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# Chapter 6

# ELEMENTS OF GROUP 6

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## 6.1 OXYGEN

A proton nuclear magnetic double-resonance technique has been used to detect the pure Oxygen-17 nuclear quadrupole resonances in molecular oxygen reversibly bonded to an iridium carrier. Application of the technique to Vaska's iridium compound $IrO_2Cl(CO)(PPh_3)_2$ showed two sets of lines and the inequivalence of charge distributions about each oxygen atom which is revealed by these results, and which is not evident in the X-ray internuclear distances, may provide new insight into the mechanism of reversible oxygen bonding.[1] The photoabsorption, photoionization and fragmentation of molecular oxygen have been measured using electron impact coincidence methods.[2] The photoabsorption measurements covered the energy range 5 - 30eV while the formation of electronic states of $O_2^+$ (p.e.s.) and the resulting ionic fragmentation (photoionization mass spectroscopy) were both measured from close to threshold up to photon energies of 75eV. The binding energies spectra of $O_2$ show peaks at 33, 47 and 57eV in addition to those reported previously and these peaks are assigned to multiple final ion states arising from photoionization of the inner valence electrons.

The diffusion of oxygen in the hexagonal close packed structure of α-titanium has been studied by nuclear microanalysis using polycrystalline samples of Ti heated in pure oxygen at atmospheric pressure at temperatures ranging from 700 to 950°C.[3] Diffusion profiles were determined which gave diffusion coefficient values with an activation energy of 48 kcal $mol^{-1}$. A kinetic model applicable to hydrometallurgical reactions occurring in an aqueous phase under an oxygen pressure has been derived.[4] In the same paper kinetic equations for the aqueous oxidation of elemental sulphur to sulphuric acid at temperatures of 160° and greater than 175° were established. The kinetics and mechanism of the oxidation of iron(II) by molecular oxygen in the presence of aqua palladium(II) ions have been described.[5] The rate of the catalytic reaction was found to be a function of the concentrations of Pd(II), Fe(II), acid, sulphate and iron Fe(III). A detailed study of these factors led to a mechanism involving the formation of a Pd(I) intermediate which undergoes oxidation by $O_2$ rather than reduction by Fe(II).

Dimensionally stable $PbO_2$ anodes on a titanium substrate have been tested for application in ozone synthesis using a variety of aqueous electrolytes.[6] At room temperature an ozone concentration of up to 13 wt% in the anodic gas ($O_3 + O_2$) was attained using an aqueous phosphate electrolyte.

The formation of $O^-$ and $O_2^-$ on silica supported vanadium-phosphorus catalysts has been investigated using e.s.r. methods. Using catalysts of varying phosphorus content it was shown that the concentration of $O^-$ and $O_2^-$ was related to phosphate ion concentration since increasing phosphorus content increases the reducibility of the catalysts and stabilizes the square-pyramidal coordination of $V^{4+}$ ions.[7]

The rates of reaction of $HO_2$ and $O_2^-$ with hydrogen peroxide (the Haber-Weiss reactions) have been studied by $^{60}Co$ γ-radiolysis as a function of pH at 23.5°C.[8] The experimental results are consistent with a chain mechanism which takes into account the dissociation of $HO_2 \leftrightarrows O_2^- + H^+$ (pK = 4.7) and the competition between the Haber-Weiss reactions ($HO_2 + H_2O_2$ and $O_2^- + H_2O_2$) and the recombination reactions of the superoxide and perhydroxyl radicals ($HO_2 + H_2O_2$ and $HO_2 + O_2^-$).

The synthesis and properties of $H_3O_2^+\ Sb_2F_{11}^-$, $H_3O_2^+\ SbF_6^-$ and $H_3O_2^+\ AsF_6^-$. The first known examples of peroxonium salts, have been reported.[9] The salts were prepared by protonation of $H_2O_2$ in anhydrous HF solutions of the corresponding Lewis acids, and isolated as metastable solids decomposing to the corresponding $H_3O^+$ salts and $O_2$ in the temperature range 20 - 50°C. Comparison of observed spectra and calculated force fields suggests that the ions are isostructural with $H_2NOH$ which possesses $C_s$ symmetry with the unique hydrogen being trans to the other two hydrogens. Attempts to protonate both oxygen atoms in $H_2O_2$ to form $H_4O_2^{2+}(SbF_6^-)_2$ resulted in $H_3O_2^+Sb_2F_{11}^-$ as the only product.

The kinetics of the formation of $H_2O_2$ in aqueous suspensions of ZnO irradiated with visible light have been studied[10] and the effects of Ti(3+) ions on the oxidation of $I^-$ by $H_2O_2$ in the presence of 0.08M HCl has been investigated by stopped flow spectrophotometry at 300nm and at 25°C.[11]

The electrochemical reduction of $H_2O_2$ in pyridine at a Pt electrode yields the superoxide ion as the major product.[12] The primary reduction step is

$$H_2O_2 + e^- \longrightarrow HO_2^- + \tfrac{1}{2}H_2 \qquad \ldots(1)$$

which is followed by a disproportionation reaction

$$HO_2^- + H_2O_2 \longrightarrow O_2^- + H_2O + OH \qquad ...(2)$$

In alkaline aqueous solutions $HO_2^-$ is oxidised at a mercury electrode by an overall two-electron process to molecular oxygen. Since $HO_2^-$ is inert at gold and carbon electrodes, the electrochemical oxidation mechanism must involve Hg(I) and Hg(II) intermediate complexes with $HO_2^-$ and/or $O_2^-$.

The photoelctron spectra of $OF_2$ and $SF_2$ have been assigned.[13]

## 6.2 SULPHUR

### 6.2.1 The Element

X-ray studies of the mixed crystals of the type $Se_nS_{8-n}$ have shown them to consist of eight-membered rings but the presence of disorder prevented a detailed structure determination and left unresolved the question as to whether homonuclear bonds are present in these compounds. A recent Raman spectroscopic study over a range of compositions have identified stretching vibrations from S-S, S-Se and Se-Se bonds, thereby indicating contrary to previous publications, that Se-Se homonuclear bonds are present in mixed crystal of the $Se_nS_{8-n}$ type.[14]

The molecular composition of liquid sulphur has been the subject of much research over many years. It was known that the homonuclear species $S_6$, $S_7$ and $S_8$ were present in the liquid but a vibrational spectroscopic study has now shown that large ring sulphur molecules of the type $S_{12}$, $\alpha$-$S_{18}$ and $S_{20}$ together with larger species $S_x$ with x = 23 to 34 are present.[15]

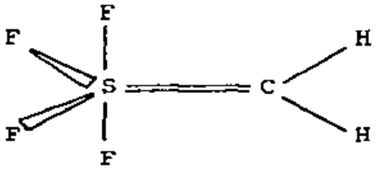
Although $S_8$ is the most stable allotrope of sulphur, the labile $S_7$ ring may be stabilised by the formation of the ion $(S_7I)^+$. The reaction of $S_8$, $I_2$ and $SbF_5$ in the appropriate ratios in $AsF_3$ has been shown to give in essentially quantitative yields the crystalline compound $S_{14}I_3(SbF_6)_3 2AsF_3$. X-ray crystallography has shown the compound to contain the novel cation $[(S_7I)_2I]^{3+}$ which consists of two $(S_7I)^+$ fragments bridged by a linear S-I-S bond.[16] This is the first structural determination of a sulphur ring with two exocyclic atoms attached, although the very unstable $S_7O_2$ has been reported.

E.s.r., u.v. and visible spectra have been recorded in an attempt to identify the species responsible for the colours in ultramarine green and blue. The two radical ions $S_2^-$ and $S_3^-$ were identified in ultramarine green whereas the ultramarine red was found to comprise largely of the nuetral molecule $S_4$.[17]

The first dico-ordinate sulphur dication $(Me_2N)_2S^{2+}$ has been prepared by treatment of $(Me_2N)_2SF_2$ with fluoride ion acceptors.[18] The diffusion of sulphur in monocrystalline nickel and cobalt oxides has been studied at temperatures between 700 and 1100°C.[19]

### 6.2.2 Bonds to Halogens

Low temperature crystal structure and electron diffraction determinations have shown that in the trigonal bipyramidal species $H_2C=SF_4$ the hydrogen atoms are located in the plane of the axial F atoms (1). These findings are now supported by the photoelectron spectrum which shows a single band at 10.65eV which is assigned to $\pi_{CS}$ ionisation.[20] *Ab initio* calculations on the same molecule also confirmed this structre showing that the alternative conformation with the hydrogen atoms in the equatorial plane is about 77 kcal $mol^{-1}$ above the stable configuration. The calculated structural parameters were in good agreement with those obtained from the low temperature X-ray and electron diffraction studies. Calculations performed on $SF_4$ indicated that the inclusion of d functions for sulphur is necessary for a quantitative description of its molecular structure and on the basis of the calculations for $O = SF_4$, a choice between the four possible molecular models derived from electron diffraction experiments was possible.[21]



(1)

A comparative study of the reactions of perfluoro-t-butyl hypochlorite and perflouromethyl hypochlorite with some simple sulphur-halogen compounds has been undertaken. While $CF_3SCF_3$, $CF_3S(O)CF_3$ and $SF_4$ readily undergo oxidative addition with $CF_3OCl$

to form $(CF_3)_2S(OCF_3)_2$, $(CF_3)_2S(O)(OCF_3)_2$ and $SF_4(OCF_3)_2$, no reaction is observed with $(CF_3)_2COCl$. In reaction with $SCl_2$ or $CCl_3SCl$, both oxidative displacement and oxidative addition occur with $(CF_3)_3COCl$ to give the tetrakis derivative $S(OC(CF_3)_3)_4$ but with $SCl_2$, $CF_3OCl$ assumes the role of fluorinating agent.[22]

Methyl sulphur pentafluoride, $SF_5$-$CH_3$, has been systematically synthesised from $SF_5Cl$ and ketene as shown in reactions (3) - (6).

$$SF_4 + Cl_2 + CsF \longrightarrow SF_5Cl + CsCl \qquad ...(3)$$

$$SF_5Cl + H_2C{=}C{=}O \longrightarrow SF_5\text{-}CH_2\text{-}COCl \xrightarrow{H_2O} SF_5\text{-}CH_2\text{-}COOH \qquad ...(4)$$

$$2SF_5\text{-}CH_2\text{-}COOH + Ag_2CO_3 \longrightarrow 2SF_5\text{-}CH_2\text{-}CO_2^- Ag^+ + CO_2 + H_2O \qquad ...(5)$$

$$SF_5\text{-}CH_2\text{-}CO_2Ag + Br_2 \xrightarrow{-AgBr} SF_5CH_2Br \xrightarrow{Zn/HCl} SF_5CH_3 \qquad ...(6)$$

The compound is stable at room temperature against HF elimination.[23]

An analytical method for characterizing the gas mixture obtained from the decomposition of $SF_6$ in a quartz reactor by an r.f. discharge has been described. A combination of gas-chromatographic, mass-spectrometric and i.r. spectrophotometric techniques has shown the presence of $SF_6$, $SO_2F_2$, $SOF_4$, $SOF_2$, $SiF_4$ and $F_2$ in the gas mixtures examined.[24] The influence of pressure, temperature, and buffer gases on the rate and selectivity of the dissociation of $SF_6$ in the filed of a $CO_2$ pulsed laser has been investigated and the photosensitised dissociation of $SeF_6$ has been brought about forthe first time.[25] The possible use of c.w. infrared lasers for studying chemical reactions has been discussed using the reaction of $SF_6$ with $SO_2$ as an example. The reaction proceeds according to the overall equation (7), but has a complex mechanism

$$SF_6 + 2SO_2 \longrightarrow SO_2F_2 + 2SOF_2 \qquad ...(7)$$

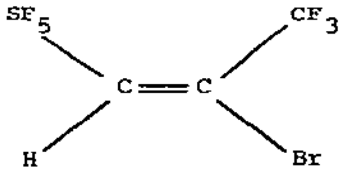
involving the participation of radicals in the first stage.[26]

The addition of $SF_5Br$ to propyne and 3,3,3-trifluoropropyne has been shown to proceed according to the equation (8).

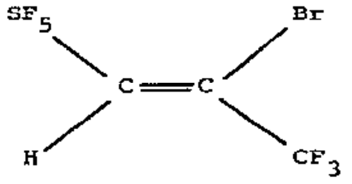
$$SF_5B + RC{\equiv}CH \longrightarrow SF_5CH{=}C(R)Br \qquad ...(8)$$

R = Me, $CF_3$.

The products are clear, colourless, hydrolytically stable liquids and the trifluoro compound could be separated into the two isomers (2) and (3) by gas chromatography.



(2)



(3)

The proton n.m.r. spectra of both products show clearly that the $SF_5$ group is attached to the olefinic carbon containing the hydrogen.[27]

The microwave spectrum of the disulphur dichloride $S_2{}^{35}Cl_2$ has been studied in the frequency range 9 - 39 GHz. Assignments were obtained for the Q-branch and some of the R-branch transitions. The $r_o$ structure of the molecule was evaluated with the S-Cl distance fixed to the electron diffraction value and the structure obtained agreed well with that deduced from the electron diffraction study.[28] A second determination of the microwave spectrum of $S_2Cl_2$ has led to precise geometrical parameters and $^{35}Cl$ quadrupole coupling constants. The S-S bond length was found to be *ca.* 10pm shorter than the standard single bond length as found for example in $S_8$; but is *ca.* 6pm longer than that found in FSSF.[29]

An improved synthesis of $SCl_3{}^+AlCl_4{}^-$ has been described in which the direct chlorination of sulphur in the presence of $AlCl_3$ takes place.[30] The negative ion-molecule reactions in sulphuryl chloride, sulphuryl fluoride and sulphuryl chloride fluoride have been described.[31]

### 6.2.3 Bonds to Nitrogen

*Polymeric Sulphur Nitride, $(SN)_x$.* In an extremely comprehensive review, Labes,Love and Nichols have covered many aspects of the chemistry of polymeric $(SN)_x$. Topics covered include preparative methods, crystal structure, band structure, chemical stability, epitaxial thin films, conductivity, specific heat, magnetoresistance, magnetic susceptibility, optical properties, X-ray and u.v. photoemission data. Halogentated $(SN)_x$ derivatives are also discussed and comparable low dimensional materials such as polyacetylene are included for comparison purposes.[32]

An investigation of the species present in the vapour of $(SN)_x$ using molecular beam electron deflection analysis has been carried out. Using this technique it is possible to study not only the mass spectrum of the vapour but also to determine the electrical polarity of the species. In agreement with previous mass spectral studies it was found that the vapour consists mainly of a tetrameric species $(SN)_4$ which was shown to be non-polar; smaller contributions were found for one or more polar species. This mass spectral data, whilst clearly showing the tetramers to differ structurally from the well known non-polar cyclic molecule $S_4N_4$ does not clearly establish the structural form of $(SN)_x$. The fragmentation pattern suggests a "quasilinear" open-chain structure which shouls have an electric dipole moment and on first sight this would appear to be in conflict with the observed non-polarity observed in this study.[33]

The reaction between polymeric sulphur nitride and IBr vapour has been shown to lead to the formation of intercalation compounds of the form $[SN(IBr)_y]_x$. A blue compound is rapidly formed with a structure similar to that of the initial $(SN)_x$. A further slow reaction leads to the formation of a brownish-blue product which is thought to be a first stage intercalation compound with an interplanar distance of 6.8Å.[34]

<u>Linear Sulphur-Nitrogen Compounds</u>. Although unstable at room temperature, the simplest nitrogen-sulphur-fluorine compound, the monomeric thiazyl fluoride, NSF, can be stabilised by incorporation as a ligand in transition metal complexes. The hexakis(thiazylfluoride) complexes of Co(II) and Ni(II) have been prepared in almost quantitative yield as shown in reaction (9).

$$6NSF + [M(SO_2)_x](AsF_6)_2 \longrightarrow [M(NSF)_6](AsF_6)_2 \qquad \ldots(9)$$

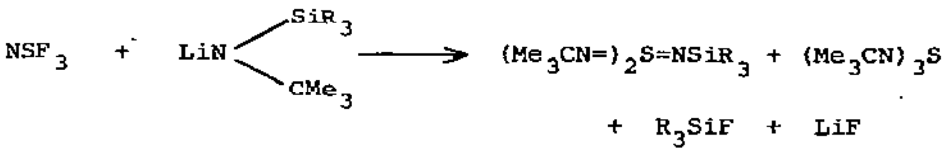
I.r. spectra of the complexes show a strong shift of the SN stretching vibration to higher wave numbers and X-ray structure analysis of the Co complex also indicates an increase in SF and SN bond strength. Spectroscopic and structural parameters of the complexes and NSF are compared in Table 1.[35]

The five coordinated aminosulphur(IV)trifluorides, $R_2NSF_3$ (counting the lone pair on the S as a ligand) and aminosulphur(VI)-

Table 1. Comparison of Molecular and Ligand NSF.

| | $\nu_{SN}$ $[cm^{-1}]$ | $\nu_{SF}$ $[cm^{-1}]$ | $d_{SN}$ $[A^{o}]$ | $d_{SF}$ $[A^{o}]$ | < NSF $[^{o}]$ |
|---|---|---|---|---|---|
| $[Co(NSF)_6]^{2+}$ | 1429 | 655 | 1.399 | 1.569 | 115.0 |
| $[Ni(NSF)_2]^{2+}$ | 1438 | 655 | | | |
| N≡S–F (gas) | 1361 | 641 | 1.446 | 1.646 | 116.5 |

oxide trifluorides, $R_2NS(O)F_3$, have been shown to lose a fluoride ion to Lewis acids to give sulphur containing cationic species $[R_2NSF_2]^+$ and $[R_2NS(O)F_2]^+$ with four coordinated sulphur. The four coordinated neutral dialkylaminosulphur(IV)oxide fluorides $R_2NS(O)F$, and amino-iminosulphur(IV) fluorides $R_2NS(=NR_4)F$, gave three-coordinated sulphur cations $[R_2NSO]^+$ or $[R_2NS{=}NR_4]^+$. The three coordinated sulphur(VI) cation $[R_2NS(O){=}NR]^+$ has also been prepared.[36] A planar three fold coordination of sulphur(VI) has also been observed in the compounds $(Me_3SiN)_3S$ and $(Me_3CN)_3S$. Both compounds exhibit a planar three fold nitrogen coordination of the sulphur but the observation of large coefficients of the temperature factors perpendicular to the $SN_3$ planes may indicate a disorder due to small deviations from planarity. The mean S-N bond lengths were found to be 150.4 and 151.5pm for $(Me_3SiN)_3S$ and $(Me_3CN)_3S$ respectively.[37] The three-coordinated sulphur(VI)-nitrogen compounds $S(=NSiR_3)(=NCR_3)_2$ and $S(=NCR_3)_3$ have been prepared by the reaction of $NSF_3$ and $LiN(SiR_3CR_3$ shown in (10). With less bulky amines the same reaction produced polymerisation products.[38]

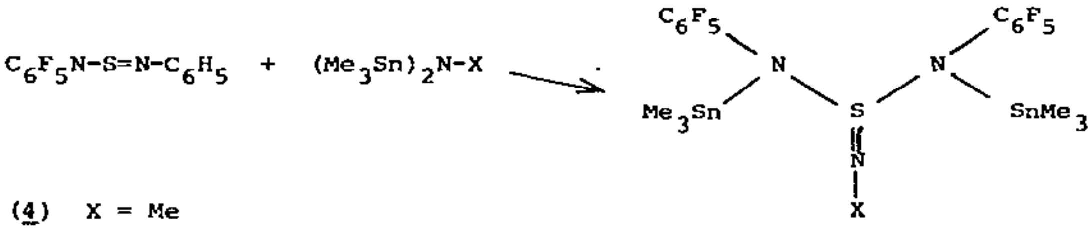


$$NSF_3 + LiN(SiR_3)(CMe_3) \longrightarrow (Me_3CN{=})_2S{=}NSiR_3 + (Me_3CN)_3S + R_3SiF + LiF \quad ...(10)$$

New preparations of salts containing the bis(chlorosulphur)nitrogen cation, $[N(SCl)_2]^+$ have been announced.[39] The preparation of salts $[N(SCl)_2]^+[X]^-$ with a variety of anions (X = $AlCl_4^-$ , $FeCl_4^-$ and $SbCl_6^-$).was achieved using thionyl chloride as a solvent for the reaction of $(NSCl)_3$, $SCl_2$ and the metal chloride, and the compound $[N(SCl)_2]^+[FeCl_4]^-$ was prepared using $S_4N_4$ as in reaction (11).

$$S_4N_4 \;+\; 8SCl_2 \;+\; 4FeCl_3 \longrightarrow 4[N(SCl)_2]^+[FeCl_4]^- \;+\; 2S_2Cl_2 \quad ...(11)$$

The reaction of N,N'-bis(pentafluorophenyl)sulphur diimide with $(Me_3Sn)_2NMe$, $(Me_3Sn)_3N$, and $(Me_3Sn)_2NC_6F_5$ shown in (12) have been shown to yield the 1:1 adducts (4) - (6).[40]



(4) X = Me

(5) X = $SnMe_3$

(6) X = $C_6H_5$ ...(12)

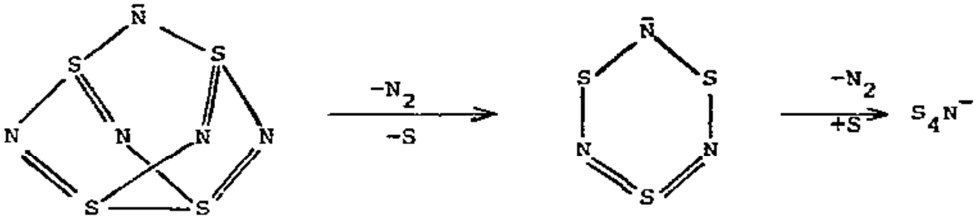
Some reactions of the derivatives of pentafluorobenzenesulphenic, sulphinic and sulphonic acid have been described. From the reaction with thionyl chloride N-sulphinylpentafluorobenzene sulphenamide and -sulphonamide were prepared. N-sulphinylpentafluorobenzenesulphenamide was also prepared by the reaction of pentafluorobenzene sulphenyl chloride with N-sulphinyltrimethylsilylamine.[41]

The synthesis of $FC(NSOF_2)_3$ from either the reaction of $FCBr_3$ and $Hg(NSOF_2)_2$ or from guanidine and $OSF_4$ has been described. The compound $C(NSOF_2)_4$ has been obtained by the reaction of $CBr_4$ and $Hg(NSOF_2)_2$ or more readily from $F_2C(NSOF_2)_2$ and $B(NSOF_2)_3$.[42]

Gas phase electron diffraction patterns of $(SO_2Cl)_2NH$ have been recorded at 83 and 86°C. It was found that at the higher temperature the compound exists as a single conformer in which the two $SO_2Cl$ groups are related by $C_2$ symmetry. The following principal structural parameters, S=O 1.417Å, S-N 1.625Å, S-Cl 2.016Å, $<$ SNS 129°, $<$ NSCl 103°, and NSO 109°, were determined.[43]

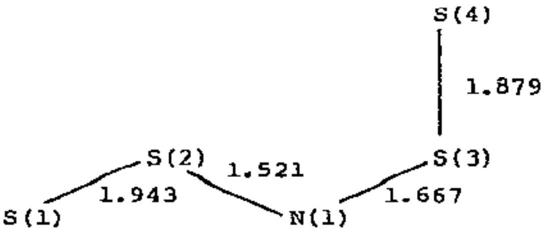
Localized molecular orbitals have been calculated for the simplest N-sulphinosulphimide, $H_2SNSO_2H$, and of its conjugated acid. A three centre S(IV)NS(VI) $\pi$ bond is formed which is localized mainly on the nitrogen atom. The S(IV)N and S(V)N $\sigma$ bonds as well as the nitrogen lone-pair are considerably delocalized onto the neighbouring sulphur atoms. In all cases the sulphur d-orbitals participate in bonding.[44]

The thermal decomposition of $(Ph_3P)_2N^+S_4N_4^-$ in acetonitrile (equation 13) has been shown to lead sequentially to the corresponding salts ofthe $S_3N_3^-$ and $S_4N^-$ anions.



...(13)

A crystal structure determination on the salt $(Ph_3P)_2N^+S_4N^-$ shows that the anion is a planar <u>cis-trans</u> chain with nitrogen in the middle of four sulphur atoms (7). Bond angles found were

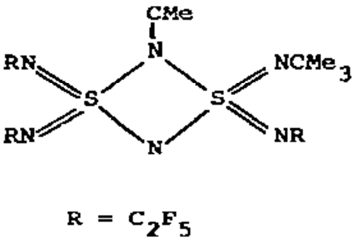


(7)

S(1) - S(2) - N(1) 110.4, S(2) - N(1) - S(3) 120.8, S(4) - S(3) - N(1) 110.6°. The sickle shape of the anion is in marked constant to the <u>cis-cis</u> structure of the isoelectric cation $NS_2Cl_2$ and the staggered conformation of $S_5^{2-}$.[45]

<u>Cyclic Sulphur-Nitrogen Compounds</u>. A review of the structure of cyclic sulphur-nitrogen compounds has suggested that the scope and variety of such rings becomes more comprehensible if they are classified on the basis of the coordination numbers of sulphur rather than the more usual basis of the formal oxidation state.[46]

The shape of the $(S-N)_2$ ring has been shown to be highly dependent upon the ligands. The ring is non-planar in (8) but planar in (9).



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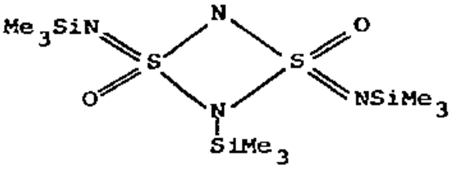
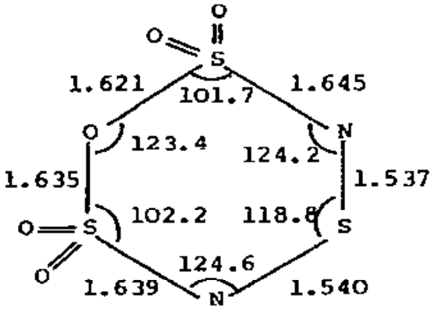


(9)

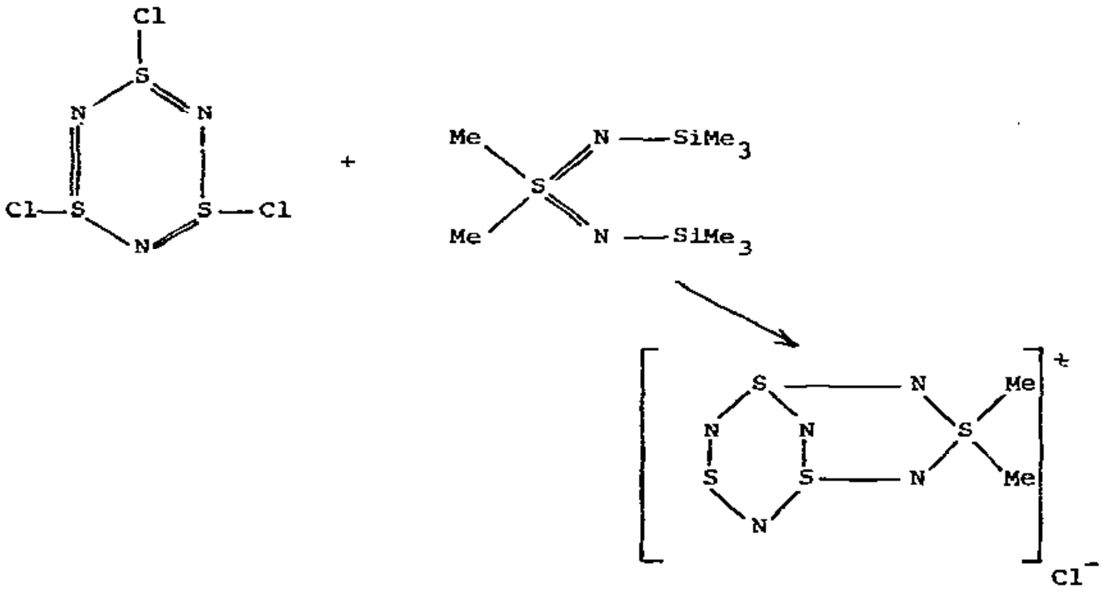
Compound (8) was prepared from $(Me_3CN:)_3S$ and $C_2F_5$-NCO and (9) from $(Me_3SiN:)_3S$ and i-$C_3F_7$-NSO. Crystal structure determinations showed (8) to have an SNS angle of 95.7° and transannular S···S and N···N distances of 2.517 and 2.240Å : bond lengths within the ring were between 1.664 and 1.728Å. The deviations of the ring S and N atom from the averaged plane of the ring were +0.1 and -0.1Å respectively. Compound (9) showed a planar ring with S···S 2.477, N···N 2.257 and S-N distances between 1.666 and 1.683Å.[47]

A structure determination on monoclinic $S_3N_2O_5$ reveals a six-membered $S_3N_2O$ ring containing a non-symmetrically bonded oxygen atom (10). $S_3N_2O_5$ was also shown to react with $S_4N_4$ in boiling methylenechloride to yield the compound $S_4N_4SO_3$.[48]



(10)

The reaction of $S_3N_3Cl_3$ with $Me_2S(NSiMe_3)_2$ or $N(SnMe_3)_3$ has been shown to give the bicyclic compounds (11) to (14)(equation 14).



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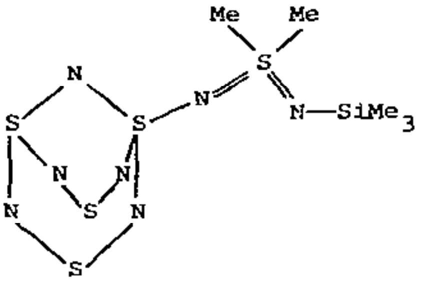

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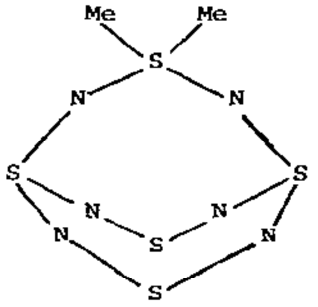

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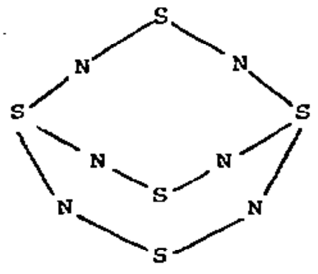
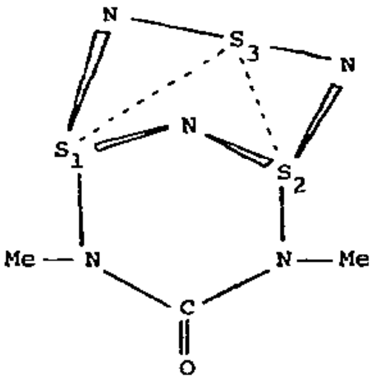


(14)

A single crystal structure determination showed (14) to have a basket structure with a transannular S-S distance of 2.425Å. A similar structure was assumed for (13) on the basis of similarities in i.r. spectra.[49]

$(NSO)_3(C_6H_5)_2Cl$ has been shown to react with secondary amines by nucleophilic substitution to give diphenylsuphanuric amides without cleavage of the trithiazine ring.[50]

An X-ray structure determination has shown that the new bicyclic cation $[S_3N_5Me_2CO]^+$ contains a three-membered ring of sulphur atoms bridged by three nitrogen atoms and a urethane group (15). The compound was prepared by the reaction of $S_3N_3Cl_3$ with $Me_2S{:}NMeC(O){-}MeS{:}Me_3$ in $CCl_4$.[51] Sulphur-sulphur distances found were $S_1{-}S_2$ = 2.703, $S_1{-}S_3$ = 2.802 and $S_2{-}S_3$ = 2.830Å.



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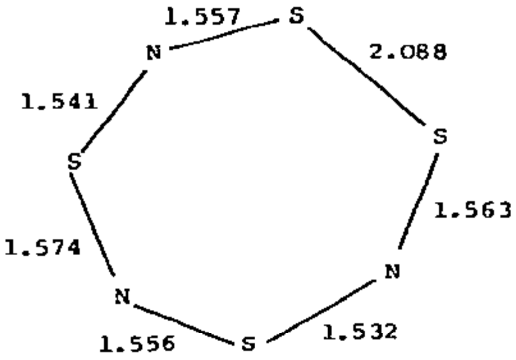


(16)

The crystal structure of thiotrithiazyl tribromide, $(S_4N_3^+)(Br_3^-)$ has been determined. The geometry of the $S_4N_3$ ring (16) was found to be essentially the same as that found in the nitrate salt but the S-S distance of 2.088Å was slightly longer in the bromide.[52] Mass spectrometric techniques have been used to identify the pyrolysis products of $S_4N_4$ vapours passed over quartz wool and silver wool at 80 to 400°C. At 200°C the major product was $S_2N_2$ accompanied by smaller amounts of $S_3N_3$ and $S_4N_2$. At higher temperatures (>300°C) $S_2$, SN and $N_2$ became major products.[53]

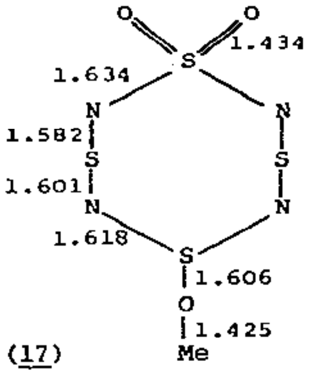
The preparation of new thiazyl halides, $N_4S_4X_2$ (X = F, Cl) have been reported. The chloride is a product of the chlorination of $S_4N_4$ whilst the fluoride may be prepared by reaction of the chloride with NaF.[54-56] X-ray powder diffraction data has been published for $N_4S_4Cl_2$ and a unit cell determined from Weissenberg data.[57] It has been known that gas-phase bromination of solid $S_4N_4$ leads to polymerisation and the formation of conducting $(SNBr_{0.4})_x$, but reaction with liquid bromine leads to a stable tribromide $S_4N_3Br_3$. In contrast the reaction of $S_4N_4$ with bromine in carbon disulphide solution results in a mixture of $S_4N_3Br_3$, $S_4N_3Br$ and a novel ionic compound $CS_3N_2Br_3$.[58]

A number of novel platinum complexes containing binary sulphur-nitrogen ligands have been reported. Starting from tetrakis(triphenylphosphine)platinum(0) and $S_4N_4$ or tetrasulphurtetraimide the compounds $(Ph_3P)_2PtS_4N_4$, $(Ph_3P)_2Pt(N_2S_2)$ and $(Ph_3P)_2PtS_2N_2H_2$ have been reported.[59]

The nucleophilic substitution of a cyclic sulphur-nitrogen compound has been observed for the first time. A surprisingly stable salt (17) has been obtained by the reaction of $S_4N_4O_2$ and sodium methoxide.

$$S_4N_4O_2 \quad + \quad NaOMe \longrightarrow \underset{(\underline{17})}{[S_4N_4O_2OMe]^{-}Na^{+}} \qquad \ldots(15)$$

A single crystal determination on the tetraphenylphosphonium salt of (17) showed the conformation of the eight-membered ring to resemble that of $S_4N_4$. The $S_4N_4$ skeleton can therefore be regarded as consisting of two annelated 5-membered rings with a weak central S-S bond (2.484Å).[60]



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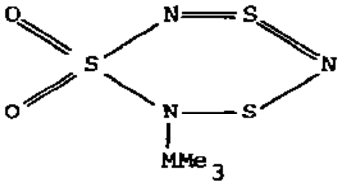
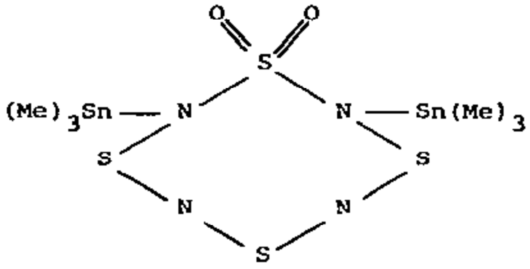


(18)

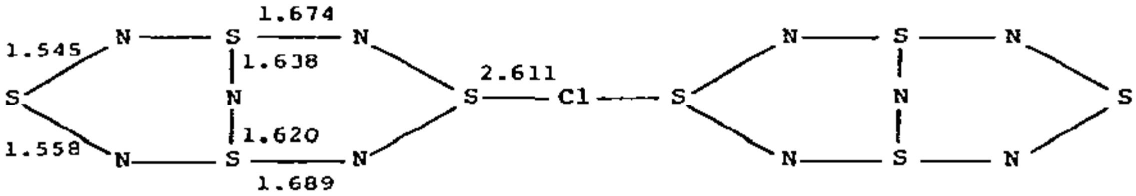
Reaction of $S_4N_4O_2$ with $N(MMe_3)_3$ M = Si, Sn, in a 1:1 ratio for the Si compound and a 3:2 ratio for the Sn compound has been shown to give the compound (18). These six-membered rings are the first examples in which the sulphur atoms have the formal oxidation states of 2, 4 and 6. A crystal structure determination on the tin compound showed a planar ring system for five of the atoms but the nitrogen atom coordinated to the tin atom lay 0.78Å above the plane.[61] Reaction of $S_4N_4O_2$ with $N(SnMe_3)_3$ in a molar ratio of 1:1 leads to the eight-membered trimethyltin substituted compound (19).



(19)

A single crystal structure determination was carried out on the compound which was also found to be highly diamagnetic.[62]

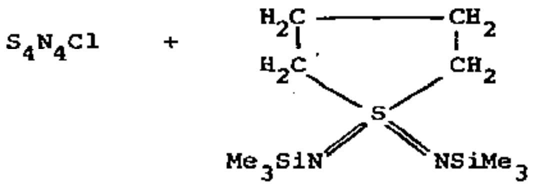
The new sulphur-nitrogen halide, $S_4N_5Cl$ has been prepared from the reaction of $S_3N_3Cl_3$ and $Me_3SiN{=}S{=}NSiMe_3$ in $CCl_4$. An X-ray structural study shows it to have a polymeric, predominantly ionic structure in which bicyclic $S_4N_5{}^+$ cations are symmetrically bridged by $Cl^-$ ions (20).

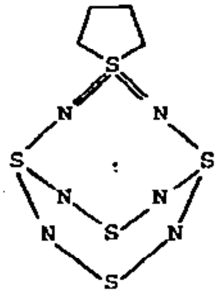


(20)

Reaction of (20) with $AgF_2$ or $SbCl_5$ gives $S_4N_5F$ or $S_4N_5SbCl_6$ respectively.[63]

The spirocyclic derivative (21) has been prepared by the reaction of $S_4N_4Cl$ with thiacyclopentane-S,S-bis(trimethylsilylimide).

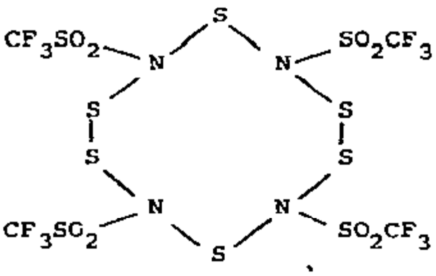




(21)

An X-ray structure analysis confirmed the spiro-linkage of the thiacyclopentane ring to the sulphur atom of the bicyclic SN skeleton.[64]

The reactions of $SCl_2$ and $S_2Cl_2$ with $CF_3SO_2(R_3Sn)N\text{-}SS\text{-}N(SnR_3)SO_2CF_3$ have been shown to yield the ten- and twelve-membered ring compounds (22) and (23). These are the largest neutral sulphur-nitrogen rings of coordination number two at the sulphur atom known to date.[65]



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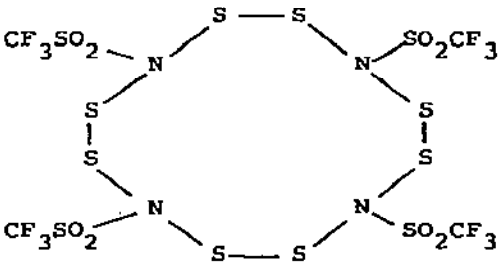
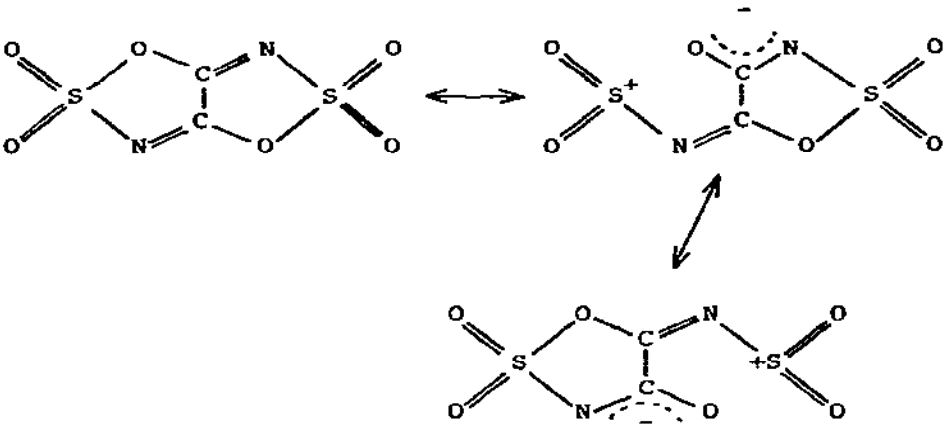


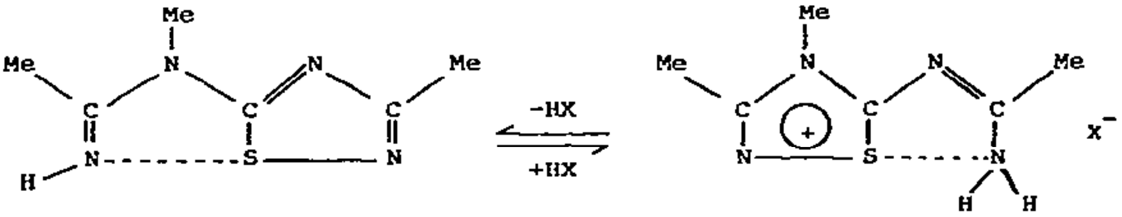
(23)

An X-ray structural investigation has shown that the product of the reaction of $(CN)_2$ and $SO_3$ in the molar ratio 1:2 is best formulated as a 1:3; 2,4 cycloadduct. The extremely long S-O bonds in the ring (1.712Å) and the short C-O (1.294Å) and exocyclic S=O (1.395Å) bonds suggest bond-no-bond resonance of the type in equation (17).[66]

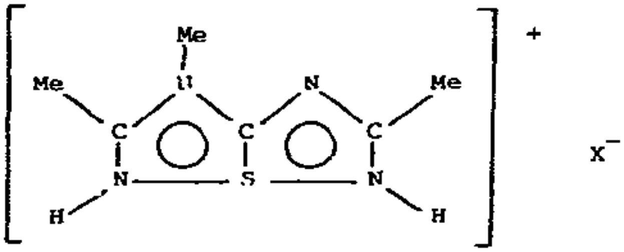


...(17)

Dynamic bond switching at π-hypervalent sulphur has now been demonstrated. Compounds (24) and (25) rapidly equilibrate and the reaction is thought to involve the thiathiophthene analogous system (26). The intramolecular N···S interaction in (24) was confirmed by an X-ray structural study.[67]



(24) (25)



(26)

### 6.2.4 Bonds to Oxygen

The extraction of sulphur dioxide from aqueous solution by dihexylsulphoxide and petroleum sulphoxides has been studied. The extraction process takes place by a solvate mechanism with the formation of compounds of composition $SO_2.S$.[68] The formation of transition metal complexes with very weak nitrogen and oxygen donors, e.g. $NSF_3$ and $OPX_3$ (X = F, NCO), has been observed in liquid sulphur dioxide.[69] The metals Ti, V, Mn, Fe, Co, Ni, Cu, Zn and Cd have been shown to react with the mixed non-aqueous solvent DMSO-$SO_2$ to form metal disulphates. Other metals Ce, Pr, Eu, Dy or U dissolve in the solvent but product identification was not possible. The existence of the $[SO_2]^-$ radical ion and of ion pairs containing a metal ion and $[SO_2]^-$ was demonstrated for solutions of metals in non-aqueous solvents containing $SO_2$. A correlation was established between dielectric constant, donor number and the reaction of metals in such solvents.[70] $SO_2$, $SOF_2$, $POF_3$ and $COF_2$ have been shown to form 1:1 oxygen-bridged adducts with $AsF_5$ and $SbF_5$ using Raman spectroscopy at different temperatures. $SO_2F_2$ behaves as a still weaker base but still forms an oxygen-bridged adduct with $AsF_5$ but not with $SbF_5$ - a reversal of the usual Lewis acidities. The relative base strengths of the molecules studied was found to be $POF_3 > SO_2 > SOF_2 > COF_2$.[71]

A study of the corrosion of nickel and cobalt by $SO_2$ has shown that the morphologies of scale formation and corrosion kinetics are very similar. In both cases a sulphide layer forms close to the metal with an outer layer consisting of two phases, an oxide and a sulphide, the latter being dispersed as inclusions in the oxide.[72]

Phenyl mercury chelates have been shown to take up 1 mole of $SO_2$ from a medium of liquid $SO_2$ to form mono-insertion products. I.r. studies showed the products to be O-sulphinates with the insertion taking place between the mercury atom and the phenyl group.[73]

Transition-metal-$SO_2$ complexes have been examined in an effort to correlate structural geometry with the stretching frequency $\nu(SO)$. Although in a majority of cases a correlation was observed a sufficient number of exceptions made accurate structural prediction unreliable. However, certain combinations of physico-chemical properties were found which, without exception, enabled diagnosis of specific coordination geometry to be made.[74] The insertion of $SO_2$ into the tungsten-alkyl bond of alkyl($\eta^5$-cyclopentadienyl)-tricarbonyltungsten(II) has been shown to be markedly promoted by the Lewis acids $BF_3$ and $SbF_5$. In some cases the reaction of the complex proceeded 20,000 times faster with $SO_2$-$BF_3$ than with $SO_2$ alone.[75]

A crystal structure determination of α-$NaHSO_4$ has shown disorder of one of the hydrogen atoms. This disorder, which was deduced from S-O bond lengths and O···O distances, causes a peculiar hydrogen bonding scheme with one of the hydrogen bonds extending across a centre of symmetry.[76] The structure of ammonium thiosulphate has been shown to consist of $NH_4$ and $S_2O_3$ tetrahedra interconnected by hydrogen bonds. All but two of the hydrogen atoms were located by difference methods and one of the $NH_4$ groups was thought to be disordered at room temperature.[77] A very short, and asymmetrical hydrogen bond has been found in the structure of $Na_3H(SO_4)_2$. The structure is dominated by a framework of Na coordination polyhedra built up by the intersection of two non-coplanar systems of chains and, to some extent, condensed into (010) layers. The S tetrahedra are approximately close packed in (010) layers and form $(SO_4H.SO_4)^{3-}$ dimers via the very short asymmetrical H-bond with O···O = 2.434, O-H = 1.03Å and $\angle$O-H···O = 177°.[78]

The unit cell parameters of the soluble modification of $CaSO_4$ have been determined and the various characteristic structural features of the polymorphic forms examined. The conversion of the soluble form to the insoluble state was shown to correspond to a type 2 phase transformation.[79] The structural differences between the α- and β- modifications of $CaSO_4.5H_2O$ have been established for the first time. Probable structural models characterised by ordered and random arrangements of the water molecules were proposed.[80]

Phases of the composition $Ca_{10-x}Na_x(PO_4)_{6-x}(SO_4)_xF_2$ have been obtained by the substitution of phosphate by sulphate ions in the $Ca_{10}(PO_4)_6F_2$ lattice. The stepwise introduction of sulphate produced an increasing distortion of the lattice although the lattice parameters of the pseudo-hexagonal unit cell were practically invariant.[81] Three sulphur apatites have been prepared, all of which crystallised in the hexagonal space group $P6_3/m$, with the formulae, $BaS(AsO_4)_2SO_4$, $SrS(AsO_4)_2SO_4$ and $SrS(PO_4)_2SO_4$.[82]

The crystal structure of the acid sulphate of indium(III) hydrate has been determined. The structure can be described in terms of layers consisting of In atoms joined to four others by sulphate groups. The coordination around the In is completed by water molecules forming an $InO_4(OH_2)_2$ distorted octahedron. These layers are linked together by oxonium ions with one $H_5O_2^+$ ion joining two sheets by short hydrogen bonds. In view of these results the compound should be formulated as $(H_5O_2)^+[In(H_2O)_2(SO_4)_2]^-$.[83]

The transformation of the room temperature form N-$PbSO_4$ to the high temperature cubic form H-$PbSO_4$ has been observed using the high temperature Guinier technique.[84] Sulphatopolytitanic acids have been shown to be formed when hydrated $TiO_2$ is dissolved in sulphuric acid. Their subsequent reaction with $H_2SO_4$ leads to the formation and precipitation of monosulphatoorthotitanic acid (titanyl sulphate dihydrate).[85]

A crystal structure determination has shown that $Mn(OH)SO_4.2H_2O$ contains two types of $Mn^{3+}O_2(OH)_2(H_2O)_2$ octahedra sharing opposite vertices via OH groups to form chains along the b-axis, with each two adjacent octahedra also being linked via bridging $SO_4$ tetrahedra.[86]

Double sulphates of composition $K_2Ni(SO_4)_2.xH_2O$ where x = 6, 2 or 0, and $K_2Ni_2(SO_4)_3$ have been investigated. Dehydration of the hexahydrate in the presence of water vapour takes place in two stages with the final decomposition products being NiO and $K_2SO_4$. There is a considerable decrease in the symmetry of the sulphate groups on going from the hexahydrate to the dihydrate and to the anhydrous double sulphate.[87] The thermal behaviour of $ZnSO_4.7H_2O$,[88] $CdSO_4$,[89] $MgUO_2(SO_4)_2.5H_2O$ and $MgUO_2(SeO_4)_2.6H_2O$[90] have been studied and the lattice parameters and the space groups of the rubidium-hafnium and caesium-hafnium double sulphates have been determined.[91]

The i.r. spectrum of amidofluorosulphuric acid and its mercury salt (prepared for the first time) have been measured and assigned.[92] Gold(III)fluorosulphate has been found to be a good fluorosulphate ion acceptor. The ion $[Au(SO_3F)_4]^-$ was found in solid crystalline materials of composition $M|Au(SO_3F)_4|$ with M = Cs, K, Li, NO or $ClO_2$. Gold(III)fluorosulphate is thought to be monosolvated and acts as a moderately strong acid in $HSO_3F$ according to the reaction[93]

$$H[Au(SO_3F)_4] + HSO_3F \longleftrightarrow Au(SO_3F)_4^- + H_2SO_3F^+$$

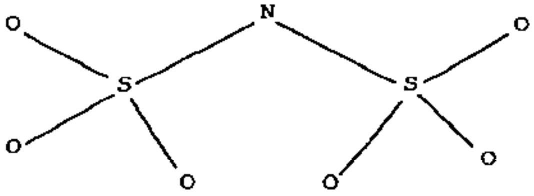
A number of phase systems involving sulphates have been studied; for conciseness these are collected together in Table 2.

Table 2. Sulphate phase systems studied.

| System | Reference |
|---|---|
| $NH_4SO_3NH_2-(NH_4)_2SO_4-H_2O$ | 94 |
| $H^+$, $NH_4{}^+$ \|\| $SO_4{}^{2-}$, $SO_3NH_2{}^- - H_2O$ | 95,96 |
| $Al_2(SO_4)_3 - K_2SO_4$ | 97 |
| $Zr(SO_4)_2 - H_2O$ | 98 |
| $K_2SO_4 - MnSO_4$ | 99 |
| $CO_2SO_4 - NiSO_4 - Ce_2(SO_4)_3 - H_2O$ | 100 |
| $Cs_2SO_4 - NiSO_4 - H_2O$ | 101 |
| $Co_2SO_4 - Ce_2(SO_4)_3 - H_2O$ | 101 |
| $CoSO_4 - MgSO_4 - H_2O$ | 102 |
| $CoSO_4 - Rb_2SO_4 - H_2O$ | 103 |
| $Ce_2O_3 - TiO_2 - SO_2 - H_2O$ | 104 |
| $Rb_2SO_4 - M_2(SO_4)_3$ M = La, Pr, Gd or Yb | 105 |
| $Rb_2SO_4.8H_2O - M_2(SO_4)_3$ M = Pr to Dy | 106 |
| $Co_2SO_4 - Pr_2(SO_4)_3 - H_2O$ | 107 |
| $NiSO_4 - Pr_2(SO_4)_3 - H_2O$ | 107 |

Various carbon catalysts, e.g. active charcoals and carbon black, have been compared as catalysts for the oxidation of sulphurous acid.[108] A thermodynamic analysis has been carried out using tautomeric equilibria and pKa values for sulphurous acid in aqueous solution. Free energy of formation values (kcal $mol^{-1}$) were calculated for dimethyl sulphite (-91.45) and $SO(OH)_2$ (-129.26), the free energy of covalent hydration of $SO_2$ was found to be 1.6 kcal $mol^{-1}$ and the free energy charge for tautomerization of $SO(OH)_2$ to $H-SO_2-(OH)$ as +4.5 kcal $mol^{-1}$.[109] It has been found that there is no range of $SO_3$ concentration in oleum solutions in which sulphur and ozone are present simultaneously in the dissolved state. At concentrations of $SO_3$ lower than 9%, homogeneously dissolved sulphur is precipitated whilst at concentrations above 9% a sharp drop in ozone concentration is observed.[110]

A determination of the crystal structure of $K_3N(SO_3)_2H_2O$ has shown the $\{N(SO_3)_2\}^{3-}$ ion to have the configuration (27) with bond distances S-N 1.606, and S-O 1.468Å and bond angles S-N-S 120.83 and N-S-O 108.70°.[111] Crystal structure determinations have also



(27)

been carried out on the compounds $\alpha$-$MnSO_3.3H_2O$,[112] $\alpha$-$FeSO_3.3H_2O$[113] and $\beta$-$FeSO_3.3H_2O$.[114]

The following series of phase changes and decompositions of $Na_2S_2O_3$ have been determined. The transformations $\alpha \to \beta \to \gamma$ are

$$\begin{tikzcd}
\text{monoclinic } \alpha \arrow[r, "330^{o}"] & \text{trigonal } \beta \arrow[d, "\text{cooling}"] \arrow[r, "338^{o}C"] & \text{b.c.c } \gamma \arrow[d, "440^{o}C"] \\
Na_2S_2O_3.5H_2O \arrow[r, "-H_2O"] & \text{orthorhombic } \alpha' & Na_2SO_4 + Na_2S_5
\end{tikzcd} \quad ...(18)$$

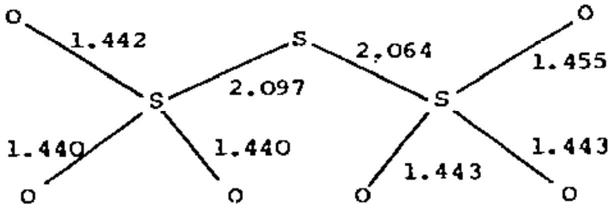
all said to be reversible but equilibrium displacement by distillition of sulphur accelerates decomposition even for the $\beta$-phase and maintaining low sulphur pressures leads to the formation of $Na_2SO_3$. The $\beta$- and $\alpha$-phases were found to be superionic conductors.[115]

The formation of sodium dithionite, $Na_2S_2O_4$, from $SO_2$ and sodium formate in a three phase system has been shown to proceed via the double salt $Na_2S_2O_5.NaOOCH$ which was isolated in a crystalline form.[116]

In the crystal structure of $Sb_2(S_2O_7)_3$ there are three $S_2O_7$ groups with mean bond lengths of S-O (bridge) 1.618, $SO_2$ (terminal) 1.423, and S-O···Sb 1.48Å. The average value of the bond angle S-O-S was found to be 121.4°.[117]

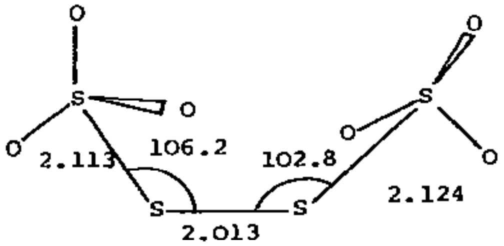
Measurements of the Gibbs free energies of transfer of the peroxodisulphate anion from water into aqueous methanol have shown results which are all consistent with the expected pattern for the electrostatically determined order of hydration (solution), i.e. $SO_4^{2-} > S_2O_8^{2-} > CN^- \sim Cl^-$. A similar picture was thought to apply for acetone-water mixtures but the inadequacies of the stability data for $K_2SO_4$ prevented a complete study being carried out.[118]

A further structure determination of $K_2S_3O_6$ has confirmed earlier results but gives a significant difference for the symmetry of the trithionate ion (28). The two S-S bonds are not of equal length being, 2.064 and 2.097Å, while one S-O bond is appreciably longer (1.455Å) than the other five (1.440 - 1.443Å).[119]



(28)

The structure of $K_2S_4O_6$ shows two tetrathionate ions in the asymmetric unit which are comparable in geometry but with rotational displacement of the $SO_3$ groups around the terminal S-S bonds, see (29) and (30). In both ions the central bond is



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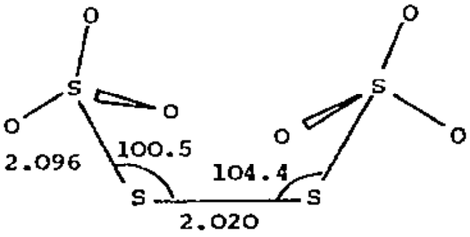
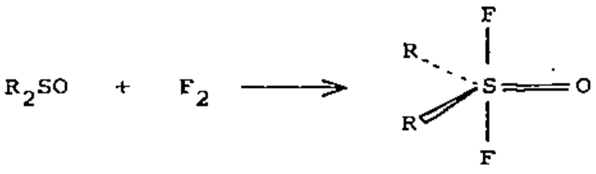


(30)

shorter than the outer pair and the sulphur skeleton is bent at nearly a right angle about the central S-S bond. The structure is held together by an extensive network of ionic interactions between the O atoms (S-O 1.434 to 1.454Å) and the K ions.[120]

Electron spin resonance studies of radicals derived from exposure of dithionate, tetrethionate and thiosulphate anions to γ-rays at 77K have been carried out.[121]

The direct fluorination of sulphoxides has led to the formation of diarylsulphur(VI)oxide difluoride (31). Treatment of (31) with BF$_3$ or PF$_5$ leads to fluorine transfer and the formation of the ionic compounds $[R_2S(O)F]^+BF_4^-$ and $[R_2S(O)F]^+PF_6^-$ respectively. Reaction with Ph$_3$P surprisingly gives rise to transfer of both fluorine atoms and the formation of the sulphoxide and Ph$_3$PF$_2$.[123]



(31)

### 6.2.5 Sulphides

The adsorption of H$_2$S and CH$_3$SH on Al$_2$O$_3$ at 303K has been studied. It was found that the number of Lewis acid sites formed by incompletely coordinated Al cations rose to a maximum when the Al$_2$O$_3$ was preheated at 600°C, and that the H$_2$S and CH$_3$SH molecules react irreversibly with these sites forming Al ← S bonds.[123] I.r. studies have provided evidence for an H$_2$S and CO$_2$ interaction on γ-Al$_2$O$_3$ to form thiocarbonate surface species which lead to the formation of carbonyl sulphide.[124]

The calculated molecular geometries of HSSH, FSSF and F$_2$SS have been found to be in good agreement with experiment when polarization functions are taken into account. The as-yet uncharacterised isomer H$_2$SS was predicted to be as stable with respect to HSSH as F$_2$SS is to FSSF.[125]

A study of the vibrational spectra of alkali-metal polysulphides has shown that Rb$_2$S$_4$ has no defined composition but that Cs$_2$S$_4$ is well defined and similar to Na$_2$S$_4$. On melting Na$_2$S$_4$ still exists as $S_4^{2-}$ chains but the Rb and Cs compounds disproportionate to $S_3^-$ radicals and probably the monosulphide. On quenching a melt of $Cs_2S_6$ to room temperature a double-branched chain structure, the thio- analogue of dithionite, $S_2S_4^{2-}$ was thought to be observed.[126] Raman studies have shown that $Rb_2S_2$ exists as $S_2^{2-}$ in both the solid and liquid states, but $Cs_2S_2$ disproportionates to $Cs_2S$ and $Cs_2S_3$ at 100° but may be rebuilt on increasing the temperature of the melt. On temperising $Rb_2S_3$ and $Co_2S_3$ at temperatures greater than 100°C, additional Raman bands were observed which were thought to result from rotating $S_3^{2-}$ ions. Only the $S_3^{2-}$ anion was observed in melts of $Rb_2S_3$ and $Cs_2S_3$.[127]

$Cs_2S_2$ has been prepared in the form of transparent yellow needles by ammonothermal synthesis at a temperature of around 300° and pressures between 2 and 3 kbar. The compound was found to crystallise in an orthorhombic unit cell in the space group Immm. The structure was built up from $S_2^{2-}$ polyanions with an S-S distance of 2.107Å.[128]

The crystal structure of $Ga_2S_2Te$ indicates that the Ga atoms are in fourfold, the Te atoms in twofold and the S atoms in threefold coordination. The structure is essentially built up of $GaS_3Te$ tetrahedra which share all four corners.[129] A new phase modification of $Tl_2S$ has been observed which appears on heating $Tl_2S$ above 450°C.[130]

The reaction in equation (19) has been found to have $\Delta H^o_{298}$ =

$$Ge + GeS_2(g) \longrightarrow 2GeS(g) \qquad \ldots(19)$$

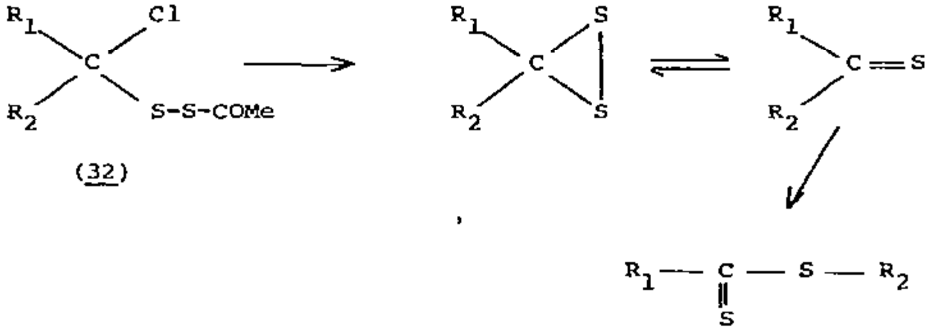
138kJ from a combination of chemical transport, mass spectrometric and thermogravimetric observations.[131] Thermochemical data has been obtained for compounds in the phosphorus-sulphur and phosphorus-selenium systems.[132] The reaction of $As_2S_3$ with $SO_2$ in HCl (concentration range 0.02 to 3.0M) has been studied. Solution of $As_2S_3$ was shown to take pace by the formation of thiosulphuric acid but at concentrations of HCl greater than 2M and pressures of $SO_2$ less than 1 atms, no solution was observed.[133]

A study of non-crystalline arsenic pentasulphide has shown that the average As atom has three bridging sulphur neighbours at 2.30Å, and one terminal sulphur atom at 2.12Å. The molecular structure was though to be derived from the unknown $As_4S_{10}$ cage molecule.[134]

The preparations, crystal structures and physico-chemical properties of compounds of the type $ABX_2$ where A = alkali metal, B = As, Sb or Bi, and X = S, Se or Te have been reviewed.[135] The hexagonal compound $K_4Tl_2S_3$ and the monoclinic compound $K_7TlS_4$ have been observed in the $K_2S$ - $Tl_2S$ system. Hexagonal $Rb_4Tl_2S_3$ was the only compound found in the $Rb_2S$ - $Tl_2S$ system.[136] X-ray diffraction and differential thermal analysis studies have shown that $La_2S_3$ and $Ce_2S_3$ react with Ge and Sn monosulphides at the polymorphic transition temperatures of the latter to form compounds of the composition $Ln_2MS_4$.[137]

Isolated tetrahedral $PS_4^{3-}$ ions with P-S bonds between 2.029 and 2.061Å have been found in the structure of $K_3PS_4.4H_2O$.[138] In the compound $Na_3SbS_4.9H_2O$ finite groups of octahedrally coordinated Na atoms of the type $(H_2O)_3Na(H_2O)_3Na(H_2O)_3NaS_3$ and $SbS_4$ tetrahedra share common corners via three of the four sulphur atoms;[139] whilst in $Cs_2Sb_8S_{13}$ $SbS_3$ ϕ-tetrahedra and $SbS_4$ ϕ-trigonal bipyramids are connected together to form sheets separated by Cs ions.[140] The same basic units are also present in $RbSb_3S_5.H_2O$,[141] and $K_2Sb_4S_7.H_2O$.[142] In the compound $NH_4SbS_2$ $SbS_4$ pseudo-trigonal bipyramids are connected to form chains.[143]

The intermediacy of the $>$CSS ring and/or its $>$C=S=S isomer appears likely from new experiments. The reaction of (32) with morpholine leads via the unstable α-chloroalkyldisulphanes and the dithio esters (33) to stable products.[144]



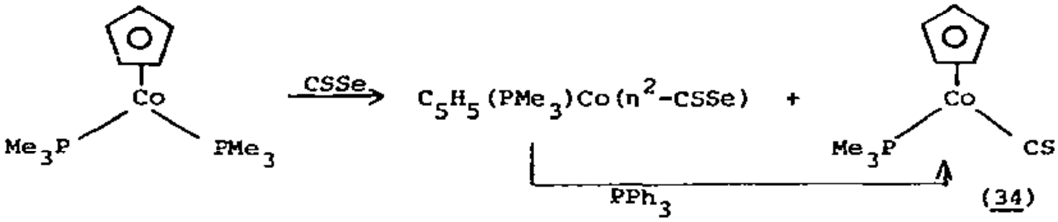
(32)

(33)

...(20)

It is thought that the use of CSSe as a source of CS should facilitate, or ever make possible in some cases, the synthesis of thiocarbonyl metal-complexes. The first examples of this reaction are the preparation of (34) and the compound $C_5H_5(PMe_3)Rh(CS)$

obtained from the corresponding ethylene complex.[145]

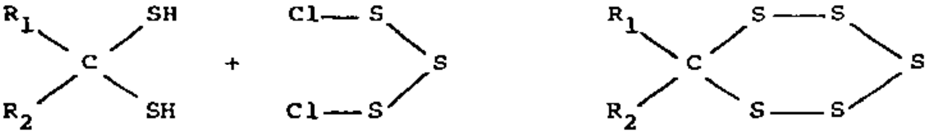


(34)

...(21)

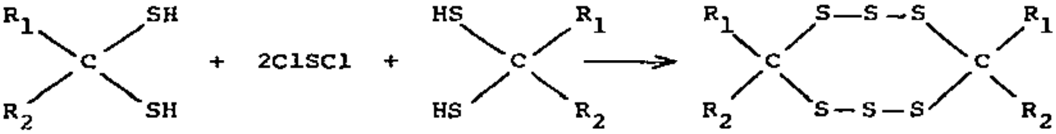
Bands due to $\nu NCS_2^-$ and $\nu NCSe_2^-$ in dithio- and diselenocarbamate ions respectively have been discussed in the light of the stretching modes in model thio- and seleno-carbonyl compounds.[146] Theoretical studies of the binding and reactions of disulphides with alkali and alkaline earth metals have been reported.[147] The comparative usefulness of six sulphur, sulphenyl, selenyl and seleninyl chlorides for the conversion of aldoximes to nitriles have been examined under similar reaction conditions.[148]

The conformation of the seven-membered ring in benzopentathiepine,[149] 1,2,4,5-benzotetrathiepin and 3-methyl-1,2,4,5-benzotetrathiepin,[150] has been shown to be of the chair form. The synthesis of a series of new pentathianes and hexathiocanes by the reactions in equations (22) and (23) has been announced.[151]



...(22)

$R_1 = R_2 = H, Me, CH_2C_6H_5, CH_2-(CH_3)_3-CH_2$



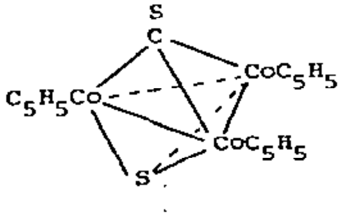
...(23)

$R_1 = R_2 = H, CH_2(CH_3)_3CH_2; \ R_1 = H, R_2 = Me.$

The preparation of the sulphanes $[(CH_3O)_3Si(CH_2)_2]S_n$ for n = 1 - 4 and the corresponding mercaptane have been reported. The $^{13}C$ and $^{1}H$ n.m.r. spectra were measured and i.r. and Raman spectra discussed in the light of both C-S and S-S bonding.[152] The colourless N-dicyandithiocarbamic acid has been prepared by reaction between a suspension of $K[S_2C-N(CN)_2]$ in diethyl ether and a solution of HCl in $(C_2H_5)_2O$ at 0°C.[153] Alkali metal salts of the acid may be prepared by reaction of dicyanamides with $CS_2$ and the corresponding hydroxide. The reaction between $Ba[S_2C-N(CN)_2]_2$ and $(NH_4)_2SO_4$ in aqueous solution leads to the formation of $NH_4[S_2C-N(CN)]$.[154] The oxidation of N-dicyandithiocarbamate ions with $I_2$ has been shown to form the pale yellow N-tetracyanothiuram disulphide, $(NC)_2N-CS-S-S-SC-N(CN)_2$.[155]

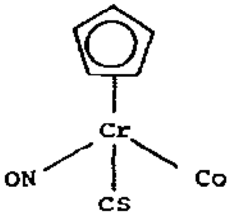
The sulphidation of niobium by $H_2S$ has been studied and from weight gain data it was shown that niobium sulphidizes some two orders of magnitude more slowly than Mo and some six orders of magnitude more slowly than Cr.[156] The phase equilibria in the composition range $NbS_2$ - $Nb_{1.5}S_2$ have been studied.[157] Platinum sulphide has been found to undergo a high pressure phase transformation at 30 kbar to give a phase isomorphous with PdS.[158] The self diffusion of iron in ferrous sulphide[159] and the crystal structure of a metastable form of $Fe_7S_8$[160] have been studied.

Available data on the force constants and lengths of C-S, transition metal-S, and C-Se bonds have been analysed and empirical relationships established.[161] The ligand CS has been shown to further follow the pattern already well established in carbonyl chemistry in that the complex (35) with a $\mu_3$-thiocarbonyl bridge has now been prepared.



(35)

This preparation completes the series $L_nM\text{-CS}$, $L_nM_2(\mu_2\text{-CS})$, $L_nM_3(\mu_3\text{-CS})$.[162] Three new chromium complexes (36 - 38) with the rare combination CS/NO have been synthesized. From the spectra of these compounds it was deduced that CS in (36) is a more effective acceptor than CO in $CpCr(CO)_2(NO)$ but in the cation (38), CS is a weaker acceptor than CO in $[CpCr(CO)(NO)_2]^+$.[163] Di- and trinuclear transition metal complexes with the structural units (39) and (40) present in the same molecule have now been made possible by studies on the basic metal/heteroallene/acid or Lewis acid metal system.



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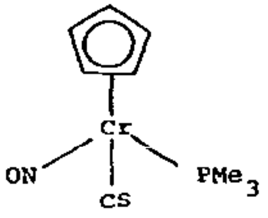

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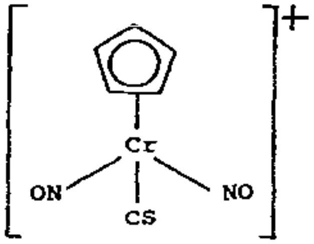

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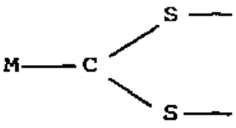
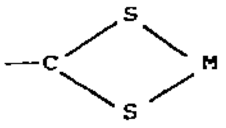
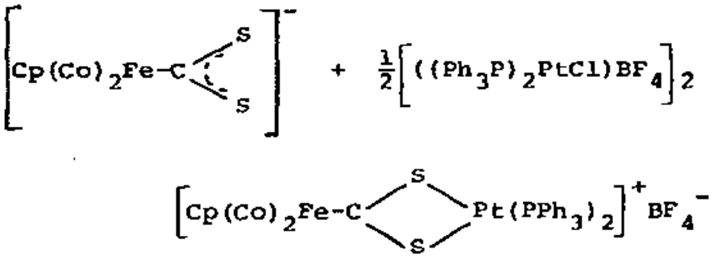


(39)



(40)

An example of such a directed synthesis is given in equation (24).[164]

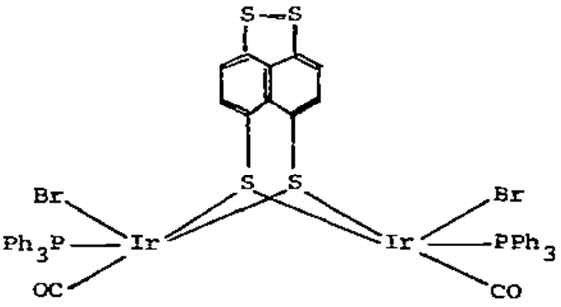


...(24)

A new bridging mode of $CS_2$ in the form of an asymmetrical bridge between the two Co atoms in the dication $[(triphos)Co(CS_2)Co(triphos)]^{2+}$ has been observed. One cobalt is π-bonded to a C=S group while the other one forms two σ-bonds to the two S atoms.[165]

A crystal structure determination on the complex anion $Mo_4(NO)_4S_{13}^{4-}$ has provided another example of the significance of $S_2^{2-}$ ligands for the stabilization of unusual coordination compounds of the transition metals. The ion contains sulphur in five different bonding states and particularly noteworthy are the four $S_2^{2-}$ ligands each of which is coordinated both end-on (to one Mo atom) as well as side-on (to another Mo atom).[166] Reaction of $Co_2WOS_3$ with $CuCl_2$ and $PPh_3$ has led to the preparation of a complex containing Cu, W and S atoms in a cubabe-like skeleton; such structures containing Cu and S were formerly unknown.[167]

The first di(μ-S)-bridge between two metal atoms has been observed in the tetrathionaphthalene complex (<u>41</u>).[168]



(<u>41</u>)

The reaction of $AgNO_3$, $PPh_3$ and $(NH_4)_2WS_4$ in a dichloromethane-water system has been shown to yield the complex $(PPh_3)_3Ag_2WS_4$ which contains the tetradentate $WS_4^{2-}$ ligand.[169]

A short literature survey on phosphine-coordinated $d^8$-metal tetrasulphides and the synthesis of such compounds using sodium polysulphides has been given.[170] Sulphur clusters have also been observed in the iron complex $[Fe_4S_4(SR)_4]^{2-}$,[171] and several complexes of Mo.[172,173,174]

The published data on rare-earth polysulphides has been analysed in an attempt to obtain a sytematic classification.[175] The preparation, properties and structures of erbium sulphides,[176] and the crystal structures of $CeS_2$[177] and $Ce_6O_6S_4$[178] have been described. A study of the microscale preparation and characterization of $^{248}Cm$ monochalcogenides has shown that although isostructural with the corresponding americium compounds, they exhibit smaller lattice constants which is the reverse of the case for the monopnictides of the two elements.[179]

The reaction of thallium sulphide and FeS has been shown to produce the compound $TlFeS_2$ with a structure made up of $[FeS_2^-]_\infty$ chains. Tetragonal or monoclinically distorted tetragonal ternary phases were also observed with the composition $Fe_xTl_2S_4$ (x = 2.6 to 3.6).[180] The structure and magnetic properties of the new ferromagnetic compound $TlFe_{1+x}S_2$ (x = 0.25 to 0.85) and the monoclinic phase $Tl_3Fe_2S_4$ have also been characterised.[181] Reaction of the fused alkali metal carbonates with Cu and S at temperatures between 600 and 790°C have been used to prepare the ternary compounds $Na_3Cu_4S_4$,[182] $K_3Cu_8S_6$ and $Rb_3Cu_8S_6$.[183] The compound $Na_3FeS_3$ has been prepared by the reaction of $Na_2CO_3$ with iron sponge at 1,000°C under a stream of $H_2S$, and a structure determination showed that the Fe and S atoms form isolated $Fe_2S_6$ anions.[184] The magnetic susceptibility of $NaCeS_2$ has the 3+ oxidation state but below 4.8K ferromagnetic ordering exists and only at temperatures above 150K does the compound show Curie-Weiss behaviour.[185] The effect of transporting agents on the chemical transport of the ternary sulphide $Co_yFe_{1-y}S_x$ using $GeI_2$ or $HI(NH_4I)$ as transporting agents has been explained on the basis of a thermodynamic model.[186] The compounds $Ag_2BeGeS_4$,[187] $Ag_7GeS_5I$,[188] $Cu_2SrGeS_4$ and $Cu_2BaGeS_4$[189] have been prepared and their crystal structures determined for the first time.

An analysis has been made of the factors in the interchangeability of atoms in chalcogenide glass forming systems and a simple classification proposed.[190] The glass forming region of the $Na_2S$-$XS_2$ (X = Si, Ge), $Na_2S$-$P_2S_5$,[191] and GeS-GeSe[192] systems have been investigated. Several phase systems involving sulphides have been reported and these are collated in Table 3.

## 6.3 SELENIUM

### 6.3.1 Bonds to Halogen

The reaction of heated selenium with highly diluted fluorine has been shown to lead to a mixture of lower selenium fluorides that may be trapped at low temperature. The new species $SeF_2$ and FSe-SeF have been unambiguously identified by i.r. spectra of $^{76/82}Se$ on purpose substituted compounds. During the u.v. photolysis

Table 3. Sulphide phase diagrams.

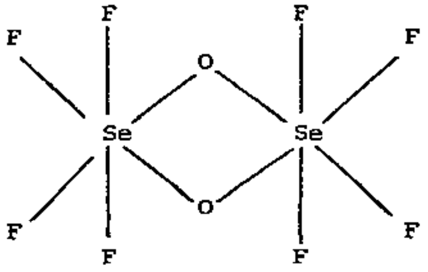
| System | Reference |
|---|---|
| $K_2S - Tl_2S$ | 193 |
| $Rb_2S - Tl_2S$ | 193 |
| $AgInS_2 - SnS_2$ | 194 |
| $CuInS_2 - SnS_2$ | 194 |
| $In_2S_3 - Pb$ | 195 |
| $PbIn_2S_4 - Pb$ | 195 |
| $BiCl_3 - Bi_2S_3$ | 196 |
| $As_2S_3 - TlSe$ | 197 |
| Sn - Sb - S | 198 |
| $Na_2S - ZnS$ | 199 |
| $FeS - In_2S_3$ | 200 |
| Fe - S - U | 201 |

FSe-SeF was found to be partially converted into $Se{=}SeF_2$.[202]

Selenium tetrafluoride and the oxide difluoride have been prepared in a pure state and various thermodynamic values determined. The temperature and heat of fusion of both compounds and the heat of vaporisation of $SeOF_2$ were found to be $SeF_4$ $T_{fusion} \approx -30$ to $-48^{\circ}C$, $\Delta H_{fusion} = 1.21 \pm 0.58 kJ\ mol^{-1}$; $SeOF_2$ $T_{fusion} = 15^{\circ}C$, $\Delta H_{fusion} = 8.075 \pm 0.6\ kJ\ mol^{-1}$, $\Delta H_{vaporisation} = 46.9 \pm 0.8\ kJ\ mol^{-1}$.[203] The standard heats of formation of $SeF_4$ and $SeOF_2$ have been determined by hydrolysis in normal NaOH solution, values obtained were $SeF_{4(\ell)}$ $\Delta H^{o}_{f298} = -849.4 \pm 24.3\ kJ\ mol^{-1}$ and $SeOF_{2(\ell)}$ $\Delta H^{o}_{f298} = -574.0 \pm 15.9\ kJ\ mol^{-1}$.[204]

The compounds $[(C_2H_5)_2NH_2]_2[PS_3F]F$ and $[(C_2H_5)_2NH_2]_2[PS_2SeF]F$ have been prepared from the reaction of diethyl ammonium trithiophosphite with fluoride ions and sulphur and selenium respectively. A structure determination of the selenium compound showed it not to be a phosphoranate with a $[PS_2SeF_2]^{3-}$ anion but to be a double salt of $[PS_2SeF]^{2-}$ with $F^-$.[205]

The molecular structures of $Se_2O_2F_8$ and $Te_2O_2F_8$ have been determined in the gas phase by electron diffraction. The skeleton of both molecules is a planar four-membered ring (42) with Se-O 1.779Å, < Se-O-Se 97.5°, Te-O 1.918Å and < Te-O-Te 99.5°. The



(42)

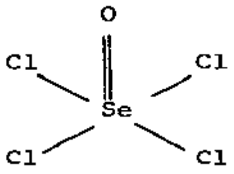
configuration around the chalcogen atoms deviates considerably from octahedral in that the equatorial bonds are approximately 0.03 to 0.04Å shorter than the axial bonds.[206] The thermal decomposition of $Se_2O_2F_8$ and $Te_2O_2F_8$ has been studied by mass spectrometry. $Se_2O_2F_8$ begins to decompose at approximately 250°C with the principal products being $SeF_4$ and $O_2$; $SeOF_2$ is a minor product. Decomposition was found to be complete at about 500°C and some decomposition to monomeric $SeOF_4$ was observed between 200 and 350°C. $Te_2O_2F_8$ did not begin to decompose until 400°C, and the final products were $TeF_4$, $O_2$ and $TeOF_2$ but no evidence for $TeOF_4$ was found.[207]

Triphenyl selenonium chloride hydrate ($Ph_3SeCl.H_2O$) has been prepared and its structure determined. The structure consists of triphenyl selenonium cations, $Cl^-$ and water molecules linked by a secondary bonding scheme involving shorter than van der Waals Se···Cl (3.530Å) and S···O (3.147Å) distances. The salt is monomeric (Se···Se 7.414Å) with five coordinate selenium and has a packing arrangement which differs from that of the six coordinate dimeric dihydrate $Ph_3SeCl.2H_2O$. Attempts to obtain the anhydrous salt by slow evaporation were unsuccessful.[208]

The Raman spectra of four chloroselenate anions, $SeOCl_3^-$, $SeCl_6^{2-}$, and $SeO_2Cl^-$ have been reported, the latter two for the first time. The spectra are consistent with a pyramidal $SeO_2Cl^-$ ion ($C_s$), a trigonal-bipyramidal $SeOCl_3^-$ ion with two axial Cl atoms ($C_s$), a square pyramidal $SeCl_5^-$ ion ($C_{4v}$) and an octahedral $SeCl_6^{2-}$ ion. Evidence for chloride bridging was found for some compounds containing the $SeOCl_3^-$ and $SeCl_5^-$ ions.[209] The preparation of several compounds containing the oxotetrachloroselenate(IV) ion, $SeOCl_4^{2-}$, have been described. Raman spectra of MeCN solutions with $Et_4NCl:SeOCl_2$ mole ratios from 1:1 to 4.7:1 indicate that an equilibrium is present of the form shown in (25). The spectrum

$$SeOCl_3^- + Cl^- \rightleftharpoons SeOCl_4^{2-} \qquad \ldots(25)$$

of the 1:1 solution is that of $SeOCl_3^-$ but as the chloride content is increased while $SeOCl_2$ concentration is held constant this spectrum decreases and that of the new species increases, becoming 100% at a mole ratio of 4.7:1. The Raman spectrum is consistent with the new species having a square pyramidal structure (<u>43</u>) with the oxygen axial and <u>trans</u> to the lone electron pair.[210]



(<u>43</u>)

The crystal structure of the oxide chloride $Cu_5Se_2O_8Cl_2$ has been determined.[211]

A study of the Se-Br system has shown it to contain two phases with congruent melting points, α-SeBr (+5°C) and α-$SeBr_4$ (+123°C). Both compounds also form β-phase modifications which are metastable and are irreversibly transformed to the α-form by annealing. A single crystal structure determination showed that both α- and βforms of $SeBr_4$ contained tetrameric cubane-like molecular units $[SeBr_4]_4$ with Se-Br bridge distances of 2.97 and 2.99Å and Se-Br terminal distances of 2.37 and 2.35Å in the α-phase modification.[212]

Hexabromoselenium(IV) acid, $H_2SeBr_6.8H_2O$ has been prepared from solution of $SeBr_4$ in concentrated aqueous HBr. A low temperature crystal structure determination shows the acid to contain regular octahedral $SeBr_6^{2-}$ ions with Se-Br distances between 2.553 and 2.579Å and $H_5O_2^+$ hydronium ions with an O···O distance of 2.55Å. The remaining water molecules are involved in a hydrogen bonding system with O···O distances between 2.64 and 2.75Å and O···Br distances of 3.42 and 3.51Å. On the basis of the structural information the compound should ideally be formulated as $(H_5O_2)_2SeBr_6.4H_2O$.[213]

### 6.3.2 Bonds to Oxygen

A structure determination has shown oxonium hydrogen selenate to contain $HSeO_4^-$ ions, hydrogen bonded to each other to form chains with OH···O lengths of 2.715Å, and $H_3O^+$ ions hydrogen bonded to $HSeO_4^-$ ions with $OH_3^+$···O distances of 2.571, 2.577 and 2.632Å. The Se-O distances ranged from 1.610 to 1.625Å and the Se-OH distance was 1.710Å.[214] The crystal structure of the piezoelectric compound $LiHSeO_3$ consists of $HSeO_3^-$ ions forming spiral chains of $SeO_3$ groups interlinked with hydrogen bonds. The $HSeO_3^-$ ion has a pyramidal configuration with two short Se-O bonds of lengths 1.654 and 1.664Å and one long Se-OH bond of length 1.792Å.[215]

The thermal decomposition and structure of double selenites of scandium and the alkali metals, $MSc(SeO_3)_2.nH_2O$, have been studied. All the compounds decompose in stages: dehydration takes place between 120 and 240°C, followed by removal of the excess of $HSeO_3$ groups and in the range 600 to 700°C the diselenites $MSc(SeO_3)_2$ are converted to the final products $Se_2O_3$ and the alkali metal selenites and selenates.[216] The rare earth selenates $Ln_2(SeO_4)_3.8H_2O$ (Ln = Y, Tb to Lu) have been prepared and were found to be isostructural. Thermal decomposition studies at temperatures up to 1,000°C showed the sequence of reactions in equation (26).[217] Isopotential points in the electrosorption of

$$Ln_2(SeO_4)_3.8H_2O \longrightarrow Ln_2(SeO_4)_3 \longrightarrow Ln_2(SeO_3)_3 \longrightarrow$$

$$Ln_2(SeO_3)_2 + Ln_2O_2(SeO_3) \longrightarrow Ln_2O_3 \qquad ...(26)$$

selenite, selenate, selenide and tellurite at the platinum rotating disc electrode have been measured.[218]

### 6.3.3 Selenides

The preparation and structure of the new isotypic compounds $SrIn_2Se_4$ and $BaIn_2Se_4$ has been described. Both compounds crystallize in the orthorhombic space group Fddd and are built up from $InSe_4$ tetrahedra connected by common corners and edges to form layers with the alkaline earth ions between them.[219] The equilibrium diagrams of the $In_2Se_3$-NiSe and $In_2Se_3$-CoSe systems have been studied and the presence of extensive liquid immiscibility regions observed.[220] $^{21}P$ and $^{77}S$ n.m.r. spectra have been measured for a range of phosphorus(V) selenides, diphosphorus(V) diselenides and triphosphorus(V) triselenides in the inert solvent $CH_2Cl_2$ and in liquid $SO_2$; a 1:1 donor:acceptor complex was observed for both the mono- and diselenides with $SO_2$.[221]

The reaction of some arsanes of the type $Me_2As-(CH_2)_n-AsMe_2$ with sulphur and selenium has been shown to result in the formation of the sulphides and selenides, respectively, $Me_2As(X)-(CH_2)_n-AsMe_2$ or $Me_2As(X)-(CH_2)_n-As(X)Me_2$ (X = S, Se). Chelate complexes with the salts $CoX_2.6H_2O$ ($X = Cl^-, Br^-, I^-, NO_3^-$) were also prepared and their spectra discussed.[222]

The new compounds $NaAsSe_2$, $NaSbSe_2$, $NaSbTe_2$ and $NaBiTe_2$ have been prepared and their structures determined.[223] Polythermal sections of the As-Se-Zn system have been studied and the regions of existence of solid solutions based on α- and β-$Zn_3As_2$ have been found.[224] X-ray powder diffraction studies have shown that $RbSb_3Se_5$ crystallizes in the orthorhombic space group Pnma and unit cell parameters were determined.[225] The $Bi_2Se_3$-MnSe system has been studied and the incongruently melting compounds $Mn_3Bi_2Se_6$ and $MnBi_2Se_4$ were observed.[226] A determination of the crystal structure of $BaSb_2Se_4$ has shown that half of the Sb atoms form ψ-tetrahedra with three Se atoms, the other half forming ψ-trigonal bipyramids with four Se atoms. These polyhedra are connected by corners and edges to form twisted chains which are ordered into sheets with the Ba ions between them.[227] The structure of the synthetic ion selenide 3C-$Fe_7Se_8$ has been shown to be isomorphous with the corresponding sulphide with an average Fe-Se bond length of 2.57Å.[228] The non-stoichiometric selenides $In_{3.3}Mo_{15}Se_{19}$ and $In_{2.9}Mo_{15}Se_{19}$ have been shown to contain the units $Mo_6Se_8$ and $Mo_9Se_{11}$; the former has already been observed in chalcogenides of the type $MMo_6X_8$ (X = S, Se, Te) but $Mo_9Se_{11}$ represents a new structural element, and may be regarded as being formed by the fusion of two $Mo_6Se_8$ units.[229]

The integral enthalpies of mixing of the liquid mixtures, AgCl + $Ag_2Se$, AgI + $Ag_2Se$, AgCl + $Ag_2Te$, AgBr + $Ag_2Te$ and AgI + $Ag_2Te$ have been determined. The systems exhibit endothermic effects which were attributed to a misfit energy resulting from the substitution of ions of different size in the polymeric network of these melts.[230] The Pd-Se system has been studied and it was shown that as well as the well known phases, $PdSe_2$, PdSe, $Pd_{17}Se_{15}$, and $Pd_4Se$ there also exists the new phases $Pd_7Se_4$, $Pd_3Se$, $Pd_{3.5}Se$ and $Pd_{4.5}Se$.[231] Members of the system $PdSe_2$ and $RhSe_2$ and their high pressure phase transformations studied.[232] The new compounds $Sm_2PbSe_4$ and $Sm_2Pb_4Se_7$ have been observed in a study of the $PbSe-Sm_2Se_3$ system.[233]

### 6.3.4 Other Compounds Containing Selenium

A new synthesis of carbonyl selenium, SeCO, has been described. The compound is obtained almost quantitatively from the selenocarbamate (**44**), and sulphuric acid.[234] The first reactions of

$$2Et_2NH \;+\; CO \;+\; Se \longrightarrow \left[Et_2NH_2\right]^+ \underset{(\mathbf{44})}{\left[Et_2N\text{-}C(O)\text{-}Se\right]^-} \xrightarrow{H^+}$$

$$SeCO \;+\; 2Et_2NH_2^{\;+} \qquad \ldots(27)$$

SeCO with organic compounds, i.e. amines and aminoalcohols, have been performed. SeCO proved to be an effective carbonylation reagent as shown in (28).[235]

$$SeCO \;+\; 2RR'NH \xrightarrow{O_2} (RR'N)_2CO \;+\; Se \;+\; H_2O \qquad \ldots(28)$$

A determination of the structure of tris(selenourea)sulphate selenourea solvate dihydrate, $(su)_3SO_4su.2H_2O$, has shown the tris(selenourea) ion to possess an approximately linear three selenium system with an Se-Se-Se bond angle of 168.29° and Se-Se bond lengths of 2.6336 and 2.6639Å. The atoms in each selenourea group of the ion are coplanar.[236] The crystal structures of selenium dithiocyanate and selenium diselenocyanate have been determined. The dimensions of the selenium dithiocyanate molecule are Se-S 2.2136, S-C 1.695Å, < S-Se-S 101.59, < Se-S-C 99.12, < S-C-N = 178.2° and the dihedral angle S-Se-S/Se-S-C = 94.8°. The selenium diselenocyanate molecule has the bond distances Se-Se 2.3343, Se-C 1.852Å, and bond angles Se-Se-Se 102.97, Se-Se-C 97.1, Se-C-N 176.9° and the dihedral angle Se-Se-Se/Se-Se-C 93.2°.[237] The compound $Re_2Br_2(CO)_6(Se_2Ph_2)$ has been shown to be a binuclear complex containing a diphenyl diselenide bridge.[238] Alkyl selenoxides and selenones have been shown to be completely ionized as bases in chlorosulphuric acid whereas the phenyl compounds and their nitro-derivatives were only weakly basic.[239]

## 6.4 TELLURIUM

### 6.4.1 Bonds to Halogens

The Raman and i.r. spectra of $Na^+$, $K^+$, $Rb^+$, $Co^+$, $NH^+$, $C_5H_5NH^+$ and $n\text{-}Bu_4N^+$ salts of the $TeF_5^-$ ion have been reported, together with the $^{19}F$ n.m.r. spectra of the $n\text{-}Bu_4N^+$ salt. The i.r. spectra were all assigned on the basis of $C_s$ symmetry and no n.m.r. evidence was found for $TeF_6^-$.[240] The telluride ion has been shown to form soluble, polynuclear cationic complexes with Hg(II) in sulphuric acid media. The compounds $Hg_5TeCl_8$ and $Hg_4Te(SO_4)_3$ were prepared and characterized.[241] A further noble gas compound with the ligand $OTeF_5$ group has been reported following the reaction in equation (29). The Compound is light sensitive and is decomposed

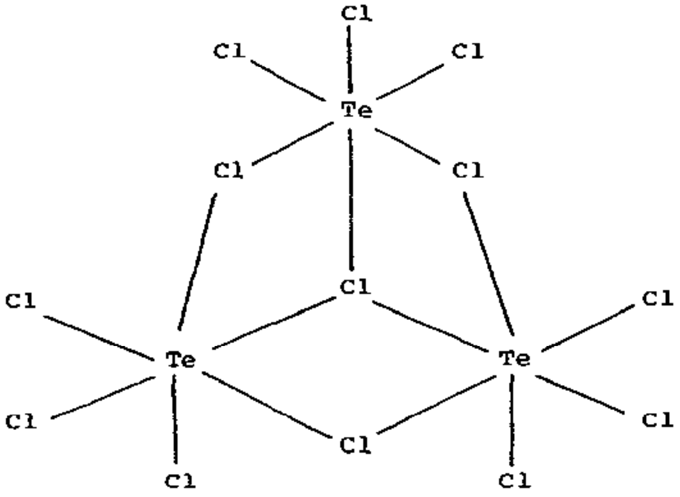
$$XeF_6 + 2B(OTeF_5)_3 \xrightarrow[n\text{-}C_5F_{12}]{-40^\circ C} 2BF_3 + Xe(OTeF_5)_6 \qquad \ldots(29)$$

(equation 30) either thermally at -10°C or by exposure to daylight

$$Xe(OTeF_5)_6 \longrightarrow Xe(OTeF_5)_4 + F_5TeOOTeF_5 \qquad \ldots(30)$$

at temperatures as low as -230°C. The red violet colour of the compound was attributed to the bonding state of hexavalent Xe, which possesses a non-bonding electron pair since $Te(OTeF_5)_6$ which has no such pair is colourless. Attempts to prepare an analogous krypton compound were unsuccessful.[242]

The trimeric chlorotellurate(IV) ion $Te_3Cl_{13}^-$ may be obtained in benzene solution as a degradation product of the cubane-like tetrameric chloride $Te_4Cl_{16}$ but may be isolated by crystallization in the form of salts with large cations. A structure determination shows the $Te_3Cl_{13}^-$ ion to have approximate $C_{3v}$ symmetry (45), consisting of three edge sharing octahedra with a central triply bridging dichlorine atom. Bond distances found were Te-Cl (triply bridging) 2.924 to 2.984, Te-Cl (double bridging) 2.706 to 2.863,

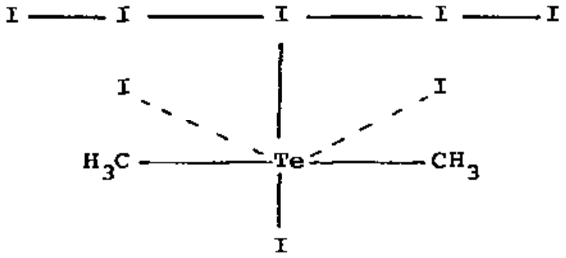


(45)

and Te-Cl (terminal) 2.320 to 2.388Å.[243]

A determination of the room temperature crystal structure of $[Me_4N]_2[TeBr_6]$ has shown it to crystallize in the cubic space group Fd3c; this clearly deviates from previous results on the analogous tetramethylammonium hexahalometallates which were reported to crystallize in the antifluorite space group Fm3m with the $K_2PtCl_6$ structure type.[244]

The structure of $(C_5H_6N)_6TeCl_6$ contains $TeCl_6^{2-}$ ions in the form of layers which alternate with double layers of $C_5H_6N^+$ ions.[245] From a crystal structure determination, $Me_2TeI_4$ is an adduct of $Me_2TeI_2$ with $I_2$, linked by intermolecular I-I bonds and weak Te-I bonds (46), and does not contain Te(VI).[246]

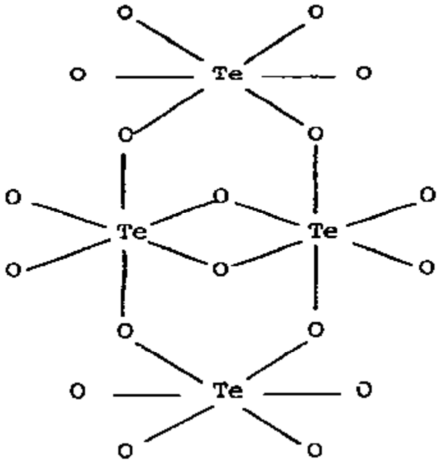


(46)

## 6.4.2 Bonds to Oxygen

The structure of an adduct of orthotelluric acid and urea has been shown to consist of infinite $Te(OH)_6.2CO(NH_2)_2$ layers connected through hydrogen bonds. Extensive hydrogen bonding also exists within the layers.[247] $Na_2TeO_3.5H_2O$ contains pyramidal $TeO_3^{2-}$ ions with Te-O distances in the range 1.850 to 1.862Å and O-Te-O angles close to 99.5°. The structure is built up from chains of $Na(H_2O)_6$ octahedra joined by sodium atoms in square planar coordination as $NaO_2(H_2O)_2$ units.[248] A crystallochemical study of the tellurates(IV) of the divalent elements Ca, Ba, Zn, and Cd, shows four types of compound $MTeO_3$, $M_2Te_3O_8$, $MTe_2O_5$ and $MTe_4O_9$. In inert atmospheres the compounds are only decomposed on melting (572 to 989°C) but in an oxygen atmosphere oxidation takes place at about 550°C to give tellurates(VI) such as $CaTeO_4$ and $BaTeO_4$ or mixed valence tellurates such as $CdTe_2O_4$.[249] $BaTeO_3$ has been shown to exist in two phase modifications and single crystals of both forms can be obtained from the reaction of $BaCO_3$ with $TeO_2$. Both structures contain isolated, pyramidal $TeO_3$ groups.[250] A systematic study of the ternary system $NH_3$-$TeO_3$-$H_2O$ has led to the formation of several new compounds. Of these, $(NH_4)_2Te_3O_8(OH)_4$ contains $[Te_3O_8(OH)_4]_n$ octahedral chains linked together through hydrogen bonds (47). The chains form cavities in which are found the $NH_4^+$ ions.[251]

The structures of the isostructural compounds $CaTeO_4$ and $SrTeO_4$ have been determined from X-ray powder data; both were found to contain strings of Te-O octahedra similar to those found in $Na_2TeO_4$.[252] The compound $BaTe_2O_6$ has been prepared from BaO-$TeO_2$ melts in the presence of air at 973K and its structure determined.



(47)

Octahedral $Te(VI)O_6$ (Te–O distances 1.902 and 1.224Å) and pyramidal $Te(IV)O_5$ groups (Te–O distances 1.830 and 2.126Å) are connected by common corners to form $Te_2O_6$ layers.[253] Compounds of the composition $Ba_6B(III)_2 \square Te(VI)_3O_8 \mathrel{\hat{=}} Ba_2B(III)_{2/3} \square_{1/3} Te(VI)O_6$ with B(III) = Pr, Nd, Sm – Lu or Y crystallize with a perovskite lattice, and the cell parameters decrease as the size of B(III) falls (B(III) = Pr a = 8.52Å, Lu a = 8.33Å). In contrast to the corresponding perovskites with U(VI) and W(VI), no polymorphism was observed.[254] A study of the ternary systems $MO - ThO_2 - TeO_2$ and $MO - UO_3 - TeO_2$ (M = Ba, Ca) has identified double tellurates(IV) of actinides and alkaline earths with the compositions $M_5Th(TeO_3)_7$, $M_2U(TeO_3)_5$ and $M_3(UO_2)(TeO_3)_4$. The phase diagram of the system $Th(TeO_3)_2 - BaTeO_3$ was also determined.[255] The compound $Rh_2TeO_6$ has been prepared by the solid state reaction of $Rh_2O_3$ and $TeO_2$ in air. The compound has the trirutile structure and shows five i.r. adsorption bands in the range 980 to 380 $cm^{-1}$.[256]

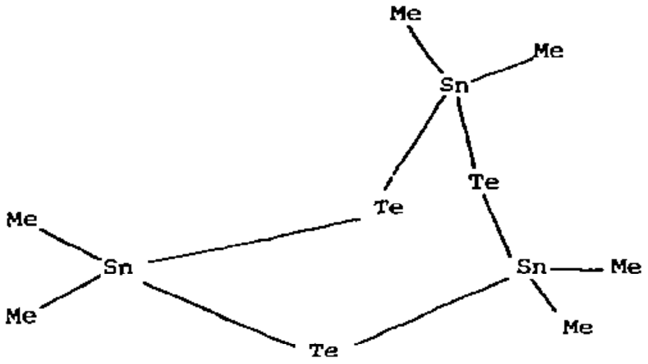
The $TeO_2(OH)_4^{2-}$ ions in the ammonium salt are monomeric and are interconnected by hydrogen bonds and the $NH_4^+$ ion. The coordination of the Te(VI) atom is octahedral with Te–OH and Te–O distances of 1.958 and 1.879Å respectively.[257] The structure of the mixed oxotellurate, $NH_4(Te(IV)Te(VI)O_5(OH))$, is built up from sheets of $Te(VI)O_6$ octahedral chains and $Te(IV)O_5$ pyramids linked together through $NH_4^+$ cations. In the latter, the Te(IV) atom forms one short axial bond at 1.920 and four long equatorial bonds at 2.090Å.[258] The crystal structures of two phosphotellurates, $Te(OH)_6 \cdot 2(NH_4)_2HPO_4$ and $Te(OH)_6 \cdot Na_2HPO_4 \cdot H_2O$ have been determined. The main features of these structures is the coexistence of two different types of anions ($(Te(OH)_6$ and $PO_4$) in the unit cell.[259]

### 6.4.3 Tellurides

The new compounds $CaAl_6Te_{10}$ and $CaGa_6Te_{10}$ have been prepared and their crystal structures determined. Both compounds show very similar dense packing of the Te atoms but differ in the distributions of the $M^{3+}$ element in the distorted tetrahedral sites and the calcium atoms in the distorted octahedral sites.[260] The first hypotelluroaluminosilicate, $Na_3(AlSi)Te_4$ has been prepared. Its structure may be described as a variant of the $\alpha$-$NaFeO_2$ type with one half of the octahedral sites occupied by Na ions and the other half occupied by a random distribution of Na ions and Al-Si dumbbells in a 1:1 ratio.[261] A recent measurement of the heat capacity of $Ge_{0.5}Te_{0.5}$ in both the solid and liquid states shows that the excess heat capacity is positive in the liquid state, decreases with increasing temperature and vanishes at about 450K above the melting point. This behaviour agrees well with the previous postulation of heteroassociations in Ge-Te liquid alloys based on measurements of the enthalpy of formation.[262] An X-ray diffraction study of germanium telluride has shown that the thermal disordering of the crystal structure is due to Frenkel defects, the concentration of which depends on temperature and degree of departure from the stoichiometric composition.[263]

$K_6(Ge_2Te_6)$ and $K_6(Sn_2Te_6)$, the first members of the families of tellurodigermanate and telluro-distannates, have been prepared and their structures determined. Both contain $X_2Te_6$ groups (X = Ge, Sn) in a staggered conformation, connected by potassium atoms in distorted octahedral or trigonal prismatic environments. The average Ge-Te distance was found to be 2.579Å and Sn-Te 2.724Å.[267] The compound $(Me_2SnTe)_3$ has been synthesized by a new route and is the first Sn(IV)-Te compound to have been subjected to an X-ray structure determination. The compound contains a cyclic skeleton (<u>48</u>) made up of alternating Sn and Te atoms with an Sn-Te bond length of 2.75Å.[265]

From X-ray crystallography $AmTe_{1.73}$ has the anti-$Fe_2As$ type structure, made up of layers of Te atoms interleaved with puckered



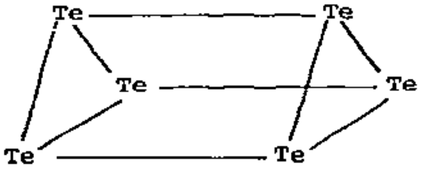
(48)

double layers of composition AmTe. The deviations from the stoichiometry $AmTe_2$ result from random vacancies in the pure tellurium layers. The Am-Te bond distance of 3.21 to 3.27Å suggests a bond intermediate between ionic and covalent.[266]

Glass formation has been investigated in the Ga-Te-S system[267] and the following phase systems have also been studied; Na - Sb - Te,[268] $Bi_2Te_3$ - $Ce_2Te_3$,[269] HgTe - $Sb_2Te_3$,[270] $Bi_2Te_3$ - HgTe,[270] and EuTe - $M_2Te_3$ and YTe - $Me_2Te_3$ where M = Sb or Bi.[271]

### 6.4.4 Other Compounds Containing Tellurium

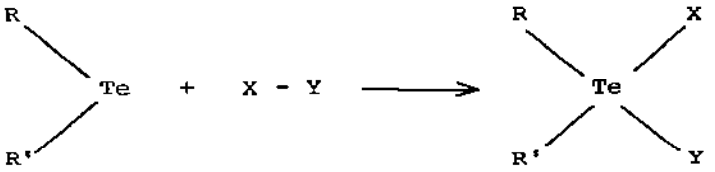
The reaction of elemental tellurium with $AsF_5$ in $AsF_3$ or $SO_2$ as solvent yields the compounds $Te_6(AsF_6)_4.2AsF_3$ and $Te_6(AsF_6)_4.2SO_2$ respectively. Both compounds contain the novel trigonal prismatic $Te_6^{4+}$ species (49) and consist of $Te_6^{4+}$ and $AsF_6^-$ ions and either $AsF_3$ or $SO_2$. The cation in the $SO_2$ adduct is quite regular but is slightly distorted in the $AsF_3$ adduct. The Te-Te bond distances in the



(49)

triangular faces range from 2.662 to 2.694Å whilst those between the faces are considerably longer, ranging from 3.062 to 3.145Å. From measurements of electronic spectra the species previously identified in highly acidic media as $Te_n^{n+}$ is actually the $Te_6^{4+}$ cation.[272]

The trimethyl telluronium cation in $Me_3TeBPh_4$ is pyramidal and disordered across a mirror plane such that two half-occupancy tellurium atoms, separated by 1.321Å share two methyl carbon atoms of full occupancy and have each a methyl carbon at half-occupancy. The mean Te-C distance is 2.14Å and the mean C-Te-C angle 92°. Secondary bonding interactions are absent, resulting in this being the first structural example of three-fold coordination of tellurium(IV).[273] A structure determination has shown that the tellurium atom in $Te(HOCH_2CH_2(CH_3)NCS_2)_4$ is dodecahedrally coordinated to the eight sulphur atoms of the four ligands with Te-S bond lengths of 2.714 and 2.758Å to each ligand.[274] It has been reported that diaryltellurium(II) can readily insert between N-halogen bonds as shown in (31).



...(31)

X - Y = N-bromobenzamide, N-bromophthalimide, N-bromosuccinimide, N-chlorophthalimide and N-chlorobenzotriazole. These reactions provide rare examples of organotellurium amides and also represent the first examples of mixed halo amides containing Te-C bonds.[275]

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