Coordination Chemistry Reviews, 103 (1990) 162–236
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

Chapter 6
ELEMENTS OF GROUP 6

M.G.Barker

6.1 OXYGEN 163

6.2 SULPHUR

6.2.1 The Element 168
6.2.2 Bonds to Halogens..171
6.2.3 Bonds to Nitrogen 174
6.2.4 Bonds to Oxygen 190
6.2.5 Sulphides 194
6.2.6 Bonds to Carbon..203

6.3 SELENIUM

6.3.1 The Element and Cationic Species..207
6.3.2 Bonds to Halogens..208
6.3.3 Bonds to Oxygen 210
6.3.4 Selenides 210
6.3.5 Bonds to Nitrogen..213
6.3.6 Bonds to Carbon..214

6.4 TELLURIUM & POLONIUM

6.4.1 The Element 215
6.4.2 Bonds to Halogens..215
6.4.3 Bonds to Oxygen 216
6.4.4 Tellurides..217
6.4.5 Bonds to Carbon..219
6.4.6 Other Compounds of Tellurium..219

REFERENCES 222

6.1 OXYGEN

The generation of singlet O_2 from triethylsilane and ozone at 195K in useful yields, as shown in equation (1) has been demonstrated.[1]

$$Et_3SiH + O_3 \longrightarrow Et_3SiOOOH \longrightarrow Et_3SiOH + {}^1\Delta_gO_2 \qquad \ldots(1)$$

The reaction of ozone with $MeSiH_3$ after irradiation in an argon matrix has been shown to give Me(H)SiO and irradiation of similar Me_2SiH_2 and ozone samples produces Me_2SiO. Both compounds are considered to have a silicon- oxygen double bond.[2]

The dinuclear manganese complexes, $[L_2Mn(\mu\text{-}O)_2MnL_2]^{3+}$ where L=2,2'-bi- pyridyl or 1,10-phenanthroline, have been shown to oxidise water with the formation of visible oxygen bubbles when suspended in water in the presence of an oxidant such as Ce(IV) ion. The bipyridyl complex was found to be the more efficient catalyst and both were only catalytic in the solid form.[3] The same group have also shown that a series of di- and tri-nuclear ruthenium complexes generate oxygen from water as both homogeneous and heterogeneous catalysts. Whilst the trinuclear complexes were clearly the more efficient catalysts they did undergo some decomposition during the catalytic process.[4] It has been reported that the addition of a catalytic amount of Ce(IV) salt accelerates the autoxidation of thioethers by at least a factor of 1000, even at low pressures (100 psig oxygen) and temperatures (373K), affording a synthetically useful reaction. The reaction is thought to proceed by a true catalytic pathway in which the oxygenated radical cation oxidises Ce(III) to Ce(IV) with production of the zwitterion R_2SOO^-.[5]

$$\overset{+}{R_2S}OO^{\cdot} + Ce(III) \longrightarrow \overset{+}{R_2S}OO^- + Ce(IV) \qquad \ldots(2)$$

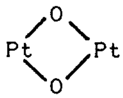
The passage of fluorine over ice at temperatures of about 223K produces a mixture of oxygen, HOF and OF_2 along with small amounts of hydrogen peroxide. The involvement of HOF in the formation of OF_2 was demonstrated by using HOF labelled both with ^{18}O and with radioactive ^{18}F. The reaction which produces the OF_2 was shown to be

$$F_2 + HOF \longrightarrow OF_2 + HF \qquad \ldots(3)$$

The OF_2 produced contained one fluorine atom from F_2 and one from HOF.[6] The substitution of oxygen-18 for oxygen-16 results in detectable upfield shifts on the n.m.r. signals of many nuclei when they are directly bonded to oxygen. These shifts can be used to follow enzymatic and nonenzymatic oxygen exchange reactions ocurring at carbon, phosphorus and nitrogen. A method for the preparation of nitrogen-15, oxygen-18 dual labelled hydroxylamine hydrochloride has been undertaken since hydroxylamine can serve as a key intermediate in the synthesis of a variety of compounds including many important heterocycles that contain N-O groupings.[7]

The vaporization of silver in a stream of oxygen at 884-994K has been measured. By varying the oxygen pressure and the activity of silver it was shown that the gas phase product was Ag_2O. After long periods of time the silver became coated with oxygen or silver oxide which decreased the concentration of Ag_2O in the gas phase.[8]

A review of oxidative damage in biological systems has shown that, despite being variable in terms of the different kinds of compounds afflicted, oxidative damage is ultimately exerted only by a small number of different reactive oxygen species.[9] Ab initio calculations have been performed on the Cu^{2+} - superoxide system by considering the effects of an ammonia ligand on copper and of an ammonium ion interacting with the superoxide. The calculations show that an intermediate Cu^{2+}-O^{2-} is stable as long as the superoxide is hydrogen bonded to the ammonium ion. A second superoxide ion may reduce Cu(II). Once Cu^{+} - superoxide is formed a pathway for the formation of a covalent bond between the superoxide ion and the ammonium proton exists. The copper-oxygen distance increases and a second proton binds the proximinal oxygen which causes electron flow from Cu(I) to the superoxide ion thus providing a Cu(II)-H_2O_2 system.[10] It has been reported that the dimer of $(Me_4N)O_2$ is actually a peroxide adduct of acetonitrile [$MeC(OO^-)$=NH], which hydrolyzes to the base adduct of acetamide [$MeC(O^-)(OH)NH_2$] and that the previously reported synthesis of $(Me_4N)O_2$ can yield substantial amounts of $(Me_4N)OH$ and $(Me_4N)OOH$. However a new synthetic route provides a purer and more consistent product in higher yields when $(Me_4N)OH.H_2O$ or $(Me_4N)_2CO_3$ is combined with KO_2 to produce $(Me_4N)O_2$.[11] The radiolysis of trimethylamine in N_2O/O_2 saturated basic solutions eventually gives dimethylamine, formaldehyde and hydrogen peroxide. The (dimethylamino)methyl radical, formed by the attack of a hydroxyl radical on trimethylamine, reacts rapidly with oxygen to give the superoxide ion radical and dimethylimonium, possibly via a short lived peroxyl radical. This is then hydrolyzed to dimethylamine and formaldehyde hydrate.[12] The photochemical decomposition of the trioxo- dinitrate ion has been shown to yield the reactive intermediate NO- which can appear in solution in singlet and triplet states. In the presence of oxygen saturated solutions triplet NO^- is converted quantitatively to peroxonitrite.[13]

The reaction between permanganate ion and hydrogen peroxide occurs in three stages: a fast initial phase, an induction period, and an autocatalytic step. The reaction is autocatalytic because manganous ion, a product of the reaction, catalyzes the reaction by combining with permanganate ion to form a complex whose breakdown products react faster with peroxide than does the complex. Retardation of the first phase to give the induction period is also due to manganous ion, which preferentially binds to permanganate, forming a relatively non-reactive intermediate, thus shutting down the first phase.[14] The oxidations of H_2O_2 and of HO_2^- by $[(bpy)_2(py)Ru(IV)(O)]^{2+}$ and $[(bpy)_2(py)Ru(III)(OH)]^{2+}$ have been studied in aqueous solution. It was proposed that $[(bpy)_2(py)Ru(III)(OH)]^{+}$ is the initial product of the oxidation of H_2O_2 by $Ru(IV)=O^{2+}$ rather than $[(bpy)_2(py)Ru(II)(OH_2)]^{2+}$, and that the oxidation of H_2O_2 by both $Ru(IV)=O^{2+}$ and $Ru(III)-OH^{2+}$ occurs by H atom (1e-1 H^+) transfer.[15] The reaction of H_2O_2, $S_2O_3^{2-}$, and cyanide at pH 7-9 has been shown to produce thiocyanate and sulphate. In the absence of cyanide a mixture of sulphate and $S_4O_6^{2-}$ was produced with low pH and excess thiosulphate favouring formation of $S_4O_6^{2-}$. The literature erroneously reports $S_3O_6^{2-}$ as the product in neutral solution.[16] The reaction between H_2O_2 and KSCN catalyzed by $CuSO_4$ exhibits three different types of bistability as a function of flow rate in that two steady states and one oscillatory state are involved. This system is one of the few in which oscillations can appear in batch configuration as well.[17] The dinuclear complex ion $[cis\text{-}Pt(II)(NH_2CH_2CH_3)_2(u\text{-}OH)]_2^{2+}$ has been shown to undergo oxidation in aqueous H_2O_2 to produce dinuclear Pt(IV) ions of the type $[cis\text{-}Pt(IV)(NH_2CH_2CH_3)_2(OH)_2(\mu\text{-}OH)]_2^{2+}$. Following the reaction by using ^{195}Pt n.m.r. spectroscopy and isolation of the major product revealed that oxidation primarily yields a D_{2h}-symmetry dinuclear compound having a four membered  ring. However, the fact that the reaction also yields lower symmetry dinuclear Pt(IV) compounds possessing this ring indicates that the oxidation, at least in part, proceeds through an "open ring" intermediate that allows isomerization to occur.[18] Near stoichiometric concentrations of H_2O_2 partially bleached the 350nm absorption band of the iron-containing superoxide dismutase from Escherichia coli. Concomitantly the high-spin Fe(III) EPR signals decreased in intensity. Thus peroxide reduces the Fe(III) ions in superoxide dismutase, which then slowly reoxidise. The pH dependence of this reaction implies HO_2^- as the actual reductant.[19]

A study of the redox chemistry of hydrogen peroxide in anhydrous acetonitrile has shown that under anhydrous conditions H_2O_2 is oxidised by a single-electron-transfer-step to HO_2, which a) is further oxidised to O_2 by a second electron transfer or b) disproportionates to H_2O_2 and O_2.[20] The net reduction of peroxotitanium(IV) by sulphur(IV) in acidic solution has been shown to proceed by a rate-determining dissociation of peroxide from TiO_2^{2+} followed by the rapid reaction of H_2O_2 and HSO_3^-. The absence of a detectable direct reaction between TiO_2^{2+} and either SO_2 or HSO_3^- is consistent with the previously proposed electrophilic nature of the peroxide moiety when coordinated to a d^0 transition-metal ion.[21]

Proton n.m.r. spectra have shown the existence of the oxonium ion in the solid basic aluminium sulphate, $3Al_2O_3.4SO_4.9H_2O$. From the results of other investigations it follows that the ion is fast bonded in the structure and that only a small amount of mobile charge carriers are present [22]. The salt $[H_7O_3]^+As(catecholate)_3]^-$p-dioxane has been shown to contain a distinct $H_7O_3^+$ unit. The proton positions were not well determined but the structure was presumed to be the same as that found by neutron diffraction. The O-O bond lengths were between 238.2 and 260.9pm and the O-O-O bond angles between 113.6 and 110.7° [23]. The inelastic neutron scattering spectrum of dodecatungstophosphoric acid hydrate shows the presence of at least one type of $H_5O_2^+$ ion, and most of the normal co-ordinates of a near planar $H_5O_2^+$ ion can be fitted to the observed spectrum, except that in the spectral region of the terminal HOH deformations, there is disagreement between the observed and calculated profiles. This was taken as evidence of disorder of the oxygen atoms about the planar positions [24].

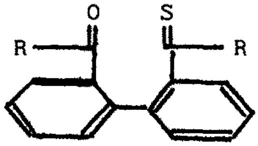
Several papers have reported the binding of dioxygen to metal complexes. X-Ray structural studies on $[Al_2(Me)_6(O_2)]^-$ showed a new bridging co-ordination mode of the dioxygen ligand, with O-O distance and stretching frequency close to the values observed in solid Na_2O_2. However on the basis of results obtained from ab initio molecular orbital-linear combination of atomic orbital calculations, a different description of the electronic structure was proposed. Despite the fact that the co-ordinated O_2 ligand carries a small negative charge, the computed bond length and harmonic frequency are close to the theoretical values expected for the gaseous O_2^- species. As a consequence the authors propose the classification of the dioxygen complex as a peroxo or superoxo complex to be of little help in elucidating the real structure of the dioxygen ligand.[25] The oxidation of some cobalt(II) pentammine complexes with molecular oxygen takes place through the formation of μ-peroxo-bridged cobalt(III) dioxygen complexes and ultimately results in either oxidative dehydrogenation of the coordinated ligand or simple "metal-centered" oxidation to form cobalt(III) complexes of the unchanged ligand and hydrogen peroxide. The cobalt (II) complexes that have undergone oxidative dehydrogenation react with dioxygen to give new dioxygen complexes that undergo further oxidative dehydrogenation.[26] Cobalt(II) ion exchanged zeolite Y has been treated with a flexible Schiff base ligand, SALEN, so as to synthesise the Co(II) complex inside the pore structure of the zeolite itself. Such a complex is rigid and of such a size that it is physically entrapped inside the pore. The complex, as its pyridine adduct, shows affinity for oxygen and forms 1:1 adducts. The adduct forms at a rate limited by the diffusion of oxygen into the zeolite and with a binding constant similar to the same species in solution.[27] The results of a thermodynamic study of base and dioxygen binding to the cobalt(II) Schiff base complex, Co(4,6-CH_3Osal-4-CF_3oph) have been compared with those reported for porphyrin complexes in order to evaluate the effect that variation in the cis ligands of the dioxygen adduct has on the cobalt-oxygen bond strength. Even though oxygen is more electronegative, the N_2O_2

ligand set of the Schiff base leads to a less acidic metal centre than the N_4 ligand set of the porphyrin and thus the Schiff base complex binds oxygen more strongly.[28] Copper(I) complexes of a series of acyclic Schiff base ligands have been shown to bind CO and oxygen at comparable rates. All the complexes bind CO reversibly in MeCN solution but the oxygen binding is partially reversible in some cases.[29] The enrichment of oxygen in an air sample that was passed through polystyrene which contained a supported Co(II) Schiff base complex as an additive has been reported. The polymer bound complexes can be cycled several times and oxygen enrichment of the permeate gases observed but ESR experiments indicated irreversible oxidation over several days.[30] Rate constants associated with the binding of oxygen to hemerythrin and hemocyanin have been determined. The changes in rate constants on replacing H_2O with D_2O indicate hydrogen bonding effects in the case of the oxy forms of hemerythrin and myoglobin but not in the case of hemocyanin. The results obtained support the recently proposed structure for binding of oxygen at the hemerythrin active site.[31] The reaction of hexa-aquamolybdenum(III) with oxygen in p-toluenesulphonic acid solutions gives the di-μ-oxo- molybdenum(V)ion $[Mo_2O_4(H_2O)_6]^{2+}$ as product. Use of isotopically labelled oxygen has demonstrated that at least some ^{18}O is taken up in the μ-oxo positions. With Mo^{3+} in large excess an intense yellow intermediate, MoO_2Mo^{6+} was observed, but there was no evidence for its formation when oxygen was in excess of Mo^{3+}.[32]

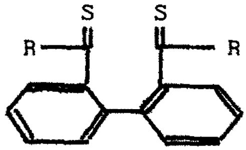
6.2 SULPHUR

6.2.1 The Element

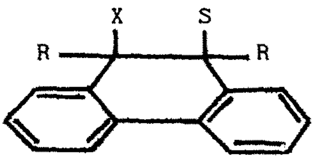
An alternative synthetic method for the preparation of the reactive dienophile S_2 by an intramolecular carbon-carbon bond forming reaction has been described. The monothione derivatives (1) were found to be blue and quite stable, however their corresponding bis(thiocarbonyl) analogues (2) which were an intense blue were found to spontaneously eject S_2 giving, via the intermediates (3), a quantitative yield of (4). The authors hope to design a stable dithione which, on gentle heating, will generate S_2 at will.[33]



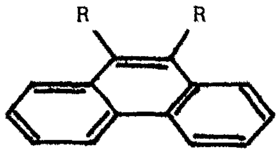
(1)



(2)



(3)

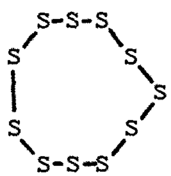


(4)

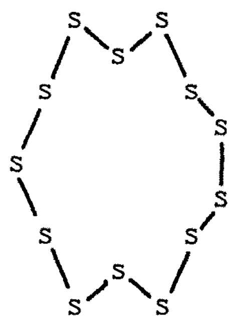
The homocyclic molecules, S_{11} and S_{13}, have been synthesized from $(C_5H_5)_2TiS_5$ and S_6Cl_2 or S_8Cl_2, equation (4).

$$(C_5H_5)_2TiS_5 \quad + \quad S_nCl_2 \longrightarrow (C_5H_5)_2TiCl_2 \quad + \quad S_{n+5} \qquad \ldots (4)$$

In S_{11} (5) the S-S distances were between 203.2 and 211.0pm with bond angles from 103.3 to 108.6° and torsional angles from 69.3 to 140.5°; Whilst in S_{13} (6) the corresponding lengths and angles were in the ranges 197.8 to 211.3pm, 102.8 to 111.1° and 29.5 to 116.3° respectively. [34]



(5)



(6)

The photochemical decomposition of pure carbon disulphide as well as of solutions of pure S_6, S_7, S_8, S_{10} and S_{12} respectively in CS_2 have been studied and products identified. In all cases mixtures of sulphur homocycles (S_n (n=5,6, ...) were formed with S_8, S_7, and S_6 being the predominant species, but traces of S_5, S_9, and S_{12} were frequently observed. S_5 was observed for the first time; being formed in the photolysis of S_7 in CS_2. [35] The exchange of sulphur isotopes between liquid CS_2 and dissolved elemental sulphur-34 (S_6, S_7, S_8, S_9, S_{10}, S_{12}) has been studied by Raman spectroscopy. No exchange was observed within 4h at temperatures below 473K and prolonged heating above this temperature only resulted in slow exchange.[36] The first detailed study of sulphur-33 NMR in the solid state has been carried out for a variety of metal sulphides and sulphates. The inherent difficulties associated with sulphur-33 NMR at natural isotopic abundance were overcome by the use of a very high magnetic field strength.[37] The chemical species in solutions of sulphur in liquid ammonia have been studied by Raman spectroscopy over a wide concentration and temperature range. The results give evidence that sulphur solubilization in liquid ammonia is in fact a redox dismutation, giving mainly the oxidised species S_4N^- and the reduced species S_6^{2-}, which is in equilibrium with the radical anion $S_3.^-$.[38] The preparation of $[K(crypt\text{-}2,2,2)]_2S_7.(H_2N\text{-}(CH_2)_2\text{-}NH_2$ and $[Kcrypt\text{-}2,2,2]_2S_6$ by reaction of K_2S_5, S and crypt-2,2,2 in ethylenediamine has been carried out. The anionic parts of the lattices were shown to consist of unbranched chains of S_7^{2-} and S_6^{2-} respectively.[39]

The mechanism of the reaction of sulphur with sodium nitrite in DMF, DMSO, and HMPA has been elucidated. The course of the complex reaction and the large number of products can be explained by assuming that at first, perthionitrates, NaS_xNO_2 are formed which, are decomposed to give either N_2O and thiosulphate, or, react with nitrite to yield nitrate and perthionitrite NaS_2NO which dissociates reversibly into sodium trisulphide and NO. The characteristic colour change during reaction from blue-green to orange-red is due to the formation of two coloured species, S_3^- (blue) and $ONSS^-$ (red).[40] The reactions of some silylphosphines with sulphur have been described and their relative reactivities in the absence of solvent discussed. $Me_2P\text{-}SiMe_3$, $MeP(SiMe_3)_2$ and $(Me_3Si)_3P$ were found to give products with the maximum sulphur content. Reactions in pentane were found to be much slower, leading to the identification of some reaction intermediates.[41] The reaction of a mixture of sulphur and selenium powders with SbF_5 in SO_2 solution has been shown to yield $(S_{0.3}Se_{1.0})_2(Sb_4F_{17})(SbF_6)$ which contains a disordered mixture of $S_xSe_{4-x}{}^{2+}$ cations. A single crystal structure determination led to the elucidation of the occupational disorder, anion-cation interactions and the geometry of the $Sb_4F_{17}{}^-$ anion.[42]

6.2.2 Bonds to Halogens

The role of d-orbitals in SF_6 has been the subject of a theoretical study using natural population and natural hybrid orbital analysis of ab-initio SCF wavefunctions. The study concludes that the sigma S-F bonds have only one-quarter contribution from sulphur orbitals and that models of SF_6 requiring sp^3d^2 hybridization should be discarded.[43]

The reactions of a series of bis(trifluoromethyl)imidosulphites with chlorine fluoride have been studied. regardless of what stoichiometry was used and although CF_3NCl_2 was always generated, it was not possible to isolate a sulphur(IV) derivative as expected from equation (5).

$$CF_3N{=}S(OR)_2 + 2ClF \longrightarrow CF_3NCl_2 + [F_2S(OR)_2] \quad ...(5)$$

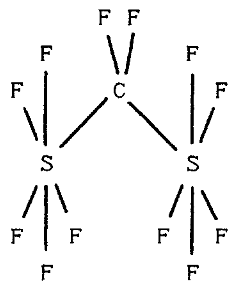
Instead, chlorine oxidatively fluorinated sulphur(IV) to a new family of cis/trans-sulphur hexafluoride derivatives in essentially the same ratio of cis:trans isomers (equation 6).[44]

$$CF_3N{=}S(OR)_2 + 4ClF \longrightarrow CF_3NCl_2 + \text{cis-/trans-}(RO)_2SF_4 + Cl_2 \quad ...(6)$$

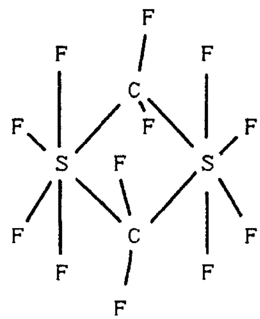
$$R = CF_3CH_2, CF_3CF_2CH_2, CF_3CF_2CF_2CH_2$$

An electron diffraction study of the gas phase structure of F_5SCCH has revealed nothing unusual in that the average S-F bond length is similar to that of several of the substituted sulphur hexafluorides, and in common with most of these the F_a-S-F_e angle is slightly smaller than 90°.[45] HC≡C-SF_5 can be transformed in a simple manner into the halogen acetylenes X-C≡C-SF_5 (X=Cl,Br,I) The compound F-C≡C-SF_5 has, however , not been obtained so far. HC C-SF_5 also reacts with $Co_2(CO)_8$ to form complexes with the formulae

$Co_2(CO)_6(HC{\equiv}C\text{-}SF_5)$, $Co_2(CO)_5(HC{\equiv}C\text{-}SF_5)_2$ and $Co_2(CO)_4(HC{\equiv}C\text{-}SF_5)_3$; the latter being a dicobalt complex containing a helical six-membered carbon chain as a ligand.[46] The structures of $(SF_5)_2CF_2$ (7) and $(SF_4CF_2)_2$ (8) have been studied by gas electron diffraction. Very long S-C bonds (190.8pm) and a large SCS bond angle (124.3°) were found for $(SF_5)_2CF_2$. These results were compared to the skeletal parameters of $(SF_5)O$ and $(SF_5)_2NF$ and a simple bonding model based on polar effects was proposed. For the cyclic $(SF_4CF_2)_2$, the SCSC four-membered ring is planar with S-C = 188.6pm, SCS = 96.2° and CSC = 83.8°.[47]



(7)

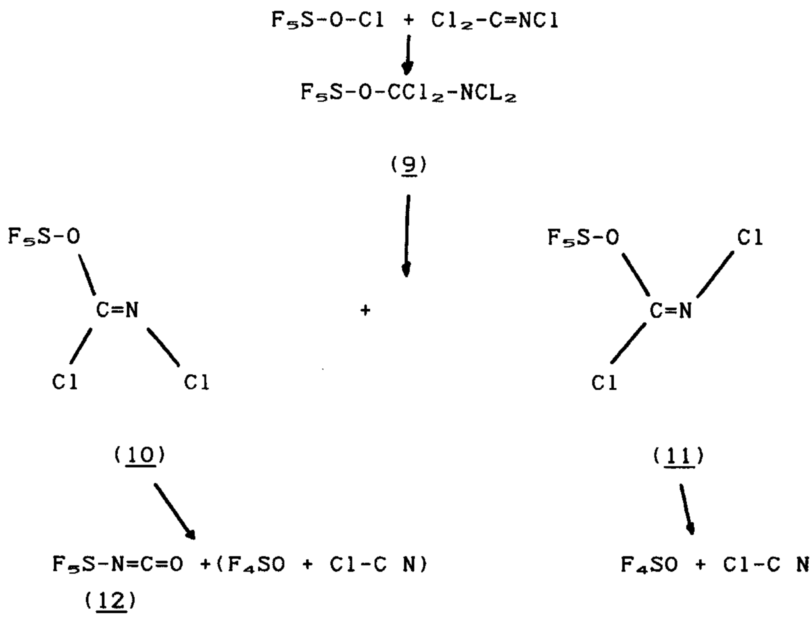


(8)

The series of known isomers, $F_5S\text{-}N{=}C{=}O$, $F_5Se\text{-}O\text{-}C\ N$, and $F_5Te\text{-}N{=}C{=}O$ has been augmented by the synthesis of $F_5S\text{-}O\text{-}C{\equiv}N$ (see Scheme 1). Compound (9) eliminates chlorine spontaneously in the presence of mercury to give the isomers (10) and (11) which could be separated by gas chromatography. The structural assignment of the isomers was made on the basis of NMR data by analogy with the isomers of $F_5S\text{-}O\text{-}CF{=}NCl$. Only isomer (10) underwent further elimination of chlorine in the presence of mercury at room temperature to give the desired $F_5S\text{-}O\text{-}C\ N$ (12) as a colourless liquid in 10% yield.[48]

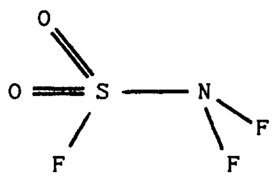
The addition of SF_5Cl on carbon-carbon double bonds has been shown to take place by a radical mechanism in which the SF_5. free radical attacks the double bonds first. The direction of the addition was not found to be changed by sterical influences in that strained derivatives were frequently obtained. In a single case the addition of TeF_5Cl on $CH_2{=}CF_2$ was possible, but the analogous reaction with

SeF_5Cl was unsuccessful.[49]



Scheme 1

FSO_2NF_2 (13) has been prepared in high yield by fluorination of FSO_2NH_2 at room temperature and its structure determined by electron diffraction. The reaction of FSO_2NF_2 with Et_2NH yields FSO_2NEt_2 and HNF_2.[50]



(13)

lengths (pm)	angles (°)
S=O = 141	O=S=O = 123
S-F = 155	O=S-F = 107
S-N = 175	O=S-N = 105
N-F = 138	N-S-F = 106
	S-N-F = 103

The intense Raman effect of SCl_4 can be used to detect small amounts of chlorine in SCl_2. Mixtures of SCl_2 and Cl_2 yield the Raman spectrum of SCl_4 at 133K, while at 298K no trace of the compound can be detected. The Raman spectra of SCl_4 and $\alpha SeCl_4$ are quite different despite the fact that both contain the ECl_3^+ (E=S or

Se) ion.[51] The vibrational frequencies of the triphenylmethanehalogenosulphanes Ph_3CSX (X=Cl,Br,I) have been assigned and the crystal structure of Ph_3CSBr determined.[52] The photoionization mass spectrum of SBr_2 has been measured and the bond energy of the S-Br bond found to be 50.9 kcal/mol..[52] The reaction of $ClSCF_2CF_2SCl$ with $Me_3C-C(O)Me$, hexene, diacetyl, cyclobutanone and $H_2C=CHC(O)CH_3$ has been shown to yield cyclic and acyclic products.[54]

The very unstable compound $CF_3S(O)I$ has been identified by correlating its UV/VIS absorptions with those of the homologous fluoride, chloride and bromide and by its decomposition products.[54] Due to its bifunctional character, S_2I_2 decomposes by inter- as well as intramolecular iodine formation. The main decomposition phase was shown to follow a first order rate law and to be strongly temperature dependent.[56] Some preparative methods for the iodosulphonium(IV) salts, $Me_2SI^+AsF_6^-$ and $Me_2SI+SbF_6^-$, have been reported. The salts are stable up to 253K and were characterized by Raman and n.m.r. spectroscopy.[57] The high pressure polymorphism of some Rare Earth sulphideiodides has been reported.[58]

6.2.3 Bonds to Nitrogen

The preparation and structures of complexes containing simple sulphur- nitrogen ligands have been reviewed. The ligands considered were: NS, NSF_n, NSCl, diimines and related complexes, $S_2N_2H^-$, $S_2N_2^{2-}$, S_3N^-, $S_2N_3^{3-}$ and several others.[59]

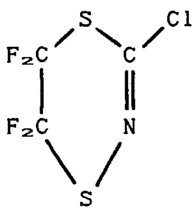
A convenient, simple synthesis of solid, pure $[SN]^+[AsF6]^-$ in approximately 75% yield by the reaction of $S_3N_3Cl_3$ and an excess of $AgAsF_6$ in sulphur dioxide solvent has been described.

$$3AgAsF_6 + S_3N_3Cl_3 \longrightarrow 3AgCl + 3[SN]^+[AsF_6]^- \qquad (7)$$

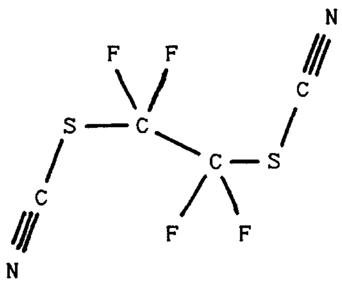
The usefulness of $[SN]^+[AsF_6]^-$ was illustrated by its reaction with elemental sulphur to give crystalline $[S_2N]^+[AsF_6]^-$ in 50% yield and its reaction with CsF in a solid/solid reaction leading to the formation of the versatile reagent NSF in reasonable purity and yield.[60]

Fragmentation of bis(tert-butyl) sulphur diimide, $S(NBut)_2$ in the presence of $Ru_3(CO)_{12}$ leads to the formation of the yellow, tetrahedrane type complex, $Ru_2(CO)_6(Bu^tNS)$ containing tert-butyl sulphur imide as a six electron ligand. According to the X-ray structure determination the N-S bond (171.6pm) is arranged perpendicular to the Ru-Ru axis.[61] The properties of the N_2S^{2-} dianion have been calculated by using Hartree-Fock-Slater and MNDO methods and related to those of N_2S and experimental results. A locally stable NSN^{2-} species with an NSN angle of 135° was characterised. This is the opposite of the neutral N_2S species where the asymmetric form is the more stable configuration.[62]

Evidence from studies on reactivity, linear free energy relationships, trapping with an amine, and activation data indicates that the unprecedented anionic sulphonylamine, $^{-}N{=}SO_2$ is involved in the alkaline hydrolysis of aryl sulphamates.[63] The reaction of $F_2S{=}NCN$ and $NC\text{-}SCF_2CF_2S\text{-}CN$ with $AgAsF_6$ has been shown to lead to the coordination compounds $(F_2S{=}NCN)_2AgAsF6$ and $(NC\text{-}SCF_2CF_2S\text{-}CN)_2AgAsF_6$. The compound $NC\text{-}SCF_2CF_2S\text{-}CN$ was formed by the reaction of $ClSCF_2CF_2SCl$ with HCN as well as with Me_3SiCN: the six-membered heterocycle (14) was formed as a by-product of the reaction.

$2\ ClSCF_2CF_2SCl + 3HCN \rightarrow NC\text{-}SCF_2CF_2S\text{-}CN +$  $+ 3HCl$ (8)

(14)

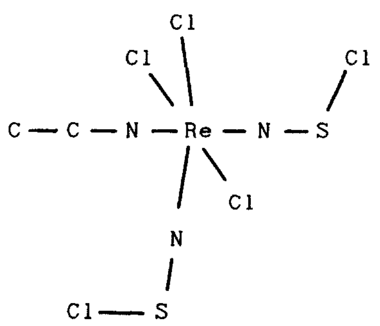


(15)

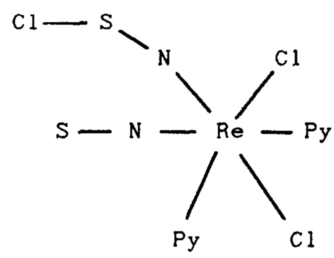
NC-$SCF_2CF_2CF_2S$-CN was investigated by X-ray structural methods and found to have the all-trans structure (15) in the solid state.[64]

14- and 15-N nmr data have been reported for compounds of the type CF_3SNXY, $(CF_3S)_2NX$ as well as $(CF_3S)_3N$ and $[(CF_3S)_2N]_2Hg$. The chemical shift values of the CF_3S-amines lie at a higher field than those of the non-fluorinated $RSNR'_2$ compounds. This was attributed to the large s-contribution of the S-N bond (sp^2 hybridization of the N atom), as a result of the electron withdrawing effect of the CF_3 group. The -I effect of the CF_3S group on the shift values is therefore not discernible. The notion of a $p\pi$-$d\pi$ interaction between the S and N atoms with nitrogen acting as a donor was not supported by this study.[65]

Black, moisture sensitive crystals of $ReCl_3(NSCl)_2MeCN$ have been obtained from $[ReCl_3(NSCl)_2]_2$ and acetonitrile in dichloromethane. The monomeric molecule (16) has a distorted octahedral coordination with meridional arrangement of the chlorine atoms and nearly linear configuration of the ReNS bonds which have lengths corresponding to double bonds.[66] The reaction of pyridine with either $ReCl_3(NSCl)_2POCl_3$ or $[ReCl_3(NSCl)_2]_2.(\mu\text{-}N_2S_2)$ and dichloromethane gives rise to the formation of $ReCl_2(NS)(NSCl)(pyridine)_2$ (17) in which each Re atom has a distorted octahedral coordination of two cis-chlorine atoms, two cis-nitrogen atoms of the pyridine and two cis-nitrogen atoms of the thionitrosyl and chloro thionitrene ligands.[67]

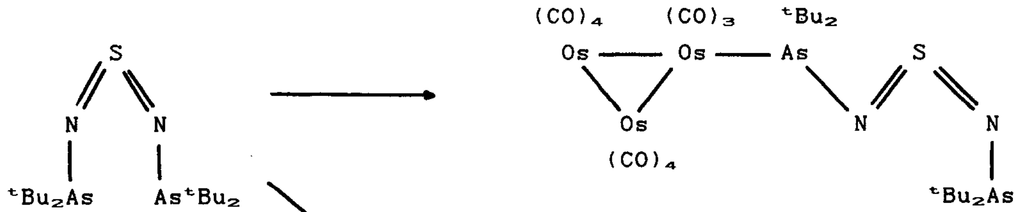


(16)

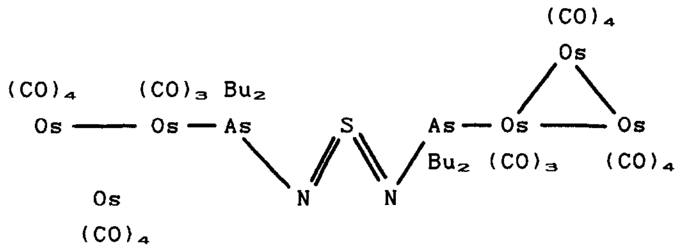


(17)

In the reaction of $S(NAs\ t\text{-}Bu_2)_2$ with the cluster $Os_3(CO)_{11}(NCCH_3)$ either one or two $[Os_3(CO)_{11}]$ units can be added to the sulphur diimide to give (18) and (19) respectively. Compound (19), which can also be obtained from the thermolysis of (18) in refluxing hexane, is the first sulphur diimide with a trans,trans configuration in the solid state.[68]



(18)



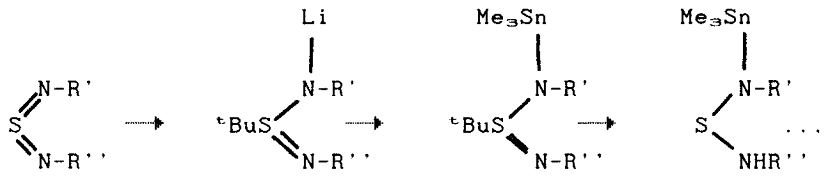
(19)

$CH_2[N(SO_2F)_2]_2$ has been obtained as an unexpected product during an attempt to prepare $N(SO_2F)_3$ from the reaction of $AgN(SO_2F)_2$ with SO_2ClF in CH_2Cl_2 solution. The compound, which is actually formed by the reaction of the silver compound with CH_2Cl_2,

$$2AgN(SO_2F)_2 + CH_2Cl_2 \longrightarrow CH_2[N(SO_2F)_2]_2 + 2AgCl \qquad ...(9)$$

is a white crystalline solid which can be sublimed in vacuo and has a structure consisting of discrete molecules.[69]

A simple method for the preparation of stannylated diaminosulphanes has been reported. The stepwise reaction of the sulphur diimides (20) with t-BuLi and Me_3SnCl gives $^tBuS(NR'')NR'(SnMe_3)$ which on heating undergo a reductive elimination of isobutene to yield the stannylated diaminosulphanes.[70]

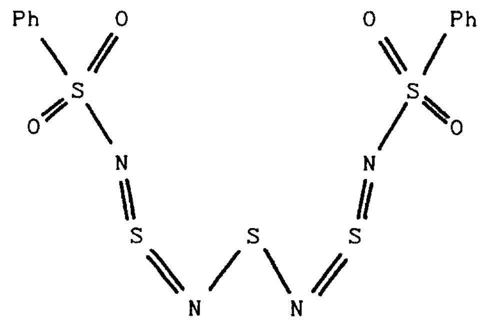


(10)

(<u>20</u>)

The compounds $N(SO_2R')_2(SO_2R'')$ have been prepared by the cleavage of aminostannanes $Me_3SnN(SO_2R')_2$ with sulphonyl chlorides $R''SO_2Cl$. A simple synthesis of the compound where R'=R''=Me from $AgN(SO_2CH_3)_2$ and CH_3SO_2Cl has been described.[71] $H_2NSO_2NWCl_4$ has been synthesised from WCl_6 and $SO_2(NH_2)_2$ and forms adducts with donor solvents such as pyridine and acetonitrile.[72] The isolation of pure bis(fluoro sulphonyl)imide has been reported.[73] Some [4+2]-cycloaddition products of perfluoroorgano-N-sulphanylamines and their oxidation products have been described. The sulphinylamines R-NSO, (R= CF_3,C_6F_5,CF_3CO) react with dimethylbutadiene to form 3,6-dihydro-4,5- dimethyl-2H-1,2-thiazine 1-oxides which can be oxidised to epoxides, epoxysultames and pyrroles. [74]

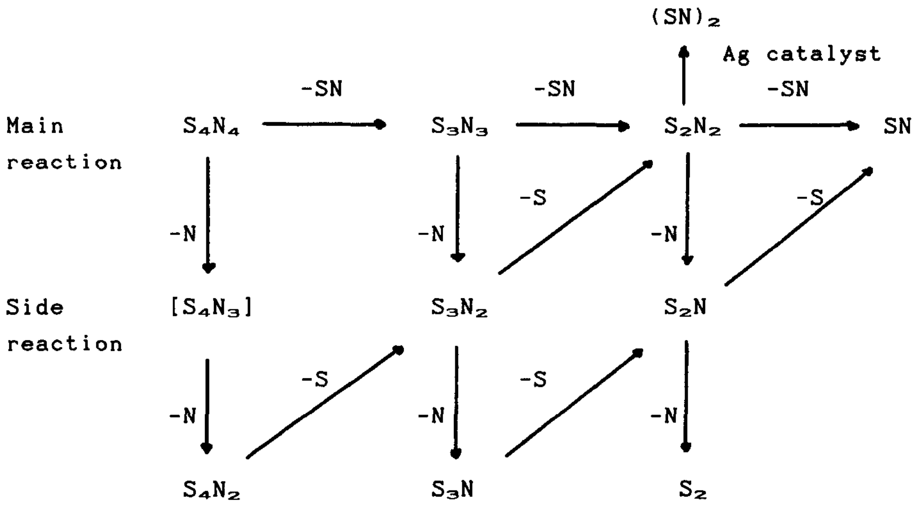
The reaction of S_4N_4 with $PhSO_2NCl_2$ has been shown to give $(PhSO_2NSN)_2S$ (<u>21</u>) which contains a S-N chain with a planar central N_4S_3 unit. The substituents at the NSN groups are in cis-trans positions.[75]



(<u>21</u>)

An improved synthesis and purification, and some properties of powdered $(SN)_x$ have been reported. Gram quantities may be prepared by reacting $(NSCl)_3$ and Me_3SiN_3 in acetonitrile, followed by the liquid SO_2 extraction of impurities. Freshly prepared samples were found to readily convert to S_4N_4 at 393K.[76]

The S_3N_3 radical, never previously characterised, has been shown to be the major semistable component of the vaporization products of the $(SN)_x$ polymer. The species can be recondensed to yield the polymer and other coloured materials. Revaporisation produces S_3N_3 in addition to S_4N_4, S_4N_2 and S_2N_2.[77] A mechanism for the polymerisation of $(SN)_x$ has been proposed on the basis of a mass spectrometric study of the thermal decomposition of S_4N_4. The proposed fragmentation scheme shows reactions in the main pathway from S_4N_4 to SN which are reversible and side reactions leading to loss of nitrogen and sulphur which are not. In the presence of silver wool the transformation of S_2N_2 to $(SN)_2$ occurs, the latter being the starting material for the polymer.[78]



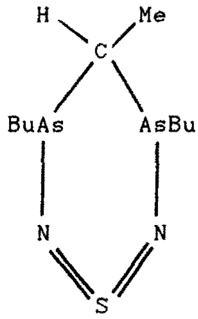
Scheme 2

A new synthesis of $[SNBr_{0.4}]_x$, by the reaction of trithiazyl chloride and $BrSiMe_3$ in CH_2Cl_2 solution at 213K has been described.[79]

The reactions of the bifunctional bis(chloroarsino) compounds

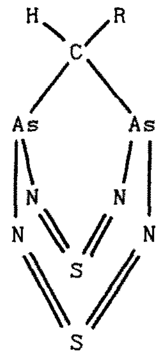
$MeCH[As(t\text{-}Bu)Cl]_2$ and $RCH[AsCl]_2$ (R=H,Me) with the salt K_2SN_2 have been shown to lead to rings (22) and cages (23) containing arsino-substituted sulphur diimides.[80]

K_2SN_2 + $MeCH[As(t\text{-}Bu)Cl]_2$ ⟶



(22)

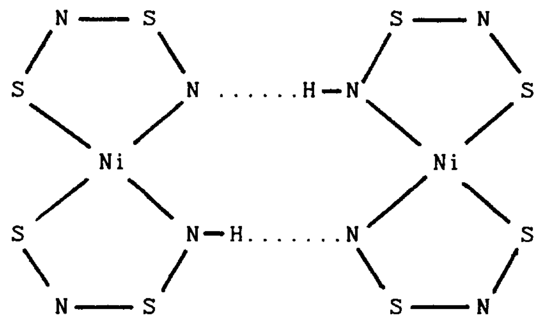
$2K_2SN_2$ + $RCH[AsCl_2]_2$ ⟶



(23)

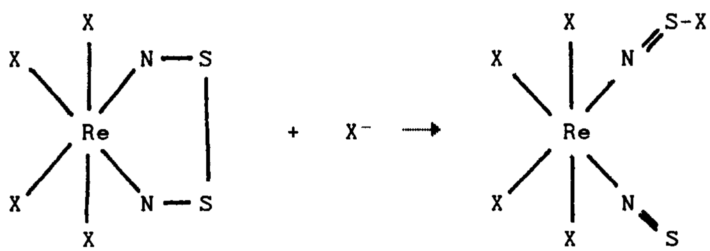
The reduction of $Ph_4P_2N_3SCl$ by triphenylantimony in methylene chloride yields a persistent radical which, on the basis of molecular orbital calculations and e.s.r. spectroscopic evidence, was thought to be the 1,2,4,6,3,5-thiatriazadiphosphinyl radical $[Ph_4P_2N_3S]$..[81]

The application of metal atom vapour synthesis to the preparation of metalla-sulphur-nitrogen compounds has been investigated. The reaction of nickel atoms with S_2N_2 gave, after extraction with methanol, $Ni(S_2N_2H)_2$ in about 15% yield. The product after cocondensation was a dark solid which did not sublime and was therefore thought to be a polymeric S_2N_2 adduct.[82] The crystal structure of $Ni(S_2N_2H)_2$ has been shown to contain two planar $[Ni(HN_2S_2)(N_2S_2)]^-$ ions linked together by hydrogen bridges to form a dimer(24).[83]



(24)

The complex $[ReCl_4(N_2S_2)]^-$ has been prepared as the PPh_4 or $AsPh_4^+$ salt by the action of $S(NSiMe_3)_2$ or diphenylacetylene on the chloronitrene complex $[ReCl_4(NSCl)_2]^-$ or from the reaction of $[ReCl_3(NSCl)_2(POCl_3)]$ with $SbPh_3$. Structural studies of $[ReX_4(N_2S_2)]^-$ (25)showed the Re atom to be part of a five membered ring with, for X=Cl, Re-N = 177, N-S = 152 and S-S = 259pm for X=Br the equivalent bond distances were 184, 153, and 264pm respectively.[84] The Nucleophilic ring cleavage of the $Re(N_2S_2)$ rings of the complexes $ReX_4(N_2S_2)]^-$ with PPh_4X in CH_2X_2 gives rise to the thionitrosyl- halothionitrenes, $(PPh_4)_2[ReX_4(NS)(NSX].2CH_2X_2$ (26) where X=Cl or Br.[85]



(25) (26)

Ruthenium trichloride reacts with trithiazyl chloride to give cis-

$RuCl_4(NS)_2$ which with triphenylmethylphosphonium chloride forms the complex $[RuCl_4(NS)_2Cl]^-$ in which a chloride ion is bonded between the sulphur atoms in chelate manner. $RuCl_4(NS)_2$ undergoes a redox reaction with PPh_4Br to give $(PPh_4)_2[(RuCl_4(NS))_2(\mu-N_2S_2)]$ which can be transformed to the bromide by treatment with Me_3SiBr. The latter compound has the ruthenium atoms linked by the nitrogen atoms of a planar N_2S_2 ring trans to which is a thionitrosyl ligand with a nearly linear Ru=N=S arrangement having an N-S bond length of 151pm.[86]

The reaction of $(Me_2SnS_2N_2$ with cis-$[MCl_2(PR_3)_2]$ in dichloromethane has been shown to provide a useful and rational route to complexes of the type $[M(S_2N_2H)(PR_3)_2][X]$(M=Pt,Pd or Co: X=Me_2SnCl_3, PF_6 or BF_4).[87] The crystal structures of the platinum complexes showed them to have stacked planar cations with significant close interactions.[88] The use of $Na(S_3N_3)$ enabled the preparation of complexes of the type $[M(S_2N_2)(PR_3)]$ to be carried out in high yield.[89]

$$[MCl_2(PR_3)_2] + 2Na(S_3N_3) \rightarrow [M(S_2N_2)(PR_3)] + S_4N_4 + 2NlC \qquad (11)$$

An improved synthesis for $MoCl_3(N_3S_2)$ from $MoCl_5$ and $(NSCl)_3$ has been given; reaction of the complex with pyridine or THF yields the respective donor-acceptor complex.[90] Preparative and structural data have been published for the following complexes containing a cyclic S_3N_2 bidentate ligand: $AsPh_4[W(O)Cl_3(HN_3S_2)$ [91], $Br_4WS_2N_3$ [92], $WCl_3(N_3S_2)(Py)$ [93], $Br_2VS_2N_3$ [94], $[N(PPh_3)_2)VCl_3(N_3S_2)].C_7H_8$ [95], $VCl_2(N_3S_2)$ [96], $VBr_2(N_3S_2)(Py)_2$ [97], $S_4N_3[MoCl_4(N_3S_2)]$ [98] and $AsPh_4[W_2Cl_4(N_3S_2)_3].CCl_4$ [99].

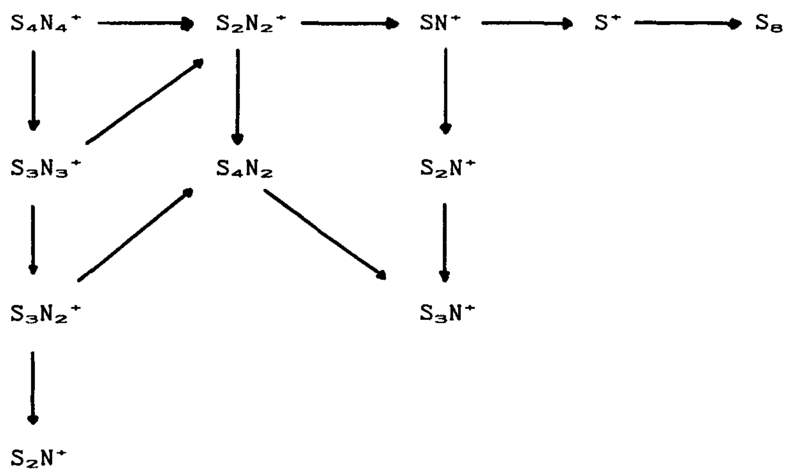
The reaction of $(NSCl)_3$ with $SbCl_5$ in thionyl chloride or methylene chloride followed by the addition of elemental sulphur has been shown to give $[S_2N][SbCl_6]$, $[S_3N_2Cl][SbCl_6]$ and $[NS_2Cl_2][SbCl_6]$. The adduct $S_4N_4.SbCl_6$ was also produced in methylene chloride.[100] The reaction of $(NSCl)_3$ with CuCl in acetonitrile solution gives $[CuCl_2(CH_3CN)]_2.(S_2N_2)$ which on thermolysis at 393K yield $(CuCl_2)_2(S_2N_2)$. [101]

S_7NH has been shown to react with $PdCl_2$ and $[Ph_6P_2N]OH$ to form the complex salt $[Ph_6P_2N][Pd(S_3N)(S_5)]$ which was isolated in two modifications both of which contained one S_3N^- and one $S_5{}^{2-}$ coordinated to the Pd atom. Reaction of S_7NH, $Pd(CN)_2$ and XOH (X=Me_4N or Ph_4P) gave salts of the type $X[Pd(S_3N)(CN)_2]$ in which one

S_3N^- chelate ligand and two CN^- ions are bound to the Pd atom. In all these complexes the coordination of the metal atom is almost square planar.[102]

The preparation of trithiadiazyl-hexafluoroarsenates by three different methods has been reported: (a) reaction of $S_3N_2Cl_2$ with $AgAsF_6$ to give $S_3N_2Cl^+AsF_6^-$, (b) halogen or radical addition to $S_3N_2AsF_6$ to give $S_3N_2Br^+AsF_6^-$ or $S_3N_2ON(CF_3)_2^+AsF_6^-$ and (c) cycloaddition of NSF to the NS_2^+ cation to give $S_3N_2F^+AsF_6^-$.[103] Complexes of $S_4N_3N(SO_2F)_2$ with the chlorides of Fe(III), Sb(V), V(III), Co(II), Ni(II), and Cu(II) have been prepared.[104]

The thermal decomposition of S_4N_4 on heating in nitrogen at 873K has been shown to be accompanied by a marked endothermic event at temperatures between 453 and 473K. the decomposition takes place with ring opening with an enthalpy change of 307.8 kJ/mole. A study of the fragmentation of S_4N_4 on electron impact has confirmed the following mechanism (scheme 3) for the thermal decomposition.[105]

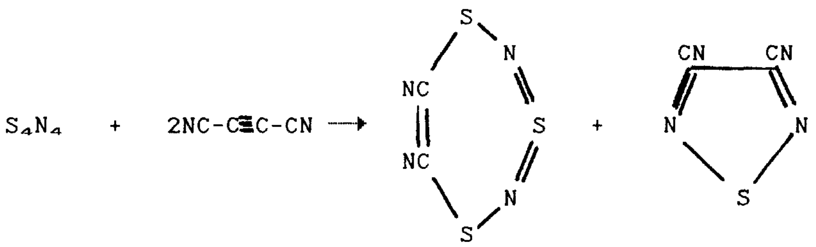


Scheme 3

The reaction of S_4N_4 with cyano and trifluoromethyl sustituted alkynes gives trithiadiazepines in good yield (equation 12). With less reactive alkynes the yields are greatly improved by $TiCl_4$ catalyst, making a range of functional derivatives of this ring system readily available.[106]

Amongst the reaction products of S_4N_4 with $SnCl_4$ in chloroform containing acetic acid and small amounts of water are the two salts

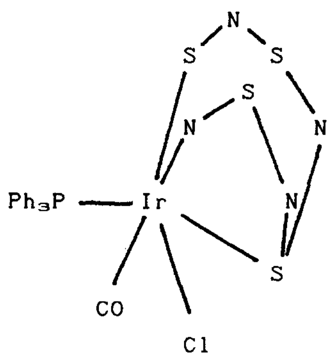
$S_4N_4H^+[SnCl_5(H_2O)]^-$ and $(S_3N_2NH_2^+)_2[SnCl_6]^{2-}$ both of which contain protonated S_nN_m units.[107]



(12)

$S_4N_4H[FeCl_4]$ and its deuterated derivative have been prepared by the reaction of S_4N_4 with $FeCl_3$ and CH_3COOH and CH_3COOD respectively. Bromination with Me_3SiBr yields $S_4N_4H[FeBr_4]$ and in this reaction $S_4N_4Br^+$ is presumed to be formed, which undergoes decomposition by elimination of Br and formation of the $S_4N_4^+$ radical cation. The latter reacts with the solvent, CH_2Cl_2 to yield the $S_4N_4H^+$ cation .[108]

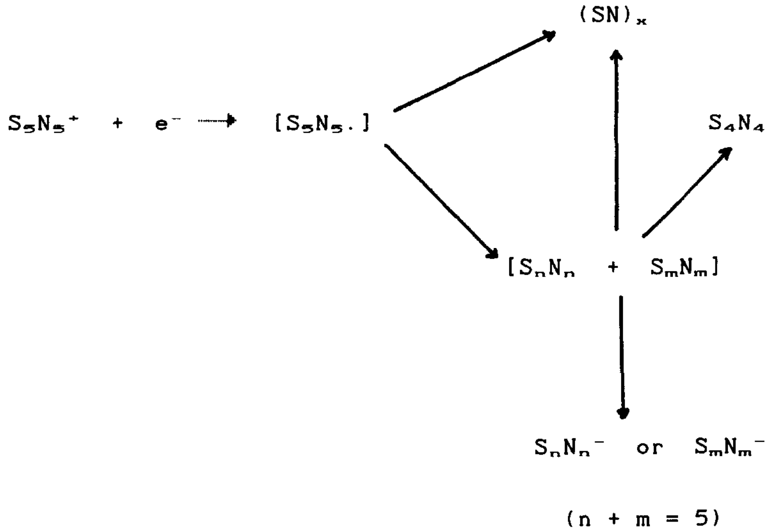
An X-ray structure determination of the product from the reaction of $[IrCl(CO)(PPh_3)_2]$ with S_4N_4 has shown that the $[IrCl(CO)PPh_3]$ fragment is inserted into the S-N bond of the S_4N_4 ring (<u>27</u>). Of the two sulphur atoms cordinated to the Ir atom, one is two coordinate whilst the other is three coordinate with the former having the expected shorter Ir-S distance of 233.5 pm compared to 239.1 pm for the three coordinate atom.[109]



(<u>27</u>)

Exposure of dilute solutions of S_8 and S_4N_4 in trichlorofluoromethane to gamma rays at 77K gave the corresponding radical cations. On annealing, the species thought to be $S_8.^+$, changes irreversibly into a species thought to be also $S_8.^+$ but in a relaxed form in which the two opposite sulphur atoms have formed a weak three-electron bond. The esr parameters of the latter species are very similar to those previously assigned to S_8^+ formed from S_8^{2+} in oleum.[110]

Aluminium chloride may be removed from $[S_5N_5][AlCl_4]$ by tetrahydrofuran to give pure $[S_5N_5]Cl$ and this reacts with tetrafluoroboric acid to give $[S_5N_5][BF_4]$. Cyclic voltammograms of the fluoroborate complex were used to derive the following mechanism (scheme 4) for the electroreduction process

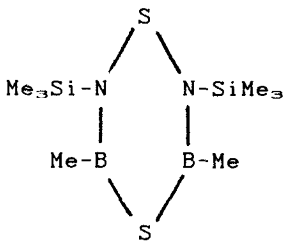


Scheme 4

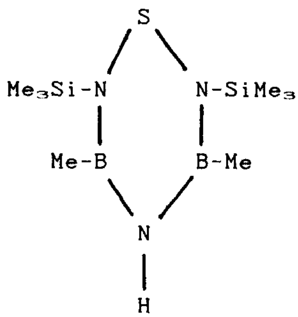
Electrodeposition of $(SN)_x$ on platinum foil and on $(SN)_x$ -film cathodes was achieved by potentiostatic electrolysis and the crystal structure of $[S_5N_5]Cl$ was determined.[111] $S_5N_5[SnCl_5(MeCN)]$ has been prepared by the reaction of $SnCl_2$ with $(NSCl)_3$ in acetonitrile suspension. The compound consists of planar $S_5N_5^+$ cations with the azulene structure.[112] The compound $(S_5N_5)_4[As_8Cl_{28}].2S_4N_4$, prepared by the reaction of $(NSCl)_3$ with As_2O_3, has planar $S_5N_5^+$

cations, octameric anions $[As_8Cl_{28}]^{4-}$ and S_4N_4 molecules with both the sulphur-nitrogen species showing positional disorder. Reaction of $(NSCl)_3$ with Sb_2O_3 and Bi_2O_3 gave $S_5N_5[SbCl_6]$ and a mixture of $S_4N_5[BiCl_4]$ and $S_4N_4Cl[BiCl_4]$ respectively. No reaction was observed between P_4O_{10} and $(NSCl)_3$.[113]

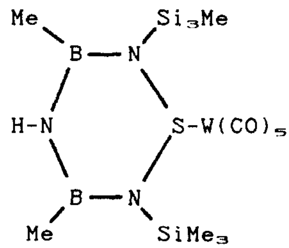
Two thermally induced N-S bond cleavage processes have been observed for EN_5S_3 heterocycles where E= CR,PR_2 or SO_2-: (i) an irreversible loss of NSN to form EN_3S_2 (for E= PR_2 and SO_2^-) and (ii) a pseudo-degenerate 1,3-nitrogen shift which exchanges all nitrogen atoms (for E=CPh).[114] The ammonolysis of the heterocycle (28) has been shown to lead to (29) which reacts with $W(CO)_5$.thf to give the complex (30).[115]



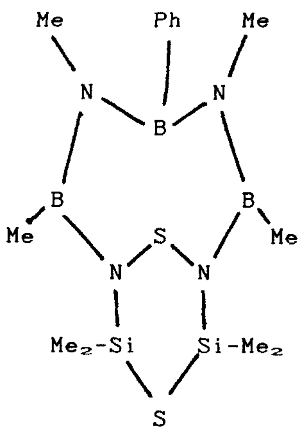
(28)



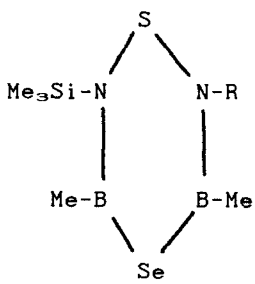
(29)



(30)



(31)

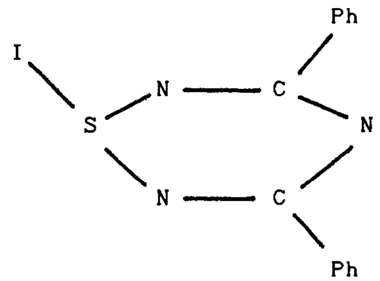


(32)

The difunctional 2,6-bis(chlorodimethylsilyl)-3,5-dimethyl derivative of (28) reacts with bis(methylamino)phenylborane to give the unexpected tricyclic product (31), the structure of which was established by X-Ray crystallography.[116]

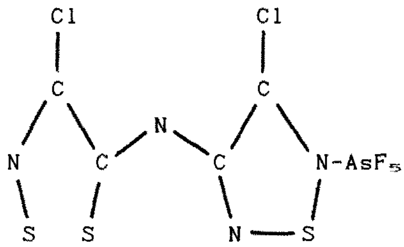
A remarkably stable derivative of (29) has been prepared in which the methyl groups attached to the boron atoms were replaced by $Me_3CN{=}S{=}N$ groups and the hydrogen on the nitrogen by a phenyl group. The heterocycle (32) was prepared by the reaction of 1,2,4,3,5-triselenadiborolane with the sulphur diimides $R{-}N{=}S{=}N{=}SiMe_3$.[117] Ammonolysis and hydrolosis reactions of further derivatives of (28) have also been studied.[118]

A crystal structure determination has shown that the N_3C_2 ring segment of (32a) is planar with the sulphur atom displaced by 25.6pm from the plane. The sulphur-iodine bond distance of 266.5pm is fractionally longer than the normal single bond distance.[119]

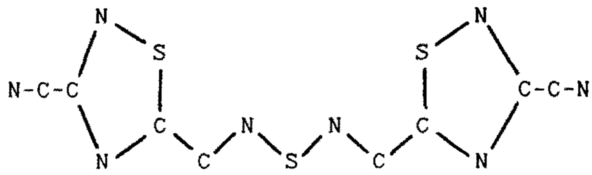


(32a)

The oxidation of 3,5-diphenyl-1,2,4,6-thiatriazinyl dimer with the nitrosonium salts $[NO]^+X^-$ ($X^-{=}BF_4^-, PF_6^-$) yields the corresponding salts of the $[Ph_2C_2N_3S]^+$ cation. Reduction of the same compound by sodium in liquid ammonia gives, following acidification, the reduced system $Ph_2C_2N_3SH$. The structures of $[Ph_2C_2N_3S]^+[PF_6]^-$ and $Ph_2C_2N_3SH.0.5CH_2Cl_2$ were determined.[120] The reaction between 1,2,4-thiadiazol-3,5-dicarbonitrile, $S(CN)_4$ and the sulphur-chlorides SCl_2 and S_2Cl_2 has been shown to proceed with the formation of $S_3(CN)_4Cl_2$ (33) and $S_3(CN)_8Cl_2$ (34). Compound (33) crystallizes with one SO_2 molecule when reacted with AsF_5 in liquid SO_2 and contains two five-membered rings joined by a nitrogen atom. AsF_5 is coordinated to one ring and the other contains an S-S bond of length 207.7pm. Compound (34) is formed by the addition of SCl_2 to two molecules of $S(CN)_4$.[121]

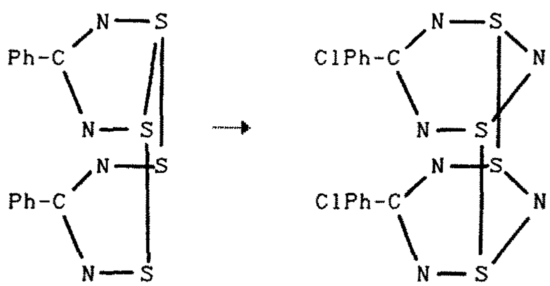


(33)



(34)

A variety of C-N-S heterocyclic radicals which are promising precursors for unsaturated C-N-S containing polymers which might be electrical conductors have been characterised. The radicals prepared include 5-methyl-1,3,2,4-dithiadiazolyl which isomerises at room temperature to 2,3,1,4-dithiadiazolyl,[122][123]: the very thermally stable, but photochemically sensitive 4,5-bis(trifluoromethyl)-1,3,2- dithiazolyl which was found to be paramagnetic in the liquid state [124] and the new thermally stable paramagnetic liquid 5-t-butyl-1,3,2,4- dithiadiazolyl.[125] Solid crystalline bis(4-aryl-1,2,3,5-dithiadiazole) has been shown to combine with two radical nitrogen atoms and/or excited nitrogen molecules in a low pressure nitrogen plasma to give (35).[126]



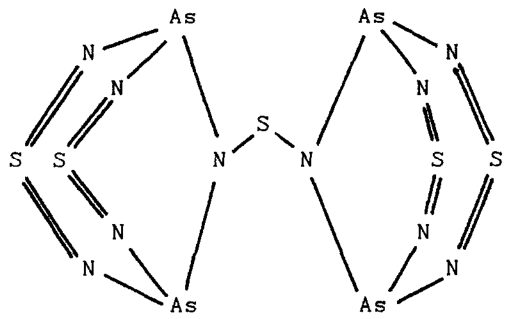
(35)

The reaction of $(NSCl)_3$ with $CoCl_2$ in acetonitrile has been shown to give $(MeCN_2S_2)_5[CoCl_4]Cl_3$ which gives $(MeCN_2S_2)Cl$ and $(AsPh_4)_2CoCl_4$ on reaction with $AsPh_4Cl$.[127]

Several studies on a number of oxidised derivatives of 3,7-bis(dimethyl- amino)-1,5,2,4,6,8-dithiatetrazocine, $(Me_2N)_2C_2N_4S_2$, have been reported. Oxidation with chlorine gives $[(Me_2N)_2C_2N_3S_2Cl]^+[Cl_3]^-$, possessing an asymetric S--Cl--S bridge, which can be converted to the corresponding PF_6^- salt which has a crystallographically symmetrical S--Cl--S bridge. Oxidation by bis(trifluoromethyl) nitroxide gives $(Me_2N)_2C_2N_4S_2(O)_2[N(CF_3)_2]_2$ which has a boat shaped conformation for the $C_2N_4S_2$ ring with the two $N(CF_3)_2$ groups occupying equatorial positions on the same side of the ring.[128] The reaction of dialkylcyanamides with NSCl units has been shown to produce either six- or eight membered rings $(Me_2NCN)(NSCl)_2$ or $(Me_2NCN)_2(NSCl)_2$. The oxidative addition of Cl_2 to 1,5-$(Me_2NCN)_2(SN)_2$ was first thought to give 1,5-$(Me_2NCN)_2(NSCl)_2$ but this is now considered to be the monochloride equivalent of the trichloride described above.[129] The reaction of $(R_2NCN)(NSCl)_2$ with $Me_3SiNSNSiMe_3$ or Me_3SiNSO produces the bicyclic compounds $R_2NCS_3N_5$ (R=Me,Et,i-Pr), the latter reagent yields an additional minor product, 1,5-$Me_2NCN(NSN)_2SCl$ which has a folded eight-membered ring with a transannular S-S bond.[130] the crystal structure of $R_2NCS_3N_5$ (R=i-Pr) shows it to have an -N=S=N- bridge weakly bonded to the sulphur atoms of a six-membered i-$Pr_2NCS_2N_3$ ring.[131] The reactions of Ph_3P and Ph_3As with the bicyclic heterocycle $PhCN_5S_3$ produce the corresponding $PhCN_4S_3NEPh_3$ (E=P or As). Both exo- and endo-isomers were characterised for the arsenic derivative.[132]

Preparative routes to 1,3,2,4-benzodithiadiazine, $C_6H_4S_2N_2$, 1,3,5,2,4- benzotrithiadiazepine, $C_6H_4S_3N_2$ and their respective norbornadiene adducts have been described.[133] The compound $[(n\text{-}C_3H_7)_4N]^+[P_4S_9N]^-$ has been synthesised from P_4S_{10} and $[(n\text{-}C_3H_7)_4N]^+[S_2P(N_3)_2]^-$. The $P_4S_9N^-$ anion has an adamantane-like structure with bridging rather than terminal nitrogen atoms.[134] The same ion has been used to prepare a salt with the cation 3,5-diphenyl-1,2,4-dithiazolium.[135]

The reaction of K_2SN_2 with arsenic halides AsX_3 (X=Cl, Br, I) does not lead to the expected cage product $As(NSN)_3As$ but to (<u>36</u>) which contains two bicyclic $[As_2S_2N_5]$ units.[136]

$6K_2SN_2 + 4\ AsBr_3 \longrightarrow$  (13)

(36)

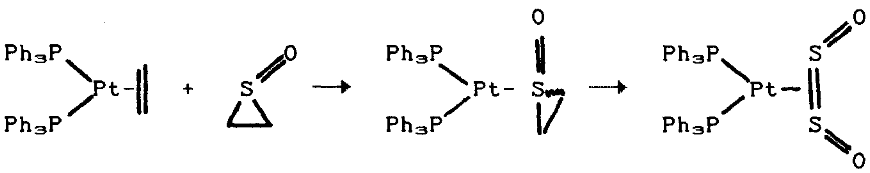
6.2.4. Bonds to Oxygen

Direct and alternating current polarograms of aqueous sulphur dioxide - water solutions show four reduction waves, more than previously reported. The first two waves probably result from the electroreduction of $SO_2.H_2O$ and HSO_3^-, the reduction of the former involving two electrons and two H+ ions and the initial product is probably H_2SO_2 which can disproportionate to sulphur and $SO_2.H_2O$ in very acidic media thus doubling the reduction current of $SO_2.H_2O$. reduction of HSO_3^- appears to occur via two paths, one a two electron/3H^+ path and the other a one electron/1H^+ path.[137] Studies of solutions of SO_2 in non-aqueous solvents have shown that Raman spectra can be used to identify the adducts SO_2.2dmso, SO_2.dmso and 2SO_2.dmso.[138] The complete phase diagrams for the SO_2-dmso and SO_2-dmf phase systems have been determined. Three stable solid species were found in the SO_2-dmf system with SO_2:dmf ratios of 2:1, 1:1 and 1:2. In the SO_2-dmso system solids were found for ratios of 2:1 and 1:1 but the species SO_2.2dmso was not found as a solid.[139] The influence of SO_2 on the chemisorption of chlorine and the kinetics of the chlorination of the higher oxides of antimony have been studied.[140] The reaction of SO_2 with BF_3 has been investigated.[141]

The reactions of some tetrahalosilanes and silane with SO_3 depend on the relative bond strengths of the Si-X bonds. SiF_4 remains unreactive even at 873K whilst $SiCl_4$ reacts at 773K to give $[(SiCl_3)_2O]$ as the major product. In contrast $SiBr_4$ and SiH_4 react at room temperature and below room temperature respectively to give

SiO_2. In all cases sulphur trioxide is reduced to the dioxide.[142] The reactions of sulphur trioxide with IF_5 have been studied.[143]

The chemistry of sulphur oxides as ligands in coordination complexes has been reviewed. The unstable oxides, SO, S_2O and S_2O_2 are discussed as well as the more familiar SO_2 complexes.[144] A good method for the complex stabilisation of sulphur monoxide is the fragmentation of thiirane S-oxide in the presence of coordinatively unsaturated or substitutionally labile transition metal complexes. That the reaction proceeds by the initial coordination of C_2H_4SO followed by elimination of ethylene has been supported by the isolation of the first thiirane S-oxide complex (37) as an intermediate in the synthesis of the disulphur dioxide complex (38) from $[(Ph_3P)_2Pt(C_2H_4)]$. [145] The complexes $[M(P^iPr_3)_2(SO)Cl]$ (M=Rh,Ir) have been shown to react with CO under mild conditions to give free SO which may be trapped by cycloaddition to an orthoquinone.[146] A general synthetic route for platinum sulphur dioxide cluster compounds has been described. Some or all of the carbonyl ligands in platinum carbonyl phosphine clusters may be replaced under mild conditions to give high yields of clusters containing the bridging sulphur dioxide ligand. In some cases changes in cluster structure takes place.[147]



(37) (38)

A simple method for the preparation of cationic organometallic sulphur dioxide complexes by metal-metal bond cleavage has been announced.[148] crystal structure determinations have been carried out on the following complexes: cis-$Na_2[Pd(SO_3)_2en]4H_2O$,[149] and $[(C_5Me_5)_2Mo_2S_4.SO_3]$.[150]

The sulphite radical anion $SO_3^{-\cdot}$, which was generated from either a Ce^{4+}-$NaHSO_3$ system at pH 2.5 or from a Ti^{3+}(edta), H_2O_2, Na_2SO_3 system at pH 9, has been shown to add to the C=O bond of some olefinic compounds in both acid and alkaline solutions although the radical is more active in acidic conditions.[151] The rate of reaction between sulphite and hexacyanoferrate(III) ions has been measured in several concentrated salt solutions and in several isodielectric water-solvent mixtures.[152] The kinetics of the reaction of dissolved nitric oxide with sulphite and bisulphite ions has been studied over a pH range of 4-10.[153] Separate peaks in the oxygen-17 NMR spectra of sodium bisulphite solutions provide direct evidence for the existence in solution of two isomers of bisulphite ion: one with the proton bonded to the sulphur atom (HSO_3^-) the other with the proton bonded to an oxygen atom (SO_3H^-). The more abundant isomer exchanges oxygen atoms with water more readily than the other and, on this evidence, was postulated as SO_3H^-.[154] The structure, stability and dehydration products of solid solutions of $Ca_3(SO_4)_2SO_3.12H_2O$ in $Ca_3(SO_3)_2SO_4.12H_2O$ have been reported.[155] Two different intercalate structures have been observed in the intercalation compounds of graphite with perfluorobutanesulphonic acid.[156] The crystal structures of three polymorphs of cadmium sulphite [157] and of the isotypic compounds $NaM_2OH(SO_3)_2$ where M is Mg,Mn,Fe,Co, or Zn have been determined.[158]

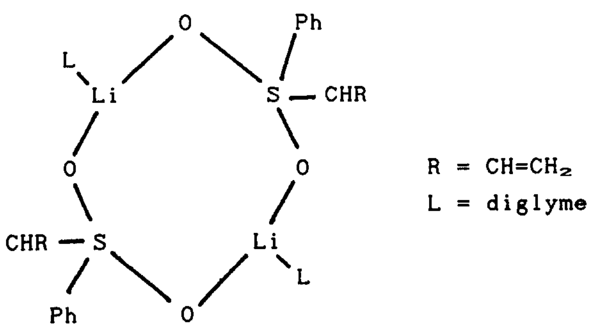
An interesting short note considers those metals for which anhydrous sulphates are not known. Whilst no general reason is proposed, the author suggests that for Nb, Mo, Tc, Ta, W, and Re it may be the ease with which these elements form metal-metal bonds and the use of inapropriate starting reagents in the syntheses that has resulted in the formation of anhydrous sulphates not being observed.[159] Sulphur dioxide has been found to reduce a number of first-row transition-metal compounds in molten alkali metal ternary sulphate eutectic, the ease of reduction being Cr(VI)>Mn(IV) >Fe(III)>Cu(II). A number of other, probably polymeric, cations (Ti,Nb,Mo, Ta, and W in their maximum oxidation states) were not reduced.[160]

The stoichiometry and temperature dependent complexation constants for reactions of protonated hexacyclen (a macrocyclic polyamine) species with sulphate anions have been determined. Three complexes were detected, 1:1 complexes of sulphate with both tri- and tetraprotonated hexacyclen species and an electrically neutral complex containing two sulphate anions per tetraprotonated macrocycle.[161] The synthesis, structure and reactivity of the alkaline earth hydrogen sulphates $M(HSO_4)_2$ of Mg,Ca,Sr and Ba have been studied.[162] Particles of $CaSO_4.0.5H_2O$ have been shown to dissolve immediately on mixing with water and subsequently form hydrated layers on their surfaces by intrusion of water molecules. These layers destruct when the dihydrate nucei are formed.[163] The reaction of thiocyanate ion with HF, H_2O_2 and iron(III) hydroxide has been shown to yield fluoro(sulpato)ferrates(II) of the type $(NH_4)_2[Fe(SO_4)F_3]$.[164]

A new method has been found for the preparation of electropositive N-bromo derivatives of sulphonimides by reaction of the Hg(II) derivatives with bromine(I) fluorosulphate. The new compounds prepared by this method, $(CF_3SO_2)_2NBr$ and $(FSO_2)_2NBr$ should be useful reagents for bromination reactions.[165] Several polyfluoroalkyl fluorosulphates, $ROSO_2F$, have been synthesized by the reaction of polyfluoro alcohols with sulphuryl fluoride or sulphuryl chloride fluoride.[166] The crystal structure of alpha-(phenylsulphonyl)allyllithium (<u>39</u>) has been determined.[167]

A method for the chromatographic separation of higher polythionates SnO_6^{2-} where n=3 to 22, has been described. The technique was applied to the detection of polythionates in bacterial sulphur secretions which were found to consist mainly of S_8 on to which are deposited long chain polythionate ions making a hydrophilic globule.[168]

Several publications have been concerned with structural studies, physical measurements and phase relations on metal sulphates: for convenience these are collected together below. Structural studies: $RbLiSO_4$ [169], $(NH_4)_3D(SO_4)_2$ [170], $Na_2SO_4(I)$ [171], $LiNaK(SO_4)_2$ [172], $Ga_9Tl_3O_2S_{13}$ [173], $KV(SO_4)_2$ [174], $3Zn(OH)_2ZnSO_4xH_2O$ [175], $Hg_3(NbF_5)_2SO_4$, $Hg_2(TaF_5)_2SO_4$ and $Hg_4(Ta_2F_{11})_2$ [176], $Na_2S_2O_3$ and $MgS_2O_36H_2O$ [177].



(<u>39</u>)

Physical measurements: Stepwise stability constants of some Se(IV) sulphato complexes,[178]; kinetics of decomposition of Ag_2SO_4, [179]; calorimetric investigations of V_2O_5 with $K_2S_2O_7$ and $K_2S_2O_7$-K_2SO_4,[180]; and the acid hydrolysis of the nitridotrisulphate ion.[181] Phase diagrams involving sulphates are collected in Table 1.

Table 1 Phase diagrams involving sulphates.

System	Ref	System	Ref
ZrO_2-H_2SO_4-K_2SO_4-H_2O &		$FeSO_4$-$MnSO_4$-H_2O	191
ZrO_2-H_2SO_4-KCl-H_2O	182	ZrO_2-H_2SO_4-Rb_2SO_4-H_2O &	192
Ag_2SO_4-H_2O	183	ZrO_2-H_2SO_4-RbCl-H_2O	
$Al(IO_3)_3$-$Al_2(SO_4)_3$-H_2O	184	K,H||SO_4,NO_3-H_2O	193
Nd_2O_3-SO_3-H_2O	185	Li_2SO_4-Na_2SO_4-H_2O	194
$VOSO_4$-K_2SO_4-H_2SO_4-H_2O	186	H_2SO_4-Na_2SO_4-$Al_2(SO_4)_3$-H_2O	195
Li,Na,KNO_3,SO_4	187	Li_2SO_4-Na_2SO_4-$CuSO_4$-H_2O	196
ZnO-Cl_2-SO_2	188	Na_2SO_4-K_2SO_4-$MgSO_4$-H_2O	197
$NaAl(SO_4)_2$-$KAl(SO_4)_2$-H_2O &	189	$CO(NH_2)_2$-Na_2SO_4-H_2O	198
$NaAl(SO_4)_2$-$RbAl(SO_4)_2$-H_2O		$CO(NH_2)_2$-Na_2SO_4-H_2SO_4-H_2O	199
$NiSO_4$-H_2SO_4-H_2O	190	Li_2SO_4-$Fe_2(SO_4)_3$	200

6.2.5 Sulphides

The reaction of ethylenediamine, sulphur and hydrogen sulphide in ethanol solution has been shown to give $[H_3N\text{-}(CH_2)_2\text{-}NH_2]_2S_6$. The compound consists of unbranched S_6^{2-} chains with helical, all trans conformation, and mono- protonated ethylenediamine cations showing uncommon synclinical conformation. A remarkable series of N-H...S bridges link the S_6^{2-} chains to form an infinite array.[201] The reaction between hydrogen sulhide and oxygen on aluminium(III) oxide has been studied.[202] The formation of the sulphur radical anions S_3^- and S_4^- in the blue and violet solutions of potassium sulphide and sulphur in acetone on adding 18C6 crown ether has been demonstrated by spectrophotometric titration under anaerobic conditions.[203] Aqueous sodium polysulphide of composition in the range $Na_2S_{2.0}$ to $Na_2S_{4.6}$ undergoes autoxidation by either air or pure O_2 at temperatures between 300 and 317K according to the equation

$$Na_2S_{2+x} + 1.5O_2 \longrightarrow Na_2S_2O_3 + x/8S_8 \quad (14)$$

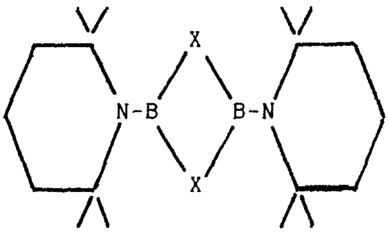
Neither sulphate, sulphite or polythionates are formed and the sulphur precipitate consists entirely of S_8.[204]

The new compound, KNaS, has been prepared by the annealing a mixture of Na_2S and K_2S. The hygroscopic, colourless compound is isostructural with $PbCl_2$ having a close packed array of S^{2-} ions with Na^+ ions in tetrahedral sites and K^+ ions out of centre in octahedral sites.[205] The kinetics and mechanism of the thermal decomposition of sodium sulphide pentahydrate to an essentially anhydrous form has been studied. A two-step dehydration reaction pathway involving an intermediate dihydrate phase was observed.

$$Na_2S.5H_2O \longrightarrow Na_2S.2H_2O + 3H_2O(g) \longrightarrow Na_2S + 2H_2O(g) \quad (15)$$

The dehydration of the dihydrate was found to be relatively more inhibited than the first step.[206] UV irradiation of sodium sulphide in aqueous solution leads to hydrogen and disulphide. Light absorption occurs by HS^- which affords the solvated electron and the HS radical. In the presence of formate, hydrogen evolution becomes catalytic with respect to HS^- with the formate being finally oxidised to carbonate.[207] Carbonate and hydrogen are also catalytically formed in the UV irradiation of an aqueous suspension of n-zinc sulphide in the presence of carbon monoxide.[208] A method of numerical analysis to describe the 11 species in aqueous polysulphide solution upon simple input of the temperature, initial concentration of sulphur, alkali metal hydroxide and hydrosulphide in solution has been evaluated.[209] The preparation of bis(tetramethylammonium)hexasulphide from tetramethylammonium chloride and Na_2S_5 in aqueous solution has been described.[210]

The i.r. spectrum of diboron trisulphide isolated in argon and nitrogen matrices has been reported. The use of partial isotopic substitution enabled the observed bands to be assigned to in-phase and out-of-phase vibrations of two -B=S residues in a non-linear arrangement. This, coupled with mass spectrometric evidence and the assumption of linear S=B-S linkages, show the shape of monomeric B_2S_3 to be based on a planar C_{2v} molecule with a B-S-B bond angle of about 120°.[211] The crystal structures of (<u>40</u>) where X= O,S or Se have been compared. All possess a crystallographically imposed centre of inversion and are therefore planar. The Group Six atom has no marked influence on the BN bond length or the internal ring angles indicating that the boron atoms are electronically saturated via the BN bonds.[212]

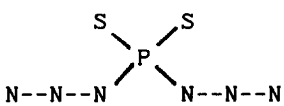


(40)

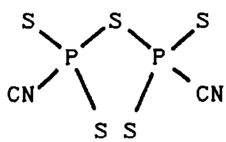
The silylsulphanes, $(MePh_2Si)_2S_n$ where n=2 to 5, have been prepared by the reaction of $MePh_2SiSNa$ with iodine or chlorosulphanes S_mCl_2 where m=1 to 3 in toluene solution. These compounds proved to be a convenient source for the generation of sulphanes and deuterosulphanes of definate chain length. Mixtures of the silylated sulphanes $(MePh_2Si)_2S_n$ with n from 1 to 10 could be prepared by heating $MePh_2SiSNa$ with an exces of cyclooctasulphur.[213] Hexa(tri-t-butoxy)disilthiane has been prepared by reaction of R_3SiSNa with R_3SiCl (R=tri-t-butoxy).[214] Lead(II)-bis-tri-t-butoxysilanethiolate is formed from $(t\text{-butoxy})_3SiSH$ and PbO by an exothermic reaction. In benzene solution the compound is monomeric but in glyme solutions a dimer is formed in which the central Pb_2S_2 ring is puckered.[215] The reactions of 2-alkoxyethanols and 2-mercaptoethanol with $(RO)_3SiSH$, $(RO)_2Si(SH)_2$, cyclo[(t-BuO2)SiS]$_2$ and SiS_2 have been investigated. Besides mixed esters of orthosilicic acid, a new group of mixed trialkoysilanethiols were obtained.[216] In the presence of Al_2Cl_6, $RGeCl_3$ reacts with $(HSi)_2E$ to yield $(RGe)_4E_6$ (R=Et,CF_3, E=S; R=CF_3, E=Se). X-ray structure determinations on the CF_3 compounds showed them to have the adamantane structure.[217] Three mixed germanium(IV) chalcogenides have been synthesized from a mixture of the component elements.[218] The band structures of SnS in the GeS and TlI modifications have been constructed, and in a 2-dimensional picture the distortion, found in the GeS modification, can be traced to a mixing of the conduction band into the valence band, similar to a second-order Jahn Teller distorsion. This picture can be used to analyse the electronic structure of related compounds such as $(Te_2)_2I_2$, InS, or HgCl.[219] The structures of two polymorphs of Cu_2ZnGeS_4 have been determined.[220] Crystal structures have also been determined for $In_{18}Sn_7S_{34}$ [221], $Hg_2PbI_2S_2$ [222], $Pb_4In_3Bi_7S_{18}$ [223], $Pb_4In_2Bi_4S_{13}$ [224], $P_2As_2S_3$ [225], and $SrEu_{1.1}Bi_2S_4$ [226].

Sulphur-phosphorus heterocycles of the composition RP(S)Sn (R=Me, t-Bu; n=7-5) have been synthesized in ring-closing reactions between the silyl or stannyl esters of trithiophosphonic acids $RP(S)(SEMe_3)_2$ (E=Si,Sn) and chlorosulphanes S_xCl_2 (x=5-3). The heterocycles are fairly stable in the solid state, in solution disproportionation to ring compounds with larger and smaller numbers of S-atoms, respectively, as well as oligerization is observed.[227] The organotrithiophosphonic esters used above were prepared in high yield from the phosphanes $RP(SiMe_3)_2$ by addition of 3 sulphur atoms (from S_8) in toluene solution.[228] From a study of the reaction of $PSCl_3$ with hexamethyl disilazane, a method for the preparation of $Me_3SiNHP(S)Cl_2$ and $[Me_3SiNHP(S)=NSiMe_3]_2$ has been developed.[229] The reaction of the pyridine adduct of dithiophosphoric acid chloride with bifunctional compounds has been used to prepare some 5 or 6-membered cyclic dithiophosphates.[230,231] The rule of topological charge stabilization has been applied to some cage type structures related to adamantane. Examples include P_4S_3, P_4S_4, P_4S_5, and P_4S_6 as well as many other sulphides and selenides of main group elements.[232] The reaction between PCl_3 and H_2S in the presence of a base has been shown to yield P_4S_5 and $[PS_2Cl_2]^-$ according to the mechanism shown in Scheme 5.[233]

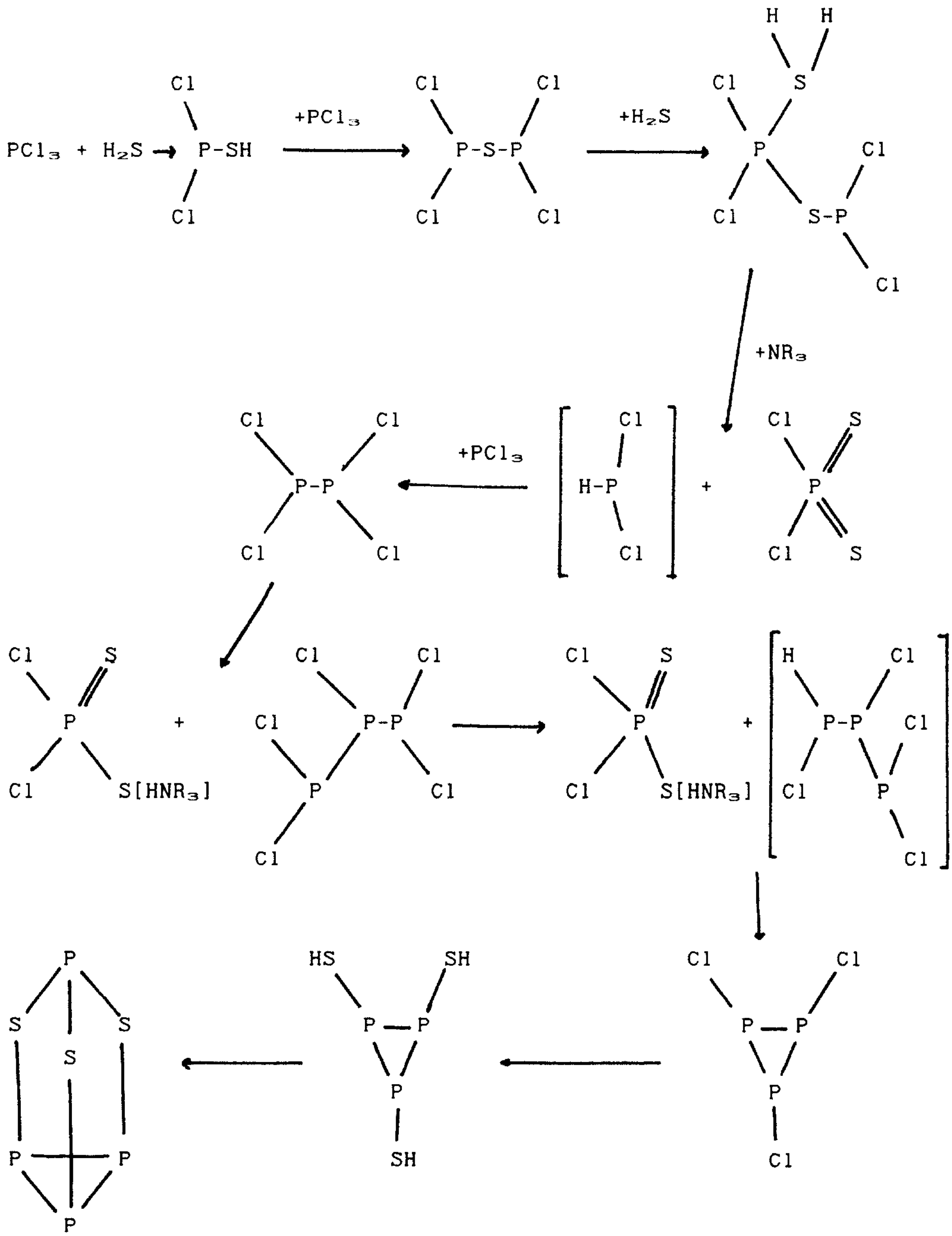
Phosphorus-31 n.m.r. spectra have been measured and assigned for some compounds with the alpha- tetraphosphorus trisulphide skeleton.[234] The diazidodithiophosphate anion,$PS_2(N_3)_2^-$,(41) can be isolated with a large cation such as Ph_4As^+. The anion is formed by the reaction of P_4S_{10} with NaN_3 in acetonitrile. Reaction of NaCN with P_4S_{10} in the same solvent gives the $(NCPS_2)_2S^{2-}$ ion (42).[235]



(41)



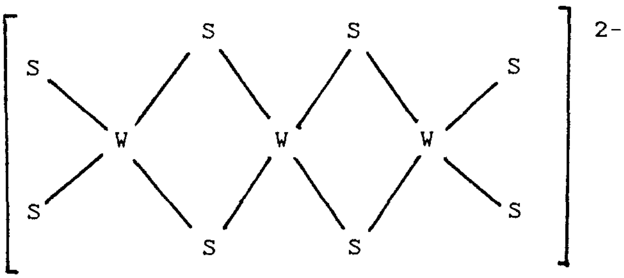
(42)



Scheme 5

The heats of formation of the arsenic sulphides, As_2S_3, As_2S_4, As_4S_3, and As_4S_5 in the gaseous state have been determined.[236] The sulphide As_4S_4 has been used as a means of preparing complexes with As-S cage molecules as ligands. Reaction of As_4S_4 with a series of Co and Fe carbonyl complexes resulted in the formation of complexes containing the As_2S_3 or As_2S_2 molecules as ligands.[237] Chalcogenostibanes of the type R_2SbER' where E=S, Se or Te and R=R'=Me, Et, have been prepared by complete exchange reaction of the corresponding distibanes and chalcogenides. The derivatives, $Me_2SbTeMe$ and $Et_2SbTeMe$ were found to be thermochromic.[238] The sulphur rich compound $[AsPh_4]_4[Bi_2S_{34}]$ has been found to contain the $[Bi_2S_{34}]^{4-}$ ion with a remarkable structure. The two Bi atoms are joined by a S_6^{2-} chain with an all trans conformation, and are each coordinated to two bidentate S_7^{2-} ligands such that the BiS_7 eight membered ring has approximately the boat-chair conformation.[239] The compound $(p\text{-}CH_3C_6H_4)_4Bi_2$ has been shown to react with sulphur or selenium to form the corresponding derivatives $(R_2Bi)_2E$, E=S or Se.[240] Since revised structural data on many of the phases MPS_3 (M = Mn, Fe, Co, Ni, Cd) have been published recently, their electronic structure has been re-examined by means of extended Huckel tight binding calculations.[241] $NiPS_3$ and $ZnPS_3$ have been prepared in new amorphous forms which show high reactivity in chemical or electrochemical insertion.[242]

The structure of $Tl_{0.82}V_5S_{3.64}$ has been shown to consist of distorted vanadium-chalcogen octahedra connected by face and edge sharing, with thallium inserted into the large quasi-rectangular channels in the three dimensional framework. No magnetic ordering was observed between 74 and 290K but a slight discontinuity at 170K suggests a phase transition.[243] The three known monomeric species $[VS_4]^{3-}$, $[VOS_3]^{3-}$, and $[VO_2S_2]^{3-}$ have been observed by high-field vanadium-51 n.m.r. spectroscopy, together with the previously unobserved ions $[VO_3S]^{3-}$, $[V_2S_7]^{4-}$, $[O_3VSVO_3]^{4-}$, $[SO_2VSVO_2S]^{4-}$, and the monoprotonated monomers.[244] A new class of catalysts for the reduction of molecular oxygen to water in acid environments has been discovered which show electrocatalytical activity comparable to that of platinum. They are Chevrel type chalcogenides with the stoichiometry $Mo_{6-x}M_xX_8$ where M is a transition metal and X is a chalcogenide.[245] Structural data for the high pressure modifications of $SnMo_6S_8$, $PbMo_6S_8$, $HgMo_6S_8$ and Mo_2S_3 have been published.[246] EXAFS analysis has been used to study the structural changes that occur during the lithiation of the amorphous materials MoS_3, WS_3 and WSe_3 and the crystalline material $NbSe_3$. For the amorphous materials, an increase in the number of metal-metal bonds was observed, as well as a significant decrease in the metal-metal distance. A reduction in the number of metal-chalcogenide interactions was also apparent and an increase in the metal-chalcogenide distance.[247] The central tungsten atom in the ion $W_3S_8^{2-}$ ion (43) has been shown to be at the centre of a square plane of sulphur atoms: the terminal tungsten atoms having tetrahedral coordination.[248]



(43)

The Raman and resonance-Raman spectra of the ions $[M'(MS_4)_2]^{2-}$ where M' = Ni, Pd, or Pt and M = Mo or W, which correspond to (43) with the central atom as M', have been measured.[249] The crystal structure of a new ternary phase in the Cu-Ta-S system, $Ta_2Cu_{0.8}S_6$, has been shown to be related to the structures of the known chalcogenides $CuTaS_3$ and TaS_3.[250] The structures of $CuTaS_3$ and Nb_2Se_9 have been redetermined.[251] The new intercalation compound $[Fe_6S_8(PEt_3)_3]_{0.05}TaS_2$ has been synthesized by flocculation of TaS_2^- layers dispersed in water-N-methylformamide; the orientation of the intercalated cluster has been determined.[252] Stable 2D zeolitic-type materials containing iron sulphide pillars have been prepared by ion exchanging a smectite clay with polyhydroxide cations of iron, followed by a sulphiding treatment at elevated temperature.[253] Ruby red crystals of Na_5FeS_4, the first thioferrate(III) with discrete tetrahedral anions, FeS_4, have been prepared by heating together a stoichiometric mixture of sodium sulphide, iron and sulphur.[254]

A single crystal X-ray structural analysis has shown that the anion of $(PPh_4)_2(NH_2Me_2)(NH_4)[Pd_2(S_7)_4]$, $[Pd_2S_{28}]^{4-}$ forms a 30-membered cage containing an entrapped cation, NH_4^+. The four equivalent S_7^{2-} ligands are so arranged that the sulphur atoms have alternatingly small (373.3-408.0pm) and large (453.3-492.1pm) distances from the centre of the cage.[255] The position of the equilibrium, equation (16) has been shown to be solvent dependent with aromatic bases and PPh_3 favouring the formation of copper(I) adducts.[256]

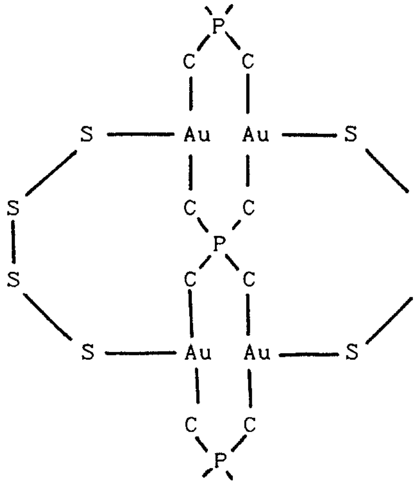
$$2Cu[S_2P(OR)_2]_2 \rightleftharpoons 2Cu[S_2P(OR)_2] + [(RO)_2P(S)S-]_2 \qquad (16)$$

Orange $[(PPH_3)_2N][Ag(S_9)].S_8$ has been prepared by reaction of a definite S_x^{2-} solution with $AgNO_3$. X-ray structural studies showed the anion $[Ag(S_9)]^-$ to have a symmetric conformation with a ten-membered ring system.[257] To determine which of the two known gold sulphides (containing Au(I) or Au(III)) are formed in the reaction of Au(III) with different allotropes of sulphur the following reactions were carried out. When Au(III) in the form of $Au_2(SO_4)_3$ in concentrated acid was reacted with electrolytically formed short-chain sulphur, monovalent gold sulphide was formed. If H_2S is allowed to react with the same solution Au_2S_3 was formed. Alternatively, if ordinary alpha-sulphur, S_8, was used the an equimolar mixture of Au_2S and Au_2S_3 were formed.[258] The addition of approximately equimolar ammounts of aqueous ammonium polysulphide solution to the gold(II)ylide dimer, $[Au(CH_2)_2P(C_6H_5)Br]_2$ in thf results in the formation of the red product (<u>44</u>) whilst the use of Na_2S gave (<u>45</u>).[259]

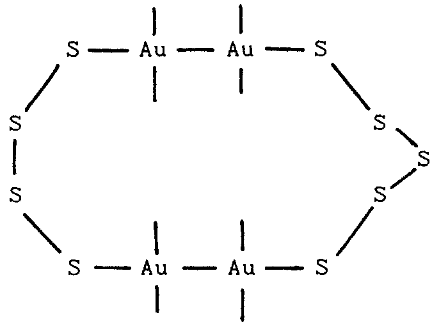
The dissolution of synthetic ZnS in aqueous sulphuric acid with and without added oxygen has been studied in an autoclave at temperatures up to 473K. In the absence of oxygen, hydrogen sulphide is produced and the equilibrium (17) is established.

$$ZnS + H_2SO_4 \rightleftharpoons Zn^{2+} + SO_4^{2-} + H_2S(aq) \qquad (17)$$

In the presence of oxygen the H_2S is oxidised to elemental sulphur and H_2SO_4.[260]



(44)



(45)

A process for the complete transformation of cyanide to SCN^- photochemically has been described. The method, which uses Rh-loaded CdS suspension, visible irradiation and an alkaline sulphide medium is efficient even in the presence of air and at very high cyanide concentrations.[261] The rate of reduction of plutonium(VI) and neptunium(VI) by bisulphide ion in neutral and mildly alkaline solutions has been studied.[262] Structural studies have been published for the following sulphides: $(UO_2)ErS_3$,[263,264], ZnS polytypes, [265], Eu_2CuS_3,[266], $[(MeC_5H_4)_3U]_2S$,[267], $[(n\text{-}Pr)_4N][Ga(SR)_4]$ R=Et,Ph,[268].

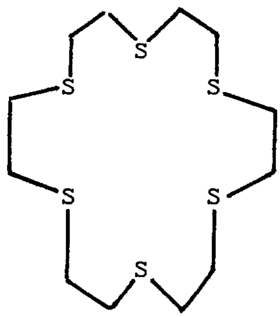
Phase relations of sulphides are given in Table 2.

Table 2. Sulphide Phase Systems

System	Ref.	System	Ref.
As_2S_3 -SnSe	269	SmS - Ga_2S_3	278
Na_2S - Tl_2S	270	Tl - Cd - S	279
In - Bi - S	271	Yb - As - S	280
Bi_2S_3 - DyF_3	272	La_2S_3 - La_2O_3 - Ga_2S_3	281
$CoCr_2S_4$ - $CoCl_2$	273	Cd - Ge - S	282
Sn - Bi - S	274	$NiCr_2S_4$-$NiGa_2S_4$	283
Cu - Tl - S	275	P_4S_3-P_4Se_3-As_4S_3-As_4Se_3	284
As_2S_3 - SmS and		MeX-Ln_2X_3	285
As_2S_3 - Sm_2S_3	276	Ga_2S_3 - Eu_2O_2S	286
As - S	277	Ga_2S_3 - Pr_2O_3	287

6.2.6 Bonds to Carbon

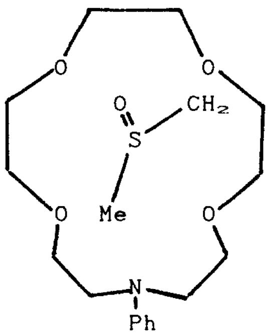
Whereas oxygen donor polyether crown ligands and related ionophores are known to bind, sometimes highly selectively, Group I and II metal ions, the corresponding polythia ligands appear to bind Transition metal ions more effectively. Complexes of the ligand (46) with Pd or Pt have been prepared in which the conformation of the macrocycle in the isomorphous $[Pd(46)]^{2+}$ and $[Pt(46)]^{2+}$ cations is an S-shaped double boat. The M^{2+} ion at the molecular inversion centre is coordinated to four sulphur atoms in a square planar arrangement with the remaining two sulphur atoms making only weak interactions with the metal ion.[288]



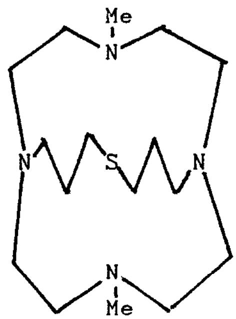
(46)

The structures of complexes of 1,4,7 trithiacyclonane, a macrocyclic ligand, with Ag(I) and Cu(I) have been shown to depend on the hardness/ softness of the anion used. When the anion is soft, such as I^-, a distorted tetrahedral structure is formed in which the ligand functions as a tridentate ligand and the fourth position is occupied by the anion. With hard anions such as ClO_4^- or NO_3^-, oligomers are formed in which the ligand is bridging and a distorted tetrahedral configuration results.[289] Hexathia-24-crown-6 has been shown to wrap around Ni(II) to form an octahedral cation with meridional stereochemistry.[290] Crown ethers have been shown to activate DMSO in reaction with aromatic amines to produce colored quinone dyes. It is thought that the crown ether complexes with DMSO through the sulphur atom which in the presence of amine as base produces nucleophilic species such as (47).[291]

The synthesis of the new thia-aza cage (48) and of its Cu(II) complex have been described. The electronic spectra of the Cu(II) complexes show the same features both in the solid state and in solution and are diagnostic of a distorted square pyramidal structure.[292]

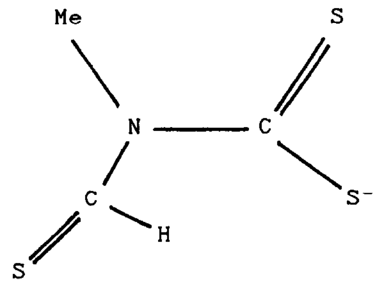


(47)



(48)

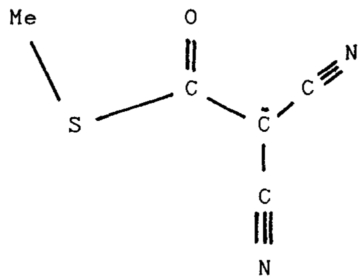
Alkylidenesulphur tetrafluorides, $R_2C=SF_4$ exhibit a strong sulphur-carbon bond that can be described as a double bond. The existence of an equilibrium between a CS and a CC double bond in the case of $CF_3-CH=SF_4/CF_2=CH-SF_4$ allows the estimation of the C=S bond energy at about 377kJ as compared with 255kJ for the average C-S bond energy.[293] Contrary to other sulphines, $(CF_3)_2C=SO$ reacts with amines, alcohols and HCl to yield derivatives of the corresponding sulphinic acid. Reaction with HBr gives a C-brominated sulphenyl bromide and sulphinyl bromide via a redox reaction. $(CF_3)_2C=SO$ also reacts with 2,3-dimethylbutadiene to give the corresponding cyclic adducts, which could be oxidised to cyclic sulphones with m-chloroperbenzoic acid.[294] Starting from carbon diselenide or carbon selenide sulphide the electrochemical preparation of heterocyclic dichalcogenolates $C_3X_5^{2-}$ has been described.[295] The crystal and molecular structure of tetra-n-butylammonium N-methyl-N-thioformyldi-thiocarbamate shows the anion to have the conformation shown in (49).[296]



($\underline{49}$)

$Ca[S_2CC(CN)_2].5H_2O$ has been synthesized and its structure determined. Calcium has a distorted bicapped trigonal-prismatic coordination of six O and two N atoms. Two O atoms are coordinated to two different Ca^{2+} ions to form dimeric units with each $S_2CC(CN)_2$ ligand bridging different dimeric units via its N atoms. The S atoms of the ligand are not included in the coordination sphere of the Ca ions but are involved in several O-H..S hydrogen bonds.[297] The ion $(S_2C_4N_2)^{2-}$ has been shown to exhibit two anodic maxima in the cv diagram. The reaction product of the first step is the dimer $[(NC)_2C{=}C(S)S{-}S(S)C{=}C(CN)_2]^{2-}$ which was shown to consist of two planar $(S_2C_2N_4)$ units which are orientated perpendicular within the anion.[298] The crystal structure of $K_2[S_2C{-}C_6H_4{-}CS_2].2H_2O$ has been determined.[299] The anion $[OSC{-}N_2H_2{-}CSO]^{2-}$ and the molecules $CH_3S{-}CO{-}N_2H_2{-}CO{-}SCH_3$ and $CH_3O{-}CS{-}N_2H_2{-}CS{-}OCH_3$ have been shown to exhibit non-planar structures in the solid state with the dihedral angles between either of the two strictly planar R-CX-NH groups of each molecule being 78.8°, 77.5° and 104.5° respectively.[300] The reaction of $K_2[S(O)C{=}C(CN)_2]$ with CH_3I yields the mono-S-methyl product in which the potassium has a monocapped trigonal prismatic coordination and the methyl group is directed towards the oxygen atom ($\underline{50}$). Oxidation of the oxothiolate gives $[(NC)_2C{=}C(O){-}S{-}S{-}(O)C{=}C(CN)_2]^{2-}$ in the first oxidation step which has two planar $[S(O)C{=}C(CN)_2]$ units perpendicularly orientated.[301]

Hydrogen bonded complexes of dialkyl sulphides and alkanethiols with HF have been prepared by condensing the argon diluted reagents at 12K. Infrared spectra of the $(CH_3)_2S..HF$ complex suggest that the latter has a weaker hydrogen bond than the $(CH_3)_2O..HF$ complex.[302] Structural studies have shown that the S-S bond length in Me_2SSMe^+



(<u>50</u>)

is relatively long whilst in $(MeS)_3^+$ and $(MeSe)_3^+$ the chalcogen-chalcogen bond lengths are almost normal for single bonds. Each cation involves a three coordinated chalcogen atom, the former having an all-cis conformation and the latter two being fairly similar with the chain-end methyl groups in trans positions to each other.[303]

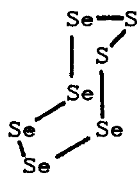
The reactions of CS_2 with hydrazine,[304] N,N-diphenylformamide,[305]-[308] and acetamide[309]-[313] have been reported. The reaction of COS with hydrazine in the presence of NaOMe has been shown to produce $Na_2[SOC\text{-}NH\text{-}NH\text{-}COS]$.[314] A series of copper thioxanthates have been prepared and characterized.[315] In reaction mixtures of acetylenes, RC≡CR, and $ClSSCl/AlCl_3/H_2CCl_2$ or $S_8/SbCl_5/H_2CCl_2$ at 250K the formation of 1,2-dithiete radical cations, $R_2C_2S_2.^+$ has been observed. On warming to 300K 1,4-dithiine radical cations, $R_4C_4S_2.^+$ were produced. Their generation can also be achieved by the reaction of 1,2-dichloroethene or 1,1,2,2-tetrabromoethane derivatives with $Na_2S_2/AlCl_3/H_2CCl_2$, a method well suited for ^{33}S isotope marking.[316] The synthesis of perhalogenated 1,3,5-trithiane 1,1,3,3,5,5-hexaoxides and their reaction with bases has been reported.[317] Dithiocyanogen, NCS-SCN has been attached as a ligand to a Transition metal for the first time by reacting it with $AgAsF_6$ in liquid sulphur dioxide.[318] The reaction of dithiocyanogen and trithiocyanogen with hexafluoroacetone (HFA) leads to the cycloaddition products $(SCN)_2.4HFA$ and $S(SCN)_2.4HFA$. These are the first reactions of $(SCN)_2$ and $S(SCN)_2$ without cleavage of the S-S bonds.[319] Spectroscopic studies of dimethyl(methylthio)- and dimethyl(phenylthio)sulphonium salts, $Me_2SSR^+A^-$ ($A=AsF_6^-$ or $SbCl_6^-$, have been reported.[320] Solvolysis of thiocarbonyl fluorides in HF/SbF_5 or FSO_3H/SbF_5 has been shown to yield dithietan-2-ylium ions reaction of which with base F^- in the solvent system HF gives dithietanes.[321] A series of allyl methyl sulphoxides $R^1R^2R^3C\text{-}S(O)\text{-}CH_2CH\text{-}CH_2$ with R^1,R^2,R^3=F,Cl,CF_3 as well as the corresponding sulphones have been synthesised.[322]

Tetrathiosquarate has been shown to act as a bridging bi(chelate) ligand in complexes with Cu,Ag,Rh Au,Pt and Pd and as a mono chelate in complexes with Ni and Zn.[323]

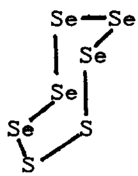
6.3 SELENIUM

6.3.1 The Element and Cationic Species.

The structure of decaselenium bis fluorosulphate, $Se_{10}[SO_3F]_2$ has been shown to contain the Se_{10}^{2+} cation of the bicyclo[4,2,2]decane type and fluorosulhate anions. The Se-Se bond lengths in the cation vary from 224.6 to 245.0 pm.[324] Selenium-77 NMR studies have been performed on natural- abundance and enriched samples of $Se_8(AsF_6)_2$ and $Se_{10}(AsF_6)_2$ in SO_2 and $100\%H_2SO_4$. The Se_8^{2+} species was found to be rigid in solution at all temperatures from 203K to room temperature although there was some evidence for slow exchange at higher temperatures. The Se_{10}^{2+} species appears to undergo structural isomerism in SO_2 solution at ambient temperatures to give two forms, one of which disproportionates below 273K to give Se_8^{2+} and the other was tentatively identified as Se_{17}^{2+} or, less likely, Se_{18}^{2+}.[325] Selenium-77 nmr studies have also been used in the characterization of selenium and selenium sulphide ring molecules.[326] The sulphide, Se_5S_2 has been shown to crystallize



(51)



(52)

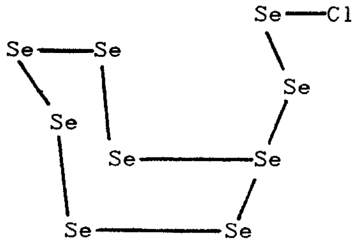
as a mixture of the two isomers (51) and (52), the ratio of which is temperature dependent. Se_5S_2 can be prepared from titanocene pentaselenide and S_2Cl_2 and reaction of the former with

SCl_2 yields Se_5S and with Se_2Cl_2, Se_7. It seems likely that a chair configuration will be adopted by Se_7.[327]

The reaction of Se_4^{2+} with $W(CO)_6$ and $Fe_2(CO)_9$ in SO_2 has been shown to give the mixed cationic cluster $[FeW(CO)_8Se_2]^{2+}$ which has a tetrahedral core structure.[328]

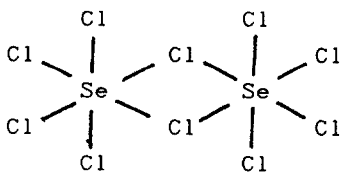
6.3.2 Bonds to Halogens.

The new compound $(Se_9Cl)^+(SbCl_6)^-$ has been prepared by the reaction of Se with $NOSbCl_6$ in SO_2. The compound contains the first example of a seven membered Se ring (53).[329]

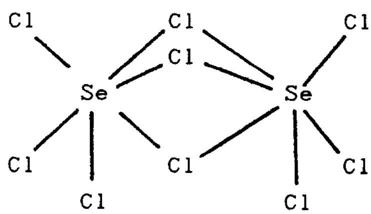


(53)

The $Se_2Cl_{10}^{2-}$ and $Se_2Cl_9^-$ anions have been prepared and isolated as $AsPh_4^+$ salts from the reaction of $(SeCl_4)_4$ with stoichiometric quantities of chloride ions in $POCl_3$ solutions. X-Ray diffraction studies show in each case two distorted octahedral $SeCl_6$ groups connected through a common edge in (54) and a common face in (55). The terminal Se-Cl bonds (average 231.7pm in (54), 222.3pm in (55)) are much shorter than the bridging bonds (average 266.1pm in (54)and 265.2pm in (55)). The stereochemical activity of the Se(IV) lone pair causes severe distortion of the central Se_2Cl_2 ring in the centrosymmetric $Se_2Cl_{10}^{2-}$ ion.[330]



(54)



(55)

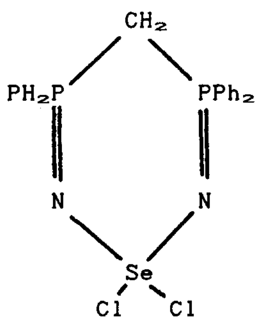
The crystal structure of $[SeCl_3][AuCl_4]$ has been shown to consist of centrosymmetric $[SeCl_4.AuCl_4]_2$ dimers with a distorted octahedral coordination geometry at the selenium atom. The compound is not isostructural with the tellurium analogue.[331] The addition of R_4NX, R= Et, ^nPr or ^nBu, to a solution of SeX_2, X= Cl or Br, in acetonitrile solution results in the formation of tri- and tetrahaloselenate(III) complexes. The R_4NSeCl_3 complexes were shown to be relatively unstable, being readily destroyed by laser light:

$$2R_4NSeCl_3 \longrightarrow (R_4N)_2SeCl_6 + Se \qquad (17)$$

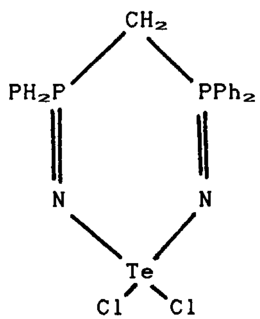
and especially to hydrolysis:

$$2SeCl_3^- + H_2O \longrightarrow SeOCl_3^- + 2HCl + Cl^- + Se \qquad (18)$$

The Raman spectra of solutions of SeX_3^- and SeX_4^- were consistent with T-shaped and square planar structures respectively.[332] The bis-silylated phosphorane $Me_3SiNP(Ph_2)CH_2(Ph_2)PNSiMe_3$ reacts with $SeOCl_2$ and $TeCl_4$ to form the new heterocyclic compounds (56) and (57) respectively.[333]



(56)



(57)

Equilibrium measurements in the Se-O-Cl system have shown that solid $SeCl_4$ and liquid Se_2Cl_2 exist as condensed compounds whereas only $SeCl_2$ exists in the gas phase. Thermodynamic data were derived from the decomposition sublimation of $SeCl_4$, the decomposition of Se_2Cl_2 and the evaporation and decomposition of $SeOCl_2$.[334]

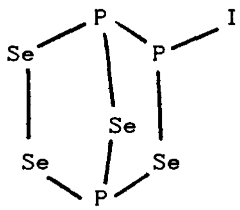
The structure of $(NH_4)_2SeBr_6$ has been shown to contain octahedral $SeBr_6^{2-}$ units in an antifluorite array of cations with the Se-Br distance 257.7pm. In contrast the $SeBr_6^{2-}$ ion in $[H_3N(CH_2)_3NH_3]SeBr_6$ is statistically distorted with Se-Br distances from 254.7 to 259.5pm.[335] The $Se_4I_4^{2+}$ cation has been prepared by the reaction of Se_4^{2+} and iodine in SO_2 solution. The 77-selenium NMR spectrum is consistent with an $I_2Se^+SeSeSe^+I_2$ structure for the cation and the equilibrium of $Se_4I_4^{2+}$ with lesser amounts of SeI_3^+ and $Se_6I_2^{2+}$.[336]

6.3.3 Bonds to Oxygen

The reaction of SeO_2 with CeO_2 at 543K leads to the formation of $CeSe_2O_6$ which has a structure consisting of zig-zag strings of CeO_8 distorted, edge-sharing, Archimedean antiprisms linked by Se atoms in three-fold coordination.[337] The oxidation by SeO_2 of imines containing an alpha methylene group has been shown to give alpha iminocarbonyl compounds.[338] The solubilities of some phases in the system M_2O_3-SeO_2-H_2O where M=Al, Ga, or In have been determined.[339] H_2SeO_3 has been studied by neutron diffraction and has been shown to have tetrahedral SeO_4 groups connected by hydrogen bonds with O..O distances of 261.5 and 262.1pm at 243K.[340] $CsHSeO_4$ has been shown not to be isomorphous with any other $MHSeO_4$ or $MHSO_4$ compound.[341] The structure of $KHSeO_4$ is however isomorphous with $KHSO_4$ and displays a similar hydrogen bonding scheme but with shorter bond lengths.[342] The polarographic and amperometric behaviour of simple solutions of selenites and selenates as well as binary mixtures of the two in HCl solution have been investigated.[343] Structural studies have been carried out on $SrSe_2O_5$,[344] and $ZnSeO_3$ and $CuSeO_3$.[345]

6.3.4 Selenides.

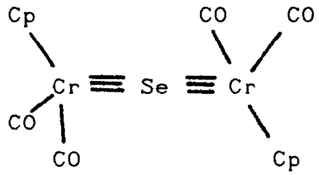
The decomposition and synthesis of hydrogen selenide under light pulses of 300-600 microsecond duration has been studied.[346] The crystal structure of $LiInSe_2$ has been determined from single crystal data. The compound is isostructural with beta-$NaFeO_2$.[347] Studies have been carried out on the systems $ZnIn_2S_4$-$ZnIn_2Se_4$-In_2Se_3-In_2S_3[348] and $TlInSe_2$-$TlGaTe_2$.[349] The compound $Na_4Sn_2Se_6.13H_2O$ has been prepared by reaction of $SnSe_2$ with alkali metal selenide. The ion contains isolated $Sn_2Se_6^{4-}$ anions consisting of two edge shared tetrahedra which are in contact with the hydrated Na^+ ions via an extensive hydrogen bridge system.[350] A new series of lead chalcogenide anions $Pb_2Se_3^{2-}$ and $Pb_2Te_3^{2-}$ has been obtained by extraction of the appropriate ternary or quaternary Zintl phases of the type $KPb_xSe_{(3-n)/3}Te_{n/3}$ with ethylenediamine in the presence of 2,2,2-crypt. The crystal structure of $(2,2,2\text{-crypt-}K+)_2Pb_2Se_3^{2-}$ contains four trigonal-bipyramidal $Pb_2Se_3^{2-}$ anions in the unit cell.[351] A Raman and resonance Raman study of P_4Se_3 has been carried out.[352] P_3Se_4I may be prepared by the reaction of molten P_4Se_3 and I_2. The structure of the molecule is derived from the structure of $P_4Se_3I_2$ by substitution of a P-I group by a selenium atom(58). The mean P-Se bond length is 225.0pm and the Se-Se length is 236.9pm. The molecule is stabilized by two weak intramolecular P-Se and P-I bonds.[353]



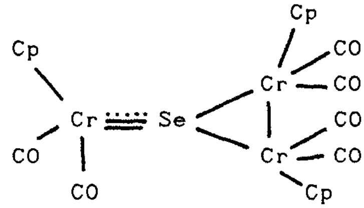
(58)

The compound $Ba_2AsSe_4(OH)_2H_2O$ has been prepared by the reaction of $Ba(OH)_2$ with As_2Se_3 in aqueous solution. Its structure contains isolated $AsSe_4^{3-}$ tetrahedra with C_s symmetry.[354] The alkali selenoarsenates(III), $KAsSe_3.H_2O$, $RbAsSe_3.1/2H_2O$ and $CsAsSe_3.1/2H_2O$ have been prepared by hydrothermal reaction of the respective alkali carbonate with As_2Se_3 at a temperature of 408K; all contain polyselenoarsenate anions $(AsSe_3^-)_n$ in which the basic units are tetrahedra linked together through Se-Se bonds into infinite chains.[355] The photoelastic trends for some 60 different infrared-transmitting chalcogenide glasses (mixed sulphide-selenides of As, Ge and Sb) have been studied.[356] The selenide, $CsSb_2Se_4$, prepared by hydrothermal reaction of Cs_2CO_3 and Sb_2Se_3 at 388K, contains polyselenoantimonate anions which display both (Sb)Se-Sb and (Sb)Se-Se(Sb) bridges.[357]

The first example of a planar Cr_3Se multiple bond system (60) generated by the selective reduction of (59) with cobaltocene has been described.[358]



(<u>59</u>)



(<u>60</u>)

The reaction of the ionic complex $K[(\eta^5-C_5Me_5)Cr(CO)_3]$ with Se_2Cl_2 has been shown to give the diselenium compound $(\eta^5-C_5Me_5)_2Cr_2(CO)_5Se_2$ which is converted to $(\mu-Se)[(\eta^5-C_5Me_5)Cr(CO)_2]_2$ with triphenylphosphine.[359] The control of magnetic phase transitions via reversible electron/ion transfer reactions at 300K using copper selenospinels, $Cu_{1+y}Cr_2Se_4$, as the model system has been reported.[360] The crystal structure of $MoSe_2$ has been refined from single crystal data.[361] The reactions of $Se_4(AsF_6)_2$, $Se_8(AsF_6)_2$ and $Se_{10}(SbF_6)_2$ with $Mo(CO)_6$ and $W(CO)_6$ in liquid SO_2 give diamagnetic products of the type, $[M_2(CO)_{10}Se_4][EF_6]_2$ in high yields. The structure of $[W_2(CO)_{10}Se_4][AsF_6]$ consists of two centrosymmetrically related pentagonal-bipyramidal $W(CO)_5(\eta^2-Se_2)^+$ groups linked by weak Se-Se bonds. The interactions between the diselenide groups are analogous to those observed in the $Se_4S_2N_4^{2+}$ cation.[362] Complexes containing a tetraselenide ligand, $[(C_5Me_5)_2M_2Se_5]$ have been prepared by the stepwise addition of selenium to the M-M double bond of $[(C_5Me_5)_2M_2(\mu-CO)_2]$ where M is either Co or Rh.[363] The new layered chalcogenides Ta_2NiSe_7 and Ta_2PtSe_7 have been prepared and characterized. The layers are comprised of Ta atoms in octahedral and bicapped-trigonal-prismatic chalcogen environments and Ni or Pt in octahedral sites.[364] The use of hydrogen selenide for the synthesis of binuclear palladium complexes and their conversion into novel dimetallic selenoxides has been described.[365] Anomalous temperature-dependent decomposition of dimethyl zinc and its reaction with hydrogen selenide under metal-organic vapour phase epitaxy growth conditions have been studied and the results correlated with the optimum growth of zinc selenide epitaxial layers on single crystalline GaAs substrates.[366] Sharp line cathodoluminescence spectra at 8K from Tm and Er ions implanted into hexagonal ZnS and ZnSe crystal platelets have been obtained.[367]

The mononuclear complexes [$M(CO)_5(MeSeCH_2SMe)$] (M=Cr,Mo or W) have been prepared and are present in solution as isomers with both S-M and Se-M bonding. In addition to the facile pyramidal atomic inversion of the metal-co-ordinated sulphur and selenium atoms, a novel 1,3-metal shift between the two different ligand atoms occurs.[368] Selenium exclusion from a Pt-Se-Pt bond sequence and selenium insertion into a Pt-P bond has been described.[369] the reaction of [$Pt(PPh_3)_4$] with closo-$SeB_{11}H_{11}$ affords [$PtH(PPh_3)_3$][$SeB_{10}H_{11}$] and [2,2-$(PPh_3)_2$-1,2-$SePtB_{10}H_{10}$].CH_2Cl_2. The same paper reports an attempt to provide more information on Se-B bonding from a crystal structure determination of $SeB_{11}H_{11}$; however scrambling of the Se atom and eleven B-H groups over the twelve dodecahedral positions precluded any precise determination of Se-B bond distances.[370]

Phase diagram studies involving selenides are given in Table 3.

Table 3 Selenide Phase Systems

System	Ref.	System	Ref.
As_2Se_3 - PbS	371	SnSe - Ce_2Se_3	380
As_2Se_3 - NiSe	372	Tl - Ge - Se	381
As_2Se_3 - CdS	373	Tl - In - Se	382
As - Se	374	Yb - As - Se	383
Sn - Bi - Se	375	AsSe - SmSe	384
CdSe - $GeSe_2$	376	SnSe - TlSe	385
SnTe-InSe & SnTe-Tl_2Se	377	SmSe - Ga_2Se_3	386
TlSe-FeSe & TlSe-CoSe	378	$CuSbSe_2$ - Cr_2Se_3	387
Cu_2Se - $SnSe_2$ - Cr_2Se_3	379	Sb_2Se_3-$FeSb_2$ & Sb_2Se_3-Fe_3Sb_2	388

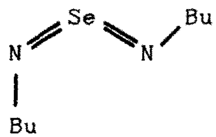
6.3.5 Bonds to Nitrogen

The reaction of trimethylsilyl azide with mesitylene selenenyl chloride has been shown to give mesitylene selenenyl azide, and reaction of tris(trimethylsilyl) amine with benzene selenyl chloride gives tribenzene selenene amide.[389]

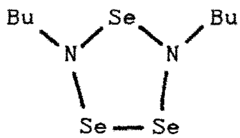
$$ArSeCl + Me_3SiN_3 \longrightarrow ArSeN_3 + Me_3SiCl \qquad (19)$$

$$3PhSeCl + (Me_3Si)_3N \longrightarrow (PhSe)_3N + 3Me_3SiCl \qquad (20)$$

The first seleninylamine, t-BuNSeO, has been prepared from t-$BuNH_2$ and $SeOCl_2$ in a 3:1 molar ratio. The selenium diimide (61) was isolated from the corresponding reaction of $BuNH_2$ and $SeCl_4$ in a 6:1 molar ratio. The compound decomposes to give cyclic $Se_3(NBu)_2$ (62).[390]



(61)



(62)

1,1 dichloro-3,5 diphenyl 4H-1,2,4,6 selenatriazene has an Se-N-C-N-C-N ring in a boat conformation with the selenium atom displaced 34.8pm, and the opposite nitrogen atom which is bonded to a hydrogen atom displaced 13pm from the plane of the boat bottom.[391]

6.3.6 Bonds to Carbon.

A structure has been suggested for the amorphous, polymeric carbon selenide $(C_2Se_3)_n$ obtained by heating $(CSe_2)_n$ in vacuum.[392] Trifluoromethyl selenyl thiocarbonyls have been shown to react with $CF_{3-n}Cl_nSCl$ or CF_3SeCl the corresponding disulphanes or selanesulphanes. Oxidation of $CF_3SeC(S)X$, X=CF_3Se,CF_3SCl with 3-Cl-$C_6H_4C(O)OOH$ yields the compounds $CF_3Se(X)C$=S=O. Only decomposition products were obtained from the reaction of $(CF_3Se)_2CSe$ and Cl_2, CF_3SeCl, CF_3SCl or 3-Cl-$C_6H_4C(O)OOH$. The preparation of compounds of the type RN=Se=NR where R=Me_3Si, $CF_3C(O)$ or CF_3SO_2 were also described.[393] The o-benzenediselenolate ligand may be conveniently prepared by sodium borohydride reduction of poly- (o-phenylene diselenide), which is readily synthesized from o-dibromo- benzene and sodium diselenide.[394] 3-Alkyl-1,2,3-diselenaboroles have been shown to react with n- and i-alkyl isocyanates and hexamethyl diisocyanate to form

2,3-dihydro-4H-1,3,2-selenazaborin-4-ones.[395]

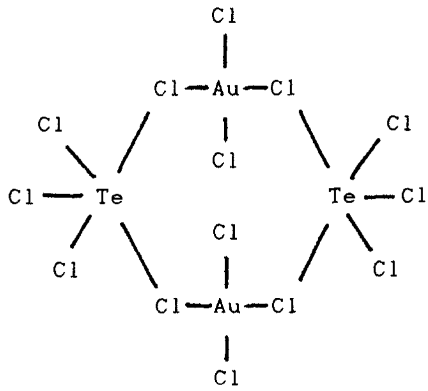
6.4 TELLURIUM & POLONIUM

6.4.1 The Element.

An extension of the REX relativistically parametrized extended Huckel LCAO molecular orbital method to periodic solids has been outlined. The method which gives a simple and systematic approach to the description of the spin-orbit splitting of energy bands, has been applied to tellurium and polonium, with trigonal-helical and simple cubic structures respectively. the helical structure of tellurium is described as a distortion of a simple cubic structure with the distortion quenched in the case of polonium by its very large spin-orbit coupling.[396]

6.4.2 Bonds to Halogens

Some rules for the stereochemistry of the lone pair electrons in the TeX_6^{2-} ion where X= Cl,Br and I, have been proposed. The structure of 1,2-ethane- diammonium hexachloro tellurate(IV) has been shown to be isostructural with the corresponding stannate.[397] $(Me_4N)_2TeCl_6$ has been shown to have an antifluorite-like arrangement of Me_4N^+ cations and $TeCl_6^{2-}$ anions. The remaining holes in this array can be filled with MeCN molecules forming the inclusion compound $(Me_4N)_2(MeCN)TeCl_6$. In the parent compound the $TeCl_6$ octahedra are almost regular but in the inclusion compound the ion is statistically distorted with the approximate point symmetry 4mm. The solvent molecules can be removed at temperatures above 320K.[398] The preparations, Raman spectra and crystal structures of the compounds, $(SCl_3)(SbCl_6)$, $SBr_{1.2}Cl_{1.8})(SbCl_6)$, $(TeCl_3)(AlCl_4)$, $(TeCl_3)(AsF_6)$, $(TeCl_3)(SbF_6)$ and $(TeF_3)_2SO_4$ have been reported. All the MX_3^+ cations in these compounds are involved in significant anion-cation secondary bonding interactions of varying strengths and geometries. The tetrachloroaluminate salt of $TeCl_3^+$ was found to have a different modification from that previously reported.[399] The compound $Te_3^+AuCl_4^-$ also has a structure involving secondary interactions which link the ions to form centrosymmetric $(TeCl_3.AuCl_4)_2$ dimers (63). The cation polyhedra, including secondary Te...Cl interactions, is a square pyramid with mean Te-Cl bond lengths of 229.4pm and Te..Cl distances of 302.8pm.[400]



(63)

The five coordinate Te(IV) complexes, $[R_2TeCl_2.L]$, where R= Ph or p-$MeOC_6H_4$ and L= a series of tertiary phosphine selenides, have been obtained by the reaction of R_2TeCl_2 and L under anhydrous conditions. The complexes possess distorted octahedral symmetry around a central Te atom which is surrounded by five groups and a lone pair occupies the vacant site. Diphosphine selenide is thought to act as a bridging ligand between two tellurium atoms as found in the diphosphine complexes of other metals.[401] The reaction of $MoTe_2$ with S_2Cl_2 has been shown to yield $MoS_2Cl_3.2TeCl_4$ at 373K and $2MoS_2Cl_3.TeCl_4$ at 412K. Raman spectra indicate that both compounds contain the S_2 ligand.[402]

6.4.3 Bonds to Oxygen

The polarographic behaviour of tellurite ions in universal buffer solutions of pH from 7.1 to 11.2 has been investigated. Reduction took place in two steps at pH 7.1 and in one step at pH 8.5 to 11.2, with no observed reduction below pH of 7.1.[403] The Caesium tellurium oxides Cs_2TeO_3, $Cs_2Te_2O_5$, $Cs_2Te_4O_9$ and $Cs_2Te_4O_{12}$ have been prepared by heating mixtures of TeO_2 and the alkali metal carbonate in an argon atmosphere. The first two oxides have structures related to perovskite whilst the remainder have structures of the inverse pyrochlore type. Unusually the structure of $Cs_2Te_4O_{12}$ contains almost regular TeO_6 octahedra with Te-O bond lengths of

210.4pm.[404] The ternary oxides $PbTeO_3$ [405] and $HgTeO_3$ [406] both contain slightly distorted TeO_3^{2-} trigonal-pyramids. Structural studies have also been made on the compound $Na_6[TeW_6O_{24}]22H_2O$ [407] and a zinc tellurite glass.[408]

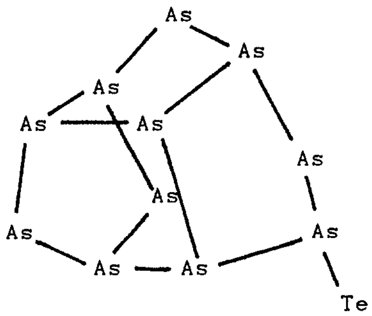
The compound $[N(n\text{-}Bu)_4^+][H(OTeF_5)_2^-]$ has been prepared by the reaction of $HOTeF_5$ and $[N(n\text{-}Bu)_4^+][OTeF_5^-]$. The anion is unusual in that it contains a very strong O-H-O hydrogen bond with an O..O distance of 259.5pm. Therefore, despite the fluorine-like behaviour of the $OTeF_5$ moiety, the O-H-O hydrogen bond in the $H[OTeF_5)_2^-$ anion does not rival the bifluoride ion as the strongest, shortest hydrogen bond.[409] The compound $[TlOTeF_5(mes)_2]_2$ has been shown to provide an example with which to gauge the variability or constancy of two recently discovered features, Tl(I)-arene coordination and bridging $OTeF_5$ groups. $TlOTeF_5$ was also prepared and found to be soluble in aromatic hydrocarbons.[410]

The new pyrochlores $Pb_2[M_{1.5}Te_{0.5}]O_{6.5}$ where M= Ti, Zr, Sn or Hf, have been prepared and crystal data determined.[411] The following phase systems involving tellurium oxides have been determined: $Li_2O\text{-}TeO_2\text{-}TiO_2$ [412], $CaO\text{-}MoO_3\text{-}TeO_2$ [413], and Ce-Mo-Te-O [414].

6.4.4 Tellurides

Solutions of sodium polytelluride in liquid ammonia have been studied by UV-visible spectroscopy. Na_2Te_2 and Na_2Te_3 were identified as distinctive, spectroscopically identifiable species but Na_2Te_4 was found to be a mixture of Na_2Te_3 and insoluble Te. No evidence for a higher polytelluride was found but a species postulated to be NaTe was found as a precursor to Na_2Te.[415] A separate group of authors has however prepared $NaTe_3$ by the reaction of sodium and tellurium in liquid ammonia. The compound contains chains of Te_6^{2-} linked together by their terminal atoms to produce infinite strings which may be built up of cubane-like clusters Te_{12}^{6-}.[416] The compounds, $[Ba(en)_3]Te_3$ and $[Ba(en)_{4.5})]Te_3$, have been prepared by reaction of the elements in ethylenediamine and their crystal structures determined.[417]

The first chalcogenide of divalent aluminium, Al_7Te_{10}, has been shown to have a central, double barrelane unit, $[Te_4Al_4\text{-}Al_4Te_4]$ which contains an Al-Al bond of 260pm which is slightly longer than an expected single bond.[418] The reaction of the alloy, $K_{1.6}As_{1.6}Te$ with a <2.2.2>cryptand ligand in ethylenediamine has been shown to reult in the formation of a compound formulated as $[K(crypt<2.2.2>)]3As_{11}Te$.en. The anion, $As_{11}Te^{8-}$ has an As_{11}^{3-} framework with an exocyclic tellurium atom (64). Nine arsenic atoms are three coordinate (one to the tellurium atom) the other two being two-coordinate.[419]



(64)

The Te_2 - pressure over Mo_3Te_4 and $MoTe_2$ as well as over mixtures of Mo $+Mo_3Te_4$, $Mo_3Te_4+MoTe_2$, and $MoTe_2+Te$ have been measured.[420] the electronic structure of the ditelluromercurate(II) Zintle anion, $HgTe_2^{2-}$ has been calculated.[421] A thermodynamic analysis of the complex $Hg_{1-x}Cd_xTe$-iodine chemical vapour transport system has been the subject of a series of publications.[422,423] The crystal structures of: $LiInTe_2$ [424], $NaCu_3Te_2$ [425], and Tl_3AgTe_2 [426] have been determined. IrPTe [427] and $Li_{3.5}Mo_6Te_8$ [428] have been prepared. studies on phase systems involving tellurides are given in Table 4.

Table 4 Telluride Phase Systems

System	ref.	System	Ref.
Zn-Pb-Te	429	$SnTe-Co_3Te_4$ & $SnTe-Co_3Sn_2$	435
HgI_2 - CdTe	430	Sm - Ge - Te	436
Pb - Sn - Te	431	Yb - Bi - Te	437
Ln - U - Te	432	Nd - Bi - Te	438
PbTe - $FeTe_2$	433	GaTe-Co & GaTe-Ni	439
V - O - Te	434	Tb - Pb - Te	440
		HoTe - InTe	441

6.4.5 Bonds to Carbon

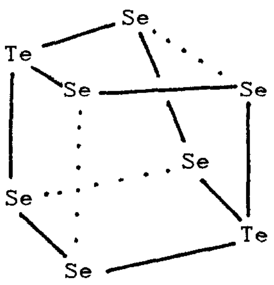
Ph_3TeF_3 has been prepared by the reaction of Ph_3TeF and XeF_2 and the crystal structure of the mer- isomer determined. Reaction of this isomer with PF_5 gave $Ph_3TeF_2^+PF_6^-$.[442] The synthesis of the (2-phenylazophenyl- C,N')tellurium(II)dithiocarbamates, $Te(C_6H_4N_2Ph)(dtc)$ where dtc= dimethyl- diethyl-, or dibenzyl-dithiocarbamate, and the corresponding series of tris compounds, $Te(C_6H_4N_2Ph)(dtc)_3$ have been reported. N.m.r. and Mossbauer data suggest that the tris compounds dissociate to Te(II) compounds in solution and are better formulated as loose, charge-transfer compounds, $Te(II)(C_6H_4N_2Ph)(dtc).R'_2NC(S)S-S(S)CNR'_2$ (R'=Me, Et, or CH_2Ph).[443] The reaction between NaTeR ($R=C_6H_4OEt$-p) and $Br(CH_2)_nBr$ (n= 1,5,6,7,9, or 10) gives the bis(tellurides) $(RTe)_2(CH_2)_n$. For the single case of n=5, a tellurium salt $[RTe(CH_2)_5]Br$ may be isolated. Attempts to brominate some of the higher members of the series lead to rupture of the Te-aryl bond and the isolation of $(Br_3Te)_2(CH_2)_n$ where n=6 or 10.[444] The photochemical reaction of $(CF_3)_2Te$ with, for example,furan gives $(CF_3)_2Te_2$ as a main product. The compound reacts with mercury and cadmium to give $(CF_3Te)_2Hg$ and $(CF_3Te)_2Cd$ respectively.[445]

When an aqueous dioxane solution of Na_2SO_3 or $Na_2S_2O_5$ is added to a solution of p-ethoxyphenyltellurium trichloride ($RTeCl_3$) the related ditelluride, R_2Te_2 is formed. The first step in the reaction has been shown to be the hydrolysis of the trichloride to give the aryltellurate, $RTeO_2^-$. If the water content of the solvent is low this acid-catalysed step becomes rate determining, but more usually the step is rapid and the slow step is the reduction of $RTeO_2^-$ by HSO_3^- to give $RTeO^-$ which is believed to dimerize to R(HO)TeTe(OH)R before being reduced by another mole of bisulphite to the ditelluride.[446] The synthesis and spectroscopic characterisation of titanocene-benzene-1,2-ditellurolate, the first example of a tellurium analogue of the dithiolene chelates has been reported.[447] The preparation and crystal structure of $Pt(1,2\text{-}Te_2C_6H_4)(PPh_3)_2$ was reported later by different authors.[448]

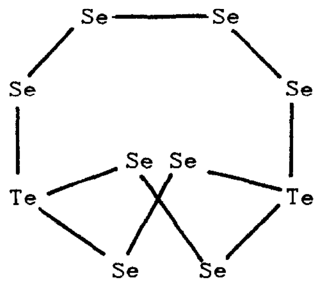
6.4.6 Other Compounds of Tellurium.

The preparation of the compounds $(Te_2Se_8)(MF_6)_2$ (M=As (<u>65</u>),or Sb), $(Te_{4.5}Se_{5.5})(AsF_6)_2$ (<u>66</u>), and $(Te_2Se_6)(Te_2Se_8)(AsF_6)_4(SO_2)_2$ (<u>67</u>) and the determination of their crystal structures has been reported. Compound (<u>67</u>) contains the cations $Te_2Se_6^{2+}$ and

$Te_2Se_8^{2+}$, hexafluoroarsenate anions and SO_2 solvent molecules. The novel $Te_2Se_6^{2+}$ cation (68) is not isostructural with the previously known cations Se_8^{2+} or S_8^{2+} but adopts a bicyclo[2.2.2]octane structure with tellurium in the three-coordinate positions. In both (65) and (67) the $Te_2Se_8^{2+}$ cations (69) have slightly different dimensions from those observed in the previously reported compound $(Te_2Se_8)(AsF_6)_2(SO_2)$. In (66) the $Te_{4.5}Se_{5.5}^{2+}$ cation is a disordered mixture of $Te_xSe_{10-x}^{2+}$ cations.[449]



(68)



(69)

The P-Te bond length in $(tert\text{-}C_4H_9)_3PTe$ of 236.8pm corresponds to a bond order near to 1.5. The distance may be influenced by the tert-C_4H_9 groups but the ^{125}Te n.m.r. shift has been shown to fall well within the common R_3PTe range, and the Te-P coupling constant is about 140 Hz smaller than in other tellurophosphoranes.[450] the reaction of R_3PTe with the compound $[Fe(Cp)(CO)_2(thf)$ has been shown to yield cyclopentadienyliron telluro- phosphorane cations $[Fe(Cp)(CO)_2(TePR_3)]^+$, which, from n.m.r. data, appear to have pi-bonding between the iron and tellurium atoms.[451] The reaction of a ditelluride solution with $M(ClO_4)_2.6H_2O$ (M=Co,Ni) in the presence of $MeC(CH_2PPh_2)_3$ has been shown to yield the compounds $[((triphos)M)_2(Te_2)].2C_4H_8O$ which contain the Te_2 unit bridging side-on between two M(triphos) moieties.[452] The reaction of $Te_4(SbF_6)_2$ with $W(CO)_6$ in SO_2AsF_3 produces $[W(CO)(Te_3)][SbF_6]_2$ which contains a three-membered tellurium ring coordinated in pi-fashion to the $W(CO)_4$ fragment.[453]

The structure of $[Te(C_3H_5OS_2)_2]$ shows the immediate environment about each tellurium atom of the asymmetric unit to be planar and comprised of four sulphur atoms derived from two asymmetrically chelating xanthate ligands; two such molecules are related so as to form loose associated dimers via weak intermolecular Te..S interactions.[454] New examples of [Te(IV)($S_2C.NR_2$)$_4$ compounds have been synthesized where R= i-Bu, Ph or CH_2Ph. [455]

REFERENCES

1 E.J.Corey, M.M.Mehotra and A.U.Khan, J. Am. Chem. Soc., 108 (1986)2472
2 R.Withnall and L.Andrews, J. Am. Chem. Soc., 108(1986)8118
3 R.Ramaraj, A.Kira and M.Kaneko, Angew. Chem., Int. Ed. Engl., 25(1986)826
4 R.Ramaraj, A.Kira and M.Kaneko, Angew. Chem., Int. Ed. Engl., 25(1986)1009
5 D.P.Riley and P.E.Correa, J. Chem. Soc., Chem Commun., (1986)1097
6 E.H.Appelman and A.W.Jache, J. Am. Chem. Soc., 109(1987)1754
7 G.Rajendran and R.L.Van Etten, Inorg. Chem., 25(1986)876
8 H.Schafer and W.Kluy, Z. Anorg. Allg. Chem., 536(1986)53
9 H.Sies, Angew. Chem., Int. Ed. Engl., 25(1986)1058
10 M.Rosi, A.Sgamellotti, F.Tarantelli, I.Bertini and C.Luchinat, Inorg. Chem., 25(1986)1005
11 K.Yamaguchi, T.S.Calderwood and D.T.Sawer, Inorg. Chem., 25(1986)1289
12 S.Das, M.N.Schuchmann, H.-P.Schuchmann and C.von Sonntag, Chem. Ber., 120(1987)319
13 C.E.Donald, M.N.Hughes, J.M.Thompson and F.T.Bonner, Inorg. Chem., 25(1986)2676
14 R.H.Simoyi, P.De Kepper, I.R.Epstein and K.Kustin, Inorg. Chem., 25(1986)538
15 J.Gilbert, L.Roecker and T.J.Meyer Inorg. Chem., 26(1987)1126
16 J.E.Schiller, Inorg. Chem., 26(1987)948
17 M.Orban, J. Am. Chem. Soc., 108(1986)6893
18 S.Al-Baker and J.C.Dabrowiak, Inorg. Chem., 26(1987)613
19 D.M.Dooley, J.L.Karas, T.F.Jones, C.E.Cote and S.B.Smith, Inorg. Chem., 25(1986)4761
20 P.Cofre and D.T.Sawyer, Inorg. Chem., 25(1986)2089
21 R.C.Thompson, Inorg. Chem., 25(1986)185
22 K.Bohmhammel, P.Brand and C. Hartig, Z. Anorg. Allg. Chem., 542(1986)201
23 B.A.Borgias, G.G.Hardin and K.N.Raymond, Inorg. Chem., 25(1986)1057
24 G.J.Kearley, H.A.Pressman and R.T.Slade, J. Chem. Soc., Chem. Commun., (1986)1801
25 P.Fantucci and G.Pacchioni, J. Chem. Soc., Dalton Trans., (1987)355
26 C.J.Raleigh and A.E.Martell, Inorg. Chem., 25(1986)1190
27 N.Herron, Inorg. Chem., 25(1986)4717
28 K.S.Leslie, R.S.Drago, A.B.Griffis, D.E.Hamilton and C.J.O'Connor, Inorg. Chem., 26(1987)1951
29 S.M.Nelson, A.Lavery and M.G.B.Drew, J. Chem. Soc., Dalton Trans., (1986)911
30 R.S.Drago and K.J.Balkus, Inorg. Chem., 25(1986)718
31 G.D.Armstrong and A.G.Sykes, Inorg. Chem., 25(1986)3135
32 E.F.Hills, P.R.Norman, T.Ramasami, D.T.Richens and A.G.Sykes, J. Chem. Soc., Dalton Trans., (1986)157
33 K.Steliou, P.Salama, D. Brodeur and Y.Gareau, J. Am. Chem. Soc., 109(1987)926

34 R.Steudel, J.Steidel and T.Sandow, Z. Naturforsch., Teil B., 41(1986)958
35 E-M.Strauss and R.Steudel, Z. Naturforsch., Teil B., 42(1987)682
36 R.Steudel and B.Holz, Z. Naturforsch., Teil B., 42(1987)691
37 H.Eckert and J.P.Yesinowski, J. Am. Chem. Soc., 108(1986)2140
38 P.Dubois, J.P.Lelieur and G.Lepoutre, Inorg. Chem., 26 (1987)1897
39 P.Bottcher and H.Buchkremer-Hermanns, Z. Naturforsch., Teil B., 42(1987)272
40 F.Seel, G.Simon, J.Schuh, M.Wagner, B.Wolf, I.Ruppert and A.B.Wieckowski, Z. Anorg. Allg. Chem., 538(1986)177
41 G.Fritz and D.Hanke, Z. Anorg. Allg. Chem., 537(1986)17
42 M.J.Collins, R.J.Gillespie, J.F.Sawyer and G.J.Schrobilgen, Inorg. Chem., 25(1986)2053
43 A.E.Reed and F.Weinhold, J. Am. Chem. Soc., 108(1986)3586
44 H.L.Marsden and J.M.Shreeve, Inorg. Chem., 25(1986)4021
45 A.G.Csaszar, K.Hedberg, R.J.Terjeson and G.L.Gard, Inorg. Chem., 26(1987)955
46 J.Wessel, H.Hartl and K.Seppelt, Chem. Ber., 119(1986)453
47 K.D.Gupta, R.Mews, A.Waterfeld, J.M.Shreeve and H.Oberhammer, Inorg., Chem., 25(1986)275
48 A.Schmuck and K.Seppelt, Angew. Chem., Int. Ed. Engl., 26(1987)134
49 T.Grelberg, T.Krugerke and K.Seppelt, Z. Anorg. Allg. Chem., 544(1987)74
50 H.W.Roesky, U.Otten and H.Oberhammer, Z. Anorg. Allg. Chem., 539(1986)191
51 R.Steudel, D.Jensen and B.Plinke, Z. Naturforsch., Teil B., 42(1987)163
52 R.Minkwitz, U.Nass and H.Preut, Z. Anorg. Allg. Chem., 538(1986)143
53 R.Minkwitz, R.Lekies, H.W.Jochims, E.Ruhl and H.Baumgartel, Z. Naturforsch., Teil B., 41(1986)784
54 H. Roesky and N.Benmohamed, Z. Anorg. Allg. Chem., 545(1987)143
55 R.Minkwitz and R.Lekies, Z. Anorg. Allg. Chem., 537(1986)169
56 R.Minkwitz and R.Lekies, Z. Anorg. Allg. Chem., 544(1987)192
57 R.Minkwitz and H.Prenzel, Z. Anorg. Allg. Chem., 548(1987)97
58 H.Beck and C.Strobel, Z. Anorg. Allg. Chem., 535(1986)229
59 P.F.Kelly and J.D.Woolins, Polyhedron, 5(1986)607
60 A.Apblett, A.J.Banister, D.Biron, A.G.Kendrick, J.Passmore, M.Schriver and M.Stojanac, Inorg. Chem., 25(1986)4451
61 M.Herberhold and W.Buhlmeyer, Z. Naturforsch., Teil B., 42(1987)65
62 M.Conti, M.Trsic and W.G.Laidlaw, Inorg. Chem., 25(1986)254
63 S.Thea, G.Cevasco, G.Guanti and A.Williams, J. Chem. Soc., Chem. Commun., (1986)1582
64 H.W.Roesky, N.Benmohamed, J.Schimkowiak, B.Krebs and M.Dartmann, Z. Anorg. Allg. Chem., 544(1987)209
65 A.Haas and M.Willert-Porada, Z. Anorg. Allg. Chem., 545(1987)24
66 H-G.Hauck, U.Patt-Siebel, U.Muller and K.Dehnicke, Z. Anorg.

Allg. Chem., 546(1987)177
67 H-G.Hauck, W.Willing, U.Muller and K.Dehnicke, Z. Anorg. Allg. Chem., 534(1986)77
68 A.Gieren, T.Hubner, M.Herberhold, K.Guldner and G.Suss-Fink, Z. Anorg. Allg. Chem., 538(1986)21
69 Z.Zak and A.Ruzicka, Z. Anorg. Allg. Chem., 549(1987)67
70 D.Hanssgen and R.Plum, Chem. Ber., 120(1987)1063
71 A.Blaschette, E.Wieland, D.Schomburg and M.Adelhelm, Z. Anorg. Allg. Chem., 533(1986)7
72 M.Witt, H.W.Roesky, M.Noltmeyer and G.M.Sheldrick, Z. Naturforsch., Teil B., 42(1987)519
73 A.Ruzicka and I.Kotasova, Z.Chem., 27(1987)180
74 U.Jager and W.Sundermeyer, Chem. Ber., 119(1986)3405
75 H.W.Roesky, J.Sundermeyer, M.Noltmeyer, G.M.Sheldrick, K.Meyer-Base and P.G.Jones, Z. Naturforsch., Teil B., 41(1986)
76 A.J.Banister, Z.V.Hauptman, J.Passmore, Chi-Ming Wong and P.S.White J. Chem. Soc., Dalton Trans., (1986)2371
77 N.M.Lau, N.P.C.Westwood and M.H.Palmer, J. Am. Chem. Soc., 108(1986)3229
78 E.Besenyei, G.Eigendorf and D.C.Frost, Inorg. Chem., 25(1986)4404
79 U.Demant and K.Dehnicke, Z. Naturforsch., Teil B., 41(1986)929
80 M.Herberhold and K.Guldner, Z. Naturforsch., Teil B., 42(1987)118
81 R.T.Oakley, J. Chem. Soc., Chem Commun., (1986)596
82 J.D.Woollins, Polyhedron, 6(1987)939
83 J.Weiss, Acta Crystallogr., C43(1987)166
84 E.Conradi, H.G. Hauk, U.Muller and K.Dehnicke, Z. Anorg. Allg. Chem., 539(1986)39
85 H.G.Hauk, W.Willing, U.Muller and K.Dehnicke, Z. Naturforsch., Teil B., 41(1986)825
86 U.Demant, W.Willing, U.Muller and K.Dehnicke, Z. Anorg. Allg. Chem., 532(1986)175
87 R.Jones, C.P.Warrens, D.J.Williams and J.D.Woollins, J. Chem. Soc., Dalton Trans., (1987)907
88 R.Jones, P.F.Kelly, C.P.Warrens, D.J.Williams and J.D.Woollins, J. Chem. Soc., Chem Commun., (1986)711
89 P.A.Bates, M.B.Hursthouse, P.F.Kelly and J.D.Woollins, J. Chem. Soc. Dalton Trans., (1986)2367
90 K.Volp, W.Willing, U.Muller and K.Dehnicke, Z. Naturforsch., Teil B., 41(1986)1196
91 E.Conradi, H.Wadle, U.Muller and K.Dehnicke, Z. Naturforsch., Teil B., 41(1986)48
92 H.W.Roesky, J.Schimkowiak, M.Noltmeyer and G.M.Sheldrick, Z. Naturforsch., Teil B., 41(1986)175
93 H.Wadle, E.Condradi, U.Muller and K.Dehnicke, Z. Naturforsch., Teil B., 41(1986)796
94 H.W.Roesky, J.Schimkowiak and F.Walther, Z. Naturforsch., Teil B., 41(1986)393
95 A.El-Kholi, R.Christopherson, U.Muller and K.Dehnicke, Z. Naturforsch., Teil B., 42(1987)410
96 R.Christopherson, W.Willing, U.Muller and K.Dehnicke, Z. Naturforsch., Teil B., 41(1986)1420

97 W.Willing, R.Christopherson, U.Muller and K.Dehnicke, Z. Naturforsch., Teil B., 41(1986)831
98 H.Wadle, E.Conradi, U.Muller and K.Dehnicke, Z. Naturforsch., Teil B., 41(1986)429
99 P.Klingelhofer, H.Wadle, U.Muller and K.Dehnicke, Z. Anorg. Allg. Chem., 544(1987)115
100 A.J.Banister and A.G.Kendrick, J. Chem. Soc., Dalton Trans., (1987)1565
101 S.Ruangsuttinarupap, C.Friebel and K.Dehnicke, Z. Naturforsch., Teil B., 42(1987)337
102 J.Weiss, Z. Anorg. Allg. Chem., 542(1986)137
103 D.K.Padma and R.Mews, Z. Naturforsch., Teil B., 42(1987)699
104 P.L.Dhingra and R.K.Verma, Bull. Soc. Chim. France, (1986)367
105 V.I.Spitsyn, I.D.Kolli and E.M.Orlova, Russ. J. Inorg. Chem., 31(1986)163
106 P.J.Dunn and C.W.Rees, J. Chem. Soc., Chem Commun., (1987)59
107 K.Holl and U.Thewalt, Z. Naturforsch., Teil B., 41(1986)581
108 U.Thewalt, K.Holl, U.Demant, U.Muller and K.Dehnicke, Z. Naturforsch., Teil B., 41(1986)1061
109 F.Edelmann, H.W.Roesky, C.Spang, M.Noltmeyer and G. M.Sheldrick, Angew. Chem., Int. Ed. Engl., 25(1986)931
110 H.Chandra, D.N.R.Rao and M.C.R.Symons, J. Chem. Soc., Dalton Trans., (1987)729
111 A.J.Banister, Z.V.Hauptman, A.G.Kendrick and R.W.H.Small, J. Chem. Soc., Dalton Trans., (1987)915
112 U.Patt-Siebel, S.Ruangsuttinarupap, U.Muller, J.Pebler and K.Dehnicke, Z. Naturforsch., Teil B., 41(1986)1191
113 W.Willing, U.Muller, J.Eicher and K.Dehnicke, Z. Anorg. Allg. Chem., 537(1986)145
114 R.T.Boere, R.T.Oakley and M.Shevalier, J. Chem. Soc., Chem. Commun., (1987)110
115 C.Habben, A.Meller, M.Noltmeyer and G.M.Sheldrick, Z. Naturforsch., Teil B., 41(1986)799
116 C.Habben, A.Meller, M.Noltmeyer and G.M.Sheldrick, Angew. Chem. Int. Ed. Engl., 25(1986)741
117 C.Habben and A.Meller, Chem. Ber., 119(1986)9
118 D.Fest, C.Habben and A.Meller, Chem. Ber., 119(1986)3121
119 A.W.Cordes, S.L.Craig, M.S.Condren, R.T.Oakley and R.W.Read, Acta Crystallogr., C42(1986)922
120 R.T.Boere, A.W.Cordes, P.J.Hayes, R.T.Oakley, R.W.Read and W.T.Pennington, Inorg. Chem., 25(1986)2445
121 H.W.Roesky, J.Sundermeyer, J.Schimkowiak, Th.Gries, M.Noltmeyer and G.M.Sheldrick, Z. Naturforsch., Teil B., 41(1986)162
122 N.Burford, J.Passmore and M.J.Schriver, J. Chem. Soc., Chem. Commun., (1986)140
123 S.A.Fairhurst, K.M.Johnson, L.H.Sutcliffe, K.J.Preston, A.J.Banister, Z.V.Hauptman and J.Passmore, J. Chem. Soc., Dalton Trans., (1986)1465
124 E.G.Awere, N.Burford, C.Mailer, J.Passmore, M.J.Schriver, P.S.White, A.J.Banister and L.H.Sutcliffe,J. Chem. Soc.,

Chem Commun., (1987)67
125 W.V.F.Brooks, N.Burford, J.Passmore, M.J.Schriver and L.H.Sutcliffe, J. Chem. Soc., Chem Commun., (1987)71
126 A.J.Banister, M.I.Hansford and Z.V.Hauptman, J. Chem. Soc., Chem. Commun., (1987)63
127 S.Ruangsuttinarupap, H-D.Gross, W.Willing, U.Muller and K.Dehnicke, Z. Anorg. Allg. Chem., 536(1986)153
128 R.T.Boere, A.W.Cordes, S.L.Craig, R.T.Oakley and R.W.Reed, J. Am. Chem. Soc., 109(1987)868
129 T.Chivers, J.F.Richardson and N.R.M.Smith, Inorg. Chem., 25(1986)47
130 T.Chivers, J.F.Richardson and N.R.M.Smith, Inorg. Chem., 25(1986)272
131 T.Chivers, F.Edelmann, J.F.Richardson, N.R.M.Smith, O.Treu and M.Trsic, Inorg. Chem., 25(1986)2119
132 R.T.Boere, A.W.Cordes, S.L.Craig, R.T.Oakley and J.A.James Privett, J. Chem. Soc., Chem Commun., (1986)807
133 A.W.Cordes, M.Hojo, H.Koenig, M.C.Noble, R.T.Oakley and W.T.Pennington, Inorg. Chem., 25(1986)1137
134 H.W.Roesky, N.Benmohamed, M.Noltmeyer and G.M.Sheldrick, Z. Naturforsch., Teil B., 41(1986)938
135 J.Neels, B.Ziemer, M.Meisel and P.Leibnitz, Z. Anorg. Allg. Chem., 542(1986)123
136 M.Heberhold, K.Guldner, A.Gieren, C.Ruiz-Perez and T.Hubner, Angew. Chem., Int. Ed. Engl., 26(1987)82
137 W.L.Reynolds and Y.Yuan, Polyhedron, 5(1986)1467
138 J.B.Gill, D.C.Goodhall, B.Jeffreys and P.Gans, J. Chem. Soc., Dalton Trans., (1986)2597
139 J.B.Gill, D.C.Goodhall and B.Jeffreys, J. Chem. Soc., Dalton Trans., (1986)2603
140 L.E.Derlynkova and V.I.Evdokimov, Russ. J. Inorg. Chem., 31(1986)788
141 J.Touzin, Z. Chem., 27(1987)180
142 B.S.Suresh and D.K.Padma, Polyhedron, 5(1986)1579
143 M.Cernik, Z. Chem., 27(1987)179
144 W.A.Schenk, Angew. Chem., Int. Ed. Engl., 26(1987)98
145 I-P.Lorenz and J.Kull, Angew. Chem., Int. Ed. Engl., 25(1986)261
146 W.A.Schenk and J.Leissner, Z. Naturforsch., Teil B., 42(1987)799
147 C.E.Briant, D.G.Evans and M.P.Mingos, J. Chem. Soc., Dalton Trans., (1986)1535
148 G.Hartmann and R.Mews, Chem. Ber., 119(1986)374
149 D.K.Breitinger, G.Schottner. M.Raidel and H.P.Beck, Z. Anorg. Allg. Chem., 539(1986)18
150 H.Brunner, U.Klement, J.Pfauntsch and J.Wachter, Angew. Chem., Int. Ed. Engl., 26(1987)230
151 T.Ozawa and T.Kwan, Polyhedron, 5(1986)1531
152 A.Rodriguez, S.Lopez, M.C.Carmona-Guzman, F.Sanchez and C.Piazza, J. Chem. Soc., Dalton Trans., (1986)1265
153 D.Littlejohn, K.Y.Hu and S.G.Chang, Inorg. Chem., 25(1986)3131
154 D.A.Horner and R.E.Connick, Inorg. Chem., 25(1986)2414

155 A.Cohen and M.Zangen, J. Chem. Soc., Dalton Trans., (1987)235
156 B.Ruisinger and H-P.Boehm, Angew. Chem., Int. Ed. Engl., 26(1987)253
157 B.Engelen, W.Buchmeier and H.D.Lutz, Z. Naturforsch., Teil B., 42(1987)37
158 W.Buchmeier, B.Engelen and H.D.Lutz, Z. Naturforsch., Teil B., 41(1986)852
159 S.S.Pollack, Inorg. Chem., 26(1987)1825
160 R.I.Dearnaley, D.H.Kerridge and D.J.Rogers, Inorg. Chem., 25(1986)1721
161 R.I.Gelb, L.M.Schwartz and L.J.Zompa, Inorg. Chem., 25(1986)1527
162 E.Kemnitz, H.Worzala, D.Hass and M.Kammler, Z. Anorg. Allg. Chem., 547(1987)57
163 K.Fujii and W.Kondo, J. Chem. Soc., Dalton Trans., (1986)729
164 M.K.Chaudhuri and N.S.Islam, Inorg. Chem., 25(1986)3749
165 S.Singh and D.D.DesMarteau, Inorg. Chem., 25(1986)4596
166 T-j. Huang and J.M.Shreeve, Inorg. Chem., 25(1986)496
167 H-J.Gais, J.Vollhardt and H.J.Lindner, Angew. Chem., Int. Ed. Engl., 25(1986)939
168 R.Steudel, G.Holdt, T.Gobel and W.Hazeu, Angew. Chem., Int. Ed. Engl., 26(1987)151
169 W.Steuner, H.Wittman, H.Jagodzinski and A.Pietraszko, Acta Crystallogr., B24(1986)11
170 M.Tanaka and Y.Shiozaki, Acta Crystallogr., C42(1986)776
171 H.Naruse, K.Tanaka, H.Morikawa, F.Marumo and B.N.Mehotra, Acta Crystallogr., B43(1987)143
172 M.J.Heeg and A.hurd, Acta Crystallogr., C43(1987)161
173 J.Jaulmes, M.Julien Pouzol, J.Dugue', P.Laruelle and M.Guittard, Acta Crystallogr., C42(1986)1111
174 R.Fehrmann, B.Krebs, G.N.Papatheodorou, R.W.Berg and N.J.Bjerrum, Inorg. Chem., 25(1986)1571
175 I.J.Bear, I.E.Grey, I.C.Madsen, I.E.Newnham and L.J.Rodgers, Acta Crystallogr., B42(1986)32
176 I.D.Brown, R.J.Gillespie, K.R.Morgan, J.F.Sawyer, K.J.Schmidt, Z.Tun, P.K.Ummat and J.E.Vekris, Inorg. Chem., 26(1987)689
177 J.W.Bats and H.Fuess, Acta Crystallogr., B42(1986)26
178 E.N.Oganesyan, E.E.Katanpyan, R.A.Sarkisyan, E.I.Nabivanets and G.G.Babayan, Russ. J. Inorg. Chem., 31(1986)1083
179 V.G.Shkodin and R.V.Abisheva, Russ. J. Inorg. Chem., 31(1986)170
180 R.Fehrmann, M.Gaune-Escard and N.J.Bjerrum, Inorg. Chem., 25(1986)1132
181 D.Littlejohn, A.R.Wizansky and S.G.Chang, Inorg. Chem., 25(1986)4610
182 D.L.Motov, Yu.P.Sozinova and M.P.Rys'kina Russ. J. Inorg. Chem., 31(1986)130
183 N.M.Nikolaeva Russ. J. Inorg. Chem., 31(1986)140
184 R.M.Shklovskaya, S.M.Arkhipov, B.I.Kidyarov, T.V.daminova and V.A.Kuzina Russ. J. Inorg. Chem., 31(1986)153
185 O.A.Govorukhina, S.D.Nikitina, R.A.Popova, M.A.Letetskaya

and V.I.Belokoskov Russ. J. Inorg. Chem., 31(1986)191
186 A.A.Ivakin, P.G.Chufarova, M.P.Glazyrin and N.I.Petunina, Russ. J. Inorg. Chem., 31(1986)279
187 E.K.Akopov and S.M.Kraeva Russ. J. Inorg. Chem., 31(1986)591
188 L.E.Derlyukova, M.V.Vinokurova and V.I.Evdokimov Russ. J. Inorg. Chem., 31(1986)481
189 L.P.Kristanova Russ. J. Inorg. Chem., 31(1986)887
190 T.E.Girich, R.I.Braginskaya, A.K.Buchinskii and S.I.Reznichenko Russ. J. Inorg. Chem., 31(1986)901
191 P.I.Soroka, T.E.Girich and M.L.Simich Russ. J. Inorg. Chem., 31(1986)922
192 Yu.P.Sozinova, D.L.Motov and M.P.Rys'kina Russ. J. Inorg. Chem., 31(1986)1809
193 V.T.Orlova, E.A.Konstantinova, Ya.S.Shenkin and I.N.Lepeshkov Russ. J. Inorg. Chem., 31(1986)1811
194 V.K.Filippov and A.M.Kalinkin Russ. J. Inorg. Chem., 32(1987)120
195 I.N.Lepeshkov, V.P.Danilov, A.N.Selin, V.P.Kim, L.A.Zaitseva and N.N.Gorbacheva Russ. J. Inorg. Chem., 32(1987)275
196 V.K.Filippov and V.I.Nokhrin Russ. J. Inorg. Chem., 32(1987)440
197 L.Soliev, Ya.G.Goroshchenko, M.A.Gornikova and N.M.Patrilyak Russ. J. Inorg. Chem., 32(1987)461
198 L.A.Zaitseva, A.A.Ivanov and I.N.Lepeshkov Russ. J. Inorg. Chem., 32(1987)462
199 L.A.Zaitseva, A.A.Ivanov and I.N.Lepeshkov Russ. J. Inorg. Chem., 32(1987)901
200 L.A.Kochubei, E.V.Margulis, M.S.Tukkaeva and I.V.Makarov Russ. J. Inorg. Chem., 31(1986)904
201 P.Bottcher and H.Buchkremer-Hermanns, Z. Naturforsch., Teil B., 42(1987)267
202 M.Zolek, J.Kujawa, A.B.Mohammed Saad, O.Saur and J.C.Lavalley, Bull. Soc. Chim. France, (1987)37
203 F.Seel and M.Wagner, Z. Naturforsch., Teil B., 42(1987)801
204 R.Steudel, G.Holdt and R.Nagorka, Z. Naturforsch., Teil B., 41(1986)1519
205 H.Sabrowsky, A.Thimm, P.Vogt and B.Harbrecht, Z. Anorg. Allg. Chem., 546(1987)169
206 J.Y.Andersson and M.Azoulay, J. Chem. Soc., Dalton Trans., (1986)469
207 H.Kisch, A.Fernandez and R.Millini, Chem. Ber., 119 (1986)3473
208 H.Kisch and W.Schlamann, Chem. Ber., 119(1986)3483
209 S.Licht, G.Hodes and J.Manassen, Inorg. Chem., 25(1986)2486
210 P.Bottcher and W.Flamm, Z. Naturforsch., Teil B., 41(1986)405
211 I.R.Beattie, P.L.Jones, D.J.Wild and T.R.Gibson, J. Chem. Soc., Dalton Trans., (1987)267
212 E.Hanecker, H.Noth and U.Wietelmann, Chem. Ber., 119(1986)1904
213 J.Hahn and K.Altenbach, Z. Naturforsch., Teil B.,

41(1986)675
214 W.Wojnowski, W.Bochenska, K.Peters, E-M. Peters and H.G. von Schnering, Z. Anorg. Allg. Chem., 533(1986)165
215 W.Wojnowski, M.Wojnowski, K.Peters, E-M.Peters and H.G.von Schneering, Z. Anorg. Allg. Chem., 535(1986)56
216 W.Wojnowski and E.W.Felcyn, Z. Anorg. Allg. Chem., 546 (1987)229
217 A.Haas, H-J.Kutsch and C.Kruger Chem. Ber., 120(1987)1045
218 S.S.Batsanov, N.N.Shevtsova, I.N.Temnitskii and V.P.Bokarev, Russ. J. Inorg. Chem., 31(1986)925
219 W.Tremel and R.Hoffmann, Inorg. Chem., 26(1987)118
220 A.F.Moodie and H.J.Whitfield, Acta Crystallogr., B42 (1986)236
221 A.Likforman, M.Guittard and S.Jaulmes, Acta Crystallogr., C43(1987)177
222 R.Blachnik, W.Buchmeier and H.A.Dreisbach, Acta Crystallogr., C42(1986)515
223 V.Kramer and I.Reis, Acta Crystallogr., C42(1986)249
224 V.Kramer, Acta Crystallogr., C42(1986)1089
225 B.H.Christian, R.J.Gillespie and J.F.Sawyer, Acta Crystallogr., C43(1987)187
226 P.Lemoine, D.Carre' and M.Guittard, Acta Crystallogr., C42(1986)259
227 J.Hahn and T.Nataniel, Z. Anorg. Allg. Chem., 547(1987)180
228 J.Hahn and T.Nataniel, Z. Anorg. Allg. Chem., 543(1986)7
229 K.Dostal, J.Sikola, M.Meisel and H.Grunze, Z. Anorg. Allg. Chem., (1986)199
230 Ch.Donath and M.Meisel, Z. Anorg. Allg. Chem., 549(1987)46
231 J.Prihoda, G.Grossmann, G.Ohms and M.Meisel, Z. Anorg. Allg. Chem., 549(1987)59
232 B.M.Gimarc and J.J.Ott, J. Am. Chem. Soc., 108(1986)4298
233 E.Fluck and B.Neumuller, Z. Anorg. Allg. Chem., 534(1986)27
234 B.W.Tattershall, J. Chem. Soc., Dalton Trans., (1987)1515
235 H.W.Roesky, M.Noltmeyer and G.M.Sheldrick, Z. Naturforsch., Teil B., 41(1986)303
236 A.V.Steblevskii, A.S.Alikhanyan, A.S.Pashinkin and V.I.Gorgoraki, Russ. J. Inorg. Chem., 31(1986)945
237 H.Brunner, H.Kauermann, B.Nuber, J.Wachter and M.L.Ziegler, Angew. Chem., Int. Ed. Engl., 25(1986)557
238 H.Breunig and S.Gulec, Z. Naturforsch., Teil B., 41(1986)1387
239 A.Muller, M.Zimmermann and H.Bogge, Angew. Chem., Int. Ed. Engl., 25(1986)273
240 M.Wieber and I.Sauer, Z. Naturforsch., Teil B., 42(1987)695
241 H.Mercier, Y.Mathey and E.Canadell, Inorg. Chem., 26 (1987)963
242 P.J.S.Foot and B.A.Nevett, J. Chem. Soc., Chem Commun., (1987)380
243 W.Bensch, J.Abort, E.Amberger, H.W.Schmalle and J.Kopf, Acta Crystallogr., C42(1986)6
244 A.T.Harrison and O.W.Howarth, J. Chem. Soc., Dalton Trans., (1986)1405
245 N.Alonso Vante, W.Jagermann, H.Tribusch, W.Hanle and K.Yvon, J. Am. Chem. Soc., 109(1987)3251

246 E.P.Khlybov, G.M.Kuz'micheva and V.V.Evdokimova, Russ. J. Inorg. Chem., 31(1986)627
247 R.A.Scott, A.J.Jacobson, R.R.Chianelli, W.-H.Pan, E.I.Stiefel, K.O.Hodgson and S.P.Cramer, Inorg. Chem., 25(1986)1461
248 S.Bhaduri and J.A.Ibers, Inorg. Chem., 25(1986)3
249 R.J.Clark and J.R.Walton, J. Chem. Soc., Dalton Trans., (1987)1535
250 P.J.Squattrito, P.N.Swepston and J.A.Ibers, Inorg. Chem., 26(1987)1187
251 S.A.Sunshine and J.A.Ibers, Acta Crystallogr., C43(1987)1019
252 L.F.Nazar and A.J.Jacobson, J. Chem. Soc., Chem Commun., (1986)570
253 R.Burch and C.J.Warburton, J. Chem. Soc., Chem Commun., (1987)117
254 K.O.Klepp and W.Bronger, Z. Anorg. Allg. Chem., 532(1986)23
255 A.Muller, K.Schmitz, E.Krickemeyer, M.Penk and H.Bogge, Angew. Chem. Int. Ed. Engl., 25(1986)453
256 M.G.B.Drew, G.A.Forsyth, M.Hasan, R.J.Hobson and D.A.Rice, J. Chem. Soc., Dalton Trans., (1987)1027
257 A.Muller, M.Romer, H.Bogge, E.Krickemeyer and M.Zimmermann, Z. Anorg. Allg. Chem., 534(1986)69
258 F.E.Senftle and D.B.Wright, Z. Naturforsch., Teil B., 41(1986)1081
259 J.P.Fackler and L.C.Porter, J. Am. Chem. Soc., 108(1986)2750
260 R.Gely, J.-P. Corriou and P.Viers, Bull. Soc. Chim. France, (1987)405
261 E.Borgarello, R.Terzian, N.Serpone, E.Pelizzetti and M..Barbeni, Inorg. Chem., 25(1986)2135
262 K.L.nash, J.M.Cleveland, J.C.Sullivan and M.Woods, Inorg. Chem., 25(1986)1169
263 S.Jaulmes, M.Julien-Pouzol, M.Guittard, T.Vovan, P.Laruelle and J.Flahaut, Acta Crystallogr., C42(1986)1109
264 M.Guittard, T.Vovan, M.Julien-Pouzol, S.Jaulmes, P.Laruelle and J.Flahaut, Z. Anorg. Allg. Chem., 540/541(1986)59
265 V.Medizadeh and S.Mardix, Acta Crystallogr., C42(1986)518
266 P.Lemoine, D.Carre' and M.Guittard, Acta Crystallogr., C42(1986)390
267 J.G.Brennan, R.A.Andersen and A.Zalkin, Inorg. Chem., 25(1986)1761
268 L.E.Maelia and S.A.Koch, Inorg. Chem., 25(1986)1896
269 A.P.Gurshumov, M.I.Murguzov, Z.Z.Nadzhafova, A.M.Akhmedov and S.Sh.Eivavov, Russ. J. Inorg. Chem., 31(1986)151.
270 I.R.Polyvyannyi, V.A.Lata, L.P.Ivakina and V.I.Antonyuk, Russ. J. Inorg. Chem., 31(1986)259
271 V.M.Ragimova, Z.G.Alieva and S.A.Sadykhova Russ. J. Inorg. Chem., 31(1986)272
272 E.I.Ardashnikova, M.P.Borzenkova and A.V.Novoselova Russ. J. Inorg. Chem., 31(1986)302
273 E.S.Polulyak, E.G.Zhukov, V.A.Levshin and V.A.Fedorov Russ. J. Inorg. Chem., 31(1986)774
274 R.D.Kurbanova, S.A.Sadykhova, A.A.Movsum-Zade, and P.G. Rustamov, Russ. J. Inorg. Chem., 31(1986)864

275 M.B.Babanly, Li Tai Un and A.A.Kuliev Russ. J. Inorg. Chem., 31(1986)1056
276 T.M.Il'yasov, A.I.Mamedov and P.G.Rustamov Russ. J. Inorg. Chem., 31(1986)1194
277 A.V.Steblevskii, A.S.Alikhanyan, A.S.Pashinkin and V.A.Malyusov Russ. J. Inorg. Chem., 31(1986)1415
278 O.A.Aliyeva and O.M..Aliyev Bull. Soc. Chim. France, (1986)29
279 M.B.Babanly, F.Kh. Guseinov, A.A.Kuliev and E.A.Bashirov, Russ. J. Inorg. Chem., 31(1986)1519
280 P.G.Rustamov, T.M.Il'yasov, A.I.Mamedov and F.M.Sadygov, Russ. J. Inorg. Chem., 32(1987)87
281 I.B.Bakhtiyarov and P.G.Rustamov Russ. J. Inorg. Chem., 32(1987)569
282 A.A.Movsum-Zade, Sh.B.Alieva, M.R.Allazov and M.I.Zargarova, Russ. J. Inorg. Chem., 32(1987)574
283 H.D.Lutz, W.Buchmeier and H.Siwert, Z. Anorg. Allg. Chem., 533(1986)118
284 R.Blachnik, Th.Weber and U.Wickel, Z. Anorg. Allg. Chem., 532(1986)90
285 O.M.Aliev, G.G.Khasaev and T.Kh.Kurbanov, Bull. Chem. Soc. France (1986)26
286 I.B.Bakhtiyarov, P.G.Rustamov, S.M.Nakhmetov and V.A.Gasymov, Z. Anorg. Allg. Chem., 533(1986)186
287 I.B.Bakhtiyarov, A.N.Mamedov and M.M.Abbasov, Z. Anorg. Allg. Chem., 545(1987)197
288 A.J.Blake, R.O.Gould, A.J.Lavery and M.Schroder, Angew. Chem., Int. Ed. Engl., 25(1986)274
289 H.-J.Kuppers, K.Wieghardt, Y.-H.Tsay, C.Kruger, B.Nuber and J.Weiss, Angew. Chem., Int. Ed. Engl., 26(1987)575
290 S.C.Rawle, J.A.R.Hartman, D.J.Watkins and S.R.Cooper, J. Chem. Soc., Chem. Commun., (1986)1083
291 D.Marji, J. Chem. Soc., Chem. Commun., (1987)7
292 A.Bianchi, E.Garcia-Espana, M.Micheloni, N.Nardi and F.Vizza, Inorg. Chem., 25(1986)4379
293 T.Grelbig, B.Potter and K.Seppelt, Chem. Ber., 120(1987)815
294 M.Schwab and W.Sundermeyer, Chem. Ber., 119(1986)2458
295 R.-M.Olk, W.Dietzsch, J.Mattusch, J.Stach, C.Nieke, E.Hoyer, W.Meiler and W.Robien, Z. Anorg. Allg. Chem., 544(1987)199
296 R.Gerner and G.Kiel, Z. Anorg. Allg. Chem., 532(1986)99
297 C.Wolf and H.-U. Hummel, J. Chem. Soc., Dalton Trans., (1986)43
298 H.-U.Hummel and H.Procher, Z. Anorg. Allg. Chem., 537(1986)79
299 U.Mikloweit and R.Mattes, Z. Anorg. Allg. Chem., 532(1986)145
300 B.Fusser and R.Mattes, Z. Anorg. Allg. Chem., 547(1987)158
301 H.-U.Hummel and F.Beiler, Z. Anorg. Allg. Chem., 543(1986)207
302 L.Andrews, R.T.Arlinghaus and R.D.Hunt, Inorg. Chem., 25(1986)3205
303 R.Laitinen, R.Steudel and R.Weiss, J. Chem. Soc., Dalton Trans., (1986)1095
304 G.Gattow and S.Lotz, Z. Anorg. Allg. Chem., 533(1986)99
305 W.Eul and G.Gattow, Z. Anorg. Allg. Chem., 535(1986)148

306 W.Eul and G.Gattow, Z. Anorg. Allg. Chem., 535(1986)159
307 W.Eul, G.Kiel and G.Gattow, Z. Anorg. Allg. Chem., 535(1986)167
308 W.Eul and G.Gattow, Z. Anorg. Allg. Chem., 536(1986)119
309 W.Eul and G.Gattow, Z. Anorg. Allg. Chem., 537(1986)189
310 W.Eul and G.Gattow, Z. Anorg. Allg. Chem., 538(1986)151
311 W.Eul, G.Kiel and G.Gattow, Z. Anorg. Allg. Chem., 542(1986)182
312 W.Eul, G.Kiel and G.Gattow, Z. Anorg. Allg. Chem., 544(1987)149
313 W.Eul and G.Gattow, Z. Anorg. Allg. Chem., 545(1987)125
314 G.Gattow and S.Lotz, Z. Anorg. Allg. Chem., 533(1986)109
315 G.Gattow and H.Muller, Z. Anorg. Allg. Chem., 549(1987)139
316 H.Bock, P.Rittmeyer and U.Stein, Chem. Ber., 119(1986)3766
317 G.Arens, W.Sundermeyer and H.Pritzkow, Chem. Ber., 119(1986)3631
318 H.W.Roesky, J.Schimkowiak, K.Meyer-Base and P.G.Jones, Angew. Chem., Int. Ed. Engl., 25(1986)1006
319 H.W.Roesky, N.K.Homsy and H.G.Schmidt, Z. Anorg. Allg. Chem., 532(1986)131
320 R.Minkwitz, H.Prenzel and H.Pritzkow, Z. Naturforsch., Teil B., 42(1987)750
321 A.Haas and W. Wanzke, Chem. Ber., 120(1987)429
322 J.Holoch and W.Sundermeyer, Chem. Ber., 119(1986)269
323 R.Grenz, F.Gotzfried, U.Nagel and W.Beck, Chem. Ber., 119(1986)1217
324 M.J.Collins, R.J.Gillespie, J.F.Sawyer and G.J.Schrobilgen, Acta Crystallogr., C42(1986)13
325 R.C.Burns, M.J.Collins, R.J.Gillespie and G.J.Schrobilgen, Inorg. Chem., 25(1986)4465
326 R.S.Laitinen and T.A.Pakkanen, J. Chem. Soc., Dalton Trans., (1986)1381
327 R.Steudel, M.Papavassiliou, E.-M.Strauss and R.Laitinen, Angew. Chem., Int. Ed. Engl., 25(1986)99
328 D.J.Jones, T.Makani and J.Roziere, J. Chem. Soc., Chem. Commun., (1986)1275
329 R.Faggiani, R.J.Gillespie, J.W.Kolis and K.C.Malhotra, J. Chem. Soc., Chem Commun., (1987)591
330 B.Krebs, N.Rieskamp and A.Schaffer, Z. Anorg. Allg. Chem., 532(1986)118
331 P.G.Jones, R.Schelbach and E.Schwarzmann, Acta Crystallogr., C43(1987)607
332 J.B.Milne, Polyhedron, 6(1987)849
333 K.V.Katti, U.Seseke and H.W.Roesky, Inorg. Chem., 26(1987)814
334 H.Oppermann, U.Hanke and G.Krabbes, Z. Anorg. Allg. Chem., 542(1986)89
335 W.Abriel, Z. Naturforsch., Teil B., 42(1987)415
336 M.M.Carnell, F.Grein, M.Murchie, J.Passmore and C.-M.Wong, J. Chem. Soc., Dalton Trans., (1986)225
337 C.Delage, A.Carpy, A.H.Naifi and M.Goursolle, Acta Crystallogr., C42(1986)1475
338 H.Martin and R.Herrmann, Z. Naturforsch., Teil B.,

41(1986)1260
339 E.Popova, J.Slavtscheva and G.Gospodinov, Z.Chem., 26(1986)342
340 H.Erfang-Far, H.Fuess and D.Gregson, Acta Crystallogr., C43(1987)395
341 J.Baran and T.Lis, Acta Crystallogr., C43(1987)811
342 J.Baram and T.Lis, Acta Crystallogr., C42(1986)270
343 H.A.Azab, A.Hassan and R.M.Hassan, Bull. Soc. Chim. France, (1987)26
344 H.Effenberger, Acta Crystallogr., C43(1987)182
345 F.C.Hawthorne, T.S.Ercit and L.A.Groat, Acta Crystallogr., C42(1986)1285
346 A.I.Sabanov, I.V.Skripachev, B.E.Ulevatyi and M.F.Churbanov, Russ. J. Inorg. Chem., 311986)625
347 W.Honle, G.Kuhn and H.Neumann, Z. Anorg. Allg. Chem., 543(1986)161
348 H.Haeuseler and M.Himmrich, Z. Anorg. Allg. Chem., 535(1986)13
349 S.S.Abdinbekov and G.D.Guseinov, Bull. Soc. Chim. France, (1986)355
350 B.Krebs and H.Uhlen, Z. Anorg. Allg. Chem., 549(1987)35
351 M.Bjorgvinsson, J.F.Sawyer and G.J.Schrobilgen, Inorg. Chem., 26(1987)741
352 G.R.Burns, J.R.Rollo and R.J.H.Clark, Inorg. Chem., 25(1986)1145
353 R.Blachnik, W.Buchmeier, C.Schneider and U.Wickel, Z. Naturforsch., Teil B., 42(1987)47
354 J.Kaub, Z. Naturforsch., Teil B., 41(1986)436
355 W.S.Sheldrick and J.Kaub, Z. Anorg. Allg. Chem., 535(1986)179
356 D.Linke Z. Anorg. Allg. Chem., 540/541(1986)142
357 W.S.Sheldrick and J.Kaub, Z. Anorg. Allg. Chem., 536(1986)114
358 W.A.Herrmann, J.Rohrmann, E.Herdtweek, H.Bock and A.Veltmann, J. Am. Chem. Soc., 108(1986)3134
359 W.A.Herrmann and J.Rohrmann, Chem. Ber., 119(1986)1437
360 R.Schollhorn and A.Payer, Angew. Chem., Int. Ed. Engl., 25(1986)905
361 K.D.Bronsema, J.L.deBoer and F.Jellinek, Z. Anorg. Allg. Chem., 540/541(1986)15
362 M.J.Collins, R.J.Gillespie, J.W.Kolis and J.F.Sawyer, Inorg. Chem., 25(1986)2057
363 H.Brunner, W.Meier, B.Nuber, J.Wachter and M.L.Ziegler, Angew. Chem., Int. Ed. Engl., 25(1986)907
364 S.A.Sunshine and J.A.Ibers, Inorg. Chem., 25(1986)4355
365 G.Besenyei, C.-L.Lee and B.R.James, J. Chem. Soc., Chem. Commun., (1986)1751
366 J.I.Davies, G.Fan, M.J.Parrott and J.O.Williams, J. Chem. Soc., Chem. Commun., (1986)68
367 A.D.Yoffe and K.J.Howlett, Z. Anorg. Allg. Chem., 540/541(1986)281
368 E.W.Abel, S.K.Bhargava, T.E.MacKenzie, P.K.Mittal, K.G.Orrell and V.Sik, J. Chem. Soc., Dalton Trans., (1987)757

369 P.Peringer and J.Schwad, J. Chem. Soc., Chem Commun., (1986)1624
370 G.Ferguson, M.Parvez, J.A.MacCurtain, O.Ni.Dubhghaill, T.R. Spalding and D.Reed, J. Chem. Soc., Dalton Trans., (1987)699
371 A.P. Gurshumov, M.I.Murguzov, Z.Z.Nadzhafova, A.M.Akhmedov and S.Sh.Eivavov, Russ. J. Inorg. Chem.,31(1986)150
372 M.R.Allazov, Sh.M.Shirinov, and A.A.Movsum-Zade Russ. J. Inorg. Chem., 31(1986)257
373 P.G.Rustamov and I.I.Aliev Russ. J. Inorg. Chem., 31 (1986)439
374 A.V.Steblevskii, A.S.Alikhanyan, V.I.Gorgoraki and A.S. Pashinkin, Russ. J. Inorg. Chem., 31(1986)474
375 A.A.Sher, I.N.Odin and A.V.Novoselova Russ. J. Inorg. Chem., 31(1986)575
376 I.N.Odin, V.V.Grin'ko and A.V.Novoselova Russ. J. Inorg. Chem., 31(1986)724
377 A.Ashirov, A.P.Gurshumov,K.Dovletov and N.A.Mamedov Russ. J. Inorg. Chem., 31(1986)729
378 A.P.Gurshumov, K.Dovletov, Ch.Dovletmuradov and D.V.Mamedova, Russ. J. Inorg. Chem., 31(1986)731
379 A.A.Babitsyna and V.M.Novotortsev Russ. J. Inorg. Chem., 31(1986)1048
380 M.I.Murgusov, A.P.Gurshumov and B.Sh.Gadirov Russ. J. Inorg. Chem., 31(1986)1098
381 E.Yu.Turkina and G.M.Orlova Russ. J. Inorg. Chem., 31 (1986)1198
382 M.B.Babanly, Zo Chan Gen and A.A.Kuliev Russ. J. Inorg. Chem., 31(1986)1200
383 T.M.Il'yasov, P.G.Rustamov and L.A.Mamedova Russ. J. Inorg. Chem., 31(1986)1408
384 T.M.Il'yasov, L.A.Mamedova and Z.T.Gulieva Russ. J. Inorg. Chem., 31(1986)1562
385 M.I.Murguzov, A.P.Gurshumov, A.M.Akhmedov, M.A.Alidzhanov, D.M.Safonov and S.S.Nadzhafova Russ. J. Inorg. Chem., 31(1986)1779
386 O.A.Alieva, O.M.Aliev and P.G.Rustamov Russ. J. Inorg. Chem., 32(1987)14
387 A.A.Babitsyna and T.A.Emel'yanova Russ. J. Inorg. Chem., 32(1987)302
388 I.F.Alieva, M.R.Allazov, A.A.Movsum-Zade and P.G.Rustamov, Russ. J. Inorg. Chem., 32(1987)732
389 T.G.Back and R.G.Kerr, J. Chem. Soc., Chem Commun., (1987)134
390 M.Herberhold and W.Jellen, Z. Naturforsch., Teil B., 41 (1986)144
391 A.W.Cordes, R.T.Oakley and R.W.Reed, Acta Crystallogr., C42(1986)1889
392 H.P.Fritz and M.Weis, Z. Naturforsch., Teil B., 42(1987)669
393 F.Fockenberg and A.Haas, Z. Naturforsch., Teil B., 41 (1986)413
394 D.J.Sandman, G.W.Allen, L.A.Acampora, J.C.Stark, S.Jansen, M.T. Jones, G.J.Ashwell and B.M.Foxman, Inorg. Chem., 26(1987)1665
395 C.Habben and A.Meller, Chem. Ber., 119(1986)1189
396 L.L.Lohr, Inorg. Chem., 26(1987)2005

397 W.Abriel, Acta Crystallogr., B42(1986)449
398 W.Abriel, Z. Naturforsch., Teil B., 41(1986)592
399 B.H.Christian, M.J.Collins, R.J.Gillespie and J.F.Sawyer, Inorg. Chem., 25(1986)777
400 P.G.Jones, D.Jentsch and E.Schwarzmann, Z. Naturforsch., Teil B., 41(1986)1483
401 T.N.Srivastava, J.D.Singh and S.K.Srivastava, Polyhedron, 6(1987)219
402 V.E.Fedorov, V.P.Fedin and O.A.Kuz'mina, Russ. J. Inorg. Chem., 31(1986)331
403 A.Hassan, H.A.Azab and R.M.Hassan, Bull. Soc. Chim. France, (1987)63
404 B.O.Loopstra and K.Goubitz, Acta Crystallogr., C42(1986)520
405 P.Scian, J.Lapassett and J.Moret, Acta Crystallogr., C42 (1986)1688
406 V.Kramer and G.Brandt, Acta Crystallogr., C42(1986)917
407 K.J.Schmidt, G.J.Schrobilgen and J.F.Sawyer, Acta Crystallogr., C42(1986)1115
408 V.Kozhukharov, H.Burger, S.Neov and B.Sidzhimov, Polyhedron, 5(1986)771
409 S.H.Strauss, K.D.Abney and O.P.Anderson, Inorg. Chem., 25(1986)2808
410 S.H.Strauss, M.D.Noirot and O.P.Anderson, Inorg. Chem., 25(1986)3850
411 J.A.Alonso, C.Cascales and I.Rasines, Z. Anorg. Allg. Chem., 537(1986)213
412 V.V.Safonov, S.A.Chebotarev, A.A.Akhmedov and N.V.Ovcharenko, Russ. J. Inorg. Chem., 31(1986)579
413 V.V.Safonov, N.G.Chaban and O.V.Sorokina, Russ. J. Inorg. Chem., 32(1987)138
414 J.C.Bart, P.Forzatti, F.Garbassi and F.Cariati, Z. Anorg. Allg. Chem., 546(1987)206
415 L.D.Schultz and W.H.Koehler, Inorg. Chem., 26(1987)1989
416 P.Bottcher and R.Keller, Z. Anorg. Allg. Chem., 542(1986)144
417 R.Zagler, B.Eisenmann and H.Schafer, Z. Naturforsch., Teil B., 42(1987)151
418 R.Nesper and J.Curda, Z. Naturforsch., Teil B., 42(1987)557
419 C.Belin and H.Mercier,J. Chem. Soc., Chem Commun., (1987)190
420 G.Krabbes, Z. Anorg. Allg. Chem., 543(1986)97
421 F.U.Axe and D.S.Marynick, Inorg. Chem., 26(1987)1658
422 D.Chandra and H.Wiedemeier, Z. Anorg. Allg. Chem., 545(1986)98
423 H.Wiedemeier and D.Chandra, Z. Anorg. Allg. Chem., 545(1986)109
424 W.Honle, G.Kuhn and H.Neumann, Z. Anorg. Allg. Chem., 532 (1986)150
425 K.O.Klepp, Z. Naturforsch., Teil B., 42(1987)130
426 K.O.Klepp, Z. Naturforsch., Teil B., 41(1986)941
427 G.Kliche, Z. Naturforsch., Teil B., 41(1986)130
428 Yu.V.Mironov, P.P.Samoilov, V.E.Fedorov, V.I.Lisoivan and S.A.Gromilov, Russ. J. Inorg. Chem., 32(1987)622
429 A.A.Movsum-Zade, M.R.Allazov, A.U.Suleimanova & N.A.Seidova, Russ. J. Inorg. Chem., 31(1986)112.
430 V.A.Lyakhovitskaya, Z.I.Zhmurova and P.P.Fedorov Russ. J. Inorg. Chem., 31(1986)581

431 I.V.Saunin, T.V.Saunina and D.A.Yas'kov Russ. J. Inorg. Chem., 31(1986)741
432 V.K.Slovyanskikh, N.T.Kuznetsov and S.V.Yan'kov Russ. J. Inorg. Chem., 31(1986)762
433 Ch.Abilov, P.G.Rustamov and S.G.Agdamskaya Russ. J. Inorg. Chem., 31(1986)867
434 I.A.Khodyakova, V.A.Dolgikh, B.A.Popovkin and A.V.Novosolova, Russ. J. Inorg. Chem., 31(1986)1043
435 S.Yu.Asadova, M.R.Allazov, A.A.Mosum-Zade and P.G.Rustamov, Russ. J. Inorg. Chem., 31(1986)1361
436 O.M.Aliev, T.Kh.Kurbanov and Z.M.Mukhtarova, Russ. J. Inorg. Chem., 31(1986)1516
437 O.M.Aliev and T.F.Maksudova, Russ. J. Inorg. Chem., 31 (1986)1523
438 F.M.Sadygov, P.G.Rustamov and T.M.Il'yasov Russ. J. Inorg. Chem., 31(1986)1783
439 P.G.Rustamov, P.K.Babaeva and N.A.Askerova Russ. J. Inorg. Chem., 32(1987)458
440 I.O.Nasibov, V.K.Valiev, A.N.Khalilov, T.I.Sultanov and T.A.Dzhalil-Zade Russ. J. Inorg. Chem., 32(1987)566
441 A.B.Agaev, P.G.Rustamov and Dzh.A.Akhmedova Russ. J. Inorg. Chem., 32(1987)577
442 A.S.Secco, K.Alam, B.J.Blackburn and A.F.Janzen, Inorg. Chem., 25(1986)2125
443 M.A.K.Ahmed, A.E.McCarthy and W.R.McWhinnie, J. Chem. Soc., Dalton Trans., (1986)771
444 H.M.K.K.Pathirana and W.R.McWhinnie, J. Chem. Soc., Dalton Trans.,(1986)2003
445 J.Kischkewitz and D.Naumann, Z. Anorg. Allg. Chem., 547(1987)167
446 J.D.Miller and T.A.Tahir, J. Chem. Soc., Dalton Trans., (1987)985
447 H.Kopf and T.Klapotke, J. Chem. Soc., Chem Commun., (1986)1192
448 D.M.Giolando, T.B.Rauchfuss and A.L.Rheingold, Inorg. Chem., 26(1987)1636
449 M.J.Collins, R.J.Gillespie and J.F.Sawyer, Inorg. Chem., 26(1987)1476
450 N.Kuhn, H.Schumann and G.Wolmershauser, Z. Naturforsch., Teil B., 42(1987)674
451 N.Kuhn and H.Schumann, J. Chem. Soc., Dalton Trans., (1987)541
452 M.DiVaira, M.Peruzzini and P.Stoppioni, J. Chem. Soc., Chem. Commun., (1986)374
453 R.Faggiani, R.J.Gillespie, C.Campana and J.W.Kolis, J. Chem. Soc., Chem Commun., (1987)483
454 E.R.T.Tiekink, Acta Crystallogr., C42(1986)633
455 M.A.K.Ahmed, W.R.McWhinnie and P.Granger, Polyhedron, 5(1986)859