Coordination Chemistry Reviews, 30 (1979) 305—350

Chapter 6

THE ELEMENTS OF GROUP 6

M.G.Barker

6.1 OXYGEN

Rate constants for the reactions of oxygen atoms, $O(^3P)$, with HBr and HI have been reported.[1] Oxygen atoms were generated by modulated mercury photosensitized decomposition of nitrous oxide, and were monitored by the chemiluminescence from the reaction with nitric oxide. The results of bond energy-bond order calculations incorporating recently proposed modifications were discussed.

The treatment of charcoals, carbon blacks and activated carbon with dry oxygen containing about 3% ozone at ambient temperature has been shown to cause gasification of the carbon and chemisorption of oxygen leading to CO- and CO_2-surface complexes.[2] A part of the chemisorbed oxygen also comes off as water vapour, and any CO-surface complex is partly converted to a CO_2-surface complex on exposure to ozonised oxygen.

An analytical method for the determination of peroxide in a large excess of nitrite has been developed which enables values for the equilibrium constant in molten nitrate to be obtained.[3] The values obtained in this study suggest the formation of peroxynitrate anions. Information was also presented on the reaction of these solutions with air, when peroxide acts as a catalyst for a slow oxidation of nitrite to nitrate, with glass when a silicate is slowly formed, and with zirconium when no reaction was observed below 400°C. A soluble peroxynitrite species was also thought to be formed in the oxidation of platinum to platinum(IV) oxide in molten nitrite melts. The acid-base behaviour of oxide ions in chloroaluminate melts has been reinvestigated as part of a study of the electrochemistry of Ni(II) in these melts.[4] Precise titrations of the basic strength of the oxide ions were performed in narrow pCl ranges.

The chemistry of the superoxide ion has received considerable attention in recent years and much of the current interest centres around its production and reactivity in biological systems. The reactions of superoxide with a representative series of alkyl halides and tosylates in Me_2SO and benzene has been shown to proceed by a pathway involving an initial S_N2 displacement leading to alkyl peroxy radicals which , in a subsequent one-electron reduction, are converted to peroxy anions.[5] It was shown that processes involving the self-reaction of peroxy radicals play, at most, a very minor role in product determination. In most instances, the initially isolatable principal product is the dialkyl peroxide which, in a subsequent, base-induced reaction, is converted into alkoxide. It has been shown that the superoxide ion $O_2^{\overline{\cdot}}$ $(HO_2^{\cdot})$ is formed during the near-u.v. photooxidation of tryptophan and that the species has at least two fates, one of which is the formation of H_2O_2.[6] An investigation[7] of the chemical reactivity of the superoxide ion in some aprotic solvents has confirmed the non-oxidative nature of $O_2^{\overline{\cdot}}$. For example it was shown that it is thermodynamically unfavorable for $O_2^{\overline{\cdot}}$ to oxidise 3,5-di-tert-butylcatechol or its anion in acetonitrile by direct one electron transfer. The apparently efficient production of singlet oxygen in the reaction of $O_2^{\overline{\cdot}}$ with the oxidising agents benzoyl peroxide and lauroyl peroxide has been reported.[8] A series of observations suggests that a significant fraction of the oxygen generated in these reactions is in the excited singlet state, presumably $^1\Delta_g$. Substantial yields of the superoxide ion have been obtained when tetralkylammonium hydroxide was added to hydrogen peroxide in pyridine.[9] The ion was identified by the e.s.r. spectrum at 77K and by cyclic voltammetry.

The crystal structure of the compound $4Na_2SO_4.2H_2O_2.NaCl$ has been determined and shows several unusual features.[10] Firstly one of the nine Na^+ ions in the molecule has a coordination number of eight (a tetragonal prismatic array of oxygen atoms); secondly, tunnels in the structure running parallel to the c axis contain H_2O_2 in an apparently disordered state; and thirdly that some ordering of the H_2O_2 molecules occurs parallel to the a and b axes.

Structural data on the recently formed species $H_5O_2^+$ $SbCl_6^-$ show the presence of isolated $H_5O_2^+$ ions.[11] For the first time this species has been obtained free from association either with other weaker molecules, or with strong hydrogen bonds to other species. The measured O-O bond distance of 2.52Å is similar to that found for other room temperature hydrogen bond distances in $H_5O_2^+$ species. The environment of the $H_5O_2^+$ ion in this compound is symmetrical in all directions and the angles of the O-O-Cl contacts would indicate weak hydrogen bonds between $H_5O_2^+$ and $SbCl_6^-$.

The matrix i.r. spectrum of the O_2Br radical as obtained by the simultaneous condensation of bromine and O_2 in argon matrices on to a 10K i.r. transmitting window has been reported.[12] The frequency observed for ν_1 of O_2Br (1487 cm^{-1}) was found to lie between that observed for O_2F (1494 cm^{-1}) and O_2Cl (1441 cm^{-1}). This apparent anomaly was rationalized on the basis of a weaker O-F bond giving a higher than expected ν_1 frequency. The reaction of O_2F_2 with polymeric VF_5 in the temperature range -119 to -78°C has been shown[13] to lead first to the reaction intermediates : $F\text{-}O\cdots O\underline{\cdots}F\cdots V_2F_{10}$ or $O_2F^+ + F^- + V_2F_{10}$. On increasing the temperature a new compound $O_2{}^+V_2F_{11}{}^-$ was formed which, in turn, decomposed rapidly at room temperature. Raman studies of these species as well as of O_2F_2 in the solid were also reported.

6.2 SULPHUR

6.2.1 The Element

A low temperature (-90°C) X-ray structural analysis of S_6 has yielded improved data for the bond distances (206.8pm), bond angles (102.6°) and torsion angles (73.8°) of the D_{3d} molecule.[14] These values are in agreement with those predicted by current theories on homonuclear sulphur bonds.

Cycloheptasulphur, S_7, has been isolated in pure form from quenched sulphur melts by fractional extraction and crystallization, exploiting the tendency of S_7 to form supersaturated solutions in CS_2.[15] Precipitation was achieved by inoculation with S_7 or addition of finely ground glass. The S_7 thus obtained showed no contamination by S_8 or S_6 in the Raman spectrum and was identical with that obtained as a condensation product from $(Et)_2TiS_5$ and S_2Cl_2. The yield was about 10% of the S_7 present in equilibrium in liquid sulphur at 159°C and most of the unconverted sulphur could be processed again for the synthesis of further S_7. Raman and i.r. spectra of four allotropes of cycloheptasulphur have been reported.[16] All 15 fundamental vibrations of the S_7 molecule were observed and assigned in accordance with the molecular point group C_s. Entropy, heat capacity, and other functions of gaseous S_7 were calculated by statistical methods and evidence for pseudorotation of S_7 in the vapour state presented. The molecular structure as well as the valence force constants of S_7 were rationalized by a qualitative molecular orbital treatment.

The thermal decomposition of S_6O_2 and S_7O in CH_2Cl_2 or CS_2 solution at temperatures between 20 and 5°C has been shown to yield SO_2, polymeric sulphur and S_{10}.[17] The latter was obtained as pure single crystals in yields of 7 to 11%.with regard to the starting materials S_6 and S_7 respectively. I.r. and Raman spectra of S_{10} as well as of the new molecular addition compound $S_6.S_{10}$ were also reported. An X-ray structural study on cyclo-decasulphur, S_{10}, as prepared by the above method has shown[18] that the four S_{10} molecules in the unit cell occupy C_2 symmetry positions, but to a good approximation have the very rare point group symmetry D_2. Six atoms of the ring lie in a plane and two atoms are situated above and two below the plane (Figure 1). This conformation, which has not hitherto been observed in sulphur chemistry does not correspond to the previously predicted D_{5d} symmetry. The arithmetical mean bond lengths (205.6 pm) and valence angles (106.2°) closely correspond to the values observed in S_{12}. The lower thermal stability of S_{10} compared to that of S_8 and S_{12} was attributed to the four large torsion angles of about 123° which exceed the previously observed values in sulphur rings by more than 20°.

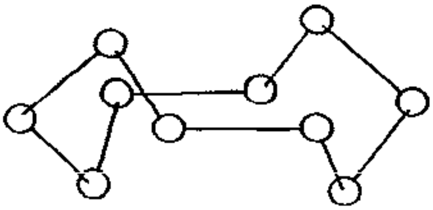


Figure 1. Molecular structure of S_{10}.

A discrepancy has been observed between the powder X-ray diffraction patterns previously reported for β-S and those recorded from samples of sulphur held at temperatures between 100 and 115°C.[19] The latter data agrees well with that calculated using single crystal data for β-sulphur.

A molecular orbital study has been used to provide explanations, in terms of the one-electron orbital energies and wave functions, for the structural changes observed on oxidation and/or reduction of S_3, S_4, S_6, and S_8.[20] For S_3 a Walsh diagram was generated which predicts successively larger bond angles in the series S_3^{2-}, S_3^- and S_3. The geometry changes upon successive double reductions of square planar S_4^{2+} to planar (C_{2v}) S_4 and finally to helical S_4^{2-} were successfully explained.

Four different cationic species have been produced[21] by the anodic oxidation of sulphur in a NaCl-$AlCl_3$ (37:63 mol.%) melt at 150°C. Good evidence was found for the existence of both S(IV) and S(II) cations. The most likely oxidation states for the two other species were thought to be +1 and +½. The spectra of S(IV) and S(II) as well the spectra of the possible S_2^{2+} and S_4^{2+} species were calculated from the measured spectra. The oxidation of elemental sulphur on heating in vacuum in silica tubes has been studied.[22] The observed changes in oxidation state were thought to be due to reaction of the sulphur with adsorbed gases and water vapour on the silica surface. This reaction may be suppressed by the chemical etching of the silica tubes followed by prolonged heating at temperatures above 600°C in vacuum.

The first derivative of cyclo-hexasulphur has been prepared.[23] Oxidation of S_6 by trifluoroperacetic acid at -10 to -20°C in dichloromethane has been shown to give two different products of the same composition of S_6O, as shown in equation (1). α-S_6O is formed when S_6

$$S_6 + CF_3CO_3H \longrightarrow S_6O + CF_3CO_2H \qquad (1)$$

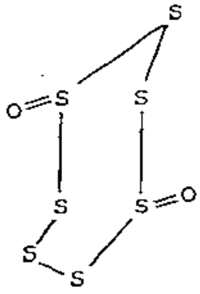
reacts with the peroxy acid at -20°C within 2 hours in the molar ratio 1:1.2 and the oxidation product is precipitated after a further 5 hours by the addition of pentane and cooling. Raman spectra showed that α-S_6O contained small amounts of S_6 in solid solution which could not be removed by repeated recrystallisations. Attempts to achieve complete oxidation of S_6 by working at a higher temperature (-10°C) and with an excess of peroxy acid led to isolation of β-S_6O which also contained traces of S_6. Raman spectra of α- and β-S_6O showed characteristic differences in wave numbers and intensities but it was thought that the two forms do not differ in molecular structure. The proposed structure for S_6O was analogous to that of S_8O with a chair-shaped S_6 ring and an exocyclic oxygen atom. Oxidation of S_8 with excess trifluoroperacetic acid gives rise[24] to the compound S_7O_2 rather than the expected S_8O_2 according to equation (2). The formation

$$S_8 + 4CF_3CO_3H \longrightarrow S_7O_2 + SO_2 + 4CF_3CO_2H \qquad (2)$$

of S_7O_2 from S_8 was thought to proceed *via* the following steps:

$$S_8 \xrightarrow{+O} S_8O \xrightarrow{+O} [S_8O_2] \xrightarrow{+O} [S_8O_3] \xrightarrow{-SO_2} S_7O \xrightarrow{+O} S_7O_2$$

The reaction product sometimes contained traces of S_7O but there was no evidence for the formation of a higher oxide of S_8. The Raman spectrum of S_7O_2 shows the typical lines of an S_7 ring as well as the SO stretching and SSO deformation vibrations characteristic of -S-SO-S- groups. The structure (1) was postulated as the basis of a comparison of the spectra of S_7O_2, S_7 and S_7O.



(1)

Raman spectral studies of elemental sulphur in Al_2Cl_6 and chloroaluminate melts have given some insight into the nature of the dissolved sulphur in these melts.[25] The Raman results show that the predominant form of sulphur in chloroaluminate melts is S_8 and that the solubility of sulphur in $AlCl_3$-containing media increases with temperature and the Lewis acidity of the solvent.

6.2.2 Bonds to Halogens

A study of SF_6 by vapour-phase electron diffraction has shown that in the gas-phase sulphur hexafluoride is a regular octahedron with an S-F bond length (r_g) of 1.561Å and mean amplitudes of vibration of 0.044Å for S-F, 0.056Å for F-F(trans) and 0.061Å for F-F(cis).[26] The influence of pressure, temperature and buffer gases on the rate and selectivity of the dissociation of SF_6 in the field of a CO_2 pulse laser has been investigated.[27] A simple three-level model for describing the macrokinetics of the dissociation was proposed and the photosensitised dissociation of SeF_6 was achieved for the first time using a pulsed CO_2

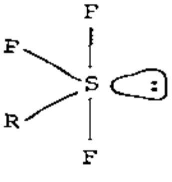
laser. The reaction of SF_6 with SO_2 under the action of quasicontinuous radiation from a CO_2 laser has been studied.[28] The reaction proceeds according to the overall equation (3). A proposed mechanism

$$SF_6 + 2SO_2 \longrightarrow SO_2F_2 + 2SOF_2 \qquad (3)$$

shows that the reaction is complex with a first stage involving the participation of radicals. The vapour phase Raman spectra of SF_6, SeF_6 and TeF_6 have been recorded with 488.0 and/or 514.5nm excitation at *ca.*0.5 atm and *ca.* 295K.[29] The intensities of the $\nu_1(a_{1g})$, $\nu_2(e_g)$, and $\nu_5(t_{2g})$ bands were determined relative to that of the $\nu_1(a_1)$ band of methane thus permitting the calculation of Raman scattering activities and differential cross sections for each band.

The systematic preparation of partially fluorinated pentafluorosulphur alkanes containing no additional halogens has been reported.[30] Thus the indirect addition of HF (via KF/formamide) to $SF_5CH{=}CF_2$, $SF_5CF{=}CF_2$, and $SF_5C(CF_3){=}CF_2$ produces $SF_5CH_2CF_3$, SF_5CHFCF_3 and $SF_5C(CF_3)_2H$ respectively. The monohydrylpentafluorosulphur-F-alkanes react readily with $S_2O_6F_2$ to form the corresponding fluorosulphates by oxidative displacement of H_2 while the dihydryl derivative undergoes cleavage to produce F-acetyl fluoride. Efforts to convert some of these materials to the unknown pentafluorosulphur ketone, $SF_5C(O)CF_3$ were unsuccessful.

The preparation of CF_3SF_3 in approximately 90% yields by the direct fluorination of CF_3SSCF_3 in a continuous flow reactor using the dilution at -120°C has been described.[31] Optimum yields were produced after 38 hours; on increasing the time CF_3SF_5 was produced such that after 72 hours this was the sole product. ^{19}F n.m.r. studies indicate that structure (2) is adopted by CF_3SF_3.



(2)

The carbon analogue of $HOSF_5$ and H_2NSF_5 has been synthesized[32] by the following route.

$$SF_5Cl \quad + \quad CH_2{=}C{=}O \xrightarrow{CFCl_3\ 20^{\circ}C} SF_5{-}CH_2{-}COCl \xrightarrow{H_2O}$$

$$SF_5{-}CH_2{-}COOH \xrightarrow{Ag_2CO_3} SF_5{-}CH_2{-}COO^-Ag^+ \xrightarrow[CFCl_3]{+Br_2}$$

$$CO_2 \quad + \quad AgBr \quad + \quad SF_5{-}CH_2Br \xrightarrow{Zn/HCl} H_3C{-}SF_5$$

In contrast to its analogues, H_3CSF_5 shows no tendency to eliminate HF at room temperature. The product of such an elimination is obtainable, however by another route, i.e.

$$SF_5{-}CH_2Br \xrightarrow[-110^{\circ}C]{n\text{-}BuLi} SF_5{-}CH_2Li \xrightarrow{-70^{\circ}C} H_2C{=}SF_4$$

N.m.r. data show that $H_2C{=}SF_4$ is not an ylide but instead shows carbene type reactions.

The reactions of RSCl ($R{=}CF_3$, CF_2Cl) with HgF_2 and AgF have been shown to give RSF and the dimeric product RSF_2SR in high yield whereas reaction with activated KF led only to RSF in low yield.[33] The dimer was thought to arise via an intermediate complex of the transition metal and sulphenic halide.

In order to obtain experimental evidence for d-orbital participation, the homologous chalcogen oxyfluorides, F_5SOSF_5, $F_5SeOSeF_5$ and $F_5TeOTeF_5$ have been prepared and their structures investigated by electron diffraction.[34,35] The results of the structural studies are shown in Figure 2 and Table 1. As indicated by the slightly increased bond angle and most drastically shortened bond, the $(p{-}d)\pi$ bonding contribution seems to be greater in the tellurium compound.

Pure bis-(pentafluorosulphur)trioxide, $SF_5O_3SF_5$, has been prepared by the photochemical decomposition of SF_5Cl in the presence of high oxygen pressures.[36] The compound is colourless with boiling and melting points of respectively 54.9 and $-55^{\circ}C$. Its i.r. spectrum shows two characteristic bands at 936 and 872 cm^{-1} and further weak bands at 743 and 730 cm^{-1}.

Improved syntheses for the compounds SF_5OOSO_2F, SF_5OOSF_5, and

Table 1. Bond lengths (Å) and bond angles (°) in the compounds $F_5X{-}O{-}XF_5$

	F_5SOSF_5	$F_5SeOSeF_5$	$F_5TeOTeF_5$	SF_6	SeF_6	TeF_6
X–O	1.586(11)	1.697(13)	1.832(12)			
$X{-}F_m$	1.560(4)	1.681(3)	1.816(4)	1.565	1.689	1.815(4)
$X{-}F_e$	1.558(8)	1.683(9)	1.820(10)			
$X{-}F_3$	1.572(34)	1.665(31)	1.799(47)			
∢ XOX	142.5(1.6)	142.4(1.9)	145.5(2.1)			
∢ F_aXF_e	87.9(0.9)	88.9(0.8)	89.8(0.9)			

m, average; e, equatorial; a, axial.

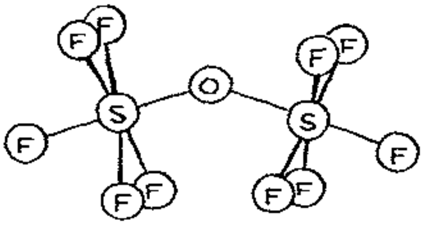


Figure 2. Molecular structure of F_5SOSF_5.

FO_2SOOSO_2F have been reported.[37] Moderate heating of CsF, SOF_4 and $S_2O_6F_2$ in a static system appears to be the preferred synthesis for SF_5OOSO_2F. 85% yields of SF_5OOSF_5 could be obtained by shortening the photolysis time to 1 hour for reaction (4), whereas ambient photolysis

$$2SF_5OCl \longrightarrow SF_5OOSF_5 + Cl_2 \qquad (4)$$

for 2-4 hours gave 94-97% yields of $S_2O_6F_2$ from reaction (5).

$$2ClOSO_3F \longrightarrow S_2O_6F_2 + Cl_2 \qquad (5)$$

Sulphur difluoride has been produced by halogen exchange of a highly diluted SCl_2-rare gas mixture with AgF or HgF_2 and then isolated as a matrix.[38] The observed vibrational frequencies are consistent with those predicted from microwave data. In addition the frequencies of

$^{34}SF_2$ were measured so that all the force constants and the bond angles could be measured. Six new azole sulphur reagents have been prepared from their trimethyl silyl derivatives and S_xCl_2 (x=1, 2). The reactions of these reagents are different from those of SCl_2 or the corresponding phthalimide reagent with thiols, amines and alcohols.[39]

The structure of trichlorosulphonium(IV) tetrachloroiodate(III) has been determined.[40] The cation has a pyramidal geometry while that of the anion is square-planar, but interionic interactions lead to a distortion of the square plane and to additional contacts to the sulphur atom. This gives a greatly distorted octahedral arrangement around sulphur with three S-Cl bonds averaging 1.988Å and three S···Cl contacts averaging 3.115Å.

The preparation of solid disulphur diiodide by the reaction of disulphur dichloride with hydrogen iodide at -90°C has been described.[41] The i.r. spectrum of the product could be assigned to a mixture of S_2I_2 and an adduct of S_2I_2 and iodine. The previously published u.v.-visible spectra of S_2I_2 have been confirmed.[42] The existence of the extremely unstable sulphinyliodide was thought to be probable but no proof for the existence of monosulphur diiodide and sulphuryl iodide could be found, in contradiction to former publications.

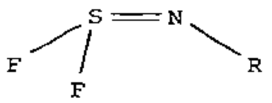
6.2.3 Bonds to Nitrogen

The gas-phase species volatilized from polymeric $(SN)_x$ treated with bromine and tetrasulphur tetranitride (S_4N_4) treated with Br_2 and ICl have been studied using mass spectrometric techniques.[43] The species observed from the bromination of $(SN)_x$ and S_4N_4 were identical consisting of Br_2, NSBr, $(SN)_4$ isomers and smaller amounts of HBr, S_2Br_2 and other sulphur-nitrogen compounds. Treatment of S_4N_4 with ICl yielded I_2, ICl, S_4N_4, NSCl, HCl, HI and small amounts of S_2Cl_2 and other S-N compounds; Cl_2 and NSI were not observed.

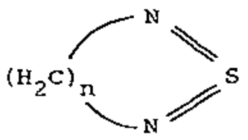
The nature and origin of the hydride species of $(SN)_x$ have been described.[44] The vapour-phase hydride species has a molecular weight of 220±12 and results from a reaction involving water during the synthesis of $(SN)_x$, probably following S_2N_2 crystal formation and prior to $(SN)_x$ sublimation. Experimental results were presented which suggest the formation of hydride species may be the first stage of a hydrolysis process leading to the formation of $(NH_4)_2S_xO_y$ salts. The most likely formulation of the hydride species was thought to be S_5N_4H, S_5N_5H or

$S_5N_5H_2$. The photopolymerization of S_2N_2 to $(SN)_x$ has been described.[45] S_2N_2 single crystals grown in tetrahydrofuran solution can be photopolymerized in their mother liquor at temperatures as low as $-65^{\circ}C$ to produce $(SN)_x$ with an electrical conductivity of about $2000\Omega^{-1}cm^{-1}$, increasing by a factor of 250 at 13K.

The structure of the compounds NSF, HSN, N_2S, N_2S_2 and H_3NS has been investigated using the L.C.A.O.-M.O. <u>ab initio</u> method.[46] The compound NSF was found to be more stable than SNF, HNS more stable than HSN, and linear NNS more stable than NSN. The order of stability of the isomers of H_3NS was predicted as $H_2SNH<H_3SN<HSNH_2<SNH_3$. N_2S_2 was shown to be square planar in agreement with recent experimental evidence. The e.p.r. spectra of radicals generated by the γ-irradiation of solutions of thiazyl fluoride in SF_6 have been reported.[47] The species NSF_2, having a terminal N atom and two equivalent F atoms, and the isomeric radical FNSF which arises from fluorine atom attack on the nitrogen atom of NSF were thought to be produced. The He(I) photoelectron spectra of the molecules (3) and (4) with S$\cdots$N multiple bonds have been assigned.[48] From the ionization energies of the O=S=O/HN=S=O



(3)



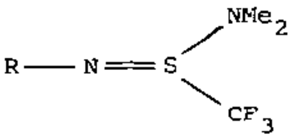
(4) n = 2,3

R = CH_3, CF_3, Cl.

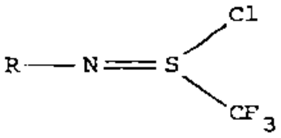
pair a parameter was deduced which proved useful in a discussion of other SN compounds such as $R_3C{-}N{=}S{=}O$ and RN=S=NR. The torsional modes in $H_3N^+SO_3^-$, $Na[O_3SNH_2]$, $SO_2(NH_2)_2$ and $Ag[O_2SN_2H_2]$ have been assigned and the barrier heights and effective force constants calculated.[49] The last two parameters increase with decreasing S-N bond length. The salt $Ag[O_2SN_2H_2]$ was shown not to contain an NH_2 group and this conclusion differs from that in an earlier publication; the SO_2 rocking and wagging modes were observed because of their associated proton motion.

S-trifluoromethyl sulphur monofluoride imides, $R{-}N{=}S(CF_3)F$, (R = CF_3CO, NC, $(CF_3)_2CF$ (5) and C_2F_5 (6)) have been prepared by the reaction of CF_3SF_3 with the appropriate N-derivative.[50] Reaction of CF_3SF_3 with cyanuric fluoride leads to the S(+2) derivative,

$(CF_3)_2N$-SCF_3. The fluorine atom in (5) and (6) may be substituted by N-silylated amines and PCl_5 to give (7) and (8) respectively.



(7)



(8)

The stepwise addition of polar reagents R-F to the formal triple-bond of NSF_3 was formerly thought impossible. The first such addition of "methyl fluoride" has now been carried out and the salt (9) and the tetrafluoride (10) isolated as stable compounds.[51] Bis(trimethylsilyl)-

$$CH_3Br + AgAsF_6 \xrightarrow[-AgBr]{+SO_2} CH_3OSO^+AsF_6^- \xrightarrow[-SO_2]{+NSF_3} CH_3NSF_3{}^+AsF_6^-$$

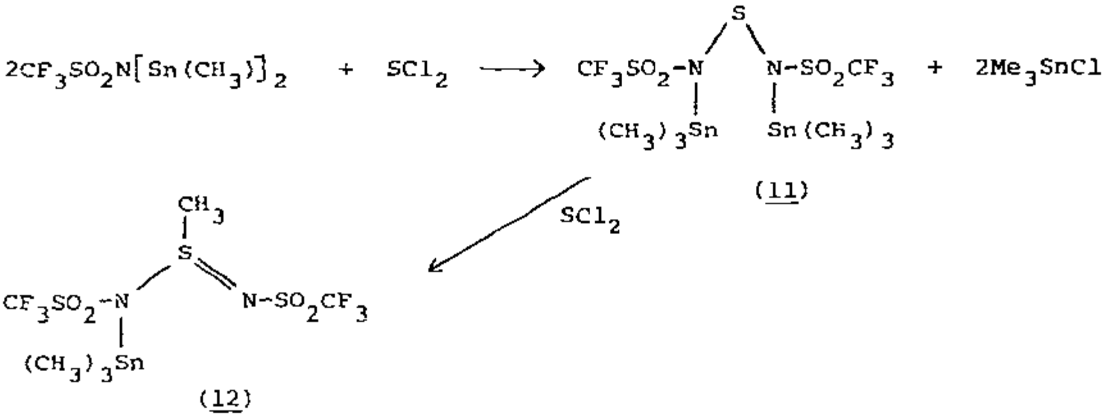
(9)

$$(9) + NaF \longrightarrow CH_3N{=}SF_4$$

(10)

sulphur diimide has been shown to react with p-tolyl- or p-chlorophenyl-sulphenyl chloride to yield the corresponding 1,7-diaryltetrasulphurtrinitrogen cation.[52] Reaction was thought to take place by two consecutive additions of an S-Cl bond to an S-N double bond, followed by the elimination of N_2 and a diaryldisulphide. A crystal structure determination of the di-4-tolyl chloride derivative shows the seven-membered SN chain assumes a *cis*, *trans*, *trans*, *cis* geometry, apparently to maximize the electrostatic interactions between itself and the chloride counterions. The values of the various S-N bond lengths indicate appreciable delocalization of charge over the entire chain.

N,N-bis(trimethylstannyl)trifluoromethanesulphonamide has been shown to react with SCl_2 in the molar ratio 2:1 to give the sulphur diamide (11). Further treatment with SCl_2 yields the methyl sulphur imide amide (12). Alkylation of sulphur with cleavage of a R_3Sn group was observed for the first time in this reaction.[53] A structural



determination on (12) showed that conventional formulation with alternate single and double bonds as shown above is unsuitable for describing the actual bonding and a correlation seems to exist between the bond lengths and the coordination numbers of the participating atoms.

Lithium bis(trifluoromethyl)sulphimide has been shown[54] to be a moderately stable precursor to several new bis(trifluoromethyl)-sulphimides, see equations (6) and (7). In general these new compounds

$$(CF_3)_2S{=}NLi \quad + \quad RX \quad \longrightarrow \quad (CF_3)_2S{=}NR \quad + \quad LiX \qquad (6)$$

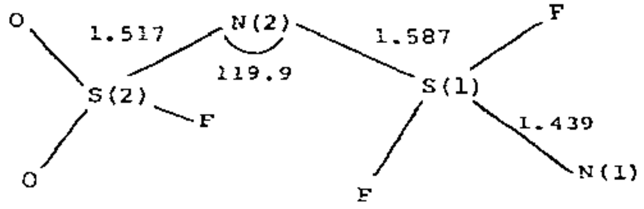
$RX = Me_3SiCl,\ CF_3C(O)Cl,\ CNCl,\ CF_3SO_2F,\ SO_2Cl_2,\ SO_2FCl,\ OPF_2Cl$

$$(CF_3)_2S{=}NLi \quad + \quad RX_2 \quad \longrightarrow \quad [(CF_3)_2S{=}N]_2R \quad + \quad 2LiX \qquad (7)$$

$RX \ = Me_2SiCl_2,\ COCl_2$

are liquids of low volatility with the exception of the carbonyl, $CO[(CF_3)_2S{=}N]_2$ which is a colourless crystalline solid, which melts at 37.5°C.

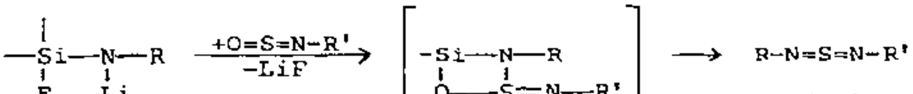
An X-ray crystal structure determination of $(AsPh_4)^+(NSF_2NSO_2F)^-$ has shown that the anion consists of two corner-sharing tetrahedra, where the corner is occupied by a nitrogen atom and the two centres of the tetrahedra by sulphur atoms.[55] The anion has, as expected, three different S-N bond lengths which can be ascribed bond orders of 2.5, 1.35 and 1.9 for S(1)-N(1), S(1)-N(2), and S(2)-N(2) respectively as shown in structure (13).



Bond lengths in Å

(13)

I.r. and Raman spectra of $S(NSiMe_3)_3$, $S(NSiMe_3)_2$ and $F_2S(NSiMe_3)_2$, three compounds containing the N=S=N system, have been reported and possible molecular structures discussed for the latter two molecules.[56] A new method for the preparation of the sulphurdiimides (14) by the reaction of lithium aminofluorosilanes with trimethylsilylthionylimide has been described.[57] N,N'-Di-tert-butylsulphurdiimide (15) has been shown to react with a series of isocyanates according to equation (8).



(14)

R=CMe$_3$ R'=SiMe$_3$

$$Me_3C{-}N{=}S{=}N{-}CMe_3 \;+\; RNCO \longrightarrow Me_3C{-}N{=}S{=}N{-}R \;+\; Me_3C{-}N{=}C{=}O \qquad (8)$$

(15)

$R = n\text{-}C_4F_9SO_2,\ 3\text{-}ClC_6H_4,\ 3\text{-}CF_3C_6H_4,\ CH_3CO,\ (O)PCl_2.$

Compound (15) also reacts with $SO_2(NCO)_2$ to yield (16) which is the first acyclic example where two sulphurdiimide groups are connected by an SO_2 group.[58]

$$(15) \;+\; SO_2(NCO)_2 \longrightarrow Me_3C{-}N{=}S{=}N{-}SO_2{-}N{=}S{=}N{-}CMe_3 \;+\; 2Me_3C{-}N{=}C{=}O \qquad (9)$$

(16)

The tetrakis-difluorooxosulphurimidato metallates(II), $M(NSOF_2)_4^{2-}$ M=Hg, Co, Pd, have been prepared[59] from $Hg(NSOF_2)_2$, $CoCl_2$ and $Pd(CH_3COO)_2$ respectively, by reaction with Ph_4PNSOF_2 or $Ph_4AsNSOF_2$. An X-ray structure determination of $[Mn(CO)_4NSOF_2]_2$ has shown it to be a dinuclear transition metal complex containing difluorooxosulphimidato bridges.[60] The bridging $NSOF_2$ groups show a strongly distorted tetrahedral symmetry with S-O and S-F bond lengths closely resembling those of other R-$NSOF_2$ compounds. The very short N-S bond of 1.434Å corresponds to a bond order of about 2.5 and indicates strong d_π-p_π bonding. The weak acid, $HNSOF_2$, has been shown to act as a base towards transition metal Lewis acids such as $M(CO)_5$ and fluoro Lewis acids such as SbF_5 to give the nitrogen bonded complexes $[M(CO)_5HNSOF_2]^+AsF_6^-$ and $F_5Sb.HNSOF_2$ respectively.[61] In superacids $HNSOF_2$ is protonated to the $H_2NSOF_2^+$ cation.

The kinetics and mechanism of the reaction between sulphamic acid and nitric acid (equation 10) have been interpreted on the basis of a three stage process.[62] The first stage is fast and involves attack by NO_2^+ on

$$HNO_3 + NH_2SO_3H \longrightarrow N_2O + H_2SO_4 + H_2O \qquad (10)$$

sulphamic acid with subsequent steps involving rearrangement and elimination (equation (11)).

$$NO_2^+ + NH_3SO_3^- \longrightarrow [NH_3SO_3NO_2] \longrightarrow O_2NNHSO_3H + H^+$$

$$O_2NNHSO_3H + NO_2^+ \longrightarrow O_2NNHSO_3NO_2 + H^+$$

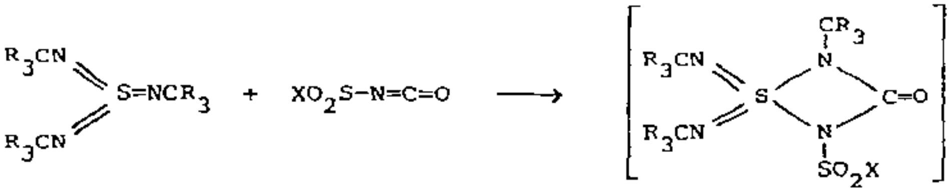
$$\downarrow$$

$$N_2O + H_2O \longleftarrow H_2NNO_2 + HSO_4^- + NO_2^+ \qquad (11)$$

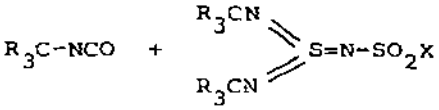
The n-propyl urea derivative, $Ph_3P{:}NSO_2NHCONHi\text{-}Pr$, has been shown to react with phosgene to give a good yield of the isocyanate $Ph_3P{:}NSO_2NCO$ which has been characterized by its reaction with alcohols and amines.[63] N,N,O-trisubstituted hydroxylamines, $R^1(R^2SO_2)NOSO_2R^2$, together with R^1NO_2 and $R^1NN(O)R^1$ are the products when hydroxylamines carrying mixed substituents such as $R^1(R^2SO_2)NOH$ are oxidised with PbO_2 in benzene.[64] Oxidation proceeds via aminyl oxide radicals, $R^1(R^2SO_2)NO\cdot$, when $R^1 = R^2 = Ph$ but when $R^1=R^2=p\text{-}ClC_6H_4$ or $p\text{-}MeOC_6H_4$, the $(p\text{-}ClC_6H_4)_2NO\cdot$ radical is also formed. Fremy's salt, $ON(SO_3K)_2$ and $HON(SO_3K)_2$ have both been shown to reduce $AgNO_3$ to silver, but the compounds $Ag_3NS_2O_3$ and $Ag_2KNS_2O_6$ both result when $HN(SO_3K)_2$ and $K_3NS_2O_3$

respectively are used.[65]

Ring Compounds. The reaction of sulphur compounds belonging to the "Y-triene" type $(RN{=})_3S$ where R = CH_3, with a slight excess of sulphonyl isocyanates has been shown[66] to give the compound (17) according to equation (12). An excess of sulphonyl isocyanate gives



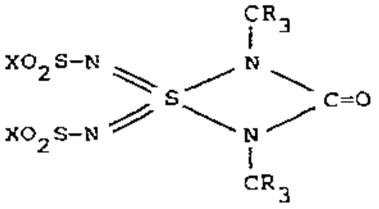
R = CH_3; X = F, Cl



(12)

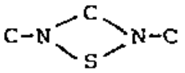
(17)

the symmetrical thiadiazetidinones(18). A single crystal structure



R = Me; X = F, Cl, CF_3.

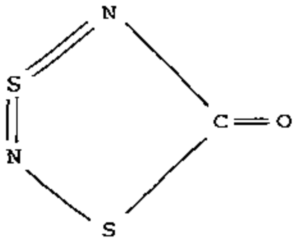
(18)

determination of (18) showed the mutually perpendicular fragments SN=S=NS and  to be almost planar with the angles in the ring, NSN 79.5, SNC 92.0, and NCN 96.5°. 1,2,3,5-Dithiadiazolium chlorides (19) have been prepared by the reaction of azines with $S_3N_3Cl_3$ according to equation (13).[67] The chloride ion in (19) has

$$3RCH{=}N{-}N{=}CHR \quad + \quad 4S_3N_3Cl_3 \longrightarrow 6\underset{(19)}{[RCN_2S_2]^+Cl^-} \quad + \quad 3N_2 \quad + \quad 6HCl \qquad (13)$$

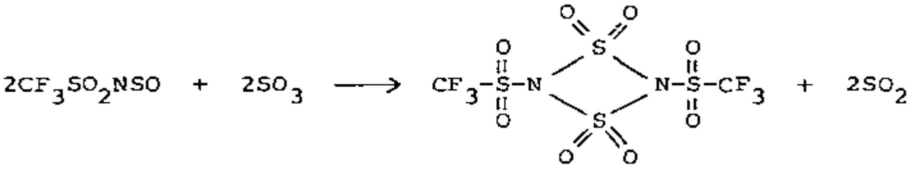
R = C_6H_5, $C(Me)_3$

been replaced by a variety of ions and on the basis of mass spectrometric investigations and X-ray analysis the cation has a delocalized ring structure. A synthesis of S_2N_2CO has been reported.[68] Structure analysis shows the compound to have a five-membered planar ring (<u>20</u>) and to form mono and bis adducts with several Lewis acids.



(<u>20</u>)

$(CF_3SO_2NSO_2)_2$, a compound with a four membered ring (<u>21</u>) has been prepared[69] from the reaction of SO_3 and CF_3SO_2NSO according to equation (14). (<u>21</u>) and $(FSO_2NSO_2)_2$ have been shown to form 1:1



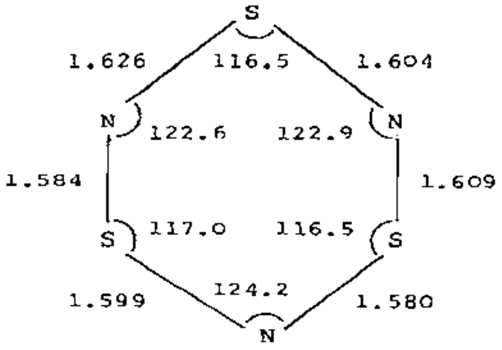
(14)

(<u>21</u>)

adducts with S_4N_4, Py, and pyridine carbonitrile, In contrast the reaction of (<u>21</u>) with aromatic nitriles yielded 1:2 cyclo addition products which were characterized by mass spectrometry.

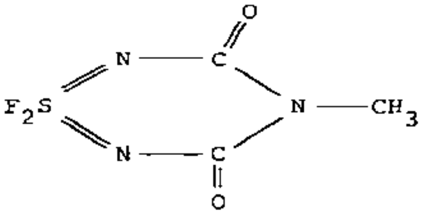
The reaction of S_4N_4 with alkali metal or tetraalkylammonium azides in ethanol has been shown[70] to produce either the tetrasulphurpentanitride ion $S_4N_5^-$ $(Li^+Na^+K^+)$, the trisulphurtrinitride ion, $S_3N_3^-$ $(Cs^+Me_4N^+Et_4N^+nPr_4N^+nBu_4N^+)$ or a mixture of the two (Rb^+). I.r. and Raman studies of the Cs salt suggest a cyclic structure with C_{3v} symmetry for $S_3N_3^-$. The potassium salt of $S_3N_3^-$ may be produced by the deprotonation of $S_4N_4H_4$ with potassium hydride.[71] The formation of $S_3N_3^-$ by reduction of S_4N_4 supports an earlier proposal that the initially formed radical anion $S_4N_4^{\cdot -}$ decomposes by an intra-molecular bond rupture. An X-ray crystallographic analysis of $[Bu_4N]^+[S_3N_3]^-$

has shown[72] that the $S_3N_3^-$ anion is a planar six-membered ring (22).

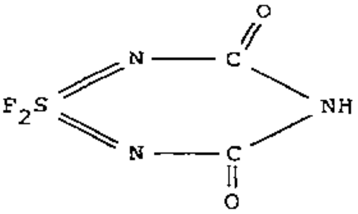


(22)

$R_3SiNSF_2NSiR_3$ has been shown to react with $(CF_3CO)_2O$ and COF_2 to give a series of acyl derivatives.[73] One of these, $COFNSF_2NCOF$, may react with $(R_3Si)_2NMe$ or $(R_3Si)_2NH$ to give the cyclic sulphur difluorodiimides (23) and (24).



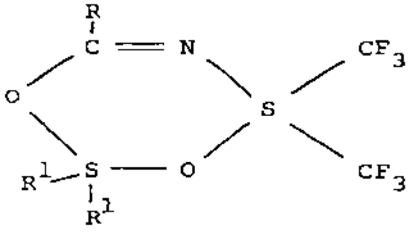
(23)



(24)

The sulphuranes (25), the first stable members of a new family with two tetra coordinate sulphur(IV) atoms bonded to carbon oxygen and/or nitrogen per molecule, have been synthesized[74] by the cycloaddition of S,S-bis(trifluoromethyl)-N-benzoyl-(or 2 phenylacetyl)-sulphimide with sulphoxides according to equation (15).

$$RC(O)N{=}S(CF_3)_2 \quad + \quad R^1_2S(O) \xrightarrow[BF_3]{(C_2H_5)_2O}$$



(15)

(25)

$R = C_6H_5,\ C_6H_5CH_2,\ C_6H_5,\ C_6H_5CH_2$

$R^1 = CH_3,\ CH_3,\ OCH_3,\ OCH_3$

Trithiazyl chloride, $S_3N_3Cl_3$, has been used to prepare[75] the first organometallic thionitrosyl following the reaction shown in equation (16).

$$Na[cpCr(CO)_3] + \frac{1}{3}S_3N_3Cl_3 \xrightarrow[-78^{\circ}C]{THF} cpCr(CO)_2(NS) + CO + NaCl \qquad (16)$$

$(NSOF)_2(CH_3NSO_2)$ has been shown to react with methanol to give sulphuric acid, aminosulphuric acid and $SO_2(NHCH_3)_2$ as products.[76] A 1:1 adduct and a monosubstituted product having the formula $(NSOF)(NSOOCH_3)(CH_3NSO_2)$ were detected as intermediates.

A determination of the crystal structure of S_4N_4 at 120K has shown that even though the compound is thermochromic and loses its orange colour on cooling, no structural transition occurs between room temperature and 120K.[77] While intermolecular distances contract 1-2% in this temperature range, the corrected S···S intramolecular distance is remarkably constant, the low temperature distances being 2.601 and 2.597Å.

A structural study of thiotriazyl nitrate $S_4N_3^+NO_3^-$ shows double bond character in the S-N bonds as found in other salts of $S_4N_3^+$.[78] The distances of one of the nitrate group oxygen atoms from the disulphide sulphur atoms are unusually short (2.620 and 2.695Å) and the N-O···S angles are such that the oxygen lone pairs may be expected to point closely toward the disulphide group.

The reaction of S_4N_4 with liquid bromine and iodine monochloride has been reported.[79] The reaction proceeds in 100% yield as shown in equation (17) Comparison of the i.r. data for $S_4N_3Br_3$ with that of

$$S_4N_4 + \frac{3}{2}Br_2 \longrightarrow \frac{1}{2}N_2 + S_4N_3Br_3 \qquad (17)$$

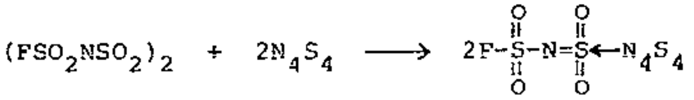
S_4N_3Cl confirmed the presence of a cyclic $S_4N_3^+$ cation and showed that the bromine was present as a Br_3^- ion. This conclusion was confirmed by X-ray studies. Though not studied in such detail, the reaction of liquid ICl with S_4N_4 appears to give a similar product as shown in equation (18). The reaction of S_4N_4 with Br_2 or ICl in the vapour

$$S_4N_4 + 2ICl \longrightarrow \frac{1}{2}N_2 + S_4N_3ICl_2 + \frac{1}{2}I_2 \qquad (18)$$

state has been shown to lead to polymerization, forming a series of highly conducting solid compounds with the approximate compositions

$(SNBr_{0.4})_x$ and $(SNICl_{0.4})_x$.[80] Solutions of IBr in CCl_4 also react with S_4N_4 at room temperature to give an analogous compound. The reaction of S_4N_4 with SO_3 in CH_2Cl_2 or with fluorosulphonic acid anhydride has been shown to give the adduct $S_4N_4.SO_3$.[81] An X-ray structure determination shows the cage of the S_4N_4 to be analogous to that observed in $S_4N_4.SbCl_5$, reconvoluted into a deformed saddle conformation with almost C_s symmetry (S-N bond lengths vary from 1.51 to 1.69Å). A structure analysis of the addition product of S_4N_4 with fluorosulphonylisocyanate shows a nucleophilic attack of a nitrogen atom of the S_4N_4 ring at the carbonyl atom of the isocyanate forming an N-C single band.[82] Although the bond distances and angles are very similar to the other Lewis acid adducts the substituted nitrogen of the S_4N_4 ring deviates significantly from a planar environment.

Reaction of S_4N_4 with N-fluorosulphonylsulphimide (previously only isolated as a cyclic dimer) has been shown[83] to yield the 1:1 adduct as shown in equation (19). A similar adduct was obtained by reaction with pyridine but reaction with benzonitrile surprisingly gave a 1:2 adduct.



$$(FSO_2NSO_2)_2 \;+\; 2N_4S_4 \longrightarrow 2F-\overset{O}{\underset{O}{\overset{\|}{\underset{\|}{S}}}}-N=\overset{O}{\underset{O}{\overset{\|}{\underset{\|}{S}}}}\leftarrow N_4S_4 \qquad (19)$$

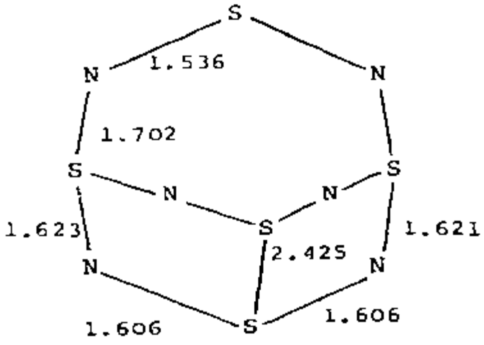
The i.r. and Raman spectra of solid and dissolved S_4N_4, $S_4N_4H_4$, $S_4N_4D_4$ and $S_3N_3Cl_3$ have been recorded and assigned on the basis of D_{2d}, C_{4v} and C_{3v} symmetry respectively.[84]

An X-ray study[85] of S_4N_5Cl, prepared from S_3N_3Cl and $Me_3SiNSNSiMe_3$, has revealed a predominantly ionic structure involving the new S-N cation $S_4N_5^+$. In the structure the chlorine atoms symmetrically bridge S_4N_5 units via the sulphur atoms bonded to two nitrogens, with an S-Cl bond distance of 2.811Å. It was thought reasonable to view S_4N_5Cl as consisting of $S_4N_5^+$ cations bridged by Cl^- ions.

A parallelism between the structural problems present in [10] annulene and the 14π system of $S_5N_5^+$ has been pointed out.[86] A comparison of six possible structural isomers of $S_5N_5^+$ within an M.O. framework led to the conclusion that an azulene-like structure is preferred.

An X-ray crystallographic study has shown that S_5N_6, prepared from $Bu_4N^+S_4N_5^-$ and bromine in methylene chloride, has a structure (<u>26</u>) in which an -N=S=N- unit bridges two sulphur atoms of an S_4N_4 cradle.[87]

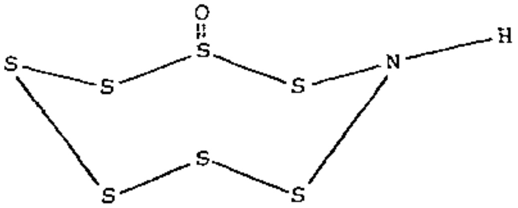
The compound S_7NSNMe_2 has been prepared by the reaction of S_7NH with



(26)

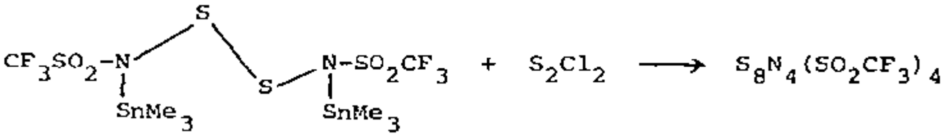
$S(NMe_2)_2$ and a crystal structure determination carried out.[88] The structure shows several interesting features. Both nitrogen atoms have an almost planar geometry indicating delocalization of the nitrogen lone pairs on to sulphur. The bonds between the ring nitrogen and the adjacent ring sulphur atoms are short (mean 1.60Å), whereas the bond from the same nitrogen to the bridging sulphur atom is longer (1.73Å) indicating single bond character.

Trifluoroperoxyacetic acid has been shown to react in 80% yield with $(S_7N)_2S$ to give colourless crystals of the known $(S_7N)_2SO$ and with S_7NH to give the new compound S_7NHO.[89] On the basis of i.r. and Raman spectra the structure (27) was proposed.



(27)

The diaminodisulphane (28) prepared from S_2Cl_2 and $CF_3SO_2N(SnMe_3)_2$ has been shown to react with further dichlorodisulphane according to equation (20) to give the novel S_8N_4 ring compound (29).[90]



(20)

(<u>28</u>) (<u>29</u>)

An X-ray structural analysis showed that the twelve membered ring has a chair conformation and contains four S-N-S units coupled via S-S bonds (2.006 - 2.009Å). The S-N bond lengths found were 1.724 - 1.732Å in the ring and those between the N-atoms and sulphonyl groups 1.650-1.657Å. The dihedral angles NSS/SSN have values of 91.3 and 94.1°.

6.2.4 <u>Bonds to Oxygen</u>

The relative proton affinities of some simple sulphur-oxygen compounds (SO_2F_2, SO_2, HSO_3F, H_2SO_4, CF_3SO_3 and H_2S) have been determined by the bracketing technique of ion-molecule reactions.[91] The proton affinities were found to fit reasonably well to a correlation curve of ionization potential vs. proton affinity and to a correlation curve of core binding energy O(1s) vs. proton affinity.

The reactions of diluted aqueous solutions of SO_2 with MnO_4^- or Ce^{4+} ions in the pH range 1-4 has been shown to produce chemiluminescence in the spectral region 450-600nm.[92] A reaction scheme was proposed in which a recombination product of primarily formed HSO_3 radicals - with a lifetime of about 1 sec. - appears as precursors of electronically excited SO_2 molecules. The radiation induced oxidation of sulphur dioxide dissolved in sulphuric acid has been studied using X-rays.[93] On the basis of previous publications a mechanism was proposed which involved the $HOOSO_2^{\cdot}$ radical as an unstable intermediate. A kinetic study of the reaction of FeS and SO_2 has shown that the first step in the reaction is the adsorption of SO_2 onto the sulphide surface followed by dissolution of the FeS with the formation of Fe^{2+} and a thiosulphurous intermediate $S_2O_2{}^{2-}$. This intermediate then reacts with $HSO_3{}^-$ to form thiosulphate which may then react with the sulphoxylate ion to produce disulphane-disulphonic acid.[94]

The pure rotational Raman spectrum of SO_3 in the vapour phase at 333K has been obtained and analysed for the first time.[95] Despite previous studies on the rates of uncatalyzed oxidations of aqueous sulphur(IV) solutions, it has now been reported that these reactions are in fact trace-metal catalyzed.[96] The previously measured rates were found to decrease by up to four orders of magnitude at high pH and by a factor of 20 at low pH in the presence of small amounts of chelating agents which complexed any trace metals present in the solution.

The replacement of the iodide ligand in the complex species $SO_2.I^-$, $SOCl_2.I^-$ and $SO_2Cl_2.I^-$ by Cl^-, Br^- and thiocyanate ions has been studied spectrophotometrically.[97] The extent of replacement was found to depend on complex stability, the nature of the replacing ligand and on the solvent used. The stability constants of $SO_2.X^-$,$SOCl_2.X^-$ and $SO_2Cl_2.X^-$ (X = Cl^- Br^- or I^-) have been determined in different mixtures of acetonitrile and dimethyl sulphoxide as solvent.[98] The electron diffraction data for sulphonyl chloride isocyanate, $SO_2Cl(NCO)$ have been shown to be consistent with two sets of geometric parameters differing in the relation between the C=O and N=C bond lengths.[99] Other parameters measured were S-N 1.656, S-Cl 2.019 and S=O 1.417Å, S-N-C 123.8, N-S=O 108.3, N-S-Cl 98.0, Cl-S=O 107.8 and O=S=O 122.8°.

N-Methylsulphonyl and N-phenylsulphonyl-N-methylhydroxylamine have been shown to result from the reactions of methylsulphonyl chloride and phenylsulphonyl with N-methylhydroxylamine.[100]

Density, viscosity, specific conductivity and freezing point measurements over the whole composition range of water-trifluoromethanesulphonic acid mixtures have been reported.[101] Some five hydrates were found in the system with water/trifluoromethanesulphonic acid ratios of 1:2, 1:1, 2:1, 4:1 and 6:1. A crystal structure determination of the tetrahydrate, $H_9O_4^+CF_3SO_3^-$, shows the triaquaoxonium ions hydrogen bonded to $CF_3SO_3^-$ ions.[102] The $CF_3SO_3^-$ ion has a staggered conformation with pseudo C_{3v} symmetry, and has one S-O bond shorter than the other two. The structure of the pentahydrate, $CF_3SO_3H.5H_2O$, shows oxonium ions and water molecules bonded to each other and to $CF_3SO_3^-$ to form a three-dimensional network.[103]

The thermal decomposition of $CaSO_3$ in an argon stream to CaO and SO_2 at temperatures up to 880°C has been shown to proceed via the intermediate reaction shown in equation (21).[104] The structure of the

$$4CaSO_3 \xrightarrow{680^oC} 3CaSO_4 + CaS \qquad (21)$$

compound $(NH_4)_2[Cu(H_2O)_6][CuSO_3]_4$ has been described in terms of distorted Cu^IO_3S tetrahedra, the ligands being atoms from four different sulphite groups.[105] Average dimensions for the SO_3 groups are S-O 1.52, O-O 2.42Å and O-S-O 105.3°.

The kinetics of the oxidation of aqueous solutions of ammonium sulphite and hydrogen sulphite have been studied.[106]

The crystal structure of the high temperature form of K_2SO_4 has been solved from powder diffraction data at 630°C.[107] The compound possesses a disordered structure in which two possible orientations of the SO_4^{2-} groups were observed. A study of the i.r. spectra of the alkali metal sulphates has shown that the frequency of the symmetrical stretching mode of the sulphate group decreases linearly from 1011 cm^{-1} to 967 cm^{-1} with increasing ionic radius of the alkali metal.[108] The crystal structure of $(NH_4)_3H(SO_4)_2$, which becomes ferroelectric at high hydrostatic pressures or by deuteration has been determined.[109] The sulphate ion forms a slightly distorted tetrahedron with three S-O bonds of 1.450 and one of 1.518Å, and carries an electric dipole moment parallel to the longest bond. A crystal structure determination on $NiS_2O_3.6H_2O$ has shown it to be isostructural with the corresponding silver salt.[110] The $S_2O_3^{2-}$ ions are less distorted from ideal tetrahedral symmetry than those of the sodium or magnesium salts and the hydrogen bonding scheme proposed for the magnesium salt is also found in this compound. A study of the compound ZnS_2O_4.pyridine has shown the structure of the dithionite ion to be very similar to that observed in $Na_2S_2O_4$ in that an eclipsed configuration with a long S-S bond (2.386Å) was found.[111] The dithionite ion in $Na_2S_2O_6 2H_2O$ has been shown to posses $D_{3d}(\bar{3}m)$ symmetry to a good approximation.[112] Bond lengths and angles found were: S-S, 2.141; S-O, 1.452Å; S-S-O, 104.6; and O-S-O, 114.1°.

The S-monoalkyl thiosulphates $M[O_3S\text{-}SR]$ with M = Li, Na, K, Rb, Cs and R = Me, Et, have been characterized by means of u.v., i.r., ^1H n.m.r. and mass spectra.[113] The reaction kinetics of glycollic acid with peroxydisulphate have been studied.[114] A free radical chain reaction mechanism was postulated to explain the observed rate law. The reaction of potassium peroxydisulphate with sodium sulphate and the thermal decomposition of aqueous solutions of potassium peroxydisulphate have been studied.[115] The adducts formed between $VO(acac)_2$ and a number of alkyl and aryl sulphoxides in dichloroethane have been investigated by means of visible and i.r. spectroscopy.[116]

It has been shown that P_4S_{10} is a mild effective reagent for the reduction of sulphoxides to sulphides and that this conversion can be achieved selectively in the presence of other reactive groups.[117] P_4S_{10} also appears to be a promising reagent for the reduction of selenoxides but will not reduce sulphones, sulphinates or sulphites.

6.2.5 Sulphides

The repulsions between valence electron pairs have been determined as a function of bond angle for H_2S (and H_2O) using the Hartree-Fock method.[118] Some agreement with the assumption of VSEPR theory were found, but it was found that bond-bond repulsions affected the equilibrium geometry more strongly than either lone pair-lone pair or bond pair-lone pair repulsions.

The characterization of the S_3^- radical anion as the blue species present in HMPA and DMF solutions of alkali polysulphides and in ultramarine blue has been extended.[119] The vibrational spectra of the red species formed by adding sulphur to blue solutions of Na_2S_4 in DMF were reported and it was concluded that the red species was the S_4^- radical anion. Both the S_2^- and S_3^- radical anions have been identified as the species responsible for the colour of ultramarine green and oxidation of the latter to ultramarine blue was associated with an increase in the S_3^-/S_2^- ratio. Resonance Raman spectra of ultramarine red revealed the presence of the species thought to be the neutral S_4 molecule. Resonance Raman Scattering studies on KI single crystals doped with S_2^- have shown the orientation dynamics of the ground state molecules to be isotope selective.[120]

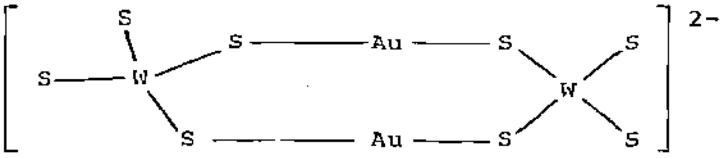
A study of the In_2S_3-Na_2S system has revealed the presence of two, previously unknown, compounds, $4Na_2S.In_2S_3$ and $5Na_2S.In_2S_3$ and has confirmed the existence of $Na_2S.In_2S_3$.[121] A new intermediate compound, Tl_4PbS_3 has been shown to be formed by a peritectic reaction at 460°C in the PbS-Tl_2S system.[122] The compound shows a polymorphic transformation at 420°C.

A new synthesis for a number of perfluoroalkyl di-, tri- and tetrasulphides ($CF_3S_nCF_3$, $C_2F_5S_nCF_3$, $C_2F_5S_nC_2F_5$, $n = 2$-4) has been developed using a low temperature glow discharge to dissociate sulphur vapour and generate trifluoromethyl radicals from hexafluoroethane.[123] The i.r. spectra of the solids $(TMA)_2C_2S_6\frac{1}{2}CS_2$ and $(TMA)_2C_2S_6$ have been investigated in the 200 to 4,000 cm^{-1} range.[124] An interpretation was carried out by using the structural and i.r. data of the CS_4^{2-} ion in the solid $K_2CS_4.CH_3OH$.

Solution of the glasses Ge_2S_3 and Ge_2Se_3 in Na_2S or Na_2Se in MeOH has been shown to lead to the compounds $Na_6Ge_2X_6.4MeOH$ ($X = S$, Se). It is thought that the formation of these compounds and the MeOH-free compounds are proof that Ge_2S_6 and Ge_2Se_6 units are present as structural groups in the glasses.[125] The sulphide Se_3S_5 has been shown to be isostructural with monoclinic sulphur (γ-S_8) with two distinct eight membered rings in the crown configuration.[126] Various disordered models were investigated but it was not possible to establish whether the structure consists of distinct Se_3S_5 rings or a mixture of Se_nS_{8-n} molecules. The average bond distances within the molecules was 2.166Å which is intermediate between the values for γ-S_8(2.044) and α-Se_8(2.318Å). An apparent bond length of 2.147Å would be predicted for Se_3S_5.

A study of the ternary system Tl-V-S has shown the existence of the following ternary sulphides, Tl_3VS_4, TlV_5S_8, $Tl_xV_6S_8$ and $Tl_2V_2S_5$.[127] The preparation of Fe_2S_2 from the reaction of stoichiometric quantities of Fe(III) in aqueous solution with Na_2S at 0°C has been shown to give a pure product. Mössbauer and i.r. spectra were measured and it was concluded that Fe_2S_3 is ordered antiferromagnetically at 4.2K.[128] It has been shown that the CoS_x phase may be deposited as single crystals by chemical transport reactions using iodine, only if x is greater than 1.06. Single crystals of Co_9S_8 have also been grown by chemical transport reactions using GeI_2 as the transporting agent.[129] Structural determinations on the cluster compounds $[Mo_2(S_2)_6]^{2-}$ [130] and $[Mo_3S_{13}]^{2-}$ [131] have shown that they both contain both terminal and bridging disulphide groups. The equivalent bonds in both the anions have roughley the same length but, as expected, the Mo-Mo distances are somewhat shorter in the former. A structural study has shown that K_2PtS_{15} is similar to $(NH_4)_2PtS_{15}.2H_2O$ and contain the Pt atom of the $PtS_{15}{}^{2-}$ anion in an octahedral environment made up from three bidentate five-membered sulphur rings.[132] The preparation and crystal structure of the hitherto unknown compound Au_2BaSnS_4 have been reported.[133]

The salt $[Ph_4P]_2[Au_2(WS_4)_2]$ has been isolated from the reaction of $Au(S_2O_3)_2{}^{3-}$ and $WS_4{}^{2-}$. Crystal structure analysis showed the anion to possess a novel ring system in which the dimeric unit (30) contains bidentate, nearly regular, tetrahedral $WS_4{}^{2-}$ ligands.[134]

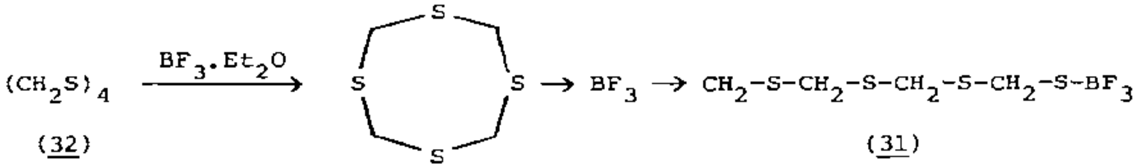


(30)

Phase equilibria in the $HgS-Tl_2S$ systems have been investigated and the compounds Tl_4HgS_3, $Tl_2Hg_3S_4$ and $Tl_2Hg_3SeS_3$ identified.[135] The homogeneity ranges of sulphide phases of La, Pr, Sm, Gd and Dy possessing the Th_3P_4 structure type have been studied.[136] Two isostructural series have been observed for β-Ln_2S_3, the first for Ln = La-Sm and the second for Ln = Sm or Gd.[137] The crystal structure of the sulphide LaS_2 has been described.[138] A structural study of the compound $Eu_3Ge_3S_9$ has shown the $Ge_3S_9{}^{6-}$ ion to have a cyclic structure with the chair conformation.[139] The equilibrium diagram for the Yb-S system has been determined in the composition range 0-62.5 at. %S at p=4.5 atm.[140] The preparation, properties, structure, and electronic structure of vanadium pentasulphide in a non crystalline form have been investigated.[141]

6.2.6 Other Compounds Containing Sulphur

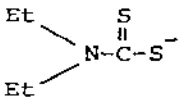
The copolymerization of tetrameric thioformaldehyde with oligomeric thioformaldehydes, substituted analogues or sulphur has been described.[142,143] It was found that the highly reactive intermediate (31), presumably formed from $BF_3.Et_2O$ and the tetrathiocane (32) according to equation (22), is able to attack trithianes, substituted tetrathiocanes, and elemental sulphur in such a way that copolymers with interesting properties are formed under mild conditions.



(32) (31)

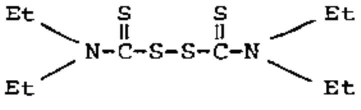
(22)

In an attempt to explore the possibility of intramolecular redox processes in metal complexes of the dialkyldithiocarbamato ligands, a detailed examination of the electrochemical behaviour of the free diethyldithiocarbamato anion (33) and its related oxidation product, tetraethylthiuram disulphide (34) has been carried out.[144]



$Et_2N-C(=S)-S^-$

(33)



$Et_2N-C(=S)-S-S-C(=S)-NEt_2$

(34)

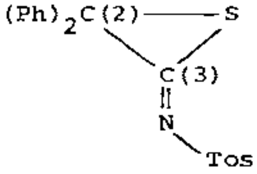
The structure of $K_2[O_2CC(S)SO].H_2O$, an oxidation product of 1,1-dithiooxalate has been determined by single crystal X-ray diffraction.[145] The dinegative ion is planar and may be considered as a peroxo thioacid anion.

Reaction of sulphenic fluorides, RSF with PF_3 has been shown to yield mercaptotetrafluorophosphoranes $RSPF_4$ (R = CF_3, CF_2Cl).[146] X-ray photoelectron spectra have been measured for several Transition metal di- and perthiocarboxylates and the binding energies of sulphur 2p orbitals reported.[147] "Bridging" sulphur atoms in perthiocarboxylate ligands were found to be more positive than terminal sulphur atoms. The gas-phase ion-molecule reactions of compounds of structure $CH_3O(CH_2)_nSCH_3$, n = 1-3 have been studied.[148] It was found that when there is a choice of forming either a sulphur-containing ion or its oxygen analogue; the sulphur ion is formed preferentially.

It has been shown that bis(thioacyl)sulphides may be obtained by treatment of acyl thioacyl sulphides with lithium alkoxides or alkyl sulphides.[149] Bis(trifluoromethyl)sulphide, tetrafluoro-1,3-dithietane, and bis(trifluoromethyl)sulphoxide have been shown to undergo oxidative addition when photolyzed with trifluoromethyl hypochlorite to form a new family of stable fluorinated sulphuranes and sulphurane oxides.[150]

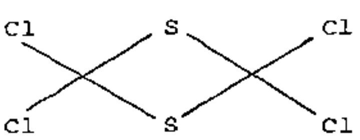
The photochemistry of several thiols in the liquid phase has been reported.[151] In all cases, products were obtained which could be rationalized as arising from the primary photoscission of the C-S bond.

Reaction of equimolar quantities of tosylisothiocyanate and diphenyl diazomethane at 0°C in anhydrous ether has been shown to yield the stable thiiranimine (35). An X-ray structure determination showed the new three-membered ring to be planar and to possess one long bond (S-C(2) = 170 pm).[152] The divalent sulphur containing ligands (36) to (38) have been shown to react with mercury(I) nitrate in methanolic solution without disproportionation to form stable

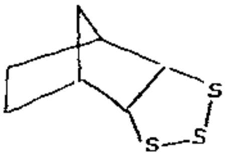


(35)

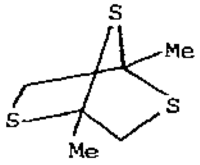
mercury(I)-sulphur compounds.[153]



(36)



(37)



(38)

The reactions of alkanethiols with CS_2 and alkali metal hydroxides have been shown to yield the thioxanthates of the types $K[S_2C\text{-}SR].H_2O$ or $M\{S_2C\text{-}S\text{-}nC_4H_9].H_2O$.[154] Red, oily thioxanthic acids, RS-CS(SH) have been prepared by reaction of the corresponding alkyl thioxanthate with dilute HCl at 0°C;[155] i.r. spectra were assigned[156] and mass spectra studied from which decomposition schemes were described.[157]

The Raman spectra and polarization parameters of the liquid dimethyl chalcogenides $CH_3\text{-}X\text{-}CH_3$ (X = O, S, Se, Te) and the i.r. spectra of the gaseous compounds have been measured.[158]

6.3 SELENIUM

6.3.1 Bonds to Halogens

The standard enthalpies of formation of crystalline selenium(IV) halides have been determined by solution calorimetry relative to that of selenium(IV) oxide.[159] The values obtained were: $\Delta H^{o}_{f,298}$ $SeCl_4$(c) -42.7±0.4 and $\Delta H^{o}_{f,298}$ $SeBr_4$(c) -17.9±0.5 kcal mol^{-1}. In a separate study,[160] an enthalpy of formation for $SeBr_4$ was obtained ($\Delta H^{o}_{f,298}$ -15.6±0.3 kcal mol^{-1}) which differed from that given previously. The reaction used in this study was that of the element with liquid bromine in an adiabatic calorimeter. Values were also obtained for liquid Se_2Br_2 (-15.6±0.3 kcal mol^{-1}) and crystalline $TeBr_4$ (-42.5 kcal mol^{-1}).

The molecular structures of selenonyl fluoride (SeO_2F_2) and sulphuryl fluoride (SO_2F_2) have been studied by gas-phase electron diffraction.[161] The geometries of both molecules are consistent with predictions from the VSEPR theory with the more important distances and bond angles for the Se compound being r(Se=O), 1.575Å; r(Se-F), 1.685Å; O-Se-O, 126.2°; F-S-F, 94.1°.

The reaction of WF_6 with Sb_2Se_3 has been shown to yield the compound $WSeF_4$.[162] The compound was shown by i.r. and ^{19}F n.m.r. spectroscopy and mass spectrometry to be isostructural with the recently reported sulphur analogue WSF_4. The reaction of PdI_2 with Se in liquid iodine has yielded single crystals of Pd_2SeI_3.[163] A structure determination showed the Pd atom to be in square planar coordination with 3I and one Se atom of a Se_2 group. The Se_2^{2-} group links four such squares to form $Pd_4Se_2I_4I_{4/2}$ units. The crystal structure of the tellurium compound, PdTeI was also described.

The reaction of the components in the systems $NdCl_3$-$TeCl_4$(and with $POCl_3$, $SeOCl_2$) and $SeOCl_2$-$TeCl_4$ (and with $POCl_3$) has been studied.[164] In the $SeOCl_2$-$TeCl_4$ system, a compound having the 1:2 composition, melting incongruently at 70°C is formed.

6.3.2 Selenium-Oxygen Compounds

The reaction of SeO_2 in aqueous solution with $Co(CN)_5OH_2^{2-}$ has been studied at pH values between 2 and 12 at 25°C.[165] The rate law was interpreted to mean that $HSeO_3^-$ was the reacting species and the proton dependence arose from the acid-base properties of an intermediate. The insertion of SeO_2 into the Sn-O bonds of bis(triorganotin)oxides $(R_3Sn)_2O$ has been shown to yield the monomeric selenites $(R_3SnO)_2SeO$.[166] Insertion of SeO_2 into the iron-methyl bond of η^5-$C_5H_5Fe(CO)_2CH_3$ gives the novel selenito complex, η^5-$C_5H_5Fe(CO)_2Se(O_2)CH_5$.[167]

The pure rotational Raman spectrum of SeO_3 monomer in the vapour state at 410K has been obtained and analysed for the first time.[168] Lattice parameter data has been obtained from single crystals of Se_2O_5 (monoclinic, $P2_{1/c}$, a = 458.5, b = 697.2, c = 1389 pm, β = 91.98°) prepared from solutions of Se(IV) and Se(VI) oxides in anhydrous selenic acid.[169]

The insertion of selenium and tellurium atoms into borane cage compounds has been performed using oxide reagents.[170] Reaction of $NaB_{11}H_{14}$ with an excess of $NaHSeO_3$ or solid TeO_2 in water-heptane under N_2 produced $B_{11}H_{11}Se$ or $B_{11}H_{11}Te$ respectively.

The crystal structures of several selenites have been determined. The paraelectric phase of $CsH_3(SeO_3)_2$ has been shown, by neutron diffraction data, to consist of H_2SeO_3 molecules and $HSeO_3^-$ ions hydrogen bonded together to form chains.[171] $Sc(HSeO_3)_3$ comprises octahedral Sc atoms linked by SeO_3 groups: the selenium atom forms the apex of a trigonal pyramid with oxygen atoms at the corners of the base triangle.[172] $FeH(SeO_3)_2$ consists of edge-sharing pairs of FeO_6 octahedra connected by one of the two non-equivalent Se atoms into layers.[173] The thermal dehydration of $ZnSeO_3.2H_2O$ and $MnSeO_3.2H_2O$ has been studied.[174]

Improved room temperature Raman spectra obtained from orientated single crystals of K_2SeO_4 have been reported and discussed.[175] The new results show that some of the earlier spectra reported for K_2SeO_4 contained spurious bands and that assignments were not entirely correct. The crystal structures of some selenates have been determined. The $RbHSeO_4$ structure has been shown to contain three independent molecules differing in the deformation of the $SeO_4{}^{2-}$ tetrahedra.[176] The structures of $ScH(SeO_4)_2.2H_2O$[177] and $HgSeO_4.H_2O$[178] have also been described.

6.3.3 Selenides

The new compounds NaCuSe, NaCuTe, KCuSe and KCuTe have been prepared and their structures determined.[179] NaCuSe and NaCuTe crystallize in a PbFCl type structure whilst KCuSe and KCuTe adopt the Ni_2In structure.

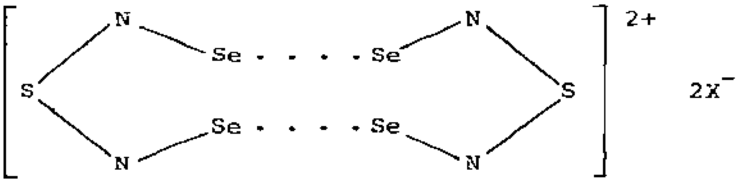
The reaction of CuSe with Cr_2Se_3 has been studied by electrical conductivity and D.T.A. measurements.[180] A mechanism for the formation of copper chromium selenospinel connected with the peritectic decomposition of CuSe was discussed. Reaction of $CuCr_2Se_4$ with the salts CuI, $CdCl_2$, NaCl and CuBr and with some salt mixtures has been studied and conditions for the preparation of single crystals of the spinel established.[181] An alternative preparation of single crystals of $CuCr_2Se_4$ has been described, based on the reaction of copper selenides with chromium trichloride.[182] Mixed crystals of the type $Cu_xZn_{1-x}Cr_2Se_4$ have been prepared and various reaction parameters described.[183]

Several phase systems involving selenium have been studied either in part or in full; these include; Tl-Pb-Se;[184] Tl-Ge-Se;[185] $TlCeSe_2$-$TlInSe_2$;[186] As_2Se_3-MnSe;[187] As_2Se_3-TlSe;[188] and M_2X-Sb_2X_3 (where M = K, Rb, Cs, and X = Se, Te).[189]

Crystal structures have been reported for the ternary selenides Ag_3AsSe_3,[190] β-Ag_9GaSe_6,[191] $Ag_4P_2Se_6$.[192] Selenides continue to be of interest as chalcogenide glasses. Studies have been carried out on glass formation in the Tl-Ge-Se and Pb-Ge-Se systems[193] and physical properties of glasses in the systems GeS-GeS_2-Sb_2S_3 and GeSe-$GeSe_2$-Sb_2Se_2 have been described.[194] The addition of organic components to selenide glasses has also been a subject of interest in this area.[195,196]

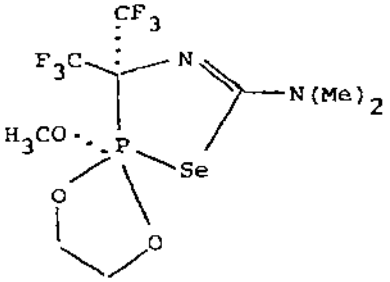
6.3.4 Other Compounds Containing Selenium

The selenium-nitrogen compound Se_4N_4 has been prepared in a new phase isostructural with S_4N_4, and the formation of two mixed sulphur-selenium-nitrogen compounds $(SSe_2N_2^+)_2(X^-)_2$ where X = Cl, Br reported.[197] On the basis of mass spectroscopic, i.r., and e.s.r. data the structure (39) was proposed for the compounds.



(39)

The reactions of SeS_2 with triphenyl compounds of Group 5 elements has been described.[198] No reaction was observed with Ph_3Sb, but with Ph_3P and Ph_3As compounds with the composition $Ph_3PS.Ph_3PSe$ and $Ph_3AsS.Ph_3AsSe$ respectively were obtained. I.r. data strongly suggested the formation of a solid solution of the type $Ph_3MS.Ph_3MSe$ rather than the formation of a sulphoselenide Ph_3MSe-$SMPh_3$. Two tri- and tetra-seleninato complexes of tin $RSn(O_2SeR)_3$ and $Sn(O_2SeR)_4$, R = C_6H_5, have been obtained from trichlorophenyltin and tetrachlorophenyltin with sodium benzeneseleninate.[199] A structure determination has shown that K_2(OSeC-CSeO) contains the 1,2-diseleno-oxalate anion with a trans planar coordination and a C-Se distance of 1.87Å.[200] The mechanism of the reaction between seleninic acids and thiols has been reported.[201] The seleninic acid derivatives R_3EO_2SeR' (E = Pb, Sn, Ge, Si, C; R = Me, Ph; R' = Me, Et, Ph) have been obtained by reaction of triorgano-Group 4 element halides, R_3EX (X = Cl, Br), with either sodium or silver seleninates.[202] Four possible reactions of phenyl vinyl selenide (CH_2=CH-SePh) have been discovered on treatment with nucleophiles or bases; Se-C cleavage, addition, metalation, or elimination.[203] The first selenophosphorane (40) has been prepared by the reaction of 5,5-bis(trifluoromethyl)-Δ^3-1,2,4-diselenazoline with 2-methoxy-1,3,2-dioxaphospholane at -30°C.[204]



(<u>40</u>)

Saturated tungstovanadium heteropolyacids of selenium(IV) have been prepared via the ether addition compounds.[205]

6.4 TELLURIUM

6.4.1 The Element

High resolution ^{125}Te and ^{123}Te Fourier transform n.m.r. spectroscopy has been used to identify the species formed in solutions of tellurium and selenium in 65% oleum at room temperature.[206] It was possible to identify all the members of this series $(Te_nSe_{4-n})^{2+}$ where n = 1 to 4 in the Te-Se-oleum system. The same technique using both ^{125}Te and ^{77}Se n.m.r. spectroscopy has been used to characterize the previously known $Te_6{}^{4+}$, $Te_4{}^{2+}$, $Se_4{}^{2+}$ and $Te_2Se_4{}^{2+}$ cations for the first time.[207] Several new mixed species in the +½ (Te_3Se^{2+}, <u>cis</u> and <u>trans</u> $Te_2Se_2{}^{2+}$ and $TeSe_3{}^{2+}$) and $\frac{1}{3}$ ($Te_3Se_3{}^{2+}$) oxidation states were also obtained. Solutions of Te in chlorosulphuric acid have also been studied using u.v. spectra, conductance and magnetic susceptibility methods.[208] Red solutions were identified as being due to the $Te_4{}^{2+}$ ion and yellow solutions the $Te_2{}^{2+}$ ion; furthermore the compounds $Te_4(SO_3Cl)_2$ and $Te_2(SO_3Cl)_2$ were isolated and characterized. The Te^- ion has been shown to be the dominant species present in molten LiCl-KCl and $LiF-BeF_2$, and the presence of higher tellurides such as Te_3^- was suggested.[209]

The equilibrium pressures of Te_2 vapour over molten $LiTe_3$ from 460 to 757°C and over solid mixtures of $LiTe_3$ and Li_2Te from 380 to 449°C have been measured using absorption spectroscopy.[210] The reduction of Te(IV) to the element by hydrazine has been investigated.[211] The influence of the concentrations of hydrogen ions, hydrazine and tellurium on the process was described and the reaction order relative to Te and hydrazine determined.

6.4.2 Bonds to Halogens

TeF_4 has been prepared by two different methods (equations 23 and 24) with sufficient purity to enable a determination of its heat of

$$TeO_2 + 2SeF_4 \longrightarrow 2SeOF_2 + TeF_4 \qquad (23)$$

$$Te + 2F_2 \longrightarrow TeF_4 \qquad (24)$$

fusion and calorific capacity.[212] Values determined were $\Delta H_{fus.}$, 3.02 kcal mol^{-1}; C_p from 298-402°K, 30 cal K^{-1} mol^{-1} for the solid, and at 423°K 31.1 cal K^{-1} mol^{-1} for liquid TeF_4.

The preparation and structures of cis and trans $F_4Te(OTeF_5)_2$, cis and trans $F_2Te(OTeF_5)_4$, $FTe(OTeF_5)_5$ and $Te(OTeF_5)_6$ have been described.[213] All the compounds were prepared by selective reactions starting with TeF_4 or $Te(OTeF_5)_4$; F_2, XeF_2 and $Xe(OTeF_5)_2$ were used as oxidizers. These new tellurium oxide fluorides are examples of the rules that the environments around tellurium have to be octahedral and that Te-O double bonds do not occur.

Elemental conductance measurements on the molten binary systems $TeCl_4$-$NbCl_5$ and $TeCl_4$-$TeCl_5$ at 240°C have shown a low degree of ionization in the melts.[214] Raman spectra of the molten 1:1 mixtures indicated the formation of $TeCl_3^+MCl_6^-$.

The crystal structure of tetrakis(ethylenethiourea)tellurium(II) hexachlorotellurate(IV) has been determined.[215] The structure is built up of $[Te(etu)_4]^{2+}$ cations and $[TeCl_6]^{2-}$ anions stacked in chains along the a axis. The coordination around the central tellurium atoms are square planar and octahedral for the cations and anions respectively. The average Te(II)-S bond length is 2.681Å and the average Te(IV)-Cl bond length is 2.530Å. Structural studies have shown that in phenylbis(selenourea)tellurium(II) chloride and phenylbis(thiourea)tellurium(II) chloride, each tellurium atom is primarily three coordinated, being bonded to one phenyl carbon atom and, in directions nearly perpendicular to the Te-C bond, to two selenourea selenium atoms or to two thiourea sulphur atoms.[216] The three centre systems Se-Te-Se and S-Te-S are nearly linear. The fourth position of a square planar arrangement around the tellurium atom is approached by the chloride ion, which lies 3.578Å from the tellurium.

The melting point diagram of the system $TeBr_4$-TeO_2 has been obtained by total pressure and D.T.A. measurements.[217] A congruently melting composition $Te_6O_{11}Br_2$ exists with a melting point of 570°C and an enthalpy of formation $\Delta H^o_{f,298}$ of -453.5 kcal/mol. The phase transition and the structure of the high temperature phase of CuTeBr have been determined.[218] Salts containing $[ArTeXY]^-$ X = Br, I; Y = Cl, Br, I; Ar = Aryl have been synthesized and preliminary crystallographic data reported.[219]

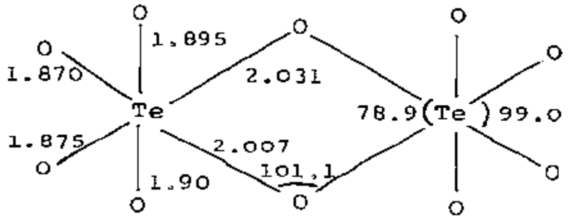
6.4.3 Bonds to Oxygen

A crystal structure determination of the cubic phase of telluric acid has shown it to possess bond distances in agreement with those of the monoclinic phase but to differ in bond angles.[220] The structure is built up of nearly ideal $Te(OH)_6$ octahedra connected via hydrogen bonds with each octahedron participating in six relatively strong and six weaker hydrogen bonds.

Solid state reactions of TeO_3 and $TeO_3.H_2O$ with M_2O and MOH (M = Na or K) have been shown to lead to the formation of the oxides Na_2TeO_4, K_2TeO_4, K_2TeO_3, $Na_4Te_2O_7$ and $K_4Te_2O_7$.[221] The interaction of TeO_3^{2-} with BH_4^- has been investigated.[222] At pH≤1.5 tellurite is reduced to Te(O) and H_2Te but in alkaline and borate buffer solutions a hydrosol of Te(O) is formed. The i.r. and laser-Raman spectra of crystalline $MgTe_2O_5$ have been measured and an assignment of the internal vibrations of the $Te_2O_5^{2-}$ ion undertaken.[223]

The stoichiometry of a tellurate-sucrose complex has been investigated by polarimetry and conductimetry.[224] The results showed that in addition to the expected 1:1 complex, a species of the type $(tellurate)_4$.sucrose is formed.

The crystal structures of several tellurates have been determined. Li_4TeO_5 contains the dimeric $Te_2O_{10}^{8-}$ ion made up of two edge sharing octahedral TeO_6 units (<u>41</u>) and may be described as having an NaCl type structure with Te and Li distributed over the cation positions.[225]



(41)

Dimeric units of the type $[Te_2O_6(OH)_4]^{4-}$ consisting of two octahedra sharing an edge have been found in the compound $Na_{0.5}K_{3.5}[Te_2O_6(OH)_4]$ $6H_2O$.[226] The structure is completed by Na^+, K^+ and water molecules held together by electrostatic interactions and hydrogen bonds. $K_2TeO_3.3H_2O$ contains pyramidal TeO_3^{2-} groups with Te-O bond lengths in the range 1.848-1.852Å and with an O-Te-O bond angle close to 100°.[227] These dimensions are considered to be representative of an unpolarized TeO_3^{2-} ion in which there is no back-bonding between the oxygen atoms and the Te^{4+} free electron pair. The structure of $K_2Te_4O_{12}$ is characterized by five oxygen coordination of the Te(IV) ion and the simultaneous presence of both Te(IV) and Te(VI) ions.[228] The compound $In_2Te_3O_9$ has been isolated in the In_2O_3-TeO_2 system and its structure shown to comprise sheets of TeO_3^{2-} anions and InO_6 groups linked in parallel chains.[229]

In the structure of $Pb_2Te_3O_8$, two of the crystallographically independent tellurium atoms are linked into endless chains parallel to the a axis by bridging oxygen atoms, and the other two are linked into isolated $[Te_3O_8]^{4-}$ ions.[230] The coordination of the tellurium atoms can be considered to be based on a tetrahedral arrangement of three oxygen atoms and a lone pair of electrons, or a trigonal bipyramidal arrangement of four oxygen atoms and the lone pair. Crystal structures have also been described for the compounds $CuTeO_4$[231] and Cu_3TeO_6.[232]

The thermal behaviour of $Co_4TeMo_3O_{16}$ and $CoTeMoO_6$ have been investigated and the thermal decomposition products identified; two new compounds Co_3TeO_6 and $Co_3Te_2MoO_{10}$ were also synthesized.[233] The reaction between tellurite, tungstate and vanadate in weakly acidic solutions have been studied.[234]

6.4.4 Tellurides

The first binary alkali-metal polytelluride, K_2Te_3, with Te_3^{2-} ions has been prepared and its structure determined.[235] The anionic components of the structure are bent Te_3 chain fragments with Te-Te distances of 280.2 and 280.5 pm which are thus shorter than in α-tellurium (283.4 pm), while the bond angle is slightly greater than in α-Te. The same ions have also been found in the compound In_2Te_5(II).[236] The structure consists of chains of four-membered Te-In rings alternating with, and cross-linked by the Te_3^{2-} polyanions. The average Te-Te distance in this unit was found to be 2.854Å with an included angle of 101.6°. The polyanions are linked by bonds of intermediate strength to form continuous chains of tellurium atoms running across the sheets of atoms.

Dimethyltin telluride has been shown to contain the first tin-tellurium six membered ring.[237] The trimeric character of the compound was derived from molecular weight, mass spectral and i.r. data. The compound $K_6(Si_2Te_6)$ the first member of a family of tellurodisilicates has been shown to contain discrete Si_2Te_6 groups in a staggered conformation.[238] The crystal structure of Ag_8GeTe_6 has also been determined.[239] The alloy CdTe has been prepared and its crystalline structure confirmed.[240] A series of new compounds $ABiTe_2$ where A is an alkali-metal have been prepared.[241] The phase and structural relations in the Rh-Te system from 66 to 74 atomic % between 400 and 1100°C have been studied.[242]

Among the phase diagrams involving tellurium that have been investigated this year are: Na_2Te-Sb_2Te_3,[243] Te-In-I,[244] $GaTe_3$-Bi_2Te_3,[245] MnTe-Bi_2Te_3,[246] Y_2Te_3-Bi_2Te_3,[247] Te-InI,[248] In_2Te_3-InI_3,[248] Ag_2Te-Tl_2Te.[249]

6.4.5 Other Compounds Containing Tellurium

Hydrogen sulphide and $TeCl_4$ have been shown to react in dichloromethane to yield substances of initially low tellurium content.[250] On fractional recrystallization an enhancement of tellurium is observed up to an atomic ratio of Te:Se = 1:5. X-ray investigation showed the compounds to have the composition TeS_7 and to be mixed crystals of S_8, TeS_7 and Te_2S_6. The compound $K_3(SH)TeS_3$ has been prepared and structurally characterized.[251] The SH^- ions are surrounded by an octahedron of K^+ ions and the TeS_3^{2-} anions from flat trigonal pyramids with Te-S distances of 234-8 pm.

Novel complexes of 2,2'-iminodiethanoldithiocarbamate (L) with Te(IV), Te(II) and Se(II), having the compositions TeL_4, TeL_2I_2, TeL_3I, TeL_2 and SeL_2 have been isolated and characterized.[252]

REFERENCES

1 D.L.Singleton and R.J.Cvetanović, Can. J. Chem., 56(1978)2934.
2 B.R.Puri and V.M.Arora, Indian J. Chem., 16A(1978)471.
3 S.S.Omer and D.H.Kerridge, J. Inorg. Nucl. Chem., 40(1978)975.
4 B.Gilbert and R.A.Osteryoung, J. Am. Chem. Soc., 100(1978)2725.
5 C.I.Chern, R.Di Cosimo, R.De Jesus and J.San Filippo, J. Am. Chem. Soc., 100(1978)7317.
6 J.P.McCormick and T.Thomason, J. Am. Chem. Soc., 100(1978)312.
7 D.T.Sawyer, M.J.Gibian, M.M.Morrison and E.T.Seo, J. Am. Chem. Soc., 100(1978)627.
8 W.C.Danen and R.L.Arundi, J. Am. Chem. Soc., 100(1978)3944.
9 J.L.Roberts, M.M.Morrison and D.T.Sawyer, J. Am. Chem. Soc., 100(1978)329.
10 J.M.Adams, R.G.Pritchard and J.M.Thomas, J. Chem. Soc. Chem. Commun., (1978)288.
11 H.M.Matheson and W.A.Whitla, Can. J. Chem., 56(1978)957.
12 D.E.Terault and R.R.Smardzewski, J. Am. Chem. Soc., 100(1978) 3955.
13 J.E.Griffiths, A.J.Edwards, W.A.Sunder, and W.E.Falconer, J. Fluorine Chem., 11(1978)119.
14 J.Steidel, J.Pickardt and R.Steudel, Z. Naturforsch., 33b(1978) 1554.
15 R.Steudel and H.-J.Mäusle, Angew. Chem. Int. Ed. Engl., 17(1978)56
16 R.Steudel and F.Schuster, J. Mol. Struct., 44(1978)143.
17 R.Steudel, J.Steidel, T.Sandow and F.Schuster, Z. Naturforsch., 33b(1978)1198.
18 R.Reinhardt, R.Steudel and F.Schuster, Angew. Chem. Int. Ed. Engl. 17(1978)57.
19 P.Taylor and T.E.Rummery, J. Inorg. Nucl. Chem., 40(1978)1444.
20 D.R.Salahub,A.E.Foti, and V.H.Smith, J. Am. Chem. Soc., 100 (1978)7847.
21 R.Fehrmann, N.J.Bjerrum and F.W.Poulsen, Inorg. Chem. 17(1978) 1195.
22 D.S.Todorovsky, A.K.Tomov and K.N.Kostadinov, Z. Anorg. Allg. Chem., 477(1978)244.
23 R.Steudel and J.Steidel, Angew. Chem. Int. Ed. Engl., 17(1978)134.
24 R.Steudel and T.Sandow, Angew. Chem. Int. Ed. Engl., 17(1978)611.
25 R.Huglen, F.W.Poulson, G.Mamantov, R.Marassi and G.M.Begun, Inorg. Nucl. Chem. Lett., 14(1978)167.
26 L.S.Bartell and S.K.Doun, J. Mol. Struct., 43(1978)245.
27 A.P.Babichev, V.D.Klimov, V.A.Kuz'menko, V.A.Legasov, and V.M.Petrov, Russ. J. Inorg. Chem., 23(1978)1105.
28 V.D.Klimov, V.A.Kuz'menko and V.A.Legasov, Russ. J. Inorg. Chem., 23(1978)1102.
29 R.J.H.Clark and N.R.D'Urso, J. Chem. Soc. Dalton Trans., (1978)170.
30 R.A.De Marco and W.B.Fox, J. Fluorine Chem., 12(1978)137.
31 R.W.Braun, A.H.Cowley, M.C.Cushner and R.J.Lagow, Inorg. Chem. 17(1978)1679.
32 G.Kleemann and K.Seppelt, Angew. Chem. Int. Ed. Engl., 17(1978)516.
33 W.Gombler, Z. Anorg. Allg. Chem., 439(1978)193.
34 H.Oberhammer and K.Seppelt, Angew. Chem. Int. Ed. Engl., 17(1978)69.
35 H.Oberhammer and K.Seppelt, Inorg. Chem., 17(1978)1435.
36 J.Czarnowski and H.J.Schumacher, J. Fluorine Chem., 12(1978)497.
37 C.J.Schack and K.O.Christe, Inorg. Nucl. Chem. Lett., 14(1978)293.
38 A.Haas and H.Willner, Spectrochim. Acta, 34A(1978)541.
39 D.N.Harpp, K.Steliou, and T.H.Chan, J. Am. Chem. Soc., 100(1978) 1222.
40 A.J.Edwards, J. Chem. Soc. Dalton Trans., (1978)1723.

41 G.Vahl and R.Minkwitz, Z. Anorg. Allg. Chem., 443(1978)217.
42 K.Manzel and R. Minkwitz, Z. Anorg. Allg. Chem., 441(1978)165.
43 R.D.Smith and G.B.Street, Inorg. Chem., 17(1978)938.
44 R.D.Smith, J.R.Wyatt, D.C.Weber, J.J.De Corpo and F.E.Saalfeld, Inorg. Chem., 17(1978)1639.
45 P.Love, H.I.Kao, G.H.Myer, and M.M.Labes, J. Chem. Soc. Chem. Commun., (1978)301.
46 M.P.S.Collins and B.J.Duke, J. Chem. Soc. Dalton Trans., (1978) 277.
47 A.R.Boate and K.F.Preston, Inorg. Chem., 17(1978)1669.
48 B.Solouki, H.Bock and O.Glemser, Z. Naturforsch., 33b(1978)284.
49 J.Howard, T.C.Waddington and E.Nachbaur, J. Chem. Soc. Dalton Trans., (1978)921.
50 I.Stahl, R.Mews, and O.Glemser, Z. Naturforsch., 33b(1978)1417.
51 R.Mews, Angew. Chem. Int. Ed. Engl., 17(1978)530.
52 J.J.Mayerle, J.Kuyper and G.B.Street, Inorg. Chem., 17(1978)2610.
53 H.W.Roesky, M.Diehl, H.Fuess, J.W.Bats, Angew. Chem. Int. Ed. Engl., 17(1978)58.
54 S.D.Morse and J.M.Shreeve, Inorg. Chem., 17(1978)2169.
55 B.Buss, D.Altena, R.Höfer and O.Glemser, J. Chem. Soc. Chem. Commun., (1978)226.
56 A.Herbrechtsmeier, F.M.Schnepel and O.Glemser, J. Mol. Struct., 50(1978)43.
57 U.Klingebiel, Z. Naturforsch., 33b(1978)950.
58 H.W.Roesky and G.Sidiropoulos, Chem. Ber., 111(1978)3460.
59 R.Eisenbarth, and W.Sundermeyer, Z. Naturforsch., 33b(1978)1194.
60 B.Buss, D.Altena, R.Mews and O.Glemser, Angew. Chem. Int. Ed. Engl., 17(1978)280.
61 R.Mews and H.C.Braeuer, Z. Anorg. Allg. Chem., 447(1978)126.
62 M.N.Hughes, J.R.Lusty, and H.L.Wallis, J. Chem. Soc. Dalton Trans., (1978)530.
63 D.E.Arrington, J. Chem. Res.(S), (1978)330.
64 J.D.Birchall and C.Glidewell, J. Chem. Soc. Dalton Trans., (1978) 604.
65 J.D.Birchall and C.Glidewell, Inorg. Chem. Acta, 28(1978)103.
66 F.M.Tesky, R.Mews, B.Krebs, and M.R.Udupa, Angew. Chem. Int. Ed. Engl., 17(1978)677.
67 H.W.Roesky and T.Müller, Chem. Ber., 111(1978)2960.
68 H.W.Roesky, E.Wehner, E.-J.Zehnder, H.-J.Deiseroth and A.Simon, Chem. Ber., 111(1978)1670.
69 H.W.Roesky, M.Aramaki and L.Schönfelder, Z. Naturforsch., 33b(1978) 1072.
70 J.Bojes and T.Chivers, Inorg. Chem., 17(1978)318.
71 J.Bojes and T.Chivers, I.Drummond and G.MacLean, Inorg. Chem., 17(1978)3668.
72 J.Bojes, T.Chivers, J. Chem. Soc. Chem. Commun., (1978)391.
73 I.Stahl, R.Mews, and O.Glemser, J. Fluorine Chem., 11(1978)455.
74 T.Kitazume and J.M.Shreeve, J. Am. Chem. Soc., 100(1978)985.
75 B.W.S.Kolthammer and P.Legzdins, J. Am. Chem. Soc., 100(1978) 2247.
76 D.L.Wagner, H.Wagner and O.Glemser, Z. Naturforsch., 33b(1978)300.
77 M.L.De Lucia and P.Coppens, Inorg. Chem., 17(1978)2336.
78 T.N.Guru Row and P.Coppens, Inorg. Chem., 17(1978)1670.
79 G.Wolmershauser and G.B.Street, Inorg. Chem., 17(1978)2685.
80 M.Akhtar, C.K.Chiang, A.J.Heeger, J.Millikan and A.G.MacDiarmid, Inorg. Chem., 17(1978)1539.
81 H.W.Roesky and B.Dederer, Z. Anorg. Allg. Chem., 440(1978)119.
82 A.Gieren, Ch.Hahn, B.Dederer, H.W.Roesky and N.Amin, Z. Anorg. Allg. Chem., 447(1978)179.
83 H.W.Roesky and M.Aramaki, Angew. Chem. Int. Ed. Engl., 17(1978) 129.

84 A.Turowski, R.Appel, W.Sawodny and K.Molt, J. Mol. Struct., 48(1978)313.

85 T.Chivers and L.Fielding, J. Chem. Soc. Chem. Commun., (1978)212.

86 R.Bartetzko and R.Gleiter, Inorg. Chem., 17(1978)995.

87 T.Chivers and J.Proctor. J. Chem. Soc. Chem. Commun., (1978)642.

88 R.B.Bruce, R.J.Gillespie and D.R.Slim, Can. J. Chem., 56(1978) 2927.

89 R.Steudel and F.Rose, Z. Naturforsch., 33b(1978)122.

90 B.Krebs, M.Hein, M.Diehl, H.W.Roesky, Angew. Chem. Int. Ed. Engl. 17(1978)778.

91 D.E.Smith and B.Munson, J. Am. Chem. Soc., 100(1978)497.

92 J.Stauff and W.Jaeschkle, Z. Naturforsch., 33b(1978)293.

93 L.T.Bugajenko and S.Schönherr, Z. Anorg. Allg. Chem., 438(1977) 279.

94 G.C.Thom, P.F.Waters and A.F.Hadermann, Inorg. Chem., 17(1978)1693.

95 N.J.Brassington, H.G.M.Edwards, D.W.Farwell, D.A.Long and H.R. Mansour, J. Raman Spectrosc., 7(1978)154.

96 A.Huss,Jr., P.K.Lim, and C.A.Eckert, J. Am. Chem. Soc., 100(1978) 6252.

97 M.A.Khan, S.Wasif and S.B.Salama, J. Chem. Soc. Dalton Trans., (1978)915.

98 S.B.Salama, S.Wasif and M.M.Omer, J. Chem. Soc. Dalton Trans., (1978)918.

99 J.Brunvoll, I.Hargittai and R.Seip, J.Chem. Soc. Dalton Trans., (1978)299.

100 M.Backhaus and C.Bliefert, Z. Naturforsch., 33b(1978)125.

101 R.Corkum and J.Milne, Can. J. Chem., 56(1978)1832.

102 J.O.Lundgren,Acta Crystallogr., B34(1978)2428.

103 J.O.Lundgren, Acta Crystallogr., B34(1978)2432.

104 R.Matsuzaki, H.Masumigu, N.Murakami and Y.Saeki, Bull. Chem. Soc. Jpn., 51(1978)121.

105 B.Nyberg, Acta Crystallogr., B34(1978)1418.

106 A.V.Gladkii, S.K.Fedorova and I.P.Skibida, Russ. J. Inorg. Chem., 23(1978)918.

107 A.J.Van den Berg and F.Tuinstra, Acta Crystallogr., B34(1978)3177.

108 R.A.Durie and J.W.Milne, Spectrochim. Acta, Part A, 34(1978)215.

109 S.Suzuki and Y.Makita, Acta Crystallogr., B34(1978)732.

110 Y.Elerman, A.Aydim Uraz and N.Armagan, Acta Cyrstallogr., B34(1978) 3330.

111 C.Th Kiers and A.Vos, Acta Crystallogr., B34(1978)1499.

112 C.Th Kiers, A.Piepenbrook and A.Vos, Acta Crystallogr., B34(1978) 888.

113 G.Gattow and B.Hanewald, Z. Anorg. Allg. Chem., 444(1978)112.

114 W.C.Vasudeva, M.R.Suliman and A.Hossady, J. Inorg. Nucl. Chem., 40(1978)1705.

115 G.G.Lezina, V.A.Lunenok-Burmakina, V.B.Emel'yanov and S.K.Rubanik, Russ. J. Inorg. Chem., 23(1978)457.

116 E.K.Jaffe and A.P.Zipp, J. Inorg. Nucl. Chem., 40(1978)839.

117 I.W.J.Still, S.K.Hasan, and K.Turnbull, Can. J. Chem., 56(1978) 1423.

118 W.E.Palke and B.Kirtman, J. Am. Chem. Soc., 100(1978)5717.

119 R.J.H.Clark and D.G.Cobbold, Inorg. Chem., 17(1978)3169.

120 W.Holzer, S.Racine and J.Cipriani, J. Raman Spectrosc., 7(1978)22.

121 I.R.Polyvyannyi, V.A.Lata, and V.I.Antonyuk, Russ. J. Inorg. Chem., 23(1978)91.

122 A.A.Gotuk, M.B.Babanly and A.A.Kuliev, Russ. J. Inorg. Chem., 23 (1978)472.

123 T.Yasumura, and R.J.Lagow, Inorg. Chem., 17(1978)3108.

124 M.Robineau and D.Zins, Rev. Chim. Minerale, 15(1978)278.

125 A.Feltz and G.Pfaff, Z. Anorg. Allg. Chem., 442(1978)41.

126 C.Calvo, R.J.Gillespie, J.E.Vekris and H.N.Ng, Acta Cyrstallogr., B34(1978)911.
127 L.Fournes and M.Vlasse, Rev. Chim. Minerale, 15(1978)542.
128 A.H.Stiller, B.J.McCormack, P.Russell and P.A.Montano, J. Am. Chem. Soc., 100(1978)2553.
129 G.Krabbes, H.Opermann and J.Henke, Z. Anorg. Allg. Chem., 442 (1978)79.
130 A.Müller, W.-O.Nolte, and B.Krebs, Angew. Chem. Int. Ed. Engl., 17(1978)279.
131 A.Müller, S.Sarkar, R.G.Bhattacharyya, S.Pohl and M.Dartmann, Angew. Chem. Int. Ed. Engl., 17(1978)535.
132 M.Spangenberg, and W.Bronger, Z. Naturforsch., 33b(1978)482.
133 Chr.L.Teske, Z. Anorg. Allg. Chem., 445(1978)193.
134 A.Müller, H.Domfield, G.Henkel, B.Krebs and M.P.A.Viegars, Angew. Chem. Int. Ed. Engl., 17(1978)52.
135 A.A.Kuliev, M.M.Asadov, R.A.Kuliev, and M.B.Babanly, Russ. J. Inorg. Chem., 23(1978)474.
136 A.A.Grizik, A.A.Eliseev, V.A.Tolstova, and G.P.Borodulenko, Russ. J. Inorg. Chem., 23(1978)330.
137 A.A.Eliseev, A.A.Grizik, F.P.Borodulenko and V.A.Tolstova, Russ. J. Inorg. Chem., 23(1978)328.
138 J.Dugué, D.Carré and M.Guittard, Acta Crystallogr., B34(1978)403.
139 G.Bugli, D.Carré and S.Barnier, Acta Crystallogr., B34(1978)3186.
140 A.A.Eliseev, G.M.Kuz'micheva, and V.I.Yashnov, Russ. J. Inorg. Chem., 23(1978)273.
141 E.Diemann and A.Müller, Z. Anorg. Allg. Chem., 444(1978)181.
142 M.Schmidt and E.Weissflog, Angew. Chem. Int. Ed. Engl., 17(1978)51.
143 E.Weissflog and M.Schmidt, Z. Anorg. Allg. Chem., 445(1978)175.
144 C.Scrimanger and L.J.Dehayes, Inorg. Nucl. Chem. Lett., 14(1978) 125.
145 S.Bielak, K.Mennemann and R.Mattes, Z. Naturforsch., 33b(1978)465.
146 W.Gombler, Z. Anorg. Allg. Chem., 439(1978)207.
147 F.M.Capece, C.Furlani, G.Mattogno, E.Paparazzo and G.Polzonetti, J. Inorg. Nucl. Chem., 40(1978)467.
148 J.K.Pau, M.B.Ruggera, J.K.Kim and M.C.Caserio, J. Am. Chem. Soc., 100(1978)4242.
149 S.Kato, K.Sugino, M.Mizuta and T.Katada, Angew. Chem. Int. Ed. Engl., 17(1978)675.
150 T.Kitazume, and J.M.Shreeve, Inorg. Chem., 17(1978)2173.
151 W.A.Pryor and E.G.Olsen, J. Am. Chem. Soc., 100(1978)2852.
152 G.L'Abbé, J.-P.Dekerk, J.-P.Declercq, G.Germain and M.V.Meerssche, Angew. Chem. Int. Ed. Engl., 17(1978)195.
153 K.Brodersen and G.Jordan, Chem. Ber., 111(1978)1221.
154 D.Horner and G.Gattow, Z. Anorg. Allg. Chem., 440(1978)246.
155 D.Horner and G.Gattow, Z. Anorg. Allg. Chem., 442(1978)195.
156 D.Horner and G.Gattow, Z. Anorg. Allg. Chem., 442(1978)204.
157 D.Horner and G.Gattow, Z. Anorg. Allg. Chem., 444(1978)117.
158 K.Hamada and H.Morishita, J. Mol. Struct., 44(1978)119.
159 A.D.Westland and R.Makhija, Can. J. Chem., 56(1978)1586.
160 V.G.Tsvetkov, Russ. J. Inorg. Chem., 23(1978)1086.
161 K.Hagen, V.R.Cross and K.Hedberg, J. Mol. Struct., 44(1978)187.
162 M.J.Atherton and J.H.Holloway, Inorg. Nucl. Chem. Lett., 14(1978) 121.
163 G.Thiele, M.Kohler-Degner, K.Wittmann and G.Zoubek, Angew. Chem. Int. Ed. Engl., 17(1978)852.
164 V.V.Safonov, E.A.Fedorov and V.G.Lebedev, Russ, J. Inorg. Chem., 23(1978)1088.
165 K.R.Ashley and Y.Jan, J. Inorg. Nucl. Chem., 40(1978)1099.
166 E.Lindner and U.Ansorge, Chem. Ber., 111(1978)2455.
167 I.P.Lorenz, Angew. Chem. Int. Ed. Engl., 17(1978)53.

168 N.-J.Brassington, H.G.M.Edwards, D.A.Long and M.Skinner, J. Raman Spectrosc., 7(1978)158.

169 Z.Zak and K.Dostal, Collect. Czech. Chem. Commun., 43(1978)2509.

170 G.D.Friesen and L.J.Todd, J. Chem. Soc. Chem. Commun., (1978)349.

171 S.Chomnilpan, R.Tellgren and R.Liminga, Act Crystallogr., B34(1978) 373.

172 J.Valkonen and M.Leskela, Acta Crystallogr., B34(1978) 1323.

173 J.Valkonen and M.Koskenlinna, Acta Crystallogr., A32(1978)603.

174 R.Ya.Mel'nikova, V.N.Makatun, V.V.Pechkovstii, A.K.Potapovich and V.Z.Drapkin, Russ. J. Inorg. Chem., 23(1978)382.

175 C.Caville, V.Fawcett and D.A.Long, J. Raman Spectrosc., 7(1978)43.

176 A.Waskowska, S.Olejnik, K.Lukaszewicz and T.Glowiak, Acta Crystallogr., B34(1978)3344.

177 J.Valkonen, Acta Crystallogr., B34(1978)3064.

178 C.Stalhandske, Acta Crystallogr., B34(1978)1408.

179 G.Savelsberg and H.Schafer, Z. Naturforsch., 33b(1978)370.

180 I.Okonska-kozlowska and J.Heimann, Z. Anorg. Allg. Chem., 447(1978) 230.

181 M.A.Chernitsyna, V.T.Kalinnikov, A.A.Babitsyna and T.A.Emelyanova, Russ. J. Inorg. Chem., 23(1978)77.

182 A.A.Babitsyna, T.A.Emelyanova, M.A.Chernitsyna, and V.T.Kalinnikov, Russ. J. Inorg. Chem., 23(1978)151.

183 I.Okonska-Kozlowska and J.Krok, Z. Anorg. Allg. Chem., 447(1978) 235.

184 Z.M.Latypov and N.R.Faizullina, Russ. J. Inorg. Chem., 23(1978)142.

185 E.Yu.Turkina, I.N.Kozhina, G.M.Orlova, and A.A.Obraztsov, Russ. J. Inorg. Chem. 23(1978)276.

186 E.M.Godzhaev, V.A.Mamedov, K.D.Orudzhev, A.A.Adilov, G.G.Guseinov, and Z.F.Mamedov, Russ. J. Inorg. Chem., 23(1978)89.

187 P.G.Rustamov, M.G.Safarov, I.I.Aliev, and T.M.Il'yasov, Russ. J. Inorg. Chem., 23(1978)84.

188 P.G.Rustamov, M.G.Safarov and I.I.Aliev, Russ. J. Inorg. Chem., 23(1978)1251.

189 L.M.Kovba, V.B.Lazarev, N.A.Moshchalkova, and A.V.Salov, Russ. J. Inorg. Chem., 23(1978)426.

190 K.Sakai, T.Koide, P.T.Matsumoto, Acta Crystallogr., B34(1978)3326.

191 J.P.Deloume, R.Faure and H.Loiseleur, Acta Crystallogr., B34(1978) 3189.

192 P.Toffoli, P.Khodadad, and N.Rodier, Acta Crystallogr., B34(1978) 1779.

193 D.Linke, M.Gitter and F.Krug, Z. Anorg. Allg. Chem., 444(1978)217.

194 D.Linke and G.Eberhardt, Z. Anorg. Allg. Chem., 442(1978)263.

195 D.Herrmann and H.Scheel, Z. Anorg. Allg. Chem., 442(1978)119.

196 D.Herrmann, W.Monheim, R.Gollmick and W.Wagner, Z. Anorg. Allg. Chem., 442(1978)125.

197 G.Wolmershauser, C.R.Brulet, and G.B.Street, Inorg. Chem., 17(1978) 3586.

198 V.Krishnam, A.Datta and S.V.L.Narayana, Inorg. Nucl. Chem. Lett., 13(1977)517.

199 E.Lindner and U.Ansorge, Z. Naturforsch., 33b(1978)341.

200 C.Matz and R.Mattes, Z. Naturforsch., 33b(1978)461.

201 J.L.Kice and T.W.S.Lee, J. Am. Chem. Soc., 100(1978)5094.

202 U.Ansorge, E.Lindner and J.Strahle, Chem. Ber., 111(1978)3048.

203 M.Sevrin, J.N.Denis, and A.Krief, Angew. Chem. Int. Ed. Engl., 17(1978)526.

204 K.Burger, R.Ottlinger, A.Frank, and U.Schubert, Angew. Chem. Int. Ed. Engl., 17(1978)774.

205 L.V.Derkach, L.Ni, and E.Herzberg, Russ. J. Inorg. Chem., 23(1978) 846.

206 C.R.Lassigne and E.J.Wells, J. Chem Soc. Chem. Commun., (1978)956.

207 G.J.Schrobilgen, R.C.Burns, and P.Granger, J. Chem. Soc. Chem. Commun., (1978)957.

208 R.C.Paul, D.Konwer, D.S.Dhillon and J.K.Puri, Indian J. Chem., (1978)253.

209 L.M.Toth and B.F.Hitch, Inorg. Chem., 17(1978)2207.

210 B.F.Hitch, L.M.Toth, and J.Brynestad, J. Inorg. Nucl. Chem., 40(1978)31.

211 G.A.Kitaev, N.M.Kondrat'eva, and L.D.Loshkareva, Russ. J. Inorg. Chem., 23(1978)1142.

212 J.Carré, P.Claudy, M.Kollmannsberger, J.Bousquet, E.Garnier and P.Barberi, J. Fluorine Chem., 11(1978)613.

213 D.Lentz, H.Pritzkow and K.Seppelt, Inorg. Chem., 17(1978)1926.

214 F.W.Poulsen, and R.W.Berg, J. Inorg. Nucl. Chem., 40(1978)471.

215 H.K.Ault and S.Husebye, Acta Chem. Scand., A32(1978)157.

216 S.Hauge, O.Johannesen and O.Vikane, Acta. Chem. Scand., A32 (1978)901.

217 H.Oppermann, V.A.Titov, G.Kunze, G.A.Kokovin, and E.Wolf, Z. Anorg. Allg. Chem., 439(1978)13.

218 U.V.Alpen, J.Fenner, B.Predel, A.Rabenau, and G.Schluckebier, Z. Anorg. Allg. Chem., 438(1978)5.

219 P.Klaeboe, C.J.Nielsen, R.Suchi and O.Vikane, Acta Chem. Scand., A32(1978)565.

220 L.Falck and O.Lundqvist, Acta Crystallogr., B34(1978)3145.

221 E.Gutierrez-Rios, M.L.Veiga and C.Pico, J. Chem. Soc. Dalton Trans., (1978)948.

222 E.S.Kotelevets, V.S.Khain and E.N.Marinova, Russ. J. Inorg. Chem., 23(1978)374.

223 E.J.Baran, Z. Anorg. Allg. Chem., 442(1978)112.

224 W.J.Popiel and M.S.Rushton, J. Inorg. Nucl. Chem., 40(1978)921.

225 J.Moret, F.Daniel, W.Loeksmanto, M.Maurin and E.Philippot, Acta Crystallogr., B34(1978)3156.

226 B.Kratochvil, J.Podlahova, and L.Jensovsky, Acta Crystallogr., B34(1978)256.

227 G.B.Johansson, and O.Lindqvist, Acta Crystallogr., B34(1978)2959.

228 F.Daniel, J.Moret, M.Maurin and E.Philippot, Acta Crystallogr., B34(1978)1782.

229 E.Philippot, R.Astier, W.Loeksmanto, M.Maurin, and J.Moret, Rev. Chim. Minerale, 15(1978)283.

230 J.C.Dewan, A.J.Edwards, G.R.Jones, and I.M.Young, J. Chem. Soc. Dalton Trans., (1978)1528.

231 L.Falck, O.Lindqvist, W.Mark, E.Philippot, and J.Moret, Acta Crystallogr., B34(1978)1450.

232 L.Falck, O.Lindqvist, and J.Moret, Acta Crystallogr., B34(1978) 896.

233 J.Sloczynski, Z. Anorg. Allg. Chem., 438(1978)287.

234 T.K.Nikitina and E.Sh.Ganelina, Russ. J. inorg. Chem., 23(1978)44.

235 B.Eisenmann and H.Schafer, Angew. Chem. Int. Ed. Engl., 17(1978) 684.

236 P.D.Walton, H.H.Sutherland and J.H.C.Hogg, Acta Crystallogr., B34(1978)41.

237 A.Blecher and B.Mathiasch, Z. Naturforsch., 33b(1978)246.

238 G.Dittmar, Acta Crystallogr., B34(1978)2390.

239 J. von Unterrichter and K.J.Range, Z. Naturforsch., 33b(1978)866.

240 F.Climent-Montoliu and A.G.Vives, Z. Anorg. Allg. Chem., 446(1978)208.

241 A.F.Trippel, V.B.Lazarer, and S.I.Berul, Russ. J. Inorg. Chem., 23(1978)390.

242 A.Kjekshus, T.Rakke and A.F.Andresen, Acta Chem. Scand., A32(1978) 209.

243 L.M.Kovba, V.B.Lazarev, N.A.Moshchalkova and A.V.Salov, Russ. J. Inorg. Chem., 23(1978)279.

244 V.V.Safonov, S.M.Chernykh and B.G.Korshunov, Russ. J. Inorg. Chem., 23(1978)271.

245 M.G.Shakhbazor, N.A.Seidova and P.G.Rustamov, Russ. J. Inorg. Chem., 23(1978)140.

246 P.G.Rustamov, S.A.Sadykhova, and M.G.Safarov, Russ. J. Inorg. Chem., 23(1978)87.

247 P.G.Rustamov, F.M.Sadygov, Z.D.Melikova and M.G.Safarov, Russ. J. Inorg. Chem., 23(1978)471.

248 S.M.Chernykh and V.V.Safonov, Russ. J. Inorg. Chem., 23(1978)465.

249 V.T.Abishov, M.B.Babanly and A.A.Kuliev, Russ. J. Inorg. Chem., 23(1978)1089.

250 M.Pupp and J.Weiss, Z. Anorg. Allg. Chem., 440(1978)31.

251 G.Dittmar and H.Schafer, Z. Anorg. Allg. Chem., 439(1978)212.

252 B.G.Sejekan, C.Janakiram and G.Aravamudan, J. Inorg. Nucl. Chem., 40(1978)211.