at 25°C to give SO_2 and a polysulphur oxide S_nO with $n > 10$. Both compounds can however be stored at -78°C without decomposition.[27]

Three studies of the isotope effects of ^{34}S and/or ^{36}S have been published. Nineteen values for ^{34}S induced isotope shifts on the n.m.r. frequency of directly bonded fluorine of 14 S(II), S(IV) and S(VI) compounds have been reported and a dependence on the S-F bond length was demonstrated.[28] Measurement of ^{34}S, ^{36}S and ^{18}O isotope effects on ^{31}P chemical shifts in thiophosphate anhydrides have confirmed the expectation that ^{36}S effects should be twice as large as the corresponding ^{34}S effects.[29] The ^{36}S-^{34}S kinetic isotope effect has been shown to be independent of isotopic composition and solvent used, and the value obtained is in the range predicted earlier for carbon and heavier atoms.[30]

The insertion of elemental sulphur into tungsten-carbon bonds has been shown to take place by the following sequential formation of complexes (5) to (7) with the mechanism shown in Scheme 1 being proposed.[31]



[M = (η^5-C_5H_5)W(NO); R = CH_2SiMe_3]

Scheme 1

6.2.2 Bonds to Halogens

Measurements of the equilibrium

$$SSF_2 \rightleftharpoons FSSF \qquad ...(7)$$

have enabled a reaction enthalpy of 11.3 kJ/mole to be evaluated. Enthalpies of formation and bond energies of SSF_2, FSSF, SF_3SF and SF_3SSF have been obtained from appearance potentials which have been measured by photoionization mass spectrometry and are shown in Table 2.[32]

Table 2. Thermochemical data from the photoionization spectra of SSF_2 and FSSF.

	ΔH_f [kJ/mol]	D(S-S)	D(S-F)	IP [eV]
SSF_2	-297	306	-	10,41
FSSF	-291	317	-	10,62
SF_2	-267	-	359	10,08
SF		-	342	10,09
SSF_2^+	706	279	182	-
$FSSF^+$	733	303	155	-
SSF^+	809	489	301	-
SF_2^+	708	-	393	-
SF^+	1022	-	332	-

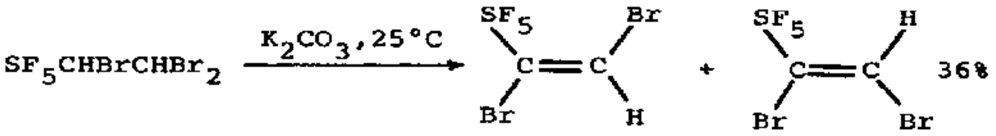
Ethynylsulphurpentafluoride has been prepared by the dehydrobromination of $SF_5CH{=}CFBr$ in 49% yield. It can also be

$$SF_5CH{=}CHBr \xrightarrow[\text{pet.ether}]{\text{KOH}} SF_5C{\equiv}CH \qquad \ldots(8)$$

obtained by a four step process (equations (9) to (12)) but the overall yield is then only 9%.[33]

$$SF_5Br + HC{\equiv}CH \xrightarrow{57°C} SF_5CH{=}CHBr \quad 80\% \qquad \ldots(9)$$

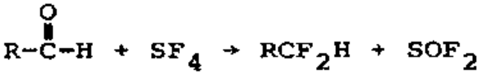
$$SF_5CH{=}CHBr \xrightarrow{Br_2,h\nu} SF_5CHBrCHBr_2 \quad 46\% \qquad \ldots(10)$$



...(11)

$SF_5CBr{=}CHBr \xrightarrow{Zn,diglyme} SF_5C{\equiv}CH$ 68% ...(12)

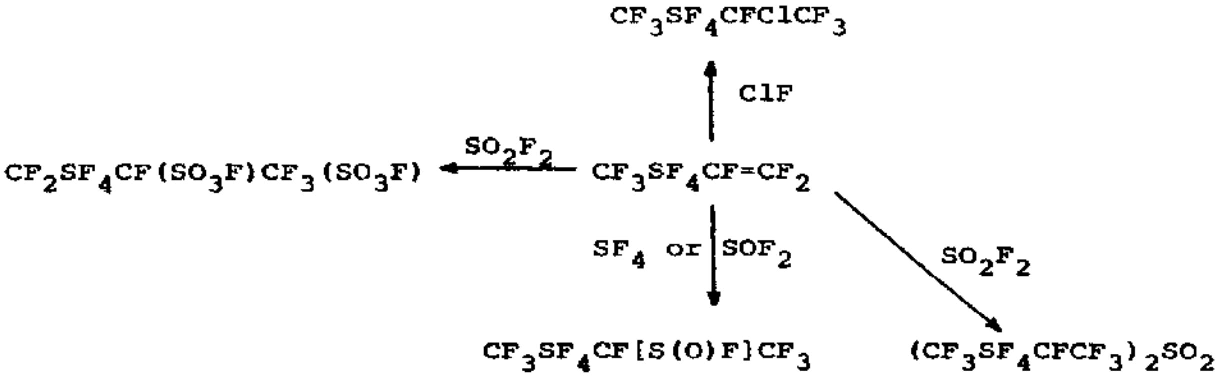
Fluorination of unsaturated aldehydes (8) with SF_4 in the presence of KF at 20°C has been shown to lead to the corresponding difluoromethyl substituted compounds.[34]



$$R-\overset{O}{\overset{\|}{C}}-H + SF_4 \rightarrow RCF_2H + SOF_2 \qquad ...(13)$$

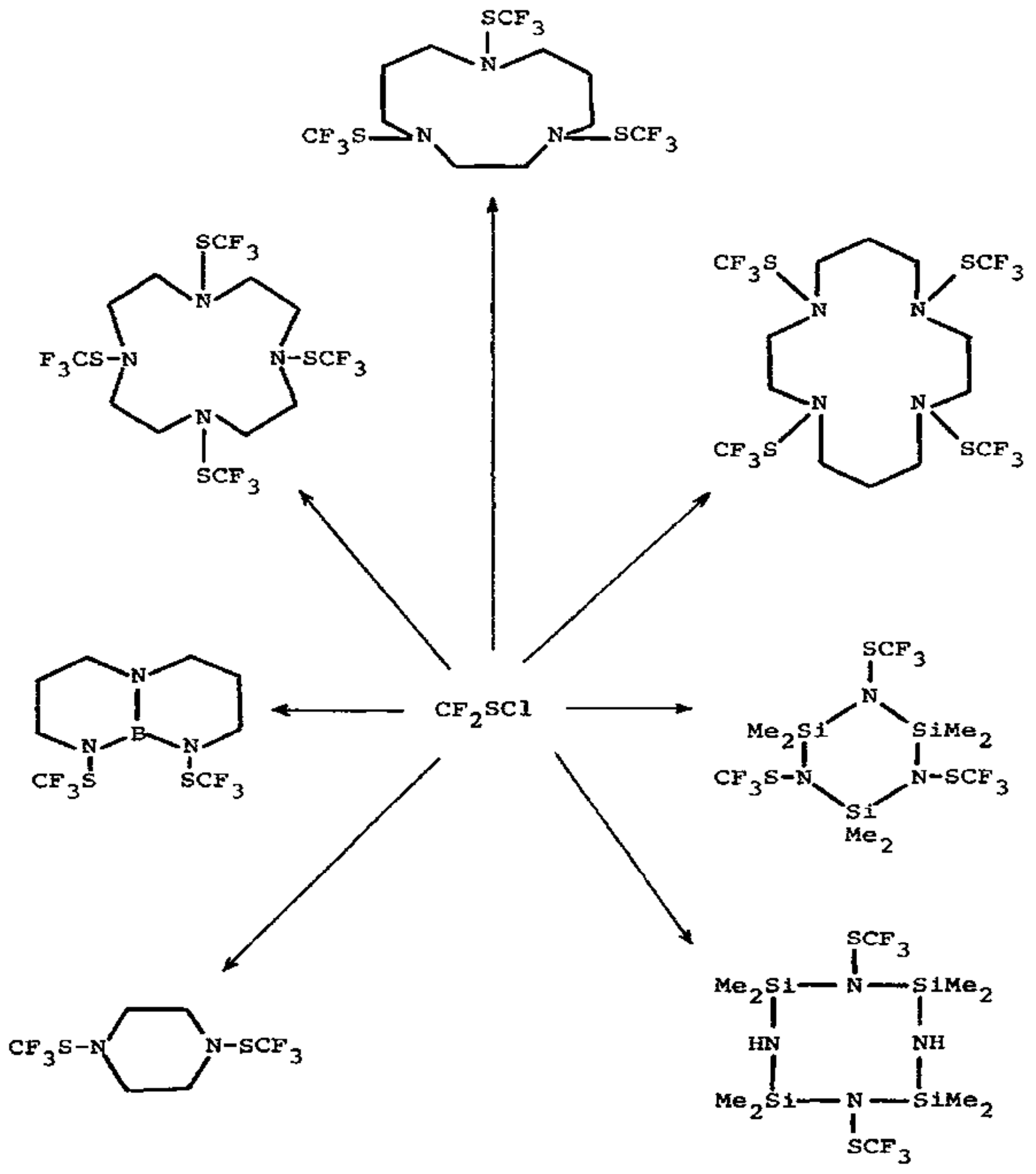
(8)

Sulphinyl fluoride has been shown to replace active hydrogen with fluorine in P-H and C-H bonds but with >N-H bonds, >NS(O)F is formed. Fluorination occurs with oxidatively unsaturated compounds such as trialkylphosphines and phosphites to form difluorophosphoranes. The yields are reduced by side reactions of the phosphorus(III) species with the sulphur and sulphur dioxide that form concomitantly with the fluorination reaction.[35] The synthesis of some new CF_3SF_4 substituted compounds have been reported. The new olefins $CF_3SF_4CF{=}CF_2$ and $CF_3SF_4CH{=}CF_2$ resulted from the dehydrochlorination of $CF_3SF_4CHFCF_2Cl$ and $CF_3SF_4CH_2CF_2Cl$ respectively. With highly hindered olefins such as $FSO_2C(CF_3)FCF_2OCF_2CF{=}CF_2$ and $CF_3SF_4CF{=}CF_2$, CF_3SF_4Cl behaved as a chlorofluorinating agent, however $CF_3C{\equiv}CH$ with CF_3SF_4Cl gave equimolar amounts of $CF_3SF_4C(CF_3){=}CHCl$ and $CF_3C(Cl){=}C(SF_4CF_3)H$. The products of the reaction of $CF_3SF_4CF{=}CF_2$ with a number of fluorides and oxyfluorides are shown in Scheme 2.[36]



Scheme 2

(Trifluoromethyl)sulphenyl, -sulphinyl and -sulphonyl derivatives of several heterocyclic amines have been prepared by the reaction of CF_3SCl with the respective heterocyclic amine. The compounds prepared are shown in Scheme 3.[37]



Scheme 3

The crystal structure of $SCl_3^+AsF_6^-$ has been determined and the following bond lengths and angles found S-Cl, 194.9 to 198.8pm, Cl-S-Cl 101.2 to 103.59°. The weighted mean S-Cl stretching frequency of the SCl_3^+ cations, was found to be directly proportional to the mean S-Cl distance, the force constant and the sulphur-anion distance (Cl_3S^+---X^-). The observation that $SCl_3^+Cl^-$ is isostructural with PCl_4^- and the large variation in the S-Cl stretching frequencies of the $SCl_3^+X^-$ salts is attributed to cation-anion interaction forces.[38] The synthesis of $CF_3SCl_2^+AsF_6^-$ has been reported. The compound was characterized by a variety of spectroscopic techniques and a crystal structure determined. Structural data for the cation are C-F = 128.8pm, C-S = 197.8pm, S-Cl = 195.9pm and F-C-F = 111.8°, Cl-S-Cl = 104.22°, C-S-Cl = 99.8°.[39]

An improved method for the preparation of CF_3SBr has been reported (equation 14):

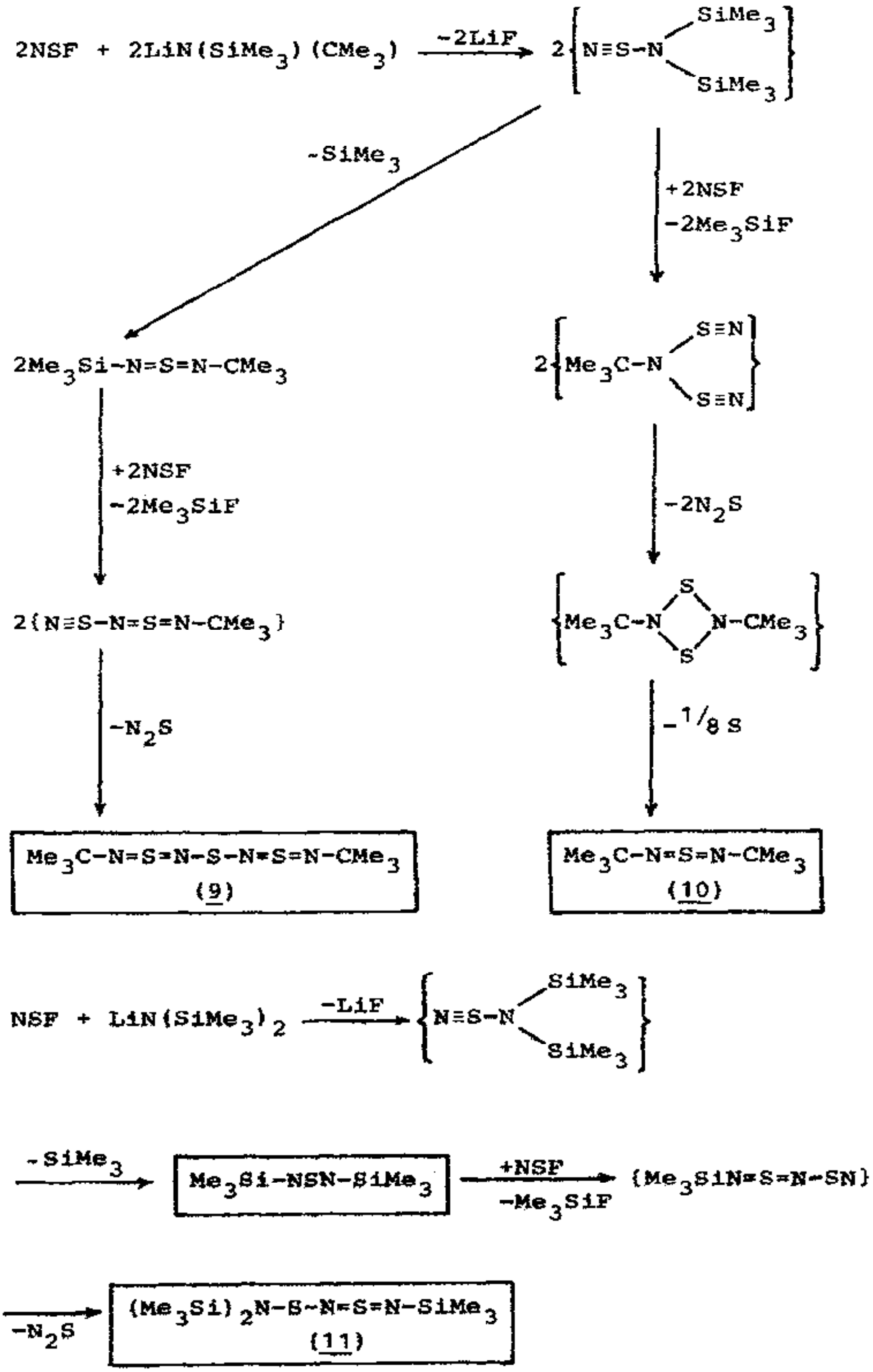
$$CF_3SCl + HBr \rightarrow CF_3SBr + HCl \qquad \ldots(14)$$

The following molecular parameters, C-F = 1.331Å, C-S = 1.814Å, S-Br = 2.162Å, CSBr = 99.4°, FCF = 108.7° were determined from electron diffraction measurements.[40] The preparation and characterization of CF_3SI have been described. CF_3SI behaves like the interhalogen compound ICl and decomposes at higher temperatures to CF_3SSCF_3 and I_2.[41]

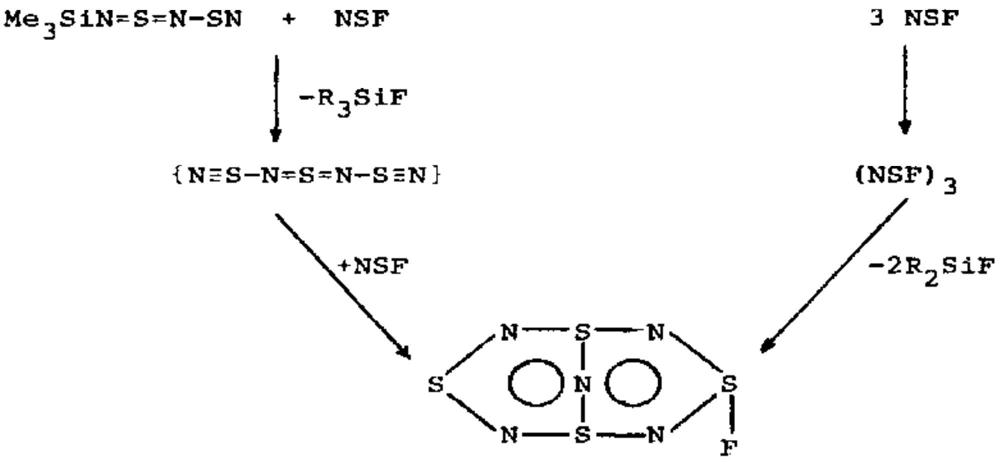
6.2.3 Bonds to Nitrogen

Linear species - The reaction of NSF with $LiN(SiMe_3)R$ where R = CMe_3 or $SiMe_3$ has been shown to give both linear, (9), (10) and (11), and cyclic, (12), thiazenes. The reaction of $(S_3N_4)_n$, with AsF_5 gives $S_4N_4.AsF_5$ in a hitherto unknown modification (13).[42]

Whereas pentacoordinated phosphoranes are well studied, little is known about the isoelectronic pentacoordinated sulphur(VI) cations. A recent paper has however shown that Me_2NSF_5 reacts with AsF_5 in liquid SO_2 at room temperature to give (14) which was found to be exceptionally stable. The salt (16) which may be expected from (15) is not stable and decomposes according to equation (16). ^{19}F-n.m.r. studies showed unequivocable proof for the formation of (14).[43]

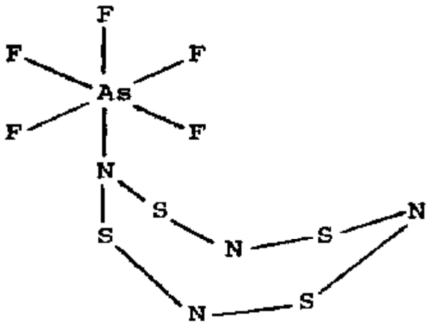

2NSF + 2LiN(SiMe3)(CMe3)
-2LiF
2{N≡S-N(SiMe3)2}
-SiMe3
+2NSF
-2Me3SiF
2Me3Si-N=S=N-CMe3
2{Me3C-N(S≡N)2}
+2NSF
-2Me3SiF
-2N2S
2{N≡S-N=S=N-CMe3}
{Me3C-N(S)2N-CMe3}
-N2S
-1/8 S
Me3C-N=S=N-S-N=S=N-CMe3
(9)
Me3C-N=S=N-CMe3
(10)
NSF + LiN(SiMe3)2
-LiF
{N≡S-N(SiMe3)2}
-SiMe3
Me3Si-NSN-SiMe3
+NSF
-Me3SiF
{Me3SiN=S=N-SN}
-N2S
(Me3Si)2N-S-N=S=N-SiMe3
(11)

Scheme 4

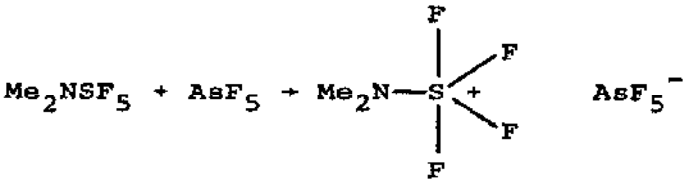


(12)

Scheme 4 (cont.)

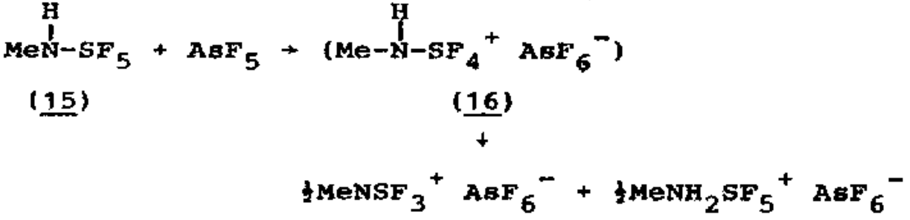


(13)



$$\mathrm{Me_2NSF_5 + AsF_5 \rightarrow Me_2N{-}\overset{+}{S}F_4 \quad AsF_5^-} \qquad \ldots(15)$$

(14)



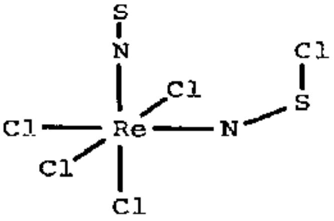
$$\mathrm{Me\overset{H}{N}{-}SF_5 + AsF_5 \rightarrow (Me{-}\overset{H}{N}{-}SF_4^+ \; AsF_6^-)}$$

(15) (16)

$$\downarrow \qquad \ldots(16)$$

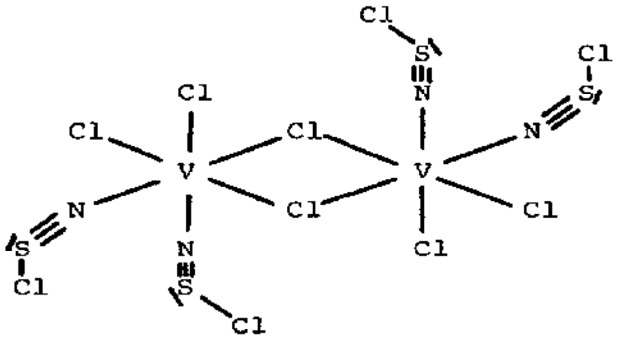
$$\mathrm{\tfrac{1}{2}MeNSF_3^+ \; AsF_6^- + \tfrac{1}{2}MeNH_2SF_5^+ \; AsF_6^-}$$

The synthesis of $[Ph_4As^+]_2[Cl_4Re(NS)(NSCl)^{2-}]CH_2Cl_2$ from the reaction of S_4N_4, Cl_4ReN and Ph_4AsCl in CH_2Cl_2 has been reported. The reaction of S_4N_4 with Re_2Cl_{10} similarly gives the salt $[Ph_4As^+][Cl_5ReNS^-]$ in a smaller yield. The anion $[Cl_4Re(NS)(NSCl)]^{2-}$ was shown to have the structure (17).[44]



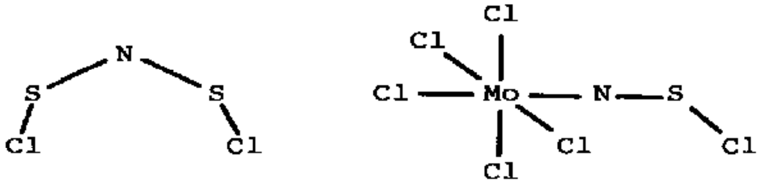
(17)

$[VCl_3(NSCl)_2]_2$ which is a chloro-bridged dimer (18) has been prepared by the reaction of VCl_4 with $(NSCl)_3$. Thermal decomposition of (18), and the reaction of VCl_4 with $(NSCl)_3$ in the presence of SCl_2 lead to the ionic species $[N(SCl)_2]_3[V_2Cl_9]$. Reaction of the recently reported complex $(AsPh_4)_2[(VCl_5)_2(N_2S_2)]$ with $(NSCl)_3$ in CH_2Cl_2 solution gives $AsPh_4[VCl_4(N_2S_2)]$ which contains the anion as a polymer with N_2S_2 bridges.[45]



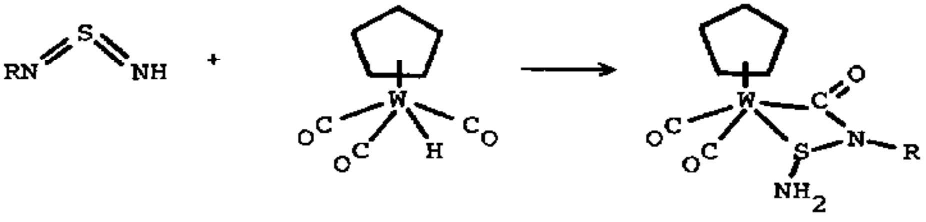
(18)

The reaction of $MoCl_4$ or $MoCl_5$ with $(NSCl)_3$ in CH_2Cl_2 has been shown to yield the chlorothionitrene complex $N(SCl)_2^+[MoCl_5(NSCl)]^-$ in which the anion (19) possesses an almost linear Mo=N=S group with bond lengths that can be interpreted as double bonds, Mo-N = 175pm, N-S 159pm.[46]



(19)

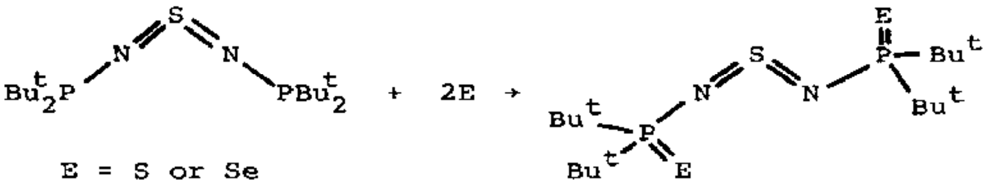
The unstable parent compound of the sulphur diimides $S(NH)_2$ has been prepared in solution by stoichiometric protonation of the anion SN_2^{2-} in K_2SN_2 with acetic acid. An analogous protonation of the salts S(NR)(NK) leads to the monosubstituted sulphur diimides S(NR)(NH) containing bulky substituents such as CMe_3 and Me_3Si which can be isolated as white solids below -40°C. The temperature dependent proton n.m.r. spectra of $S(NH)_2$ and monosubstituted diimides indicate the presence of two isomers in solution (ratio 4:1) which are reversibly interconverted.[47] $S(NH_2)$ and S(NR)(NH) react with the half-sandwich complexes $CpW(CO_3)H$ and $Cp^*W(CO_3)H$ with insertion into the W-H bond. The structures of the addition products (19') have been interpreted on the basis of a central four membered heterocycle into which an acyl group and one of the N=S bonds are incorporated.[48]



...(17)

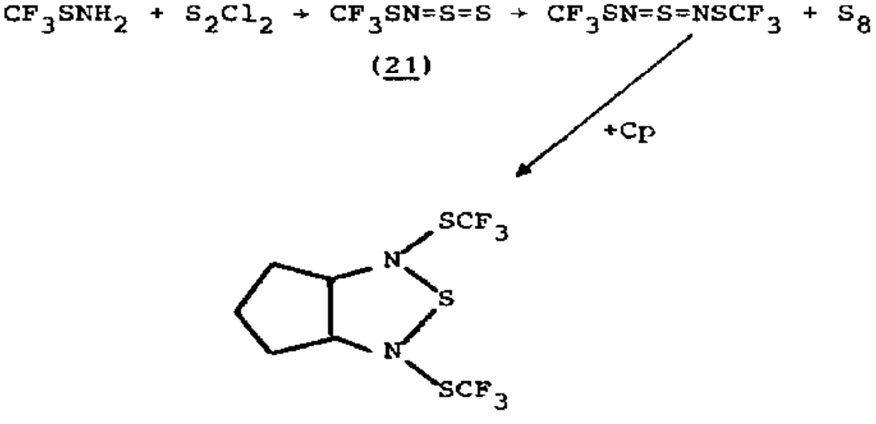
(19')

$S(N-P-Bu^t_2)_2$ has been shown to add sulphur and selenium at both phosphorus atoms to give the new chalcophosphinyl substituted diimides (20). According to X-ray structure determinations the compounds are present in the unsymmetrical configuration in the solid state but ^{31}P n.m.r. spectra give no indication of non-equivalence of the two phosphorus substituents in solution.[49]



(20) ...(18)

The oxidative halogenation of $CF_3SN(SiMe_3)_2$ with F_2 or Cl_2 has been shown to lead to the formation of $CF_3S(X){=}NX$, X = F or Cl. During the chlorination $CF_3S(Cl){=}NSiMe_3$ was isolated and shown to react with CF_3SCl to give $CF_3S(Cl){=}NSCF_3$ which could also be prepared from $(CF_3S)_2NH$ and Cl_2 at -60°C. The fluoride could be prepared similarly. In the presence of quinoline or acridine, CF_3SNH_2 condenses with S_2Cl_2 to give (21) whilst $CF_3SN{=}S{=}NSCF_3$ reacts with cyclopentadiene to give (22).

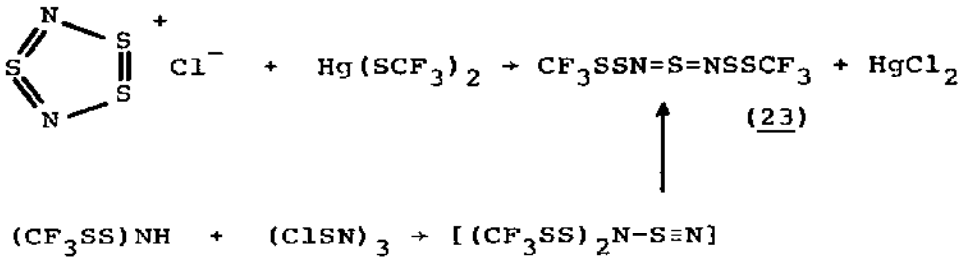


$$CF_3SNH_2 + S_2Cl_2 \rightarrow \underset{(21)}{CF_3SN{=}S{=}S} \rightarrow CF_3SN{=}S{=}NSCF_3 + S_8$$

(22) ...(19)

The reaction of $[S_3N_2Cl]^+Cl^-$ with $Hg(SCF_3)_2$ led to ring opening and the formation of (23) which could also be prepared by the reaction of $(CF_3SS)_2NH$ and $(ClSN)_3$ in the presence of pyridine[50] (equation 20).

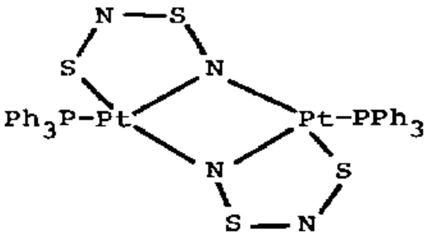
Ring Compounds - SCF calculations have been performed for S_2N_2, S_4^{2+}, $S_4N_4^{2+}$, S_4N_4, H_2S_2, $S_6N_4^{2+}$, S_8, S_8^{2+}. Molecular structures were determined by finding pairs of nuclei linked by the maximum charge density line between them i.e., a charge density analogue for the Lewis electron pair model. The relatively low S-S bonds



...(20)

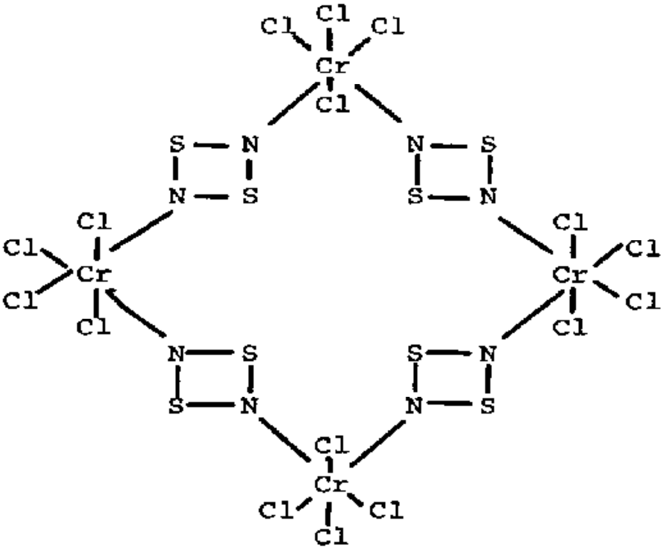
in S_4N_4 and $S_6N_4{}^{2+}$ and the cross-ring bonds found to be present in $S_8{}^{2+}$ and $S_8{}^{4+}$ exhibit the characteristics of closed shell interactions as opposed to the other S-S and S-N bonds in these molecules which are characteristic of a shared interaction.[51]

The reactions of S_4N_4 with $Pt(PPh_3)_3$ or $Pd(PPh_3)_4$ have been shown to give $[M(S_2N_2)(PPh_3)]_2CH_2Cl_2$ where M = Pt or Pd. The X-ray structure of the platinum compound shows the $[Pt(S_2N_2)]_2$ unit to be planar: the $S_2N_2{}^{2-}$ group acting as a bidentate and bridging ligand with the platinum atoms being bridged by nitrogen to form a four membered Pt_2N_2 ring (24).[52]



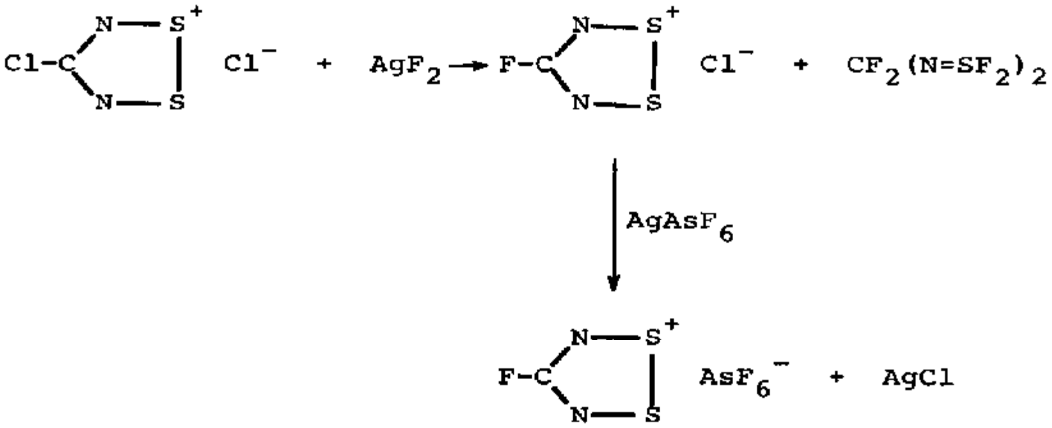
(24)

$(NSCl)_3$ reacts with metallic chromium, $Cr(CO)_6$, $CrCl_3$.3thf and CrO_3 to form mixtures in which $S_4N_3{}^+[CrCl_4(M_2S_2)]^-$ has been identified as the major product. The compound reacts with $AsPh_4$ in CH_2Cl_2 to form $(AsPh_4)_4[CrCl_4(\mu\text{-}N_2S_2)]_4.8CH_2Cl_2$ which consists of $AsPh_4{}^+$ ions, tetrameric $[CrCl_4(N_2S_2)]_4{}^{4-}$ anions (25) and included CH_2Cl_2 molecules. The chromium atoms of the anions occupy the corners of a nearly ideal square, being connected by the nitrogen atoms of planar S_2N_2 rings which are orientated perpendicularly to the Cr_4 plane. The octahedral coordination of the chromium atoms is completed by four terminal chlorine atoms the axial ones of which form short Cl---S contacts of average 310 pm to the sulphur atoms of the N_2S_2 rings.[53]



(25)

Several perhalogenated 1,2,3,5-dithiadiazolium salts have been prepared by the reactions shown in equations (21) to (23).



...(21)

$$CF_3CN + S_3N_3Cl_3 \xrightarrow[\text{steel cylinder}]{\text{liq. } SO_2} CF_3CN_2S_2{}^+Cl^- + S_5N_5{}^+FeCl_4{}^-$$

$$+ S_4N_4O_2 + CF_3CN_3S_2Cl_2 + OSCl_2 + O_2SCl_2 \qquad ...(22)$$

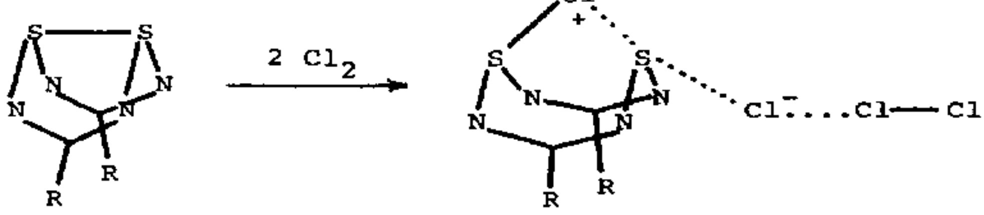
$$CF_3CN + S_3N_3Cl_3 \xrightarrow[\text{teflon autoclave}]{\text{liq. } SO_2} CF_3CN_2S_2{}^+Cl^- + S_4N_4O_2 + OSCl_2$$

$$+ O_2SCl_2 + CF_3CN_4S_3{}^+S_3N_3O_4{}^- \qquad \ldots(23)$$

Reduction of $XCN_2S_2{}^+(Cl,Br)^-$ by Zn in liquid SO_2 gave the radicals $XCN_2S_2{}^\cdot$ (X = F,Cl,Br,CF_3) in high yields. The radicals are diamagnetic in the solid state.[54]

$VBr_2(N_3S_2)$ has been synthesized from $VCl_2(N_3S_2)$ and Me_3SiBr. Reaction with PPh_4Br in CH_2Br_2 gives $(PPh_4)_2[VBr_3(N_3S_2)]_2$. The crystal structure of $VBr_2(N_3S_2)$ shows the vanadium atoms to form planar six membered rings with the N_2S_2 groups with short V–N distances (172 and 185pm). Bromine bridged dimers are associated via V–N links to form chains in a similar way as in some tetra halides.[55] The pyridene complexes $VCl_2(N_3S_2)py$ and $VCl_2(N_3S_2)(py)_2$ have been synthesized by reaction of polymeric $VCl_2(N_3S_2)$ with varying amounts of pyridene in CH_2Cl_2. Crystal structure determination of $VCl_2(N_3S_2)py$ showed the unit cell to consist of two monomeric independent molecules which differed only slightly. The vanadium atoms have trigonal bipyramidal coordination with the N atom of the pyridine molecule, and one chlorine atom in apical positions, and with one chlorine atom and the N atoms of the N_3S_2 ring in equatorial positions. The V–N bond lengths of the planar VN_3S_2 ring of 174pm correspond to double bonds.[56]

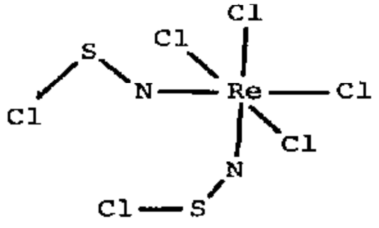
Oxidation of (26) with chlorine gas at −30°C in acetonitrile yields the ionic compound $[(Me_2N)_2C_2N_4S_2Cl]^+Cl_3{}^-$ (27) which contains a puckered $C_2N_4S_2$ cation possessing an asymmetric S–C---S transannular bridge.[57]



(26) R = NMe$_2$ (27)

...(24)

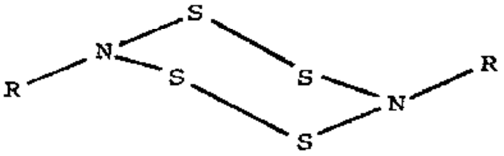
$S_4N_3^+[ReCl_4(NSCl)_2]^-$ has been shown to be a by-product in the reaction of $Re_2(CO)_{10}$ with excess trithiazyl chloride. The compound contains the well known cyclic planar $S_4N_3^+$ cation and in the anions the rhenium atom is coordinated octahedrally by four chlorine atoms and two cis-positioned NSCl ligands (28).



(28)

The mean Re-N and N-S bond lengths (177 and 158pm respectively) correspond to double bonds and the bond lengths and angles are similar to those found in $AsPh_4[ReCl_4(NSCl)_2]$; in (28) however the two chlorine atoms are both turned towards each other.[58]

Reaction of sulphur dichloride with primary amines under high dilution conditions gave compounds which contained a six membered cyclohexane type ring with the RN groups in the 3,6-positions (29).

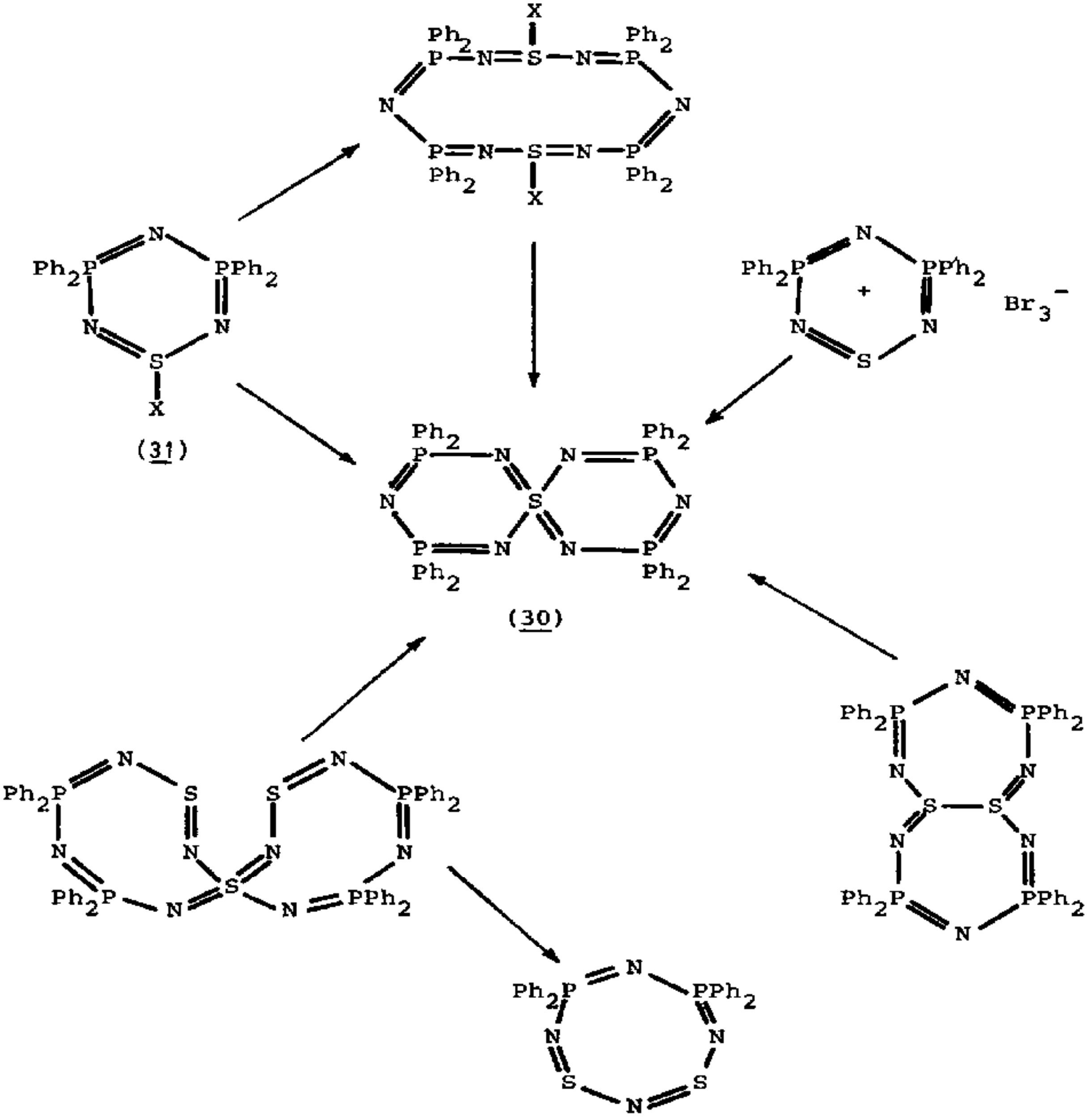


R = Et, $CH_2C_6H_5$,
$n\text{-}C_6H_{13}$,
$CH_2\text{-}CH_2\text{-}C_6H_5$

(29)

The structures have two unusual features 1) All the S-N bond lengths (average 1.716Å) are significantly longer than the previously reported values (ca. 1.67Å) found for $S_n(NH)_{8-n}$ and 2) The angles at the nitrogen atoms SNS 111.3, CNS 115.8, 116.8, reveal a substantial degree of pyramidalization: the nitrogen atoms lying 0.373 and 0.392Å from the plane of their substituents. This pyramidal (sp^3) geometry is in contrast to that observed for cyclic eight membered S-N compounds which are all essentially trigonal suggesting that the bonding has very little or no π character.[59]

The 6,6 spirocycle (30) has been prepared by the pyrolysis of several spirocyclic phosphathiazenes as shown in Scheme 5. In the case of X = NMe_2; NEt_2 or NC_5H_{10}, the 12 membered rings $(Ph_2PN)_4(NSNR_2)_2$ were isolated and shown to be intermediates in the thermal transformation of (31) to (30).[60]

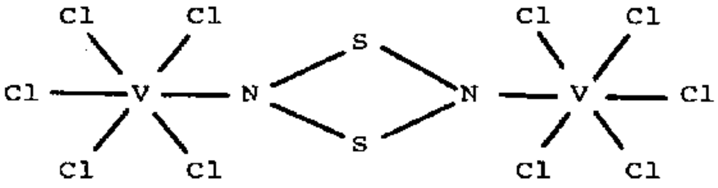


Scheme 5

The eventual synthesis of $SN^{\cdot}$ and $(S_3N_3)^{\cdot}$ by electrochemical reduction or oxidation respectively, starting from $SN^+SbF_6^-$ and $PPN^+S_3N_3^-$ have been checked by e.p.r. spectroscopy. Only the reduction of $SN^+SbF_6^-$ yielded detectable $S_3N_2^{+\cdot}$ and a radical, the e.p.r. signal of which is a quintet of triplets. This signal was not obtained by electrochemical oxidation of $CF_3CO{-}N{=}(S_3N_2)$ or $FSO_2{-}N{=}(S_3N_2)$.[61]

The vapourization of the $(SN)_x$ polymer had previously been thought to lead to the production of a linear bent $(SN)_4$ unit as the dominant gas-phase species. The HeI photoelectron spectrum of $(SN)_x$ vaporised at 140°C does however indicate that the predominant species is an S_3N_3 neutral species with no evidence for $(SN)_4^{+}$.[62]

$ZrCl_4$ has been shown to react with $(NSCl)_3$ to give $(S_3N_3Cl_2)_2Zr_2Cl_{10}$, $S_4N_4Zr_2Cl_{10}$ or $(S_4N_4Cl)_2Zr_2Cl_{10}$ depending on the reaction conditions. These compounds have an ionic structure containing the known $S_3N_3Cl^+$, $S_4N_4^{2+}$ or $S_4N_4Cl^+$ and the previously unknown $Zr_2Cl_{10}^{2-}$ ions. A crystal structure determination showed $(S_4N_4Cl)_2Zr_2Cl_{10}$ to be built up from $S_4N_4Cl^+$ ions which are nearly identical to those observed in $S_4N_4Cl(FeCl_4)$ and that $Zr_2Cl_{10}^{2-}$ contains two chloro bridges joining two edge-shared octahedra.[63] The reaction of VCl_4 and $S_3N_2Cl_2$ in CCl_4 solution gives a solid, black product mixture from which $(AsPh_4)_2[(\mu N_2S_2)(VCl_5)_2]$ can be extracted by reaction with $AsPh_4Cl$ in CH_2Cl_2 solution. The same compound can also be synthesized from $AsPh_4VCl_5$ and $S_3N_3Cl_3$ in CH_2Cl_2 solution. The centrosymmetric $[(\mu N_2S_2)(VCl_5)_2]^{2-}$ ion consists of two quadratic pyramidal VCl_5 units which are linked via the nitrogen atoms of an N_2S_2 ring (32). The N_2S_2 ring shows positional disorder having two different orientations in the crystal.[64]

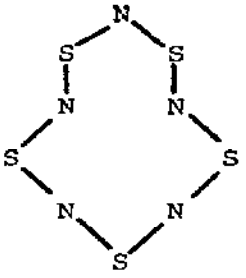


(32)

The crystal structures of $(Ph_2PN)_2(NSX)$ X = Cl, I, NMe_2Ph, have been determined. Where X = Ph the six membered P_2SN_3 ring is planar to within 0.08Å whereas the sulphur atom in the other compounds lies out of the NPNPN plane by 0.29 to 0.55Å. The average endocyclic S-N bond lengths are significantly shorter when X = Cl or I compared to when X = NMe_2 or Ph.[65] $(NSCl)_3$ has been shown to react with ruthenium complexes of the type $[Ru(\eta^5C_5H_5)X(PPh_3)_2]$ X = Cl, Br, CN, SCN or $SnCl_3$ and $RuCl_2(PPh_3)_2(pip)_2$ to yield $[Ru(NSCl)_2Cl(X)(PPh_3)_2]$ $Ru(NSCl)_2Cl_2(PPh_3)(pip)$, respectively.[66] The reaction between $(NSCl)_3$ and $RuCl_2(PPh_3)_3$ gives $RuCl_3(NS)(PPh_3)_2$ together with $[Ph_3PNH_2]Cl.CH_2Cl_2$ and Ph_3PNH.[67]

S_4N_4 reacts with $NH_4^+FeBr_4^-$ in benzene to give the 1:1 inclusion compound $NH_4^+FeBr_4^-.S_4N_4$ in which the geometry of the S_4N_4 group is almost identical to crystalline S_4N_4. The S_4N_4 molecule is surrounded by ionic neighbours in such a way that the sulphur atoms form close contacts with the bromine atoms of the $FeBr_4^-$ anions and the nitrogen atoms are close to the NH_4^+ cations.[68] The potentially explosive S_4N_4 has been thermally decomposed over silver wool in a controlled way by using a flow system under reduced pressure and the products analysed by P.E.S. of the gas phase.[69] The crystal structure of $C_{36}H_{44}CuN_4S_4^+.SF_3SO_3^-$ has been determined.[70] $S_5N_5[RuCl_3(CO)_3]0{\cdot}5CH_2Cl_2$ has been prepared from $Ru_3(CO)_{12}$ and trithiazylchloride in boiling CH_2Cl_2. Its structure consists of planar $S_5N_5^+$ cations in the azulene conformation with bond lengths SN from 155 to 159pm and octahedral $[RuCl_3(CO)_3]^-$ anions with fac geometry.[71] $S_5N_5[GaCl_4]$ was prepared in high yields from gallium and trithiazylchloride with different second products being formed in different solvents. In CH_2Cl_2, $S_4N_4Cl[GaCl_4]$ was formed whilst in CCl_4, $S_3N_2Cl[GaCl_4]$ was the second product. The latter compound may be converted to $S_5N_5[GaCl_4]$ with additional $(NSCl)_3$ and reaction of $GaCl_3$ on $S_5N_5[GaCl_4]$ gives $S_5N_5[Ga_2Cl_7]$. I.r. spectra indicate that the $S_5N_5^+$ ion has different structures depending on the ion and X-ray structural studies showed that $S_5N_5[GaCl_4]$ is isotypic with $S_4N_4[AlCl_4]$ having a heart-shaped $S_5N_5^+$ ion (33) with the possibility of disorder being present in the crystal. In $S_5N_5[Ga_2Cl_7]$ the cation has an azulene-like structure (34) but in both cases the cations are planar with all S-N bond lengths being approximately equal.[72]

In the presence of MOH (M = K, Me_4N), S_7NH reacts with $Ni(CN)_2$ to yield besides the three nuclear complex $M[(S_3NNi)_3S_2]$ the new



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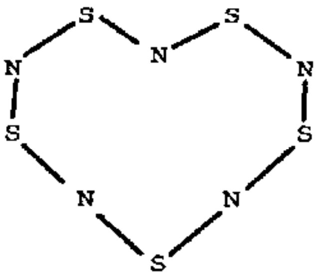
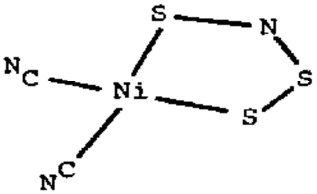


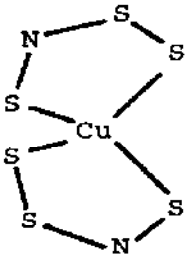
(33)

mononuclear complex $M[Ni(S_3N)(CN)_2]$. The $Ni(S_3N)(CN)_2^-$ anion is planar, nickel being coordinated by one S_3N^- chelate ligand and by two CN^- ions (35).



(35)

The reaction of $CuCl_2$, S_7NH and $(Ph_4As)OH$ gives the salts $[Ph_4As][Cu(S_3N)_2]$ or $[Ph_4As][Cu(S_3N)Cl]$ depending on the reaction conditions. The former compound has two S_3N^- chelate ligands giving a distorted tetrahedral arrangement (36) whilst the latter has one S_3N^- ligand and one Cl^- resulting in a trigonal planar environment (37).[73]



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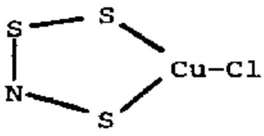
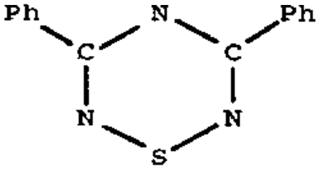


(37)

The reduction of $Ph_2C_2N_3SCl$, prepared from the reaction of benzamidine with $S_3N_3Cl_3$, with Ph_3Sb gives the radical $Ph_2C_2N_3S\cdot$ (38) whose ESR signal in CH_2Cl_2 consists of a seven-line pattern with equal hyperfine coupling constants to all three nitrogen atoms. In the solid state the radical forms a dimer consisting of a pair of cofacial $Ph_2C_2N_3S$ rings with a dihedral angle of 14° between their respective mean planes (39). The closest inter-ring contact is between two sulphur atoms at 2.666Å.[74]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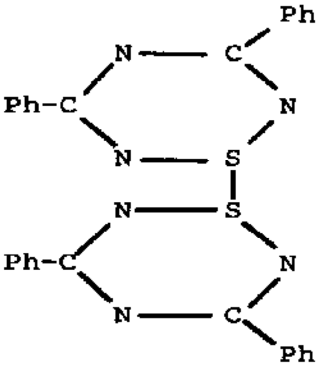
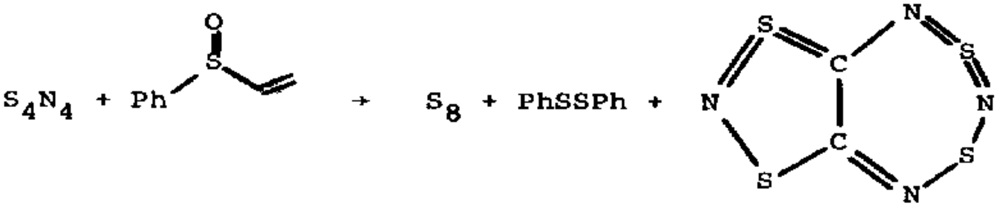

(39)

Crystalline $CH_3\overline{CSNSN}^+AsF_6^-$, $CH_3\overline{CSNSCH}^+AsF_6^-$ and $H\overline{CSNSCH}^+AsF_6^-$ have been prepared in essentially quantitative yield by the reaction of S_2NAsF_6 with MeCN, MeCCH and HCCH respectively in sulphur dioxide solution. The $CH_3\overline{CSNSN}^+$ ion is planar and both $CH_3\overline{CSNSN}^+$ and $H\overline{CSNSC}R^+$ (R = H or Me) can be regarded as 6π cyclic systems. The cations have been reduced chemically and electrolytically to form long-lived free radicals.[75]

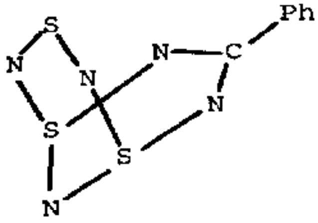
S_4N_4 and phenylvinyl sulphoxide react to give a novel planar delocalised 14π electron aromatic system, (40), in which all the S_4N_4 atoms have been retained. In the solid crystal the molecules form parallel overlapping stacks with a minimum interplanar atomic separation of 3.26Å.[76] A crystal structure determination has shown that in $C_7H_5N_5S$, the planar SNCNS and SNSNS components of the bicyclic molecule (41) make dihedral angles



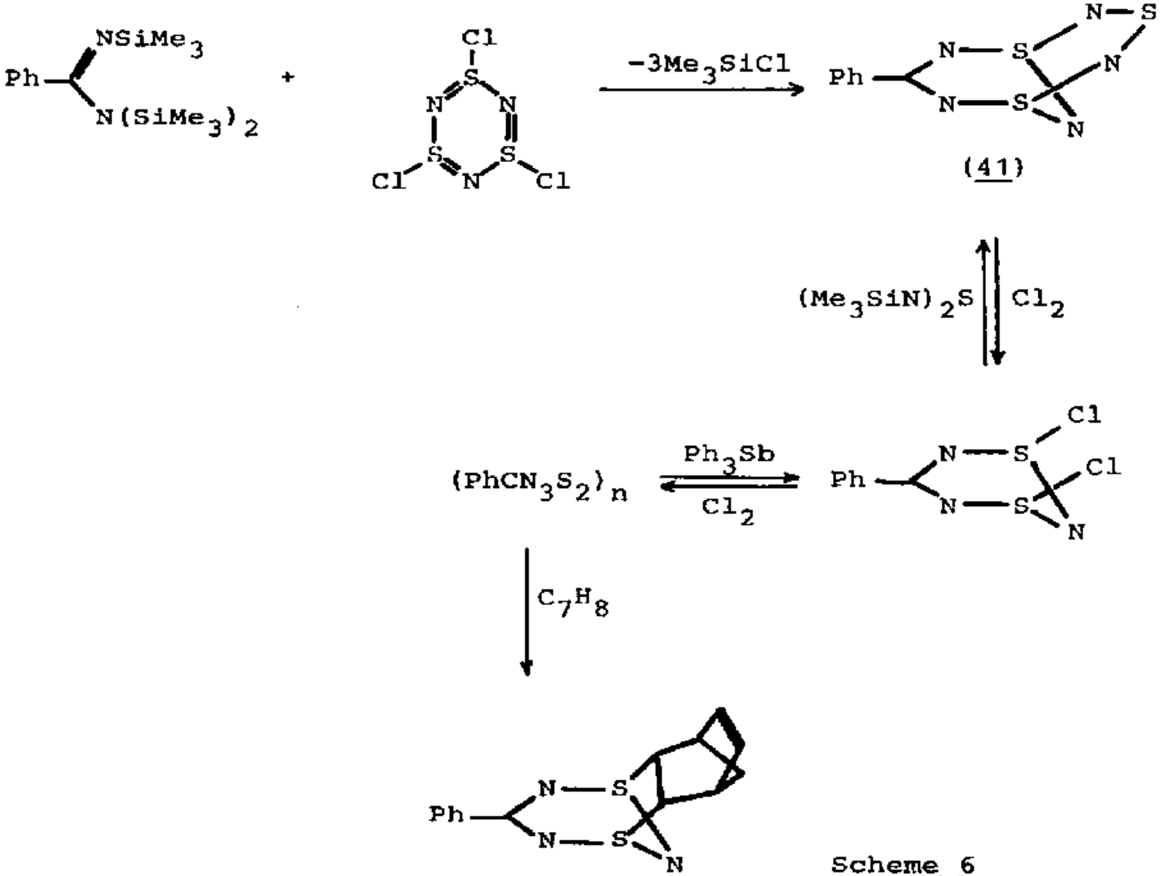
...(25)

(40)

of 137.1 and 118.3° with the SNS bridging unit. The S-N bonds connecting the NSN fragment to the CN_3S_2 ring are much longer (1.728Å) than those in the remainder of the molecule (1.546-1.630Å).[77]

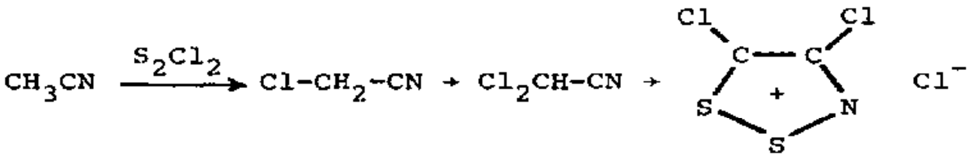

(<u>41</u>)

The reaction of $PhC(NSiMe_3)N(SiMe_3)_2$ with $S_3N_3Cl_3$ has been shown to provide a simple, efficient and rational synthesis of (<u>41</u>). The structural integrity of the CS_2N_3 ring is shown by the reactions given in Scheme 6.[78]



Scheme 6

The low temperature absorption spectra and preresonance Raman spectra of $Ph_2PS_2N_3$ and $Ph_4P_2S_2N_4$ have been measured.[79] S_2Cl_2 reacts with acetonitrile via chloro- and dichloroacetonitrile to give (42). The reactivity of (42) with proton active compounds is determined by the nucleophilic substitution of the chlorine atom attached to the carbon atom C-5. Ring cleavage with chlorine gives the compounds shown in Scheme 7.[80]



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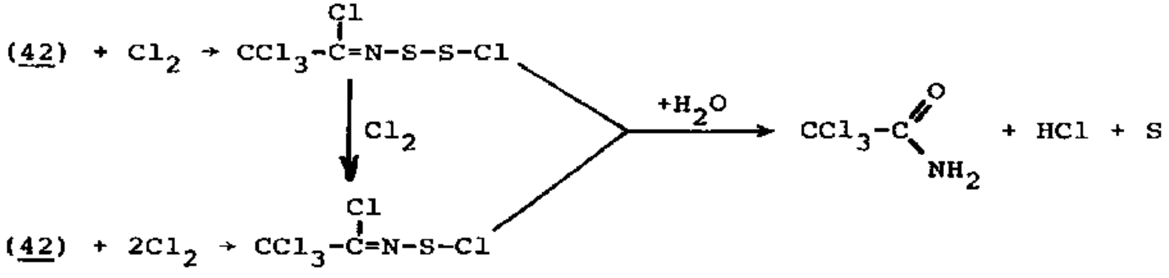
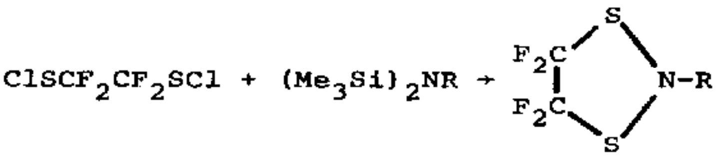


Scheme 7

The use of $ClSCF_2CF_2SCl$ as a precursor for new sulphur-nitrogen-carbon heterocycles has been described. Several of the reactions are shown in equations (27) to (29).[81]



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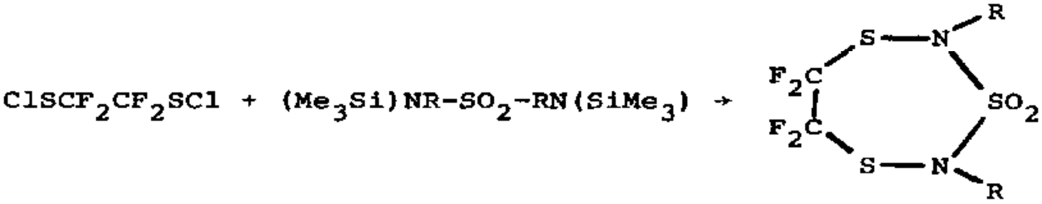

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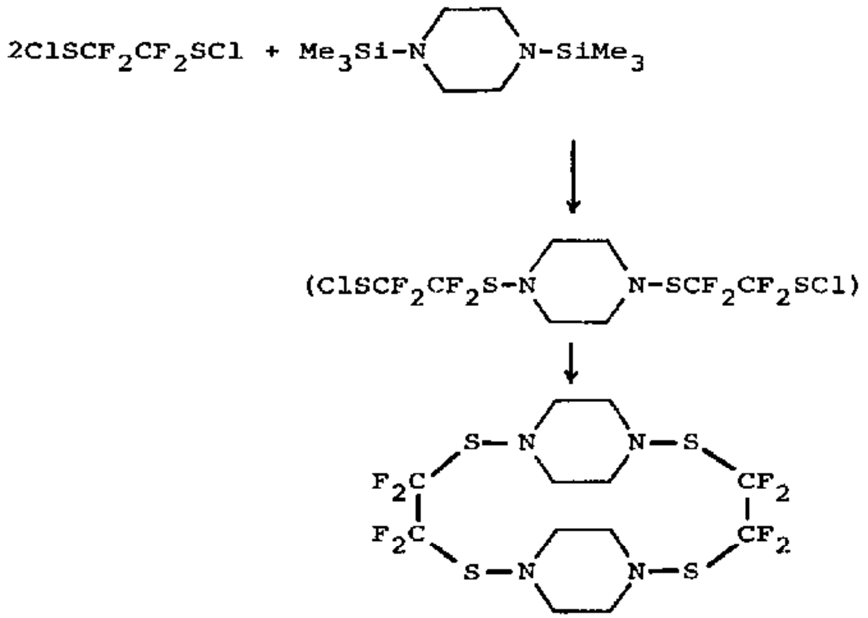


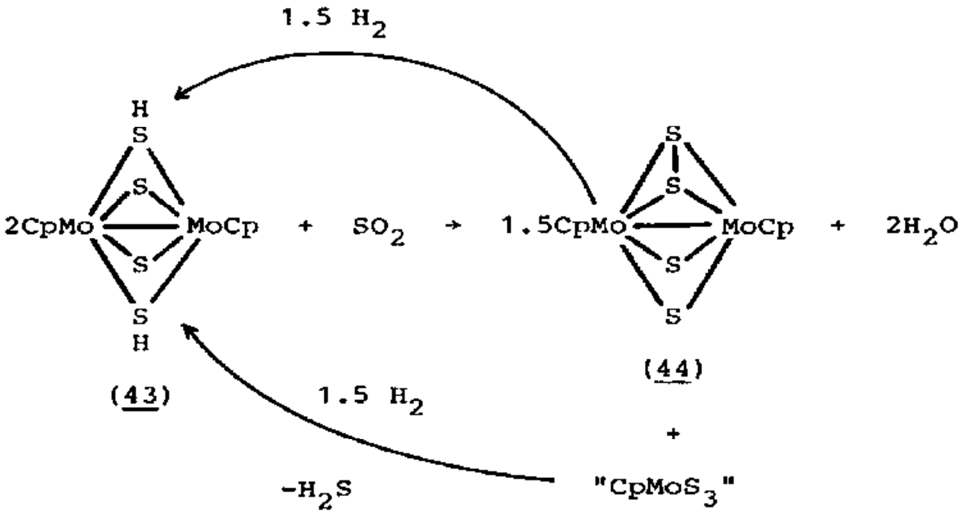
...(29)

6.2.4 Bonds to Oxygen

The organometallic molybdenum sulphur complex (<u>43</u>) has been shown to be the first example of a catalyst to effect the homogeneous catalytic hydrogenation of SO_2. The catalyst is effectively sulphur saturated and contains reducing SH groups uniquely regenerable from sulphide groups by H_2. Conversion of SO_2 to S_8 and H_2O proceeds under mild conditions with H_2 but in the absence of H_2 the stoichiometric reaction of (<u>43</u>) with SO_2 produces the known cluster (<u>44</u>). A third product of the reaction analyses as $[Me_nCpMoS_3]_n$ and contains the sulphur from the reduced SO_2 since S_8 is not formed in the stoichiometric reaction, however, if catalysis is terminated at or before complete SO_2 consumption, S_8 is the product (Scheme 8).[82]

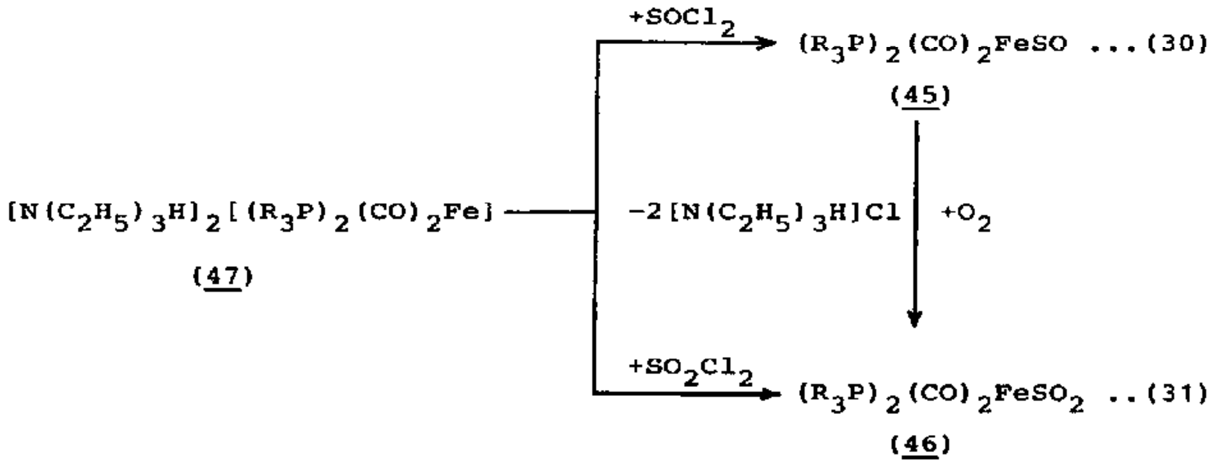
A method has been developed for the measurement of the dissociation energies of gas phase neutral dimers using photoionization spectra of mass selected ions from molecular beams generated by jet expansion. The dissociation energies obtained for trans-$C_4H_8.SO_2$ and $C_6H_6.SO_2$ were 3.85 and 4.40 kcal/-mol respectively.[83]

The synthesis of SO- and SO_2 complexes (<u>45</u>) and (<u>46</u>) follows equations (30) and (31) by nucleophilic substitution of $SOCl_2$ or SO_2Cl_2 by the same metallate (<u>47</u>). (<u>46</u>) can also be obtained by



Scheme 8

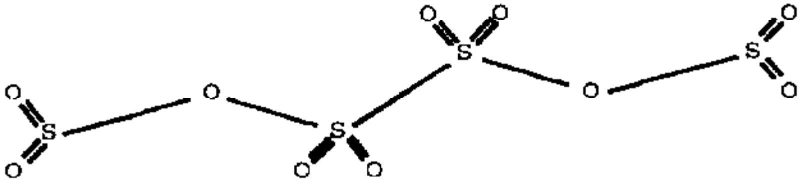
simple air oxidation of solutions of (45). Spectroscopic studies indicate a trigonal bipyramidal configuration for iron with both phosphite ligands in axial positions and the sulphur oxide ligands in equatorial positions together with both carbonyl ligands. X-ray structure analysis of (46) shows the exactly planar coordination of the sulphur atom and the nearly perpendicular orientation of the SO_2 plane to the equator plane; thus complex (46) is isolobal to SO_3.[84]



The oxides MgO, V_2O_5, CrO_3, MnO_2, CoO, CuO, Cu_2O and ZnO react with dimethyl sulphoxide-sulphur dioxide to form the metal disulphates $M_x(S_2O_7)_y$.z dmso. The oxides SnO_2, PbO_2, La_2O_3 and Ag_2O gave products of intermediate composition whilst TiO_2, Cr_2O_3, Fe_2O_3, Co_3O_4, NiO, MoO_3 and Al_2O_3 do not react with the mixed-solvent system. The mechanism of conversion of oxide into disulphate is shown in equation (32).[86]

$$MO + SO_2 \rightarrow MSO_3 \xrightarrow{SO_2} MS_2O_5 \xrightarrow{2dmso} MS_2O_7 \qquad ...(32)$$

An adduct of two SO_2 molecules and one dithionate ion forms the anion (48) of $[(\eta^6-C_6H_6)_2Cr]_2S_4O_{10}$. The SO_2 molecules are coupled to the dithionate ion *via* unusually long $S_{(SO_2)}-O_{(S_2O_6)}$ bonds (243pm).[86]



(48)

EPR spectroscopy is a very sensitive and selective method for the detection of paramagnetic species and for this reason it has been used in an attempt to determine whether SO_2 and NO_x can exert an effect on the photosynthetic process in spruce needles. Results of the study indicate that SO_2 and NO_x can effect to varying degrees the various paramagnetic species responsible for the water splitting reaction in photosynthesis.[87]

An X-ray structure investigation has shown that in $[Ir(PPr^i_3)_2(SO)Cl]$, the sulphur monoxide is coordinated in a bent η^1 fashion. Peracid oxidation transforms coordinated SO to SO_2 and CO displaces SO *via* a 5-coordinated intermediate which has been isolated.[88] The extraction of water and sulphuric acid by trilaurylamine dissolved in toluene has been studied.[89]

In the high temperature polymorph Na_2SO_4(I), up to 33% cation vacancies can be generated by substitution of Na^+ by 2 and 3+ ions. The hexagonal high temperature form and its monoclinic distortions can be quenched to room temperature and structure determinations showed them to be characterised by strong orientational disorder of the sulphate tetrahedra.[90] A crystal structure investigation concentrating on the thermal motions of oxygen and lithium in $KLiSO_4$ at various temperatures has been carried out. The thermal vibrations were explained by a coupled rotational vibration of oxygen around the sulphur atoms.[91] The solubility and reactivity of seven first-row transition-metal sulphates in the ternary eutectic Li_2SO_4-Na_2SO_4-K_2SO_4 and in the ternary eutectic containing Na_2CO_3 have been studied and the transition metal oxide products identified. Addition of potassium pyrosulphate was found to dissolve all the oxides, and in some cases with reduction[92] $Rb_3H(SO_4)_2$ has been shown to be isostructural with its ammonium analogue, having a pseudo hexagonal room temperature structure which transforms to hexagonal symmetry at elevated temperatures with changes in the O-H-O hydrogen bonds.[93] $CaSO_4.H_2SO_4$ has been identified as calcium hydrogen sulphate whereas $CaSO_4.3H_2SO_4$ is a genuine adduct. Depending on the excess of H_2SO_4, both compounds can exist together at temperatures up to 343K but above this temperature only $Ca(HSO_4)_2$ is stable.[94] $(NH_4)_3H(SO_4)_2$ contains regular tetrahedral NH_4^+ ions linked to SO_4^{2-} by hydrogen bonds. Neighbouring sulphate ions are linked by O-H---O hydrogen bonds. Protonic conductivity has been previously explained by the presence of chains which although like one of the three types found in this structural study, they do not exist in the direction of highest conductivity.[95] $(NH_4)_2H_3AsO_4SO_4$ has been shown to have a structure closely related to those of the mixed salts $M_2H_3PO_4SO_4$ (M = K, NH_4) but in the arsenate, order was observed between the two types of XO_4 groups. $[H_3AsO_4SO_4]^{2-}$ groups were found to be linked by two ammonium ions building up chains interconnected by hydrogen bonds.[96] The structural properties of several anhydrous double sulphates of Cu^{II}, $M_2Cu(SO_4)_2$, have been determined from their i.r. spectra and powder diffraction patterns.[97] The preparation of $Na_2Cu(SO_4)_2.6H_2O$ has been described. On its dehydration, oxygen atoms from the sulphate groups enter the coordination sphere of Cu^{II} and the symmetry of SO_4^{2-} becomes lower.[98] The La and Tl atoms in $TlLa(SO_4)_2.2H_2O$ have been shown to be nine coordinated by oxygen atoms, La atoms in the form of a distorted monocapped square antiprism and Tl in the form of an irregular polyhedron.[99] Several papers have described studies on phase systems involving the sulphate ion and these are collected in Table 3.

Table 3.

System	Ref.
K_2CO_3,Rb_2SO_4,H_2O	100
$(NH_4)_2HPO_4$,$NH_4H_2PO_4$,K_2SO_4,H_2O	101
UO_2SO_4,$CO(NH_2)_2$,H_2O	102
K_2SO_4,$MgSO_4$,$CuSO_4$,H_2O	103
K_2SO_4,$MgSO_4$,$CoSO_4$,H_2O	104
$K_2S_2O_7$,$V_2O_3(SO_4)_2$	105
K_2SO_4,$MgSO_4$,$ZnSO_4$,H_2O	106
K,Mg,Ca||SO_4,Cl,H_2O	107

The solubility of praseodymium and neodymium sulphates in potassium chloride solution has been measured.[108]

Bis(fluorosulphuryl)peroxide, $S_2O_6F_2$, has been shown to oxidise manganese in HSO_3F to give $Mn(SO_3F)_3$ and the ternary fluorosulphates $M_2[Mn(SO_3F)_5]$ where M = K or Cs. The oxidation of $Mn_2(CO)_{10}$ by $S_2O_6F_2$, or the further oxidation of $Mn(SO_3F)_2$ by $S_2O_6F_2$, in either the absence or presence of HSO_3F provides alternative routes to $Mn(SO_3F)_3$. Solutions of the ternary fluorosulphates in HSO_3F are unstable and produce polymeric $Mn(SO_3F)_2$. $ReO_2(SO_3F)_3$ was produced by the oxidation of rhenium or Re_3O_7.[109] The oxidation of sulphite by permanganate ions has been shown to involve Mn(VI) as an intermediate, whose fate depends on the pH.[110]

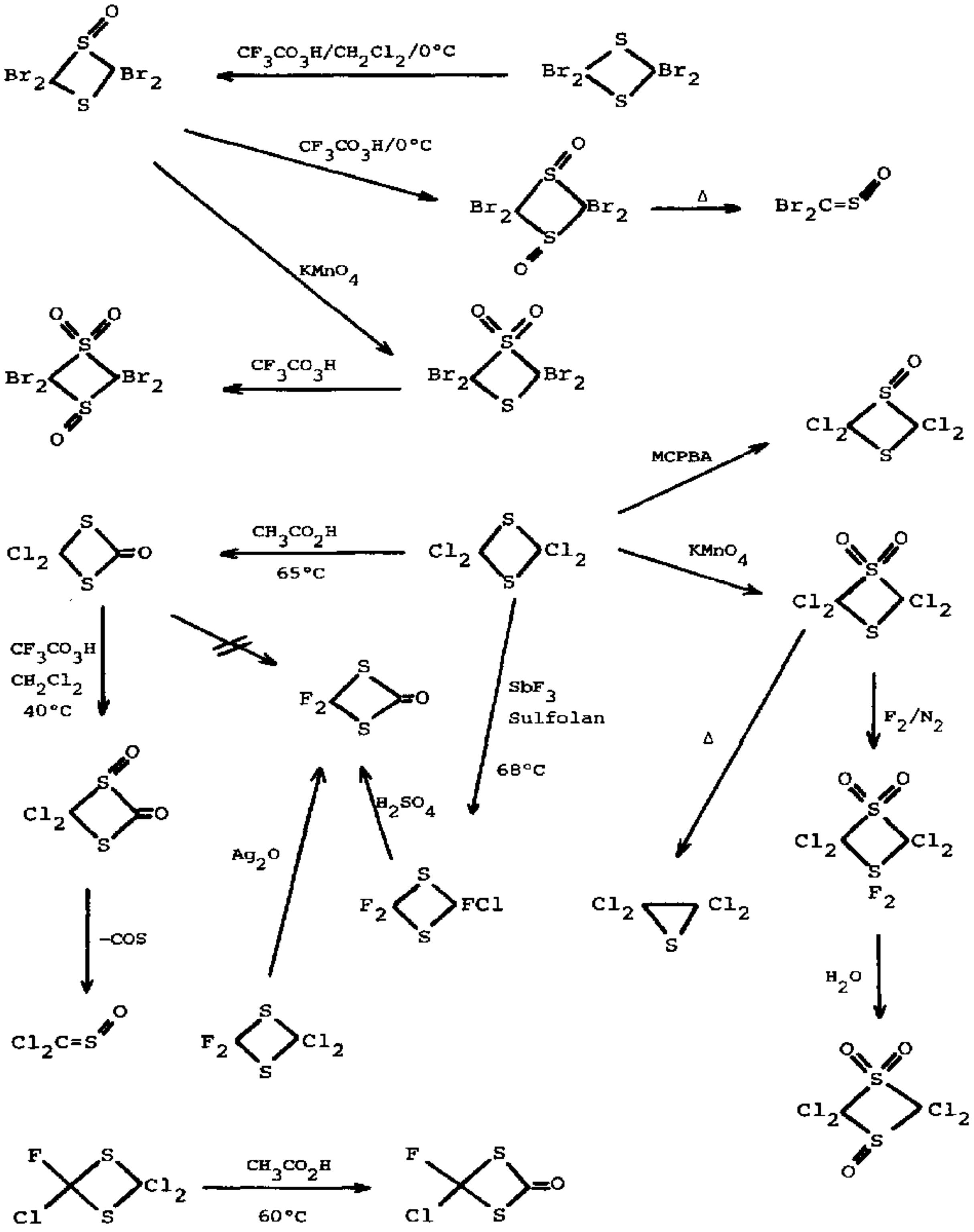
$Tl_2S_2O_5$ has been prepared by the reaction of TlOH and liquid SO_2; it slowly decomposes at room temperature to thallium(I) sulphite and SO_2. Comparison of the vibrational spectra of the thallium(I) sulphite and disulphite with the infrared spectra of the argon-matrix reaction products of Tl_2O and SO_2 indicate that these products are not simply the sulphite and disulphite as was previously suggested but that they are probably complex mixtures of several thallium-sulphur-oxygen compounds.[111] The association constants of the potassium peroxodisulphate ion pair ($K_2S_2O_8^-$) and the reaction rate between peroxodisulphate and iodide ions have been measured in several isodielectric water-solvent mixtures. The sequence of the rate constants does not follow that of the association constants, but agrees qualitatively with the sequence of transition state solvation energies calculated from excess free energies of mixing suggesting the influence of solvent structure on the reactivity.[112] The preparation and characterization of the anionic thiosulphato complexes cis$[(en)_2Co(SO_3)(S_2O_3)]^-$, and cis$[(en)_2Co(S_2O_3)_2]^-$, and of the molecular complex cis-$[(en)_2Co(NO_2)(S_2O_3)]$ have been reported.[113] The reaction of $Ag(OH)_4^-$ with different concentrations of thiosulphate ion in NaOH have been studied. At low concentrations reaction proceeds via the aquated silver(III) species $Ag(OH)_3H_2O$ and results in a monothiosulphato complex $Ag(OH)_3S_2O_3^{2-}$.[114]

Marked similarities have been found between the experimental electron density maps for $Na_2S_2O_3$ and the theoretical maps for amido sulphuric acid NH_2SO_3H. Quantum chemical calculations and determinations of the deformation density in the region of the SO bond and the lone pair on oxygen have been reported.[115] The synthesis and properties of several new, perhalogenated 1,3-dithietane S-oxides, thiiranes and sulphines have been reported, and are shown in Scheme 9.[116]

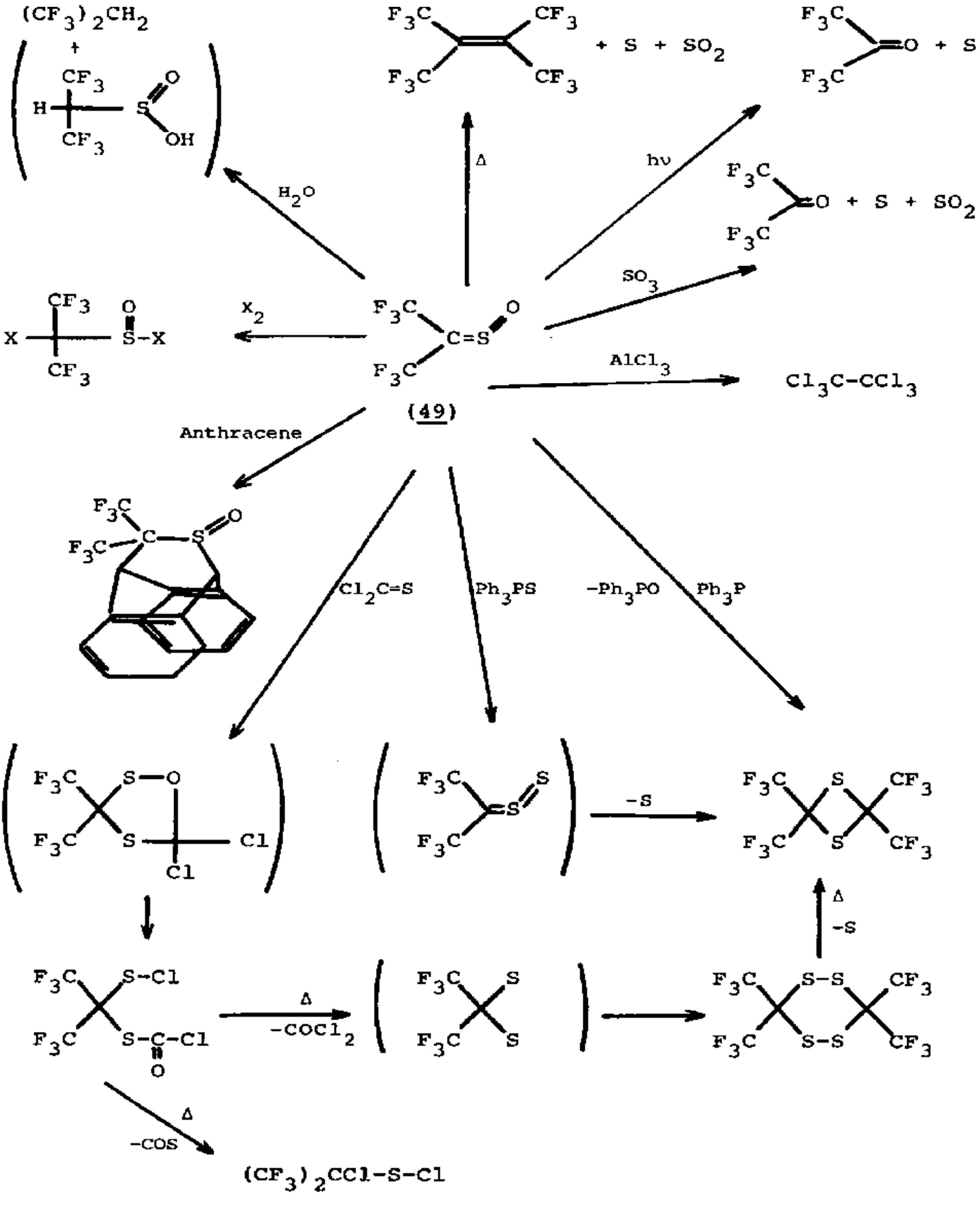
New methods for the synthesis of bis(trifluoromethyl)sulphine (49) have been reported together with the pyrolysis, photolysis and hydrolysis behaviour of the compound and its reaction with the thiocarbonyl group (thiophosgene) with anthracene and halogens (Scheme 10).[117]

Fluoromethane sulphonyl chloride has been prepared by a simple and clean method from chlorofluoromethane. Reaction of FCH_2SO_2Cl with NMe_3 leads to an inverse amine adduct of fluorosulphene, $Me_3\overset{+}{N}$-CHF-SO_2^-.[118] A series of S-oxides (50) to (54) have been prepared by the oxidation of (55) and their pyrolysis products identified (Scheme 11).[119]

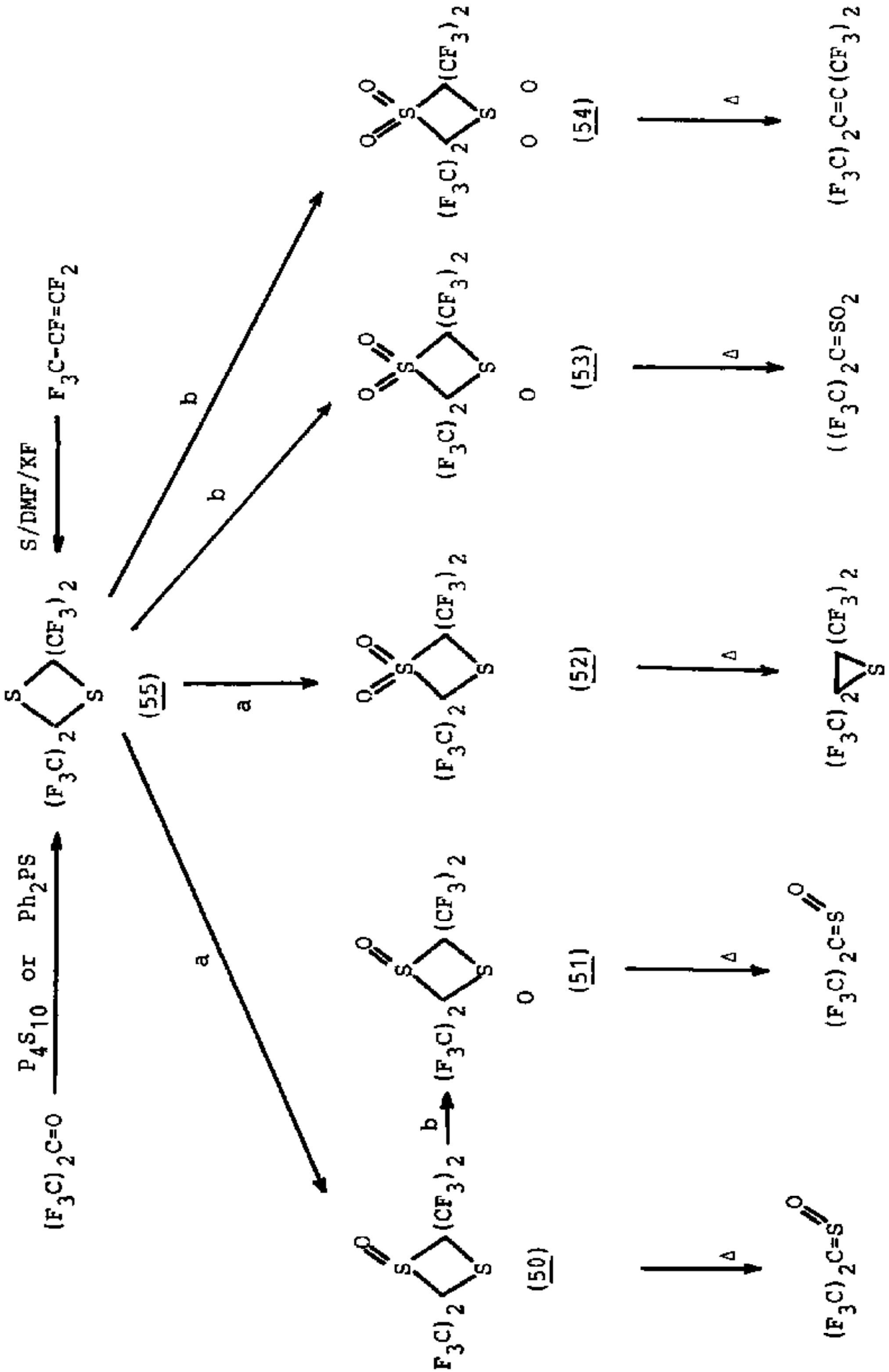
The sulphoxylates $S[OCH(R)CF_3]_2$ and the disulphides $S_2[OCH(R)CF_3]_2$ (R = CF_3 or H) have been prepared from the reaction of SCl_2 or S_2Cl_2 respectively with the lithium alcoxides $LiOCH(R)CF_3$. Reaction of $S[OCH(H)CF_3]_2$ and chlorine gives


CF$_3$CO$_3$H/CH$_2$Cl$_2$/0°C
CF$_3$CO$_3$H/0°C
Δ
KMnO$_4$
CF$_3$CO$_3$H
MCPBA
CH$_3$CO$_2$H
65°C
KMnO$_4$
CF$_3$CO$_3$H
CH$_2$Cl$_2$
40°C
SbF$_3$
Sulfolan
68°C
Δ
F$_2$/N$_2$
H$_2$SO$_4$
Ag$_2$O
–COS
H$_2$O
CH$_3$CO$_2$H
60°C

Scheme 9


$(CF_3)_2CH_2$
+
CF_3
H
CF_3
S
O
OH
H_2O
F_3C
CF_3
F_3C
CF_3
+ S + SO_2
Δ
F_3C
O + S
F_3C
hν
F_3C
O + S + SO_2
F_3C
SO_3
CF_3
O
X
S-X
CF_3
X_2
F_3C
C=S
O
F_3C
(49)
$AlCl_3$
Cl_3C-CCl_3
Anthracene
F_3C
F_3C
C
S
O
$Cl_2C=S$
Ph_3PS
$-Ph_3PO$
Ph_3P
F_3C
S
O
F_3C
S
Cl
Cl
F_3C
S
F_3C
-S
F_3C
S
CF_3
F_3C
S
CF_3
Δ
-S
F_3C
S-Cl
F_3C
S-C-Cl
O
Δ
$-COCl_2$
F_3C
S
F_3C
S
F_3C
S-S
CF_3
F_3C
S-S
CF_3
Δ
-COS
$(CF_3)_2CCl-S-Cl$

Scheme 10



a = $F_3C{-}CO(OOH)$
b = $F_3C{-}SO_2(OOH)$

Scheme 11

$ClS(O)OCH_2CF_3$ and CF_3CH_2Cl whereas the sulphur-sulphur bond in the disulphides is cleaved giving SCl_2 and the sulphoxylates.[120] The crystal structures of the compounds $S_2(SO_2Ph)_2$, $S_2(SO_2C_6H_4Me\text{-}p)_2$, $S(SO_2C_6H_4Me\text{-}p)_2$, $S_3(SO_2C_6H_4Me\text{-}p)_2$ and their selenium analogues have been determined. The selenium analogues were found to be isomorphous with the respective sulphur compounds. In the disulphonyl sulphone or -selane chains, the lengths of the terminal bonds are S-S 2.101 to 2.141 and S-Se 2.242-2.286Å and the lengths of the central bonds between bivalent atoms are S-S 1.987-2.037 and Se-Se 2.246-2.304Å.[121] An 18C6 crown complex of amidosulphuric acid has been obtained from reaction of the crown ether 18C6 with amidosulphuric acid in water, methanol and ethanol and its crystal structure determined.[122]

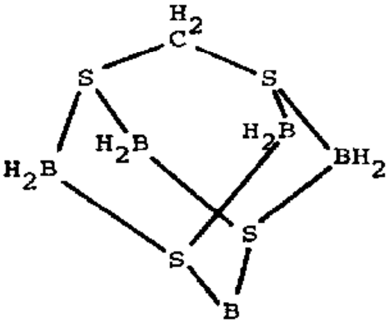
6.2.5 Sulphides

The energies of unstable negative ions formed by the addition of electrons to H_2S and $(CH_3)_2S$ have been determined by electron transmission spectroscopy. The orbitals occupied in these ions were found to be of σ^* type and to have the proper symmetry to act as acceptors of π-electron density from transition metals or aromatic systems. The electron attachment energy of H_2S was lower than that found for Me_2S consistent with the weaker π-acceptor ability of methylated compounds.[123] Several hydrogen bonded complexes of H_2S and HF and H_2Se and HF have been prepared by condensing the argon-diluted reagents at 12K. The observation of two ν_1(H-F) librational modes is consistent with pyramidal structures for the complexes. A stable reverse complex HF---HSH and a $H_2S\text{---}(HF)_2$ complex were also observed.[124] ^1H n.m.r. has been used to identify the sulphanes H_2S_9 to H_2S_{35} in benzene solution and the complete sulphane distribution in crude oils. In sulphane mixtures without solvent or in CS_2 and CCl_4 solution, H_2S_8 shows the largest downfield shift and characterization of higher sulphanes is difficult.[125]

The first interalkali metal sulphide KLiS has been prepared and its crystal structure determined. The structure is characterized by c-centered squares of lithium layers interspersed by anti parallel ordered K-S pairs forming an anti PbFCl-type structure.[126] The same group of workers have also prepared NaLiS which is also hygroscopic and has the anti PbFCl structure.[127] $Cs_2S_5.H_2O$ has been synthesized from an aqueous solution of Cs_2S (prepared from $Ba(OH)_2.8H_2O$, Cs_2SO_4 and H_2S) and stoichiometric amounts of sulphur. The characteristic features of the structure of $Cs_2S_5.H_2O$ are unbranched, zig-zag chains of $S_5{}^{2-}$ as are found in other known pentachalcogenides of the M_2X_5 type, and hydrogen bridges between terminal sulphur atoms of the chains and oxygen atoms of the water molecules.[128] The preparations, thermal decompositions i.r. and Raman spectra and phase transitions of the strontium polysulphides, SrS_2, SrS_3A and SrS_3B have been investigated. $S_3{}^{2-}$ entities were found in both forms of SrS_3.[129]

Solid state ^{11}B n.m.r. techniques have been used to study the structural nature of various phases in the systems B-S, B-Se, B-S-Se, and B-Te. It was demonstrated that the techniques could be used efficiently for the structural characterization of these hydrolytically sensitive and glass forming systems. In the B-S system the novel compound BS_2 was observed at higher S:B ratios and B_2S_3 at lower ratios whilst in the B-Se system, BSe_2 rather than the expected B_2Se_3 was observed as the only product besides a subselenide with B-B bonds. No binary B-Te compounds were detected.[130]

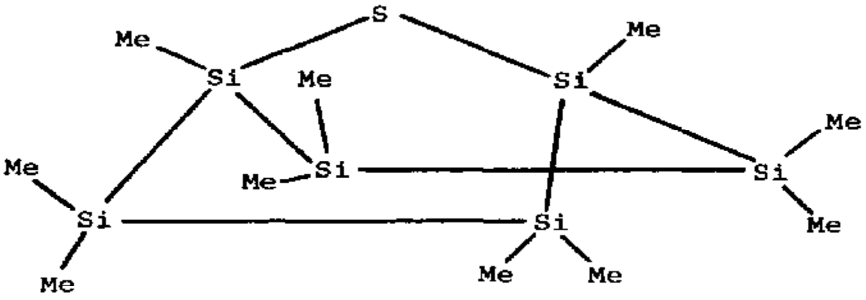
Hydroboration of CS_2 with NaB_3H_8 has been shown to yield the new compound $Na[CH_2(BH_2)_5S_4]$ isolated as the tri-dioxanate. The anion has the adamantane skeleton CB_5S_4 (<u>56</u>) and the crystal structure of the analogous compound $Ph_4P[CH_2(BH_2)_5S_4]$ was determined.[131]



(<u>56</u>)

GaS, prepared at temperatures below that required for adequate annealing exists in the form of microcrystals with a much higher stacking fault density and lower overall crystal symmetry than that found for β-GaS. High resolution electron microscopy shows this to be due to a predominance in the material of a high pressure modification of GaS present metastably in the partially annealed samples.[132] The oxide sulphide, $CaLaGa_3S_6O$, $SrLaGa_3S_6O$, $La_2ZnGa_2S_6O$ and $Sr_2ZnGe_2S_6O$ have been prepared for the first time and their space groups and lattice dimensions determined. Atomic positions were obtained from single crystal data for $CaLaGa_3S_6O$ and $La_2ZnGa_2S_6O$.[133]

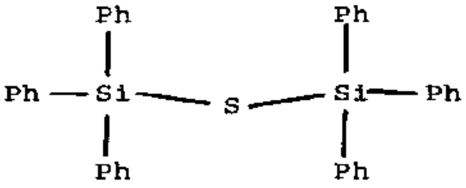
The first thiasilane derived from a polysilane, (57), has been prepared from 1,4-dichlorodecamethylhexasilacyclohexane and H_2S with elimination of HCl.[134]



(57)

Bis(triphenylsilyl)sulphide (58) has been prepared by the condensation of triphenylsilanethiol. The molecule is bent with a bond angle Si-Si-Si = 112° and with mean bond distances Si-S and Si-C of 215.2 and 187.4pm respectively.[135]

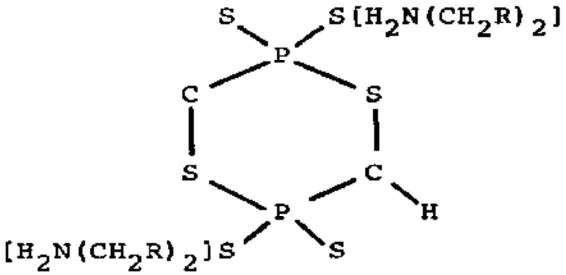
The polytypes of SnS_2 crystals grown by chemical transport reactions have been studied.[136,137] The structure of $(LaO)_4Sn_2S_6$ has been shown to consist of alternating independent layers of $(LaO)_n$ and $(SnS_3)_n$ with the former being formed of tetrahedra of



(58)

La with an oxygen atom at their centres and the latter to contain chains of distorted sulphur octahedra with Sn occupying off-centre positions.[138] The preparations of the isotypic compounds $Ba_3CdSn_2S_8$ and $Ba_6CdAg_2Sn_4S_{16}$ and the crystal structure of the former have been described.[139]

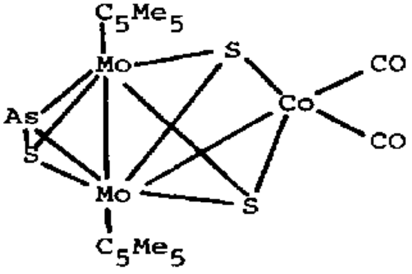
Polysulphides dissolved in non-aqueous solvents have been shown to react under anaerobic conditions with nitric oxide to yield solutions of nitrosodisulphides.[140] The reaction of P_4S_{10} with tertiary alkyl amines has been used to prepare several dialkylammonium salts of (59).[141]



(59)

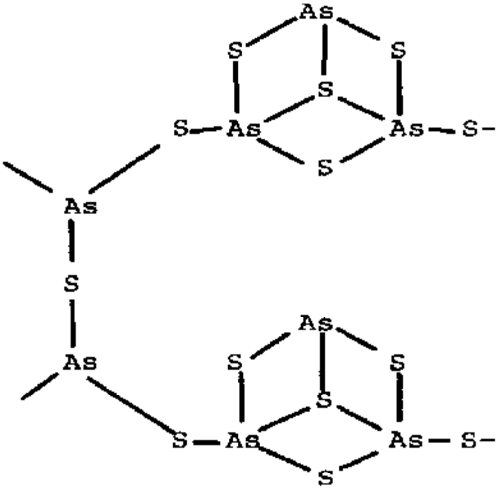
Gas phase electron diffraction, microwave spectroscopy and n.m.r. spectroscopy have been used to investigate the molecular structure of difluorophosphine sulphide, PF_2HS. The parameters obtained were r(P-F) 154.6, r(P=S) 187.5, r(P-H) 141.9pm FPF 99.1 FPS 117.2 and HPS 116.4°.[142]

$Ti_4P_8S_{29}$ has been prepared by reaction of the elements at 400°C and a crystal structure determination shows it to correspond to the constitutional formula $Ti_4^{4+}([PS_4]_4^{3-}[P_2S_6]^{2-}[P_2S_7]^{2-})$. The anion PS_4^{3-} is tetrahedral, $P_2S_6^{2-}$ is built up from two tetrahedral PS_4 units sharing an edge and the novel $P_2S_7^{2-}$ can be derived from $P_2S_6^{2-}$ by replacing one of the bridging S atoms by a disulphide group.[143] $Cs_2P_2S_6$ and $K_2P_2S_6$ have been shown to be isostructural with $Tl_2P_2S_6$ and to contain discrete $P_2S_6^{2-}$ anions. Two PS_4 tetrahedra are connected by a common edge to hexathiametadiphosphate groups.[144] HfP_2S_6 has also been prepared from the elements at temperatures between 500 and 900°C and is isostructural with TiP_2S_6.[145] The reaction of Na_2S_4 and PPh_4Cl in ethanol solution has been shown to give $[P(Ph)_4]_2S_8$.[146] The first complex (<u>60</u>) with AsS as a ligand has been obtained from the dinuclear complex $(C_5Me_5)_2MoAs_2S_3$ and $Co(CO)_8$.



(<u>60</u>)

From the bond lengths it was concluded that AsS has a bond order of 1 and functions as a 5 electron donor; the analogous PS complex was also prepared.[147] The reaction of As_2S_3 and PPh_4Cl with HCl in CH_2Cl_2 or $1,2\text{-}C_2H_4Cl_2$ gives $PPh_4[As_2SCl_5]$ and reaction with a further mole of PPh_4Cl gives $(PPh_4)_2[As_2SCl_2]$. The coordination of the As atoms in the $As_2SCl_5^-$ ion is distorted trigonal bipyramidal (including the lone pair of electrons) with the S, one Cl atom and the lone pair in equatorial positions; the two bipyramids around the two As atoms sharing a common edge. The As atoms in $As_2SCl_6^{2-}$ have a distorted octahedral coordination with the two octahedra sharing a common face with the lone electron pair in the trans positions to the sulphur atoms.[148] The reaction of ethylenediamine (en) with As_2S_3 gives $(enH_2)_3(As_3S_6)_2.6en$ which contains discrete cyclic $As_3S_6^{3-}$ anions with a six membered As_3S_3 ring in the chair conformation.[149] $Co_2As_8S_{13}$, prepared by the reaction of Co_2CO_3 with As_2S_3 in aqueous solution under pressure at 180°C, contains polymeric $As_8S_{13}^{2-}$ anions which are made up of individual As_4S_4 rings which are each connected to three further 8-membered rings via As-S-As bridges to form an infinite layer structure.[150] The analogous Rb and ammonium thioarsenates have also been prepared as monohydrates. Structure determination of the Rb compound shows it to contain the same polymeric anions $As_8S_{13}^{2-}$ (61) composed of individual As_4S_4 rings interconnected by bridging AsS_3 pyramids.[151]



(61)

$SnSb_2S_4$ and $SnSb_2Se_4$ are isostructural and are composed of ribbons of edge sharing semi-octahedra, MX_5, linked by shared S or Se atoms.[152] The reaction of $MeC(CH_2SbCl_2)_3$ with H_2S has been shown to give $CH_3C(CH_2SbS)_3$ and with NaSeH, $CH_3C(CH_2SbSe)_3$ and $CH_3C(CH_2Sb)_3Se_2$, attempts to prepare the analogous Te containing compounds were not successful.[153]

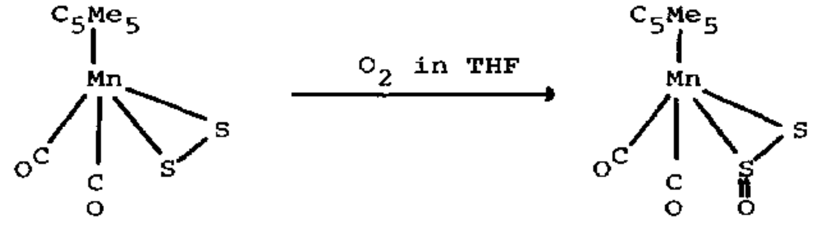
The bond structures of compounds containing one dimensional MS_2 chains with edge-sharing tetrahedra or square planar coordination at the transition metal, M, have been examined in considerable detail.[154] A new metastable modification of TiS_2 has been prepared by a topotactic solid-state reaction at room temperature in which $CuTi_2S_4$ working electrodes were anodically oxidized in aprotic copper(I) electrolytes. On the basis of X-ray powder data it was found that the new phase belongs to an unusual AB_2 structural type. This cubic form of TiS_2 is of interest as a material for reversible electrodes in secondary batteries, having advantages over the normal hexagonal layer lattice type TiS_2.[155] The effect of sodium intercalation on the electronic structure of a slab of the layer lattice form of TiS_2 has been studied using calculations employing the tight-binding method. Flattening of the slab beyond a critical value was found to increase, not only the density of states at the Fermi level for Na_xTiS_2 but also the anisotropy of electron distribution around Ti^{4+} which explains why there is an abrupt change in both the isotropic and anisotropic parts of the sodium Knight shifts during the phase transition.[156] The structure of Tl_2TiS_4 has been found to consist of infinite perthioanions $TiS_{4/2}(S_2)^{2-}$ which are separated by Tl^+ cations. The anion chains are built up from distorted octahedra, the two unshared S atoms of each being connected by a S-S bond of 2.10Å.[157] The crystal structure of the new ternary sulphide $Zn_2Ti_{18}S_{32}$ has been determined.[158] The preparation and molecular and electronic structure of the cluster compound $(CpTi)_5S_6$ have been described, the reaction stoichiometry was thought to be as shown in equation (33) although other sulphur-containing products were obtained.[159] The La atoms in $La_5V_3O_7S_6$

$$10Cp_2Ti(CO)_2 + 12H_2S \rightarrow 2(CpTi)_5S_6 + 7H_2 + 20CO + 10C_5H_6 \qquad ...(33)$$

have been shown to be nine coordinated in tricapped trigonal prisms containing four oxygen and five sulphur atoms or vice-versa whilst the vanadium atoms are in octahedral coordination with two oxygen and four sulphur atoms.[160] The niobium(IV) compounds $Nb_2X_4S_3$ (X = Br or Cl) have been prepared by the reaction of NbX_5 and Sb_2S_3 in CS_2 at 50°C and have been shown to contain the $[\overline{Nb-S-Nb-S}_2]^{4+}$ moiety.[161] The structure of $Pb_{0.15}Nb_3S_4$ consists of Pb atoms partially occupying the large channel parallel to the c axis in the Nb_3S_4 host lattice. The sulphur atoms form flat trigonal antiprisms around Pb with the lead atoms moved away from the centre which gives three long and three short Pb-S distances.[162]

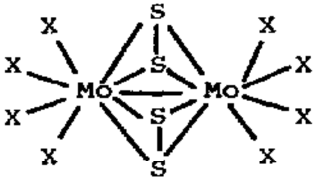
The discrepancy between the ideal stoichiometry of $LaCrS_3$ and the site contents of the unit cell $La_{72}Cr_{60}S_{192}$ which corresponds to $60La_{1.2}CrS_{3.2}$ has been the subject of some conjecture in the past. A study using EPMA and density measurements, whilst not unequivocal, suggests that there is no evidence for gross cation disorder and that the composition is probably close to $La_{1.2}CrS_{3.2}$ rather than $LaCrS_3$. The former composition implies an average cation valence of 2.91 which taking into account how the crystals were prepared seems quite plausible.[163] Oxidation of the S_2 complex (62) to the S_2O complex (63) can be achieved even with atmospheric oxygen. The pronounced acceptor character of the S_2O

ligand has been demonstrated for the first time in (63) and the bonds in coordinated S_2O are longer than those in free S_2O.[164]



(62) (63) ...(34)

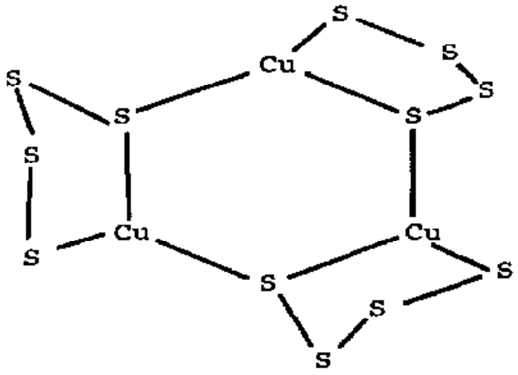
The synthesis of novel tri- and tetranuclear clusters in the Mo-Fe-S system has been accomplished by the addition of $Fe(CO)_5$ or $Fe_2(CO)_9$ to the complex $(C_5Me_5)_2Mo_2S_4$.[165] The addition of tetraalkylthiuram disulphides $[R_2NC(S)S\text{-}SC(S)NR_2]$ to MoS_4^{2-}, WS_4^{2-} and $MoO_2S_2^{2-}$ has been shown to yield the new complexes $Mo(V)(S_2)(S_2CNR_2)_3$ and $W(VI)S(S_2)(S_2CNR_2)_2$ and the known complex $Mo(VI)O(S_2)(S_2CNR_2)_2$ respectively.[166] Calculations of the electronic structures of MoS_4^{2-} and $Mo_3S_9^{2-}$ have shown that in both systems the closeness of the atomic energy levels of the sulphur atoms 3p and the molybdenum atoms 4d and 5s levels results in substantial delocalization of the molecular orbitals. Nominally non-bonding sulphur atoms (at 3-3.5Å) still interact sufficiently to split some of their bonding and antibonding levels. Both levels are however occupied so no net S-S bonding results.[167] Interactive molecular graphics have been applied to modeling steric effects in the sulphido-bridged molybdenum dimers $[CpMoS(\mu\text{-}S)]_2$. It was shown that the intramolecular van der Waals energies of the syn isomers are higher than those of the corresponding anti isomers.[168] The polypyrazolylborate complexes, $[(HB(pz)_3Mo(CO)_2]_2S$ and $[HB(Me_2pz)_3)Mo(CO)_2]_2S$ have been shown to contain a linear $[Mo\text{-}S\text{-}Mo]^{2+}$ unit with unusually short Mo-S distances of 2.180 and 2.200Å. The selenium analogue of the first complex was also prepared and shown to have a similar structure with a linear Mo-Se-Mo bridge.[169] The synthesis, spectroscopic and structural properties of a series of cyanothiomolybdates with Mo_2S, Mo_2S_2, Mo_3S_4 and Mo_4S_4 cores have been studied.[170] $Mo(S_2)Cl_3$, prepared by an improved method has been shown to react in CH_2Cl_2 with $(PPh_3Me)Cl$ to give $(PPh_3Me)_2[Cl_4Mo\mu\text{-}S_2)_2MoCl_4].2CH_2Cl_2$. The corresponding bromo complex was prepared by reaction of $MoBr_4$ with S_7NH and subsequent treatment of the reaction mixture with PPh_4Br in CH_2Br_2 solution. Both complexes are ionic with PPh_3Me^+ and PPh_4^+ cations respectively and anions $[X_4Mo(\mu-S_2)_2MoX_4]^{2-}$ (<u>64</u>).[171]



(<u>64</u>)

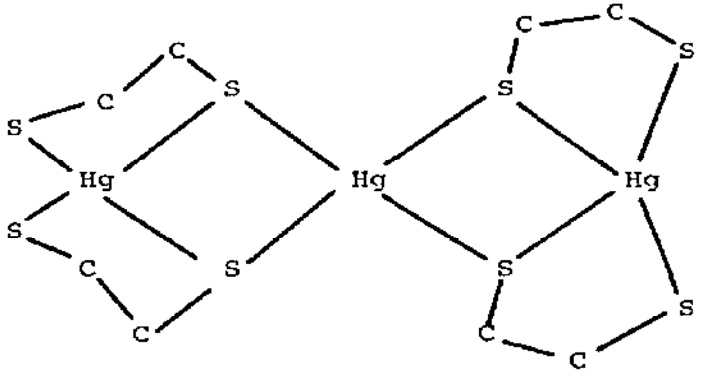
The complexes $Pd_2X_2(\mu\text{-dppm})_2$ where X = Cl, Br, have been shown to abstract sulphur from H_2S under ambient conditions to form $PdX_2(\mu\text{-S})(\mu\text{-dppm})_2$ and H_2 quantitatively. The latter can be oxidised in stages to μ-SO and μ-SO_2 derivatives, the latter losing SO_2 spontaneously to regenerate the former complex.[172] The new ternary transition metal chalcogenides Ta_2PdS_6, Ta_2PdSe_6, Nb_2PdS_6 and Nb_2PdSe_6 have been prepared and shown to possess a new laminar structural type.[173] The addition of K_2PtCl_6 to an aqueous ammonium polysulphide solution has been shown to result in the formation of $[NH_4]_2[Pt(S_5)_3]2H_2O$. Addition of concentrated HCl results in the separation of $[NH_4]_2[PtS_{17}]2H_2O$.[174]

The reaction of $Cu(CH_3COO)_2H_2O$ with a polysulphide solution gives $[Ph_4P]_2(NH_4)[Cu_3(S_4)_3].2CH_3OH$. The anion $[Cu_3(S_4)_3]^{3-}$ (<u>65</u>) consists of a central Cu_3S_3 ring and three CuS_4 rings.[175]



(<u>65</u>)

The mixed valence compound $K_3Cu_8S_6$ has been shown to possess metallic electrical conductivity at temperatures above 160K and below less-conducting structural phases. The changes in conductivity between 160 and 100K are also associated with changes in magnetic susceptibility.[176] The synthesis, characterization and physical properties of the ternary sulphides MPd_3S_4 (M = Rare Earth metal) have been described. $LaPd_3S_4$ was shown to have the ideal $NaPt_3O_4$ structure.[177] The structure of $ZnAgPS_4$ is closely related to that of the high temperature form of $ZnAl_2S_4$.[178] A general procedure for the synthesis of the polysulphido, $[M(S_x)_2]^{2-}$, complexes (M = Zn, x = 4-6; M = Cd, x = 5; M = Ni, x = 4; M = Mn, x = 5,6) has been described and some reactions carried out.[179] The reaction of $Zn(CH_3COO)_2.2H_2O$, $Cd(CH_3COO)_2.2H_2O$ or $Hg(CH_3COO)_2$ with defined alcoholic polysulphide solutions lead to the formation of $(NEt_4)_2[Hg(S_6)_2]$, $[(PPh_3)_2N]_2[Cd/S_6)_2].CH_3CN$, $(PPh_4)_2[Zn(S_6)_2]$ and $(PPh_4)_2[Hg(S_4)_2]$.[180] On varying the reaction conditions treatment of $HgCl_2$ with ethane-1,2-dithiolate and Ph_4PBr in methanol yields either $[Ph_4P]_2[Hg(SCH_2CH_2S)_4]$ which contains isolated trinuclear anions (66) or $[Ph_4P]_2[Hg_2(SCH_2CH_2S)_3]$ which has polymeric anions composed of quasi isolated binuclear subunits (67).[181]



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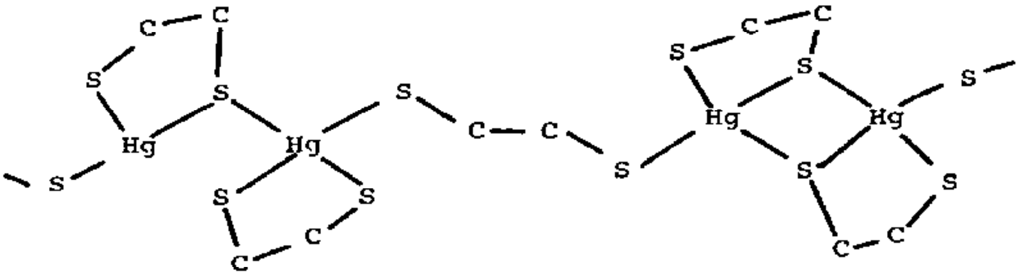


(67)

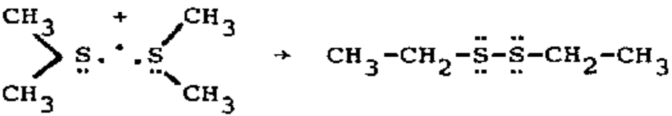
The compound $Nd_3Br_5S_2$ has been shown to contain NdS_4 tetrahedra linked in ribbons and surrounded by Br atoms. Nd atoms found in the middle of the ribbon are bonded to four sulphur atoms and four bromine atoms whilst those at the edge are surrounded by two sulphur and five bromine atoms.[182] The sulphide fluorides LnSF with Ln = Er, Yb, Lu have been shown to undergo a high pressure transformation from the β YSF type to a PbFCl type structure.[183] The structure of $EuEr_2S_4$ has been shown to be of the $CaFe_2O_4$ type with Eu atoms in 8-fold prismatic coordination.[184] The chemistry of transition metal polysulphides has been reviewed.[185]

The following phase systems involving sulphides have been studied: Ga_2S_3-Eu_2O_3,[186] GaX_3-Ga_2S_3 and InX_3-In_2S_3 (X = Cl, Br, I),[187] Ga_2S_3-Ga_2O_3,[188] Tl_2S-GeS_2,[189] Tl-Ge-Sn-S,[190] Tl-Tl_2S-Cu_2S-Cu,[191] CuTlS-Tl_2S-S.[192]

Structural studies have been carried out on the following transition metal complexes containing metal-sulphur bonds: $(PPh_4)_2[MoCl_3(N_3S_2)]_2.2CH_2Cl_2$,[193] $[\eta^5\text{-}C_5H_5)(CO)_2Mn]_2SO$,[194] $(\eta^5\text{-}C_5Me_5)_2Fe_2S_4$ and $(\eta^5\text{-}C_5Me_5)_2Co_2S_4$,[195] $(Et_4N)_6(Fe_4S_4I_4)_2Fe_2S_2I_4$,[196] $[Fe(C_6H_{22}S_3)_2](PF_6)_2$,[197] $[Co_8S_6(SPh)_8]^{4-}$ and $[Co_8S_6(SPh)_8]^{5-}$,[198] $[Fe_6(\mu_3\text{-}S)_8(PEt_3)_6]$-$(BPh_4)_2$.[199] An EXAFS study of W-Fe-S clusters containing the WS_2Fe unit has been carried out[200] and a XANES study of the Fe-Mo protein of nitrogenase and its synthetic Fe-Mo-S clusters has been reported.[201] The electronic structures of Fe-S clusters,[202] and the $MoFe_3S_4(SH)_6{}^{3-}$ ion[203] and the preparation and properties of $[Co_4S_3(SO)(CN)_{12}]^{8-}$[204] have been described. The homolytic and heterolytic Zn-S bond enthalpy have been found to be 177.4 and 740.2 kJ/mole respectively.[205]

6.2.6 Bonds to Carbon

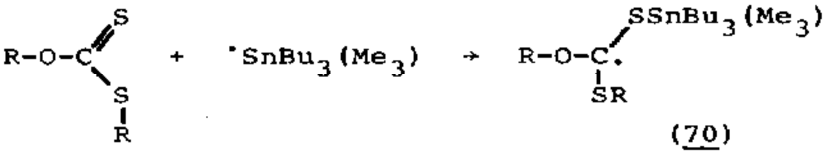
A novel rearrangement of the radical cation (<u>69</u>) with a three electron bond has been described. In the rearrangement H^+ and H are formally split off and the reaction takes place only for high concentrations of (<u>69</u>) and it is noteworthy that oxygen does not affect the yield.[206]



(<u>69</u>) (<u>68</u>) ...(35)

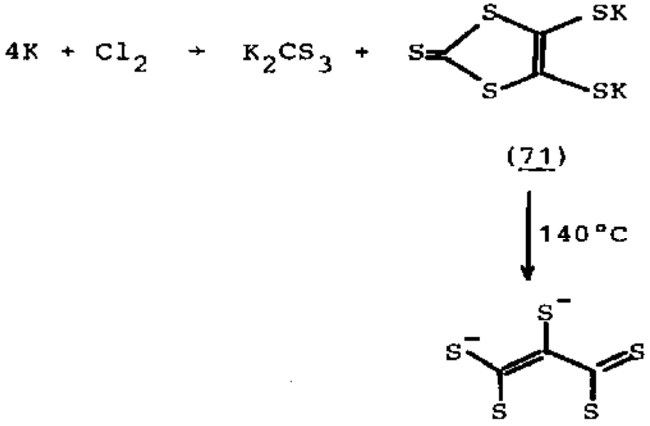
A new homogeneous organonickel reagent has been used for the reductive cleavage of the carbon sulphur bonds in thiols, sulphides and thioacetals. In a typical reaction the organosulphur compounds are treated with the reagent which is prepared in situ from an equimolar mixture of nickelocene and lithium aluminium hydride in THF. In general one equivalent of the nickel reagent is required for each carbon-sulphur bond reduced.[207]

The oxide transfer technique, involving O^{2-} transfer from Tl_2O to a suitable acceptor, has been coupled with matrix isolation for the synthesis and infrared spectroscopic characterization of the mono and dithiocarbonate anions CO_2S^{2-} and $COS_2{}^{2-}$ each in a triple ion with two Tl^+ cations. CO_2S^{2-} was characterized by sharp intense carbon-oxygen stretching vibrations at 1445 and 1202 cm^{-1} and a carbon-sulphur stretching mode at 603 cm^{-1}. The two most intense bands of the $COS_2{}^{2-}$ anion the C-O stretch and the antisymetric C-S stretch were identified at 1506 and 606 cm^{-1} respectively.[208] A study of the mechanism of reduction of dithiocarbonates(Xanthates) with tributylstannane has shown that the deoxygenation occurs by addition of stannyl radicals to give (<u>70</u>) followed by fragmentation rather than by direct S_H2 attack on sulphide sulphur.[209] Dichloromethane solutions of Sn(IV) tetrachloride with an excess of dimethyl sulphide have been shown to contain trans- and cis-$SnCl_4.2Me_2S$ isomers in dynamic equilibrium.[210]


(70)

...(36)

The crystal structure of dipotassium 1,2-dithiole-3-thion-4,5-dithiolate, $K_2C_3S_5$ has been determined. The compound was prepared by the reaction of potassium with CS_2 in DMF to give (71) which isomerizes quantitatively to $K_2C_3S_5$ after 1-2h at temperatures between 120 and 140°C.[211]

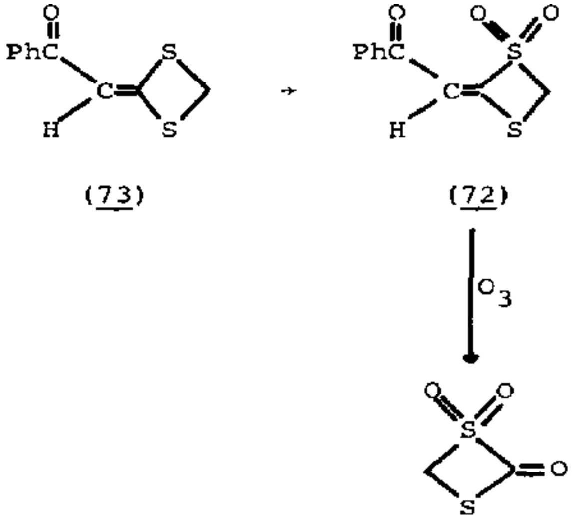

(71)

...(37)

The reaction of $HSCR_3$ (R = $SiMe_3$) with $M(NR_2)_2$ (M = Ge or Pb, R = $SiMe_3$) has been shown to give some unexpected products: cis and trans $[Ge(CH_2Ph)(NR_2)(\mu\text{-}S)]_2$ a rare example of a group four cyclodi(metal thiene); $[Pb(SCR)_3(\mu\text{-}SCR_3)]_2$ which the new ligand SCR_3 functions as both a bridging and as a terminal ligand and $[Pb(NR_2)(\mu\text{-}SCR_3)]_2$ the first simple prochiral group 4 metal(II) complex.[212]

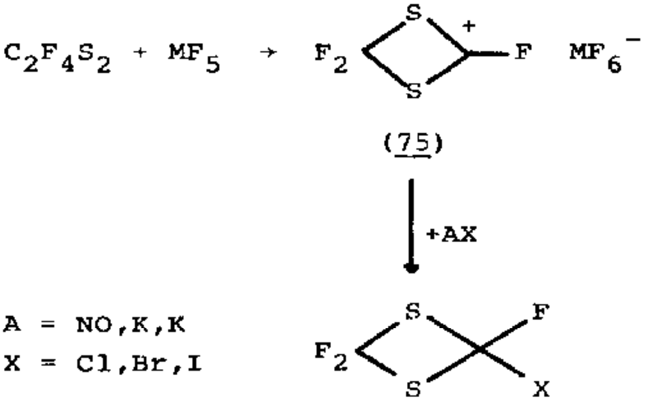
The ozonolysis of (72) prepared via oxidation of (73) has been shown to give (74) as the first 1,3-dithietane with an α oxosulphone structure. (74) can be regarded as a potential sulphene precursor but pyrolysis of (74) has not yet yielded sulphene.[213]

The reaction of $C_2F_4S_2$ with the Lewis acids AsF_5 and SbF_5 gives the stable salts (75), the addition of Cl^-, Br^- or I^- to these salts gives the stable dithietanes (76). The corresponding



(<u>73</u>) (<u>72</u>) (<u>74</u>) ...(<u>38</u>)

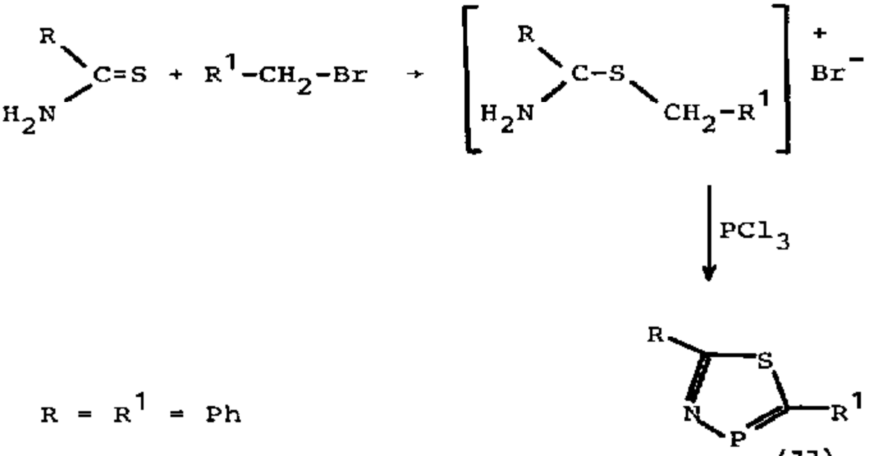
stable salt $C_2ClF_2S_2^+SbF_6^-$ also adds Cl^- or Br^- to form $C_2Cl_2F_2S_2$ and $C_2BrClF_2S_2$ respectively.[214]



(<u>75</u>) (<u>76</u>) ...(<u>39</u>)

Crystals of $F_2CS_2CF^+$ AsF_6^- have been shown to be orthorhombic with the space group Pmmn. The cation (<u>75</u>) possesses mm symmetry and does not show any short intermolecular interactions. The C-F and C-S bonds to the cationic carbon are significantly shorter than the other C-F and C-S bonds.[215]

Novel simple heteroarenes such as (<u>77</u>) can be prepared from thiocarbamides by alkylation at the sulphur atom and subsequent condensation with PCl_3.[216]

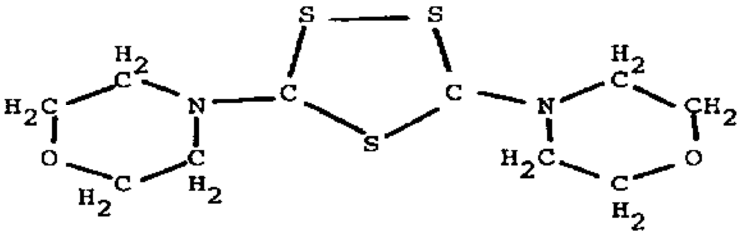


R = R^1 = Ph

(77)

...(40)

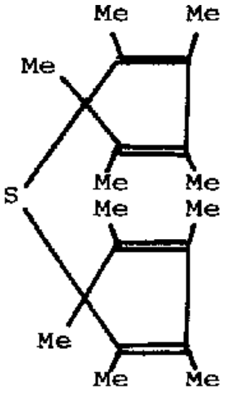
In the oxidation of thiourea by iodate in weakly acidic solution the concentration of iodide may exhibit several extrema, the number of which mainly depends on the initial ratio of the concentrations of thiourea and iodate and is at most four. The first step of the reaction results in the formation of iodide which then reacts with iodate to give iodine.[217] The reaction of $S_2[C(S)NC_4H_8O]_2$ with iodine in ratios ranging between 1:1 and 1:10 has been investigated in CH_2Cl_2 by spectrophotometric methods. The immediate production of the known 1:1 charge-transfer complex between the reagents is observed and the species evolves according to a first-order rate law to give a brown compound which has been isolated from concentrated solutions. The structure of the compound consists of $[C_{10}H_{16}N_2O_2S_3]^{2+}$ cations (78) and discrete polyiodide anions I_{16}^{4-}.[218]



(78)

The pentamethylcyclopentadienyl-sulphur compounds $S(C_5Me_5)_2$ (79) and $S_2(C_5Me_5)_2$ have been prepared by the reaction of $Li(C_5Me_5)$

with SCl_2 and S_2Cl_2 respectively. The X-ray crystal structure of $S(C_5Me_5)_2$ was determined and it was clear that the two C_5Me_5 rings are almost coplanar and are slightly staggered.



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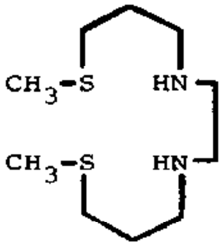


(80)

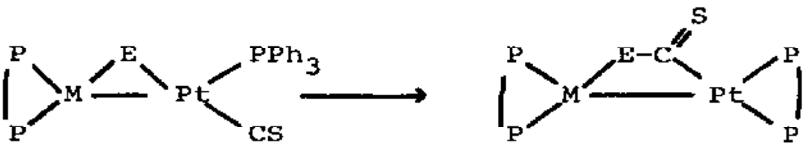
The reaction of (79) with $Fe_2(CO)_9$ results in the formation of the known cluster compound $Fe_3S_2(CO)_9$. Cyclic voltammetry experiments on (79) and C_5Me_5H suggest that oxidation occurs at the carbocyclic ring rather than at the sulphur atom and attempts to prepare cations of the type $[S(C_5Me_5)_2]^+$ were unsuccessful.[218]

Oligomeric complexes of tetrathio-oxalate with Ni(II), Cu(II) and Pd(II) have been synthesized, yielding materials having high electrical conductivities of up to 20 S cm^{-1}.[219]

The compound β-$(ET)_2AuI_2$ where ET is bis(ethylenedithio)tetrathiafulvalene, has been shown to be an organic superconductor with a transition temperature of either 3.2K[220] or 3.93-4.98K.[221]

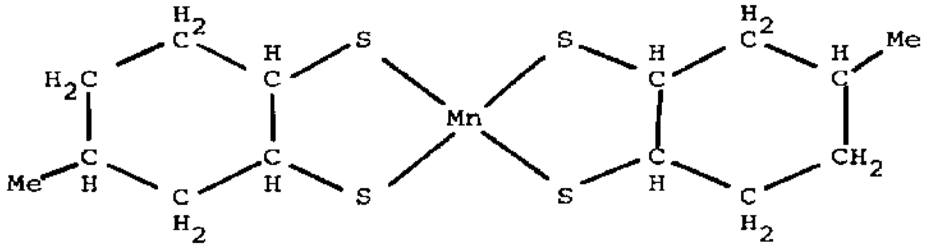
A series of cylindrical macrocyclic ligands have been synthesized by high dilution condensation of macrocyclic ligands containing 12-membered N_2S_2 and 15-membered N_2S_3 subunits following different reaction sequences.[222] The protonation of six N_2S_2 macrocycles and the open chain ligand (80), as well as their complexation with Cu^{2+} have been studied. The first protonation constant of these ligands is in the range of slightly acidified secondary aliphatic ammonium ions whereas the second is essentially determined by electrostatic factors.[223]

The reaction of $MoBr_4$ and excess dimethyl sulphide gives $SMe_3^+[MoBr_4(SMe_2)_2]^-$ the cation of which has S–C bonds of length 180pm and C–S–C bond angles of 102 and 103°. In the anion the Mo atom is octahedrally coordinated by 4 Br atoms in equatorial positions and the two sulphur atoms of the SMe_2 donor molecules in axial positions with Mo-S bond lengths of 254pm.[224] The metal initiated reformation of CS_2 (and CSSe) from the ligands CS and S (and CS and Se) can be accomplished by reaction of the binuclear complex (<u>81</u>) with biphosphane ligands.[225]



(<u>81</u>) M = Pt or Pd, E = S or Se. ...(41)

The reaction of CS_2 with $Mo(CO)_2(S_2CNEt_2)_2$ in the presence of 2 equivalents of PPh_3 results in the formation of the dinuclear complex $Mo_2(S_2CNEt_2)_3(\mu\text{-}CSC(S)S)(\mu\text{-}S_3C_2NEt_2)$. A structure determination showed that one molecule of CS_2 and two thiocarbonyl units have been incorporated in two new ligands. One ligand results from CS coupling with CS_2 to form a $-CSC(=S)S^-$ unit where the carbon bridges both metals and the sulphide chelates to one molybdenum. The second ligand appears to form by thiocarbonyl insertion into a molybdenum-sulphide bond of a dithiocarbamate (S_2CNEt_2) to give a $-SC(SC(S)NEt_2)$ moiety.[226] The reactivity of some copper(I) tetrahydroborates towards CS_2 and SCNPh (and COS[227]) and the structures of $(PPh_3)_2Cu(\mu\text{-}S_2CSCH_2SCS_2)Cu(PPh_3)$, $(PPh_3)_2Cu(S_2COEt)$ and $(PPh_3)_2Cu(S_2CNHPh).CHCl_3$ have been described.[228] The first dithiocarboxylato derivatives of gold have been obtained. The compounds have the stoichiometries $Au(CH_3CS_2)$, $Au(PhCS_2)$ and $Au(PhCS_2)(Ph_2CCS_2)$, the structures of the dithioacetic acid derivative and the mixed ligand compound have been determined.[229] The unusual planar manganese(III) sulphur complex (<u>82</u>) has been prepared by the reaction of $MnCl_4.4H_2O$ with toluene-3,4-dithiolate in methanol in the presence of atmospheric oxygen. A further product is a square pyramidal complex containing an additional apical MeOH group. Reaction under anaerobic conditions leads to the formation of the manganese(II)-sulphur complex $[Mn(S_2C_6H_3Me)_2]^{2-}$ which differs from (<u>82</u>) in that it has a strongly distorted tetrahedral coordination.[230]



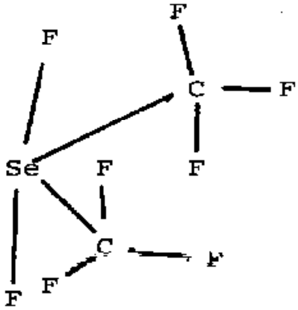
(82)

Parts 147 to 165 of the series of papers on the chemistry of chalcogenolates have been published by Gattow in the past year. The topics covered in these parts are the reaction of formamide with CS_2 to produce N-formyl dithiocarbamates,[231] N-formyl dithiocarbamic acid, H-CO-NH-CS-SH[232] and its methyl and ethyl esters.[233] The crystal structure of $K[S_2C\text{-}NH\text{-}CO\text{-}H]$ was shown to be based on a superstructure consisting of a hydrogen bridged 16 membered ring system formed by four $[S_2C\text{-}NH\text{-}CO\text{-}H]^-$ anions.[234] The N-thioformyl dithiocarbamates, $M[S_2C\text{-}NH\text{-}CS\text{-}H]$ where M = K,Rb, Cs,Tl,NH_4 and $[N(n\text{-}C_4H_9)_4]$ have been prepared,[235] and the crystal structure of the latter determined. The structure is built up of dimeric aggregates consisting of 2 tetra n-butyl ammonium cations and two $S_2C\text{-}NH\text{-}CS\text{-}H$ anions linked together by -CS-S---H-N bridges.[236] The methyl and ethyl esters of N-thioformyl dithiocarbamic acid have been prepared.[237] The 2,3-ethanedithiolates $M_2[SCH_2CH_2S]$ where M = Li,Na,K,Rb,Cs,Tl,NH_4 have been prepared and characterised[238] and their reactions with CS_2 studied.[239] N-methyl formamide reacts with CS_2 in the presence of NaH, KOH, and $Ba(OH)_2$ to form the corresponding N-methyl, N-formyl dithiocarbamate.[240] The reaction of the potassium compound in acetone-d_6 with gaseous HCl at -78°C forms the unstable $H\text{-}CO\text{-}NCH_3\text{-}CS\text{-}SH$ whose existence in solution was demonstrated by n.m.r.[241] The ethyl and methyl esters of the acid have been prepared.[242] N-methyl-thioformamide may be prepared by reaction of N-methylformamide with P_4S_{10} and it reacts with CS_2 in the presence of hydroxides to give the corresponding N-methyl-N-thioformyldithiocarbamate[243] whose oxidation with iodine forms the hitherto unknown $\overline{CS\text{-}S\text{-}S\text{-}CS\text{-}N}\text{-}CH_3$.[244] Hydrazine reacts with CS_2 to form $M_2[S_2C\text{-}NH\text{-}NH\text{-}CS_2]$ with M = Na,K,[245] the potassium salt containing anions linked together by N-H---S bridges.[246] The mixed dithiocarbamate dithiocarbimate, $Na_3[S_2C-NH-N=CS_2].7H_2O$ has been prepared by reaction of $H_2N-NH_2.H_2O$ with CS_2 and NaOH in aqueous solution[247] and the S-methyl ester of dithiocarbamic acid reacts with CS_2 in the presence of NaH or KH at -15°C to yield the hitherto unknown salts of the S-methyl ester of N-dithiomethylene dithiocarbazic acid.[248]

6.3 SELENIUM

6.3.1 Bonds to Halogens

The previously described pentafluoroselenium isocyanate $F_5Se-N=C=O$ has been demonstrated to be $F_5Se-O-C{\equiv}N$ according to electron diffraction data, ^{77}Se and $^{14,15}N$, n.m.r. and vibrational spectroscopy. The other possible isomers, the nitrile oxide, $F_5Se-C{\equiv}N-O$ and the fulminate $F_5Se-O-N{\equiv}C$ were excluded using geometrical and chemical arguements respectively. The authors point out that there are now no F_5Se-N compounds known to exist in spite of several derivatives with the $F_5S-N=$ and $F_5Te-N=$ configurations. Numerous attempts to attach a SeF_5 group to nitrogen with SeF_6 or SeF_5Cl have failed.[249] Several properties of CF_3SeF_3 have been described. Fluorination of CF_3SeF_3 with liquid F_2 or AgF_2 has been shown to lead to CF_3SeF_5 which decomposes to CF_4 and SeF_4. With water CF_4 and $SeOF_2$ are formed. Addition of ClF to CF_3SeF_3 gives CF_3SeF_4Cl, which splits mainly into CF_3Cl and SeF_4. A neutral concentrated solution of $KMnO_4$ oxidizes CF_3SeO_2H in water in good yields to CF_3SeO_3F the free acid of which is obtained with 74% $HClO_4$. The aqueous solution can be concentrated up to 90% but above this concentration spontaneous decomposition to CF_4, COF_2 and SeO_2 occurs.[250] The structure of gaseous bis(trifluoromethyl)selenium difluoride has been determined by electron diffraction. The predominant species was shown to be the monomer $(CF_3)_2SeF_2$ (83) with the CF_3 ligands occupying the equatorial sites of a framework derived from a trigonal bipyramid. The principal structural parameters are Se-F 182.7, Se-C 202.2 and C-F 131.4pm; F-Se-F 157.8, C-Se-C 118.7 and F-C-Se 108.9°. The molecule has C_2 symmetry with the CF_3 groups twisted 19.8° away from the positions in which one C-F bond is anti with respect to an Se-C bond. Comparisons with the structures of related molecules show that the change from SeF_4 to $(CF_3)_2SeF_2$, unlike that from SF_4 to $(CF_3)_2SF_2$, results in an increase in the equatorial bond angle in accordance with the predictions of the valence shell electron pair repulsion model.[251]



(83)

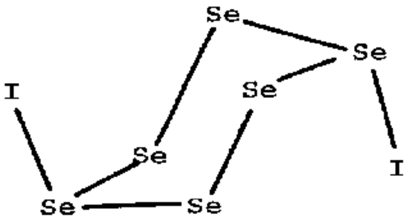
The enthalpies of formation of $SeCl_4$ and $SeOCl_2$ have been found to be -184.4 and -182.9 kJ/mole respectively.[252]

Selenium and tellurium bis(trithiocarbonates) have been found to react with Br_2 and I_2 to give the corresponding haloselenium and halotellurium trithiocarbonates. The reaction of the tellurium compound with excess Br_2 gave tribromotellurium trithiocarbonates.[253]

$Se_6I_2(AsF_6)_2.2SO_2$ has been prepared by condensing AsF_5 onto Se and I_2 over liquid SO_2.

$$6Se + I_2 + 3AsF_5 \xrightarrow{SO_2} Se_6I_2(AsF_6)_2.2SO_2 + AsF_3 \qquad ...(42)$$

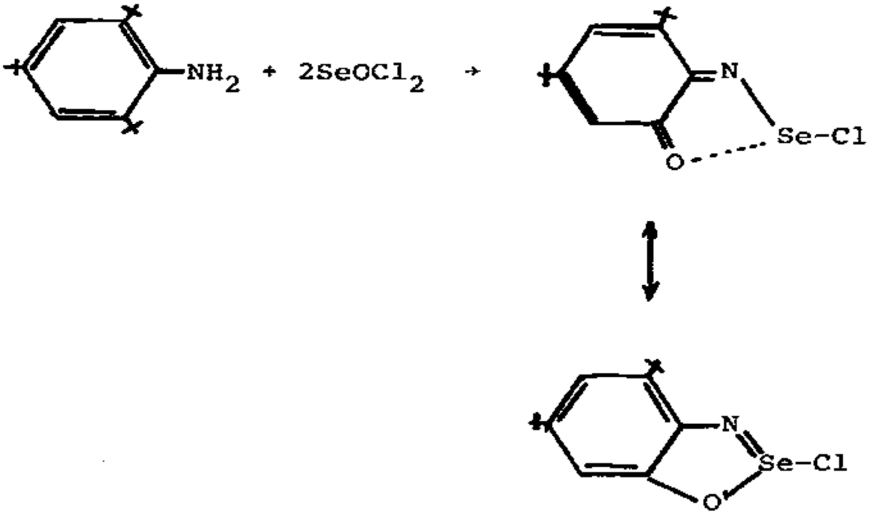
A crystal structure determination showed the cation (84) to contain a hexaselenium ring of chair conformation with iodine substituents in the axial 1,4 positions.[254]



(84)

6.3.2 Bonds to Nitrogen

A crystal structure determination has shown that in piaselenole-Piaselenolium pentaiodide, $C_6H_4N_2Se.C_6H_5N_2Se^+I_3^-.I_2$ there are no isolated I_5^- anions but layer shaped polyiodide aggregates built up by linear, asymmetric I_3^- anions and I_2 molecules. The piaselenole and its conjugate acid, the piaselenolium cation are connected in turn by a linear NH-N hydrogen bridge and by a so called $(SeN)_2$ connectivity parallelogram in which Se-N bonds (1.787Å) and very short Se-N contacts (2.691Å) are adjacent.[255] $SeCl_4$ has been shown to react with $Ph_2P{=}NSiMe_3$ by elimination of $SiMe_3Cl$ to form $Ph_3P{=}NSeCl_3$ which may be converted to $(Ph_3P{=}N)_2SeCl_2$ by reaction with a further mole of $Ph_3P{=}NSiMe_3$. 2,4,6-Tri-t-butylaniline and $SeOCl_2$ react to give (<u>85</u>). Crystal structure determinations on $Ph_3P{=}NSeCl_2$, $(Ph_3P{=}N)_2SeCl_2$ and (<u>85</u>) showed that the S-N bond lengths of 1.680, 1.735 and 1.766Å all indicate significant Se-N multiple bonding.[256]



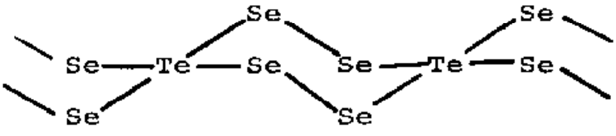
(<u>85</u>) ...(43)

6.3.3 Bonds to Oxygen

The $CdSeO_4$-H_2SeO_4-H_2O[257] systems have been investigated. As part of a study of the $CoSeO_4$-$NiSeO_4$-H_2O system, the crystal structure is isostructural with $CuSO_4.5H_2O$ and consists of $Co(H_2O)_4$ chains, µ-linked by the SeO_4.[258] The coordination and complex formation of some three valent lanthanoids (Er,Tb,Sm,La) in aqueous selenate solutions have been determined from X-ray scattering measurements. Inner sphere complexes are formed with the selenate ion with the Ln-O-Se angle being about 140° which corresponds to monodentate bonding.[259] The selenite group in $CaSeO_3.H_2O$ has been shown by a crystal structure determination to act as a bidentate ligand. The polyhedron around calcium being pentagonal bipyramidal and the selenite group forms a trigonal pyramid with Se and oxygen atoms at the apices.[260] The selenite ion in $Cu(HSeO_3)_2.H_2O$ is also in the shape of a trigonal pyramid but one Se-O bond is stretched (1.773Å) due to the hydrogen atom bonded to this oxygen; the two other Se-O bonds are of 1.673 and 1.678Å length.[261] $UO_2Se_2O_5$ has been synthesized by a gas-solid reaction at 720K between SeO_2 and UO_3. In the oxide, two pentagonal bipyramids share one edge to form U_2O_{12} entities which are linked by >Se-O-Se< groups giving rise to a lamellar structure.[262]

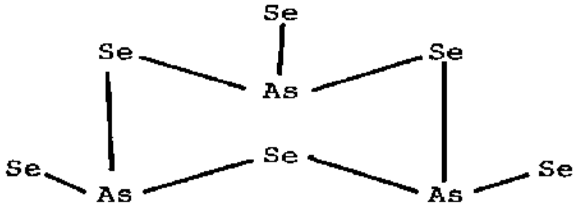
6.3.4 Selenides

Cs_2Se_5 has been prepared by reaction of the elements in liquid ammonia and shown to have the K_2S_5 type of structure. The compound is characterized by unbranched chains of Se_5^{2-} with a trans conformation. Rb_2TeSe_4 has been synthesized from a mixture of Rb_2Se_3, Se and Te at 600°C for 5 days. The compound is isotypic with Rb_2Te_5 and contains an infinite polyanion (86) of six membered rings of Te and Se connected by common vertices.[263]



(86)

The compounds $InGaSe_2$ and $InGaTe_2$ and their structures have been reported. Both crystallize in the TlSe structure type which is characterized by one dimensional linear chains of edge sharing $GaSe_4$ tetrahedra parallel to the c-axis of the tetragonal cell.[264] The new compounds Ba_2SiTe_4 and Ba_2SiSe_4 have been shown to be isotypic with the Sr_2GeS_4 structure. Ba_2SiTe_4 is the first o-telluridosilicate with discrete $SiTe_4^{4-}$ anions.[265] Investigations of the Na-Si-Se and Na-Ge-Se systems have shown the existence of $Na_4Si_4S3_{10}$, Na_2GeSe_3 and $Na_8Ge_4Se_{10}$. The first two compounds are isotypic with the corresponding sulphides and the latter with the corresponding telluride.[266] The new compound $Na_6Si_2Se_8$ has a structure in which two $SiSe_4$ tetrahedra are connected by a Se-Se bond (237.3pm) forming a discrete $[Si_2Se_8]^{6-}$ anion.[267] Na_4GeSe_4 obtained from a stoichiometric melt of Na_2Se, Ge and Se at 750°C crystallizes with a new orthorhombic structure in the space group Pnma. It is characterized by discrete $GeS_4{}^{4-}$ anions with almost regular tetrahedral geometry. Two independent anions appear in the structure with mean Ge-S bond lengths of 2.345 and 2.353Å.[268] Six polytypes of $SnSe_2$ crystals grown by chemical transport have been described.[269] At all compositions in the melt and vapour phase of the P_4Se_3-$AsSe_3$ system, compositions of the type $P_{4-n}As_nSe_3$ are formed. During long extraction with CS_2 compounds of the type $P_{4-n}As_nS_{3-m}Se_m$ are formed.[270] Low temperature (65K) single crystal, neutron diffraction studies have been carried out on the isostructural compounds Tl_3PSe_4 and Tl_3AsS_4.[271] $[Sr(en)_4]_2[As_3Se_6]Cl$ has been prepared by reaction of $SrCl_2$ with As_2Se_3 in ethylene diamine solution under reflux. The structure of the compound contains discrete cyclic $As_3Se_6{}^{3-}$ anions (<u>87</u>) with a six membered As_3Se_3 ring in the chair conformation. A bridging ethylene diamine molecule leads to the formation of $[Sr(en)_4]_n$ chains for the first of the cations but in contrast discrete $Sren_4$ units are observed for the second cation.[272]



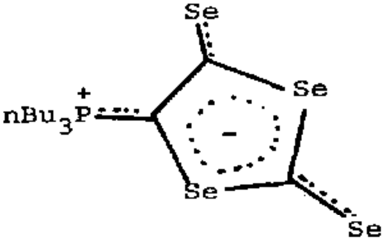
(<u>87</u>)

The anharmonic thermal vibrations in zinc sulphide, selenide and telluride have been studied.[273] The pseudo-ternary system $SmMo_6(S_{1-x}Se_x)_8$ has been investigated to determine the valence state and the effects of changing the crystal field on the magnetic behaviour of the samarium cation. The end-members and the samples with x = 6 and 7 were found to be superconducting with

$SmMo_6Se_8$ having the highest critical temperature; 6.5K.[274] The ternary chalcogenide $Nb_3Pd_{0.72}Se_7$ has been synthesized and its structure determined. The structure is a new laminar type that consists of layers of formula Nb_6PdSe_{14}, between which additional Pd atoms statistically occupy a rhombic site.[275] The following phase systems involving selenides have been studied; Cd-Ge-Se,[276] $CdSe-SiSe_2$ (and $CdS-SiS_2$),[277] SnTe-NiSe and SnTe-CoSe,[278] SnSe-Fe(Co,Ni)Se[279] and As_2Se_3-CoSe and Sb_2Se_3-CoSe.[280]

6.3.5 Bonds to Carbon

The barrier to rotation about the Se-Se bond in phenyl benzyl diselenide, $PhSeSeCH_2Ph$, has been found to be 6.3 kcal mol^{-1} as indicated by changes in the proton n.m.r. spectrum at low temperatures. This value is some 1.4 kcal mol^{-1} lower than the barrier in the corresponding sulphide.[281] Ab initio molecular orbital calculations with electron correlation have been carried out to determine the electron structure of selenoformaldehyde.[282] The propensity of several reagents to oxidize selenides to selenones has been evaluated and the scope and limitations of the methods presented.[283] The ultrasonically promoted electrochemical reduction of selenium to Se_2^{2-} and Se^{2-} has been demonstrated. After electrolysis the addition of an electrophile such as an alkyl halide leads to the synthesis of dialkyl diselenides and selenides. Ditellurides and tellurides were also prepared in the same manner.[284] The reaction of CSe_2 and nBu_3P has been shown to give (<u>88</u>) as dark red, flat prismatic crystals. It is hoped that derivatives of this new type of phosphorus ylide may exhibit the properties of an organic metal.[285]



(<u>88</u>)

The electrochemical behaviour of some dibenzodichalcogens and related compounds have been studied.[286]

6.3.6 Other compounds containing Selenium

The fundamental vibrations of eleven possible six-membered selenium sulphide ring molecules, Se_nS_{6-n}, as well as of all isomers of the two seven-membered rings, 1,2-Se_2S_5 and 1,2-Se_5S_2, have been calculated. The results indicate that Raman spectroscopy is a possible method for the identification of these compounds.[287] The compound, $(\mu Se)[V(CO)_3(dppe)]_2$ and its sulphur and tellurium analogues have been prepared by a number of routes and investigated in some detail. X-ray structural studies showed that the sulphur and selenium compounds contain a linear V-Se-V (or V-S-V) system with very short bond distances, whereas the tellurido compound has in its centre a slightly bent V-Te-V group (165.9°).[288] The reactions of $Se(SiMe_3)_2$ with $MCl_2(PPh_3)_2$ (M = Co or Ni) have been used to prepare four novel cluster compounds.[289] The reactions of tri-t-butylphosphane with selenium and tellurium have been found to proceed quantitatively with the formation of seleno- and telluro-tri-t-butylphosphorane respectively. Tri-t-butylarsane reacts with selenium to give seleno-tri-t-butylarsorane but no significant reaction was observed with tellurium.[290] The oxidative electrochemistry of iron selenocarbonyl porphyrins have been studied.[291]

6.4 TELLURIUM

6.4.1 Bonds to Halogens

Nitrosyl-pentafluorotellurate(VI) has been prepared from NOCl and $Hg(OTeF_5)_2$. The compound is ionic in the solid state and in acetonitrile solution having the formulation $NO^+OTeF_5^-$ but in the gaseous state a covalent molecule ON-$OTeF_5$ has been observed.[292] Thiazylpentafluorooxotellurate, $NSOTeF_4$, has been prepared from NSF and $B(OTeF_5)_3$ or from $NS^+SbF_6^-$ and $CoOTeF_5$. The compound is rather unstable and isomerises rapidly to give the known TeF_5NSO and polymeric products. $F_5TeNSNTeF_5$ is formed from TeF_5NSO in the BF_3 catalysed elimination of SO_2 from $NSOTeF_5$. The latter also reacts with AsF_5 to give the thiazyl salt $NS^+F_5TeOAsF_5^-$.[293] The donor-acceptor properties of the $OTeF_5^-$ ion have been studied in the presence of the acceptor species AsF_5 and $As(OTeF_5)_5$. The mixed cations $[TeF_x(OTeF_5)_{3-x}]^+$ (x = 0-3) and the neutral species $TeF_5(OTeF_5)_{4-x}$ (x = 0–2) have been characterized in solution. The novel anion $As(OTeF_5)_6^-$ was also identified.[294] The preparations of $AgOTeF_5.CH_2Cl_2$ and $[AgOTeF_5(C_6H_5CH_3)_2]_2$ and the crystal structure of the latter have been reported. The compound contains centrosymmetric dimeric molecules with planar Ag_2O_2 cores with two $OTeF_5$ groups bridging two silver atoms. Spectroscopic data also suggest that $AgOTeF_5CH_2Cl_2$ and the known compound $AgOTeF_5(CH_3CN)_4$ can also contain bridging $OTeF_5$ groups in the solid state.[295] $Au(OTeF_5)_3$, prepared from AuF_3 and $B(OTeF_5)_3$ has also been shown to contain bridging $OTeF_5$ groups.[296] A series of transition metal compounds with the $=N-TeF_5$ ligand have been synthesized by the reactions:[297]

$$2Me_3Si-NH-TeF_5 + MF_6 \rightarrow 2Me_3SiF + H_2N-TeF_5 + F_4M=N-TeF_5 \quad M = Mo,W. \qquad ...(44)$$

$$VF_5 + H_2NTeF_5 \rightarrow F_3V=N-TeF_5 + 2HF \qquad ...(45)$$

$$F_4Mo=N-TeF_5 \xrightarrow{BCl_3} Cl_4Mo=N-TeF_5 + BF_3 \qquad ...(46)$$

The amine TeF_5NHCF_3 has been prepared as a colorless, stable liquid from the reaction of $TeF_5N=CCl_2$ with HF. Further reactions of the amine with various metal fluorides, halogens and interhalogens have led to the preparation of a wide range of derivatives.[298]

The crystal structure of $[H_3N(CH_2)_3NH_3]TeCl_6$ has been shown to contain distorted $TeCl_6^{2-}$ octahedra with Te-Cl distances between 2.426 and 2.627Å.[299] The compounds $[Ph_4As]_2TeCl_4$, $[Ph_4N]_2TeBr_4.-CH_3CN$, and $[Ph_4N]_2TeI_4$ have been prepared by the reaction of Te, X_2 and excess Ph_4NX (X = Br,I) in acetonitrile solution or by heating $[Ph_4As]_2TeCl$, Te and Ph_4AsCl for several hours in the same solvent. In all the compounds Te(II) exhibits a square planar coordination and the Te-Cl, Te-Br and Te-I bond lengths were found to be 260.7(mean), 275.3 and 298.5pm respectively.[300] Tellurium double layers, between which planar layers of iodine molecules are inserted characterize the new intercalation compound $(Te_2)_2(I_2)$. The compound which contains a Te modification which was previously unknown was prepared by hydrothermal synthesis in concentrated hydrogen iodide.[301] The crystal structure of the β polymorph of $C_8H_8TeI_2$ contains tellurium in a distorted octahedral coordination with iodine occupying the axial positions with respect to two benzylic carbon atoms and two further iodine atoms in the equatorial positions. The structure differs from that of the α polymorph in the intermolecular bonding arrangements of the heavy atoms and in the polar arrangements of the molecules.[302]

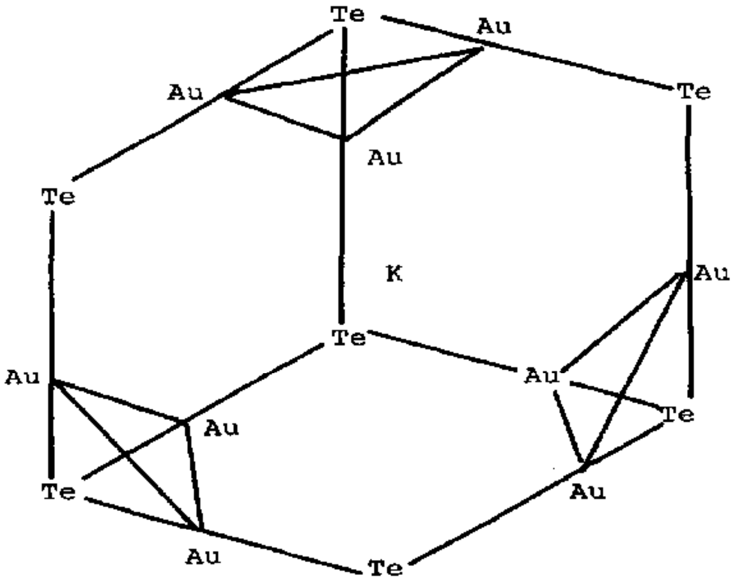
6.4.2 Bonds to Oxygen

$SrTeO_4$, prepared by hydrothermal synthesis contains TeO_6 octahedra sharing edges to form infinite chains parallel to the c axis of the crystal which are held together by Sr^{2+} ions. The structure is therefore similar to that of the β-form of Na_2TeO_4.[303] $CdTeO_3$ contains isolated, slightly distorted, trigonal TeO_3 pyramids with a mean Te–O distance of 1.89Å which are connected by cadmium atoms.[304] A new series of tellurium mixed oxides of composition $K_3M^{III}Te_3O_{12}$ (M = Al,Ga,Cr,Fe) have been prepared. The oxides all crystallize in a superlattice of the $PbTiO_2$ type.[305] The mixed oxohalide, Sb_3TeO_6Cl, has been prepared and its structure determined. The coordination of the heavy atom can be considered as a distorted trigonal bipyramid with the lone-pair directed towards one of the equatorial positions. The crystal contains parallel layers of $(Sb_3TeO_6)_n{}^+$ perpendicular to the c axis with chloride ions situated between the layers.[306] Two mixed oxides of antimony and tellurium, $Sb_2Te_2O_9$ and Sb_2TeO_7 have been synthesized by the solid-state reaction of TeO_2 and Sb_2O_3 or Sb_2O_5. Single crystals of the former were prepared by transport processes. The thermal decomposition of both oxides at temperatures above 950°C, leads to Sb_2O_4 as the only solid phase.[307] The $ZnCl_2$-TeO_2-WO_3 system has been studied.[308]

6.4.3 Tellurides

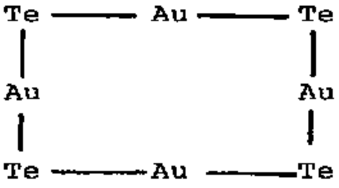
$CsTe_4$ has been prepared from a melting reaction at 570°C in sealed quartz tubes. The caesium required for the reaction was prepared in situ from mixtures of CsN_3 and Te at 350°C. $CsTe_4$ has a structure in which the tellurium atoms from a two-dimensional puckered layer built up from pseudo-trigonal bipyramidal T-shaped units $Te_4{}^-$.[309]

The electronic structure of three, one-dimensional chains containing square planar Te_5^{n-} units have been calculated using both m.o. and band theory. Two chains containing Te_5^{2-} in different conformations and one in which they are modulated by Sn were treated thus enabling the structures of Rb_2Te_5, Cs_2Te_5 and K_2SnTe_5 to be modeled. A three centre, four electron model was used to explain the elongation of the Te-Te bonds within the Te_5 unit.[310] The ternary compound $LiInTe_2$ has been synthesized by reaction of the elements and shown to crystallize with the tetragonal chalcopyrite structure which is maintained up to the melting point.[311] The high pressure form of $MnIn_2Te_4$ has been synthesized at a hydrostatic pressure of 1.5G.Pa at 1073K. The structure of the telluride comprises $MnTe_6$ octahedra (Mn-Te = 2.889Å) bridged by chains of $InTe_4$ tetrahedra (In-Te = 2.767 to 2.835Å).[312] The crystal structres of $[Ph_4P]_4[KAu_9Te_7]$, $[Ph_4P]_2[K_2Au_4Te_4(en)_4]$ and $[Ph_4P]_2[K_2Au_4Te_4(dmf)_2(CH_3OH)_2]$ have been reported. The structure of the first telluride can be described as a derivative of an $M_{12}X_8^{4-}$ cube with one corner and three edges missing (<u>89</u>). The Au_9Te skeleton has the cube distorted by compression along the pseudo three fold axis containing the unique Te atom and the missing corner.



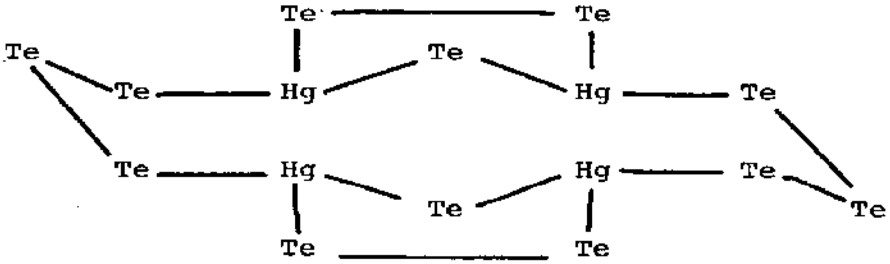
(<u>89</u>)

Both of the remaining tellurides contain planar $Au_4Te_4^{4-}$ rings (<u>90</u>) to which two K^+ ions are coordinated on opposite faces.[313]



(<u>90</u>)

The two ternary tellurides $[nBu_4N]_4[Hg_4Te_{12}]$ and $[PPh_4]_2Hg_2Te_5$ also contain unusual anion coordinations, in the former, the novel Hg_4Te_{12} anion has four mercury atoms which are coplanar and are coordinated in a distorted tetrahedral fashion to an array of two Te^{2-}, two Te_2^{2-} and two Te_3^{2-} ligands (<u>91</u>) whilst the latter contains a new polymeric anion $Hg_2Te_5^{2-}$ (<u>92</u>) which runs in a one dimensional string.[314]



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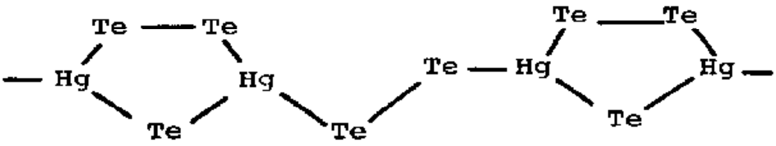
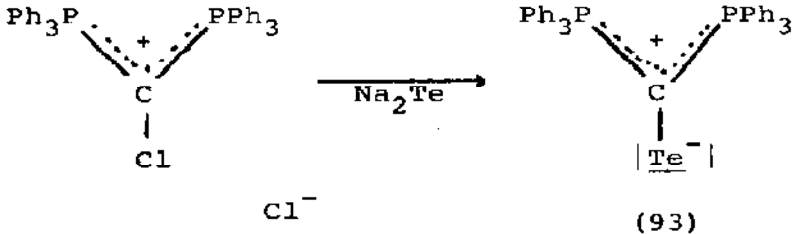


(<u>92</u>)

The following phase systems involving tellurides have been studied: Dy-Bi-Te,[315] $CdTe-La_2Te_3$,[316] Te-Sb-Te,[317] $PbTe-CoTe_2$,[318] GeTe-YbTe[319] and Nd-Bi-Te.[320]

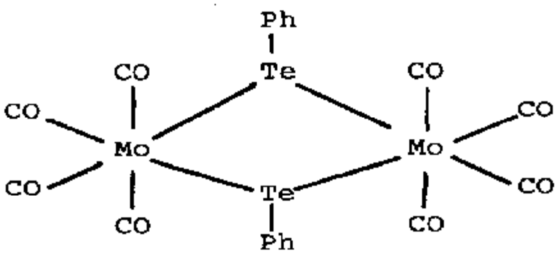
6.4.4 Bonds to Carbon

Di-p-tolylditelluride reacts with tetra-t-butyldiphosphane and tetraisopropyldiphosphane to form new tellurophosphinous acid esters p-$CH_3C_6H_4TePR_2$ (R = t-C_4H_9, i-C_3H_7).[321] The crystal and molecular structures of four, three-coordinated divalent tellurium complexes, $PhTeSC(NMe_2)_2Cl$, $PhTeSC(NMe_2)_2Br$, $PhTeSeP(NC_4H_8O)_3Cl$ and $PhTeSeP(N_4H_8O)_3Br$ have been determined. The four complexes are all three coordinated T-shaped. In a direction nearly perpendicular to the Te-C bond, tellurium is bonded to a halogen atom and in a trans position to the halogen to a tetramethylthiourea sulphur or a trimorpholylphosphine selenide selenium atom. The three centre system Y-Te-X (Y = chalcogen, X = halogen) are nearly linear.[322] $Ph_3P=C=PPh_3$ has been shown to form deeply colored crystalline 1:1 adducts with elemental S, Se, and Te. A superior synthesis for the Te compound (93) is the reaction of Na_2Te with $(Ph_3P)_2CCl^+Cl^-$. All three compounds are thermally unstable and decompose at or below room temperature.[323]



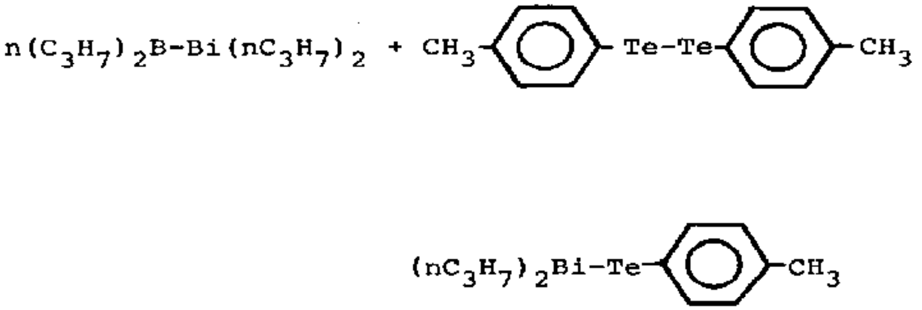
(93) ...(47)

The reaction of Ph_2Te_2 with $Mo(CO)_6$ in toluene gives a black amorphous precipitate of $Mo_n(TePh)_{3n-3}(CO)_6$ (n~4) as the main product with small amounts of $Mo_2(CO)_8(TePh)_2$. The structure of the latter shows it to be a dinuclear complex (94) with the Mo atoms bridged by two TePh ligands.[324]

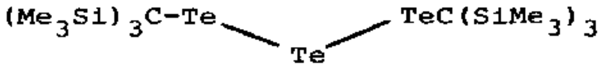


(94)

The structure of di-2-thienyl telluride has been determined.[325] The first molecule with a bismuth-tellurium bond, p-tolyltelluro-di-n-propylbismutane, has been prepared in high yield by the reaction shown in equation (48).[326]


...(48)

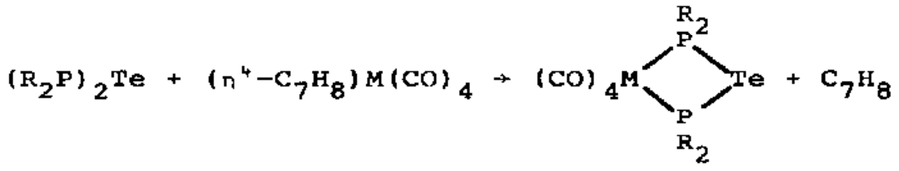
Novel polyselenides and polytellurides have been prepared by stabilizing the tris(trimethylsilyl)methyl group $[(Me_3Si)_3C]_2Te_3$. The first compound containing a three tellurium atom chain (<u>95</u>) crystallizes as a trans rotamer with a bonding angle of 103.8° at the central tellurium atom and Te-Te bond distances of 2.710Å.[327]


(<u>95</u>)

Poly(methylene ditelluride) $(CH_2Te_2)_x$, and the related polymers $(CH_2Te)_x$, $(CH_2Se)_x$ $(p\text{-}CH_2C_6H_4CH_2Te)_x$ and $(p\text{-}CH_2C_6H_4CH_2Te_2)_x$ have been found to give conductive materials when doped with bromine or iodine.[328]

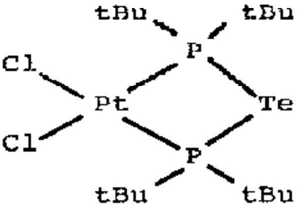
6.4.5 <u>Other compounds containing Tellurium</u>

$(R_2P)_2Te$ (R = t-Bu) reacts with $(\eta^4\text{-}C_7H_8)M(CO)_4$ (M = Cr,Mo) to form norbornadiene and the new chelate complexes (96).[329]


...(49)

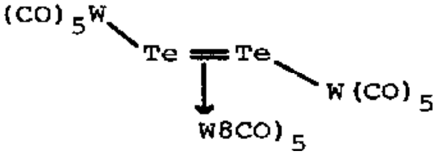
(<u>96</u>)

The compound (97) has been prepared from heterogeneous reactions $(t\text{-}Bu_2P)_2Te$ and $(PhCN)_2PtCl_2$ in methylene chloride or platinum dichloride in toluene suspension.[330]



(97)

The compound $Cp_2Mo_2FeTe_2(CO)_7$ is formed from the reaction of $Fe_3Te_2(CO)_9$ and $Cp_2Mo_2(CO)_6$ in hexane under CO_2. The four molecules in the asymmetric unit are quite similar consisting of a $CpMo(CO)_2$ fragment bridging the Te wing-tips of a $Cp(CO)_5MoFeTe_2$ butterfly. The 3.13Å Te---Te distance is well within bonding distance and is proposed to be chemically significant.[331] The reaction of $[(CO)_5W]_3Sn$ with H_2Te leads to (98) in which the Sn atom has been replaced by a Te_2 unit coordinated in an unusual manner. The Te-Te distance in (98) (268.6pm) lies between the bond length of free Te_2(g) (261pm) and that of hexagonal tellurium (283.5pm).[332]



(98)

The compounds $(Te_2Se_2)(Sb_3F_{14})(SbF_6)$ and $(Te_{3.0}Se_{1.0})(Sb_3F_{14})$-$(SbF_6)$ have been prepared by the oxidation of a 1:1 Te-Se alloy and 1:1 and 3:1 Te-Se mixtures with SbF_5 in SO_2 solution. The former contains both the ions $Te_2Se_2^{2+}$, $Sb_3F_{14}^-$ and SbF_6^- and the $Te_2Se_2^{2+}$ cation has Te-Se bond lengths of 2.446 and 2.481Å and Se-Te-Se and Te-Se-Te angles of 89.1 and 90.9 respectively. The $(Te_{3.0}Se_{1.0})^{2+}$ cation consists of a disordered mixture of the Te_3Se^{2+}, Te_4^{2+} and trans $Te_2Se_2^{2+}$ cations.[333] The crystal structure of $[Na(C_{18}H_{36}N_2O_6)]_2[Te_4]$ has been shown to contain cryptated Na^+ ions and tetratelluride anions, Te_4^{2-}, with terminal bond lengths of 2.702Å and a longer central bond of length 2.746Å. The Te-Te-Te bond angles were 109.7 and 110.0° and a Te-Te-Te-Te dihedral angle of 105.3° was found.[334]

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