anionic complex $[WCl_2F_2(\eta^2\text{-}N_3S_2)]^-$.[259] Copper(I) and silver complexes of the $[S_3N]^-$ ion are of older vintage, e.g. $[Cu(PPh_3)_2(\eta^2\text{-}SSNS)]$ and $[Cu(\eta^2\text{-}SSNS)_2]^-$.[260]
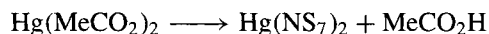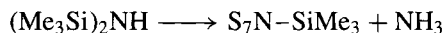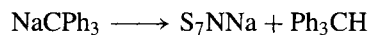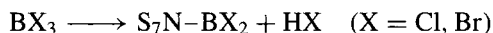
(iii) Sulfur imides, $S_{8-n}(NH)_n$ [206]

The NH group is "isoelectronic" with S and so can successively subrogate S in *cyclo*-S_8. Thus we have already seen that reduction of S_4N_4 with dithionite or with $SnCl_2$ in boiling ethanol/benzene yields $S_4(NH)_4$. Again, whereas reaction of S_2Cl_2 or SCl_2 with NH_3 in non-polar solvents yields S_4N_4, heating these 2 reactants in

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(1990). See also P. F. KELLY, A. M. Z. SLAWIN, D. J. WILLIAMS and J. D. WOOLLINS *Polyhedron* **10**, 2337–40 (1991).

[259] H. BORGHOLTE, K. DEHNICKE, H. GOESMANN and D. FENSKE, *Z. anorg. allg. Chem.*, **586**, 159–65 (1990).

[260] J. BOJES, T. CHIVERS and P. W. CODDING, *J. Chem. Soc., Chem. Commun.*, 1171–3 (1981).

polar solvents such as dimethylformamide affords a range of sulfur imides. In a typical reaction 170 g S_2Cl_2 and the corresponding amount of NH_3 yielded:

S_8 (32 g)   1,3-$S_6(NH)_2$ (0.98 g)   1,3,5-$S_5(NH)_3$ (0.08 g)
S_7NH 1,4-$S_6(NH)_2$ (2.3 g)   1,3,6-$S_5(NH)_3$ (0.32 g)
(15.4 g)   1,5-$S_6(NH)_2$ (0.82 g)

In no case have adjacent NH groups been observed.

S_7NH is a stable pale-yellow compound, mp 113.5°; the structure is closely related to that of *cyclo*-S_8 as shown in Fig. 15.43a. The proton is acidic and undergoes many reactions of which the following are typical (see also p. 729):

$$BX_3 \longrightarrow S_7N\text{-}BX_2 + HX \quad (X = Cl, Br)$$

$$NaCPh_3 \longrightarrow S_7NNa + Ph_3CH$$

$$(Me_3Si)_2NH \longrightarrow S_7N\text{-}SiMe_3 + NH_3$$

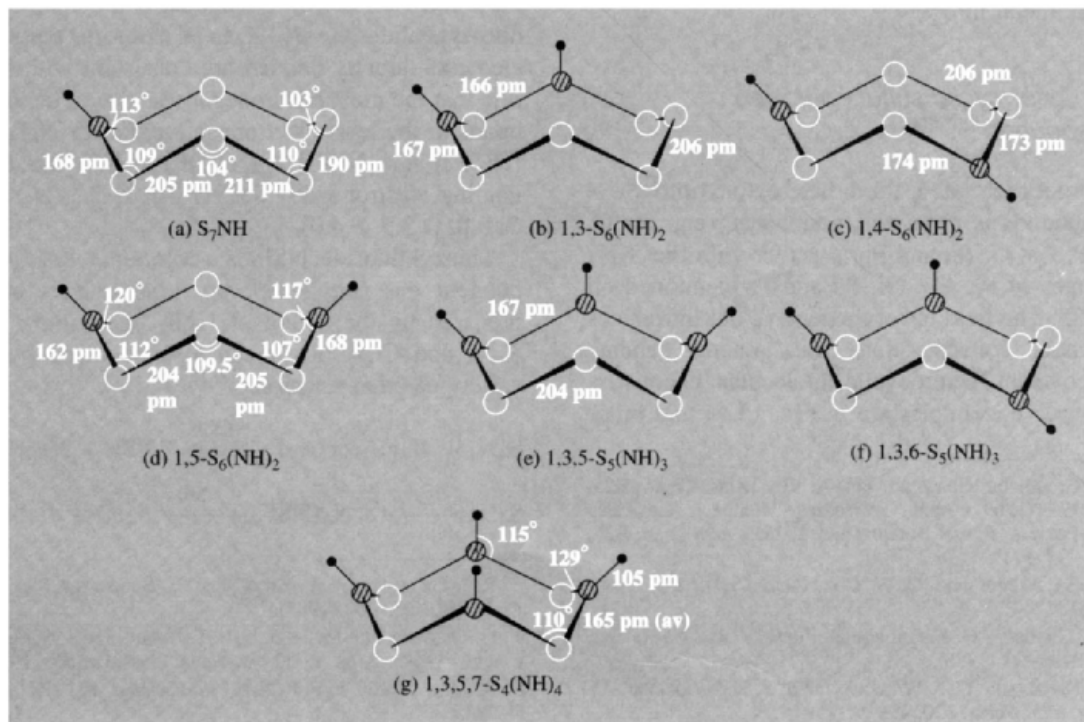$$Hg(MeCO_2)_2 \longrightarrow Hg(NS_7)_2 + MeCO_2H$$

Figure 15.43   Structures of the various cyclo sulfur imides.

The 3 isomeric compounds $S_6(NH)_2$ form stable colourless crystals and have the structures illustrated in Fig. 15.43b, c, and d.[208,261] The 1,3-, 1,4-, and 1,5-isomers melt at 130°, 133°, and 155° respectively. The 1,3,5- and 1,3,6-triimides melt with decomposition at 128° and 133° (Fig. 15.43e and f). The tetraimide, $S_4(NH)_4$ (mp 145°) is structurally very similar (Fig. 15.43g):[262] the N atoms are each essentially trigonal planar and the heterocycle is somewhat flattened, the distance between the planes of the 4 N atoms and 4 S atoms being only 57 pm. The influence of extensive intermolecular H-bonding on the structure has been studied by electron deformation density techniques.[263]

Alkyl derivatives such as $1,4\text{-}S_6(NR)_2$ and $S_4(NR)_4$ can be synthesized by reacting S_2Cl_2 with primary amines RNH_2 in an inert solvent. Compounds such as $1,4\text{-}S_2(NR)_4$ (R = $-CO_2Et$) are now also well characterized.[264] The bis-adduct $[Ag(S_4N_4H_4)_2]^+$ has been isolated as its perchlorate; this has a sandwich-like structure and is unique in being S-bonded rather than N-bonded to the metal ion.[265]

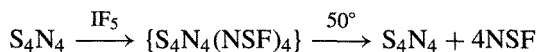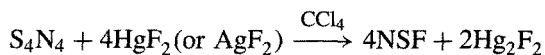### (iv) Other cyclic sulfur–nitrogen compounds [207,209]

Incorporation of a third heteroatom into S–N compounds is now well established, e.g. for C, Si; P, As; O; Sn and Pb, together with the S_2N_2 chelates of Fe, Co, Ni, Pd and Pt mentioned on p. 725. The field is very extensive but introduces no new concepts into the general scheme of covalent heterocyclic molecular chemistry. Illustrative examples are in Fig. 15.44 and fuller

details including X-ray structures for many of the compounds are in the references cited above. A selenium analogue of the dimer $S_6N_4{}^{2+}$ (p. 731) has also been prepared and structurally characterized, *viz.* $[SN_2Se_2Se_2N_2S]^{2+}$.[266]

(v) Sulfur–nitrogen halogen compounds [267–9]

As with sulfur–halogen compounds (pp. 683–93) the stability of N–S–X compounds decreases with increase in atomic weight of the halogen. There are numerous fluoro and chloro derivatives but bromo and iodo derivatives are virtually unknown except for the nonstoichiometric $(SNX_x)_\infty$ polymers (p. 728) and $S(NX)_2$ (p. 740). Unlike the H atoms in the sulfur imides (p. 735) the halogen atoms are attached to S rather than N. Fluoro derivatives have been known since 1965 but some of the chloro compounds have been known for over a century. The simplest compounds are the nonlinear thiazyl halides $N\equiv S-F$ and $N\equiv S-Cl$: these form a noteworthy contrast to the nonlinear nitrosyl halides $O=N-X$. In all cases, the pairs of elements directly bonded are consistent with the rule that the most electronegative atom of the trio bonds to the least electronegative, i.e. $\{S(NH)\}_4$, $\{N(SF)\}_{1,3,4}$, $\{N(SCl)\}_{1,3}$, O(NF), O(NCl) (formal Pauling electronegativities: H 2.1, S 2.5, N 3.0, Cl 3.0, O 3.5, F 4.0).

Thiazyl fluoride, NSF, is a colourless, reactive, pungent gas (mp −89°, bp +0.4°). It is best prepared by the action of HgF_2 on a slurry of S_4N_4 and CCl_4 but it can also be made by a variety of other reactions:[267]

$$S_4N_4 + 4HgF_2\,(\text{or }AgF_2) \xrightarrow{CCl_4} 4NSF + 2Hg_2F_2$$

$$S_4N_4 \xrightarrow{IF_5} \{S_4N_4(NSF)_4\} \xrightarrow{50°} S_4N_4 + 4NSF$$

[261] J. C. VAN DE GRAMPEL and A. VOS, *Acta Cryst.* **B25**, 611–17 (1969), and references therein. See also H. J. POSTMA, F. VAN BOLHUIS and A. VOS, *Acta Cryst.* **B27**, 2480–6 (1971).

[262] T. M. SABINE and G. W. COX, *Acta Cryst.* **28**, 574–7 (1967).

[263] D. GREGSON, G. KLEBE and H. FUESS, *J. Am. Chem. Soc.* **110**, 8488–93 (1988).

[264] J. NOVOSAD, D. J. WILLIAMS and J. D. WOOLLINS, *Z. anorg. allg. Chem.* **620**, 495–7 (1994).

[265] M. B. HURSTHOUSE, K. M. A. MALIK and S. N. NABI, *J. Chem. Soc., Dalton Trans.*, 355–9 (1980).

[266] R. J. GILLESPIE, J. P. KENT and J. F. SAWYER, *Inorg. Chem.* **20**, 4053–60 (1981).

[267] O. GLEMSER and M. FILD, in V. GUTMANN (ed.), *Halogen Chemistry*, Vol. 2, pp. 1–30, Academic Press, London, 1967.

[268] R. MEWS, *Adv. Inorg. Chem. Radiochem.* **19**, 185–237 (1976).

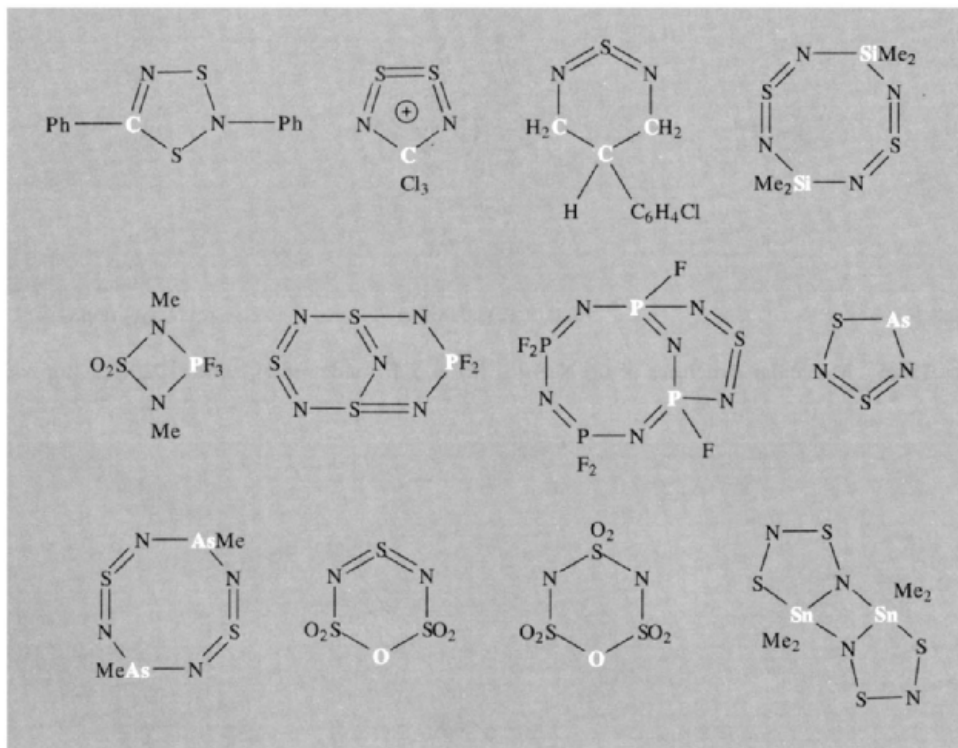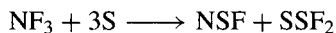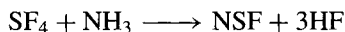[269] O. GLEMSER and R. MEWS, *Angew. Chem. Int. Edn. Engl.* **19**, 883–99 (1980).

Figure 15.44 Some heterocyclic S–N compounds incorporating a third heteroelement.

$$SF_4 + NH_3 \longrightarrow NSF + 3HF$$

$$NF_3 + 3S \longrightarrow NSF + SSF_2$$

S_4N_4 can also be fluorinated to NSF (and other products) using F_2 at $-75°$, SeF_4 at $-10°$, or SF_4. The molecular dimensions of NSF have been determined by microwave spectroscopy: N–S 145 pm, S–F 164 pm, angle at S 116.5°. The angle at S is very close to the angle at N in ONX (110–117°, p. 442). NSF can be stored at room temperature in copper or teflon vessels but it slowly decomposes in glass (more rapidly at 200°) to form a mixture of OSF_2, SO_2, SiF_4, S_4N_4 and N_2. At room temperature and at pressures above 1 atm it trimerises to cyclo-$N_3S_3F_3$ (see below) but at lower pressures it affords S_4N_4 admixed with yellow-green crystals of $S_3N_2F_2$; this latter is of unknown structure but may well be the nonlinear acyclic species FSN=S=NSF. $N_3S_3F_3$ is best made by fluorinating cyclo-$N_3S_3Cl_3$ with AgF_2/CCl_4. The tetramer cyclo-$N_4S_4F_4$ is not obtained by polymerization of NSF monomer but can be readily made by fluorinating S_4N_4 with a hot slurry of AgF_2/CCl_4. Some physical properties of these and other N–S–F compounds (p. 725) are compared in the following table:

Compound	$N\equiv S{-}F$	$S_3N_2F_2$	$N_3S_3F_3$
MP/°C	−89	83	74.2
BP/°C	+0.4	–	92.5

Compound	$N_4S_4F_4$	$N\equiv SF_3$	$FN{=}SF_2$
MP/°C	153(d)	−72	–
BP/°C	–	27.1	−6.7

The structures of $N_3S_3F_3$ and $N_4S_4F_4$ are in Fig. 15.45. The former features a slightly puckered 6-membered ring (chair conformation) with essentially equal S–N distances around the ring and 3 eclipsed axial F atoms. By contrast,
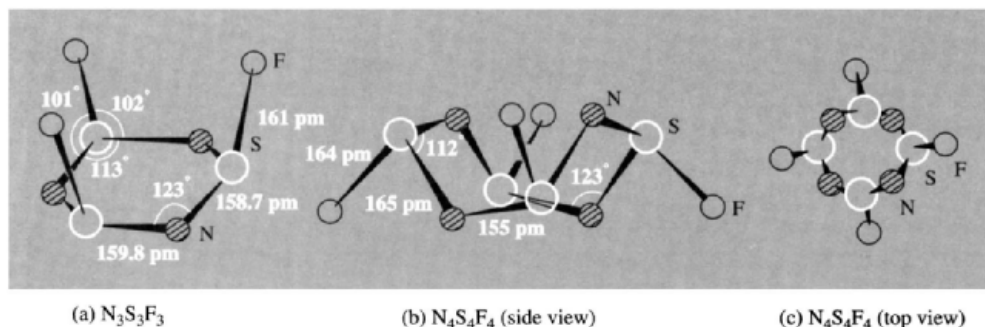
(a) N₃S₃F₃   (b) N₄S₄F₄ (side view)   (c) N₄S₄F₄ (top view)

Figure 15.45   Molecular structures of (a) $N_3S_3F_3$, (b) $N_4S_4F_4$ (side view), and (c) $N_4S_4F_4$ (top view).

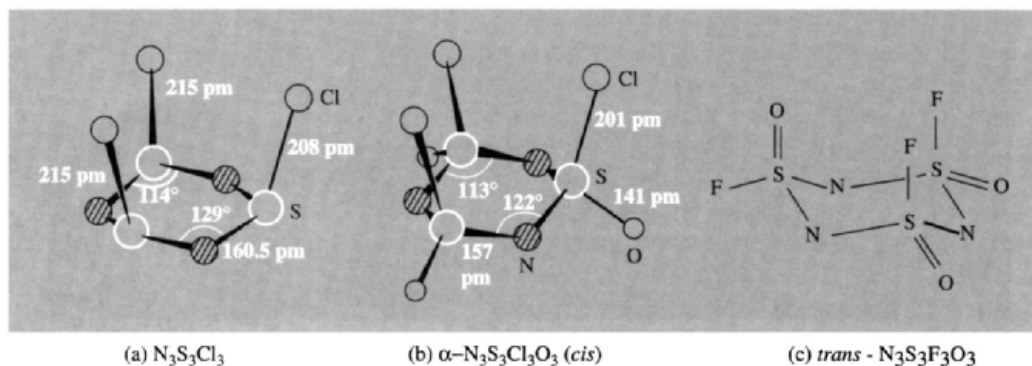(a) N₃S₃Cl₃   (b) α–N₃S₃Cl₃O₃ (*cis*)   (c) *trans* - N₃S₃F₃O₃

Figure 15.46   Molecular structure of (a) $N_3S_3Cl_3$, (b) α-$N_3S_3Cl_3O_3$ (*cis*), and (c) *trans*-$N_3S_3F_3O_3$.
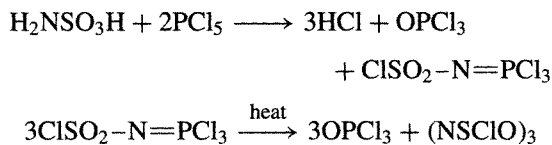
$N_4S_4F_4$ shows a pronounced alternation in S–N distances and only 2 of the F atoms are axial; it will also be noted that the conformation of the N_4S_4 ring is very different to that in S_4N_4 (p. 723) or $S_4(NH)_4$ (p. 735). It is an interesting intellectual exercise to attempt to rationalize these striking structural differences.[270] The chemistry of these various NSF oligomers has not been extensively studied. $N_3S_3F_3$ is stable in dry air but is hydrolysed by dilute aqueous NaOH to give NH_4F and sulfate. $N_4S_4F_4$ is reported to form an N-bonded 1:1 adduct with BF_3 whereas with AsF_5 or SbF_5 fluoride ion transfer occurs (accompanied by dethiazylation of the ring) to give $[N_3S_3F_2]^+[MF_6]^-$ and $[NS]^+[MF_6^-]$.

In the chloro series, the compounds to be considered are $N{\equiv}S{-}Cl$, *cyclo*-$N_3S_3Cl_3$, *cyclo*-$N_3S_3Cl_3O_3$, and *cyclo*-$N_4S_4Cl_2$; the ionic compounds $[S_4N_3]^+Cl^-$ and $[cyclo{-}N_2S_3Cl]^+Cl^-$ and $[catena{-}N(SCl)_2]^+[BCl_4]^-$; together with various isomeric oxo- and fluoro-chloro derivatives. Thiazyl chloride, NSCl, is best obtained by pyrolysis of the trimer in vacuum at 100°. It can also be made by the reaction of Cl_2 on NSF (note that $NSF + F_2 \longrightarrow NSF_3$) and by *numerous other reactions*.[267] It is a yellow-green gas that rapidly trimerizes at room temperature, and is isostructural with NSF.

By far the most common compound in the series is $N_3S_3Cl_3$ (yellow needles, mp 168°) which can be prepared by the direct action of Cl_2 (or $SOCl_2$) on S_4N_4 in CCl_4, and which is also obtained in all reactions leading to NSCl. The structure (Fig. 15.46a) is very

270 S. M. OWEN and A. T. BROOKER, *A Guide to Modern Inorganic Chemistry*, Longman Scientific and Technical, Harlow 1991, pp. 120–1.

similar to that of $N_3S_3F_3$ and comprises a slightly puckered ring with equal S–N distances of 160.5 pm and the N atoms only 18 pm above and below the plane of the 3 S atoms. $N_3S_3Cl_3$ is sensitive to moisture and is oxidized by SO_3 above 100° to $N_3S_3Cl_3O_3$; at lower temperatures the adduct $N_3S_3Cl_3.6SO_3$ is formed and this dissociates at 100° to $N_3S_3Cl_3.3SO_3$. A more efficient preparation of $N_3S_3Cl_3O_3$ is by thermal decomposition of the product obtained by the reaction of amidosulfuric acid with PCl_5:

$$H_2NSO_3H + 2PCl_5 \longrightarrow 3HCl + OPCl_3$$
$$+ ClSO_2-N{=}PCl_3$$
$$3ClSO_2-N{=}PCl_3 \xrightarrow{heat} 3OPCl_3 + (NSClO)_3$$

The compound is obtained in two isomeric forms from this reaction: α, mp 145° and β, mp 43°. The structure of the α-form is in Fig. 15.46b and is closely related to that of $(NSCl)_3$ with uniform S–N distances around the ring. The β-form may have a different ring conformation but more probably involves *cis-trans* isomerism of the pendant Cl and O atoms. Fluorination of α-$N_3S_3Cl_3O_3$ with KF in CCl_4 yields the two isomeric fluorides *cis*-$N_3S_3F_3O_3$ (mp 17.4°) and *trans*-$N_3S_3F_3O_3$ (mp −12.5°) (Fig. 15.46c). The structural assignment of the 2 isomers was made on the basis of ^{19}F nmr. Fluorination with SbF_3 under reduced pressure yields both the monofluoro and difluoro derivatives $N_3S_3Cl_2FO_3$ and $N_3S_3ClF_2O_3$, each having 3 isomers which can be separated chromatographically and assigned by ^{19}F nmr as indicated schematically in Fig. 15.47. Numerous other derivatives are known in which one or more halogen atom is replaced by $-NH_2$, $-N{=}SF_2$, $-N{=}PCl_3$, $-N{=}CHPh$, $-OSiMe_3$, etc.

A different structure motif occurs in S_4N_3Cl. This very stable yellow compound features the $S_4N_3{}^+$ cation (p. 732) and is obtained by many reactions, e.g.:

$$3S_4N_4 + 2S_2Cl_2 \xrightarrow{CCl_4/heat} 4[S_4N_3]^+Cl^-$$

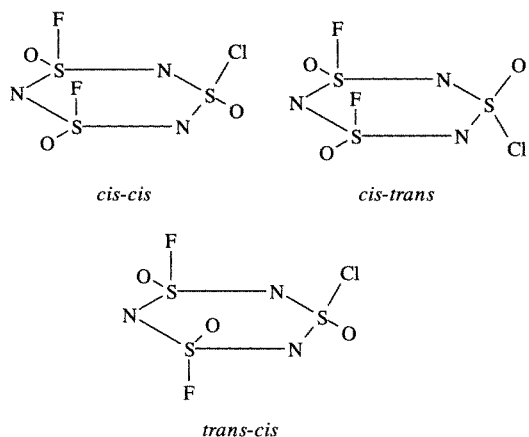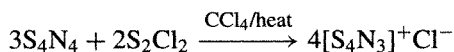*cis-cis*   *cis-trans*

trans-cis

Figure 15.47 Schematic representation of the three geometric isomers of $N_3S_3ClF_2O_3$. The three isomers of the monofluoro derivative are similar but with Cl and F interchanged.

The chloride ion is readily replaced by other anions to give, for example, the orange-yellow $[S_4N_3]Br$, bronze-coloured $[S_4N_3]SCN$, $[S_4N_3]NO_3$, $[S_4N_3]HSO_4$, etc.

Chlorination of S_4N_4 with NOCl or $SOCl_2$ in a polar solvent yields $S_3N_2Cl_2$:

$$S_4N_4 + 2NOCl \longrightarrow S_3N_2Cl_2 + \tfrac{1}{2}S_2Cl_2 + 2N_2O$$
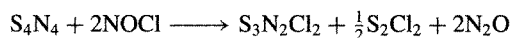
The crystal structure again reveals an ionic formulation, $[N_2S_3Cl]^+Cl^-$, this time with a slightly puckered 5-membered ring carrying a single pendant Cl atom as shown in Fig. 15.48a; the alternation of S–N distances and the rather small angles at the 2 directly linked S atoms are notable features. Reaction of $[N_2S_3Cl]^+Cl^-$ with bis(trimethylsilyl)cyanamide, $(Me_3Si)_2NCN$, in MeCN yields dark red crystals of N_2S_3NCN (i.e. $\overline{SNSNS}{=}NCN$) in which the essentially linear NCN group (176.4°) lies diagonally above the N_2S_3-ring with the angle S=N–C being 119.0°.[271] Yet a further chloride can be obtained by the partial chlorination of S_4N_4 with Cl_2 in CS_2 solution below room temperature: one of the

271 A. J. Banister, W. Clegg, I. B. Gorrell, Z. V. Hauptman and R. W. H. Small, *J. Chem. Soc., Chem. Commun.*, 1611–13 (1987).
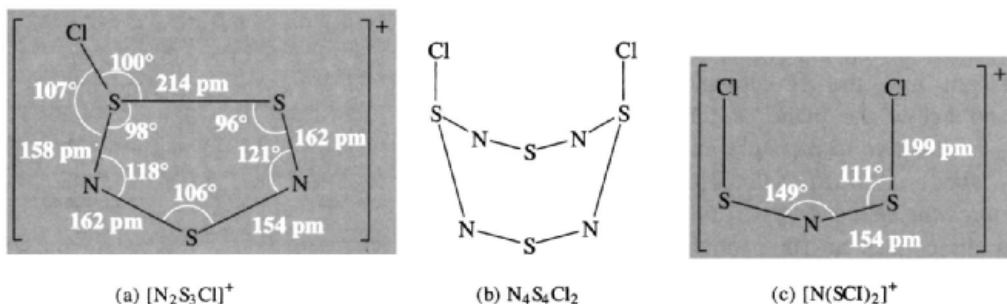
Figure 15.48 Structure of (a) the cation in $[N_2S_3Cl]^+Cl^-$, (b) $N_4S_4Cl_2$, and (c) $[N(SCl)_2]^+$.

trans-annular S···S "bonds" is opened to give yellow crystals of $N_4S_4Cl_2$ (Fig. 15.48b) and this derivatized heterocycle can be used to prepare several other compounds.[272]

Reaction of NSF_3 with BCl_3 yields the acyclic cation $[N(SCl)_2]^+$ as its BCl_4^- salt (Fig. 15.48c); the compound is very hygroscopic and readily decomposes to BCl_3, SCl_2, S_2Cl_2, and N_2.

The formation of highly conducting nonstoichiometric bromo and iodo derivatives of polythiazyl has already been mentioned (p. 728). It has been found that, whereas bromination of solid S_4N_4 with gaseous Br_2 yields conducting $(SNBr_{0.4})_x$, reaction with liquid bromine leads to the stable tribromide $[S_4N_3]^+$-$[Br_3]^-$.[273] In contrast, the reaction of S_4N_4 with Br_2 in CS_2 solution results in a (separable) mixture of $[S_4N_3]^+[Br_3]^-$, $[S_4N_3]^+Br^-$ and the novel ionic compound $CS_3N_2Br_2$ which may be $[S{=}\overline{C\text{-}S}{=}N\text{-}S{=}N]^{2+}[Br^-]_2$ or $[S{=}\overline{C\text{-}S}{=}N\text{-}S(Br){=}N]^+Br^-$. The binary halides SN_2Br_2 and SN_2I_2 are also known. Thus SF_4 reacts with $(Me_3Si)_2NI$ in $C_2F_4Cl_2$ at $0°C$ to give $S(NI)_2$ as a shock-sensitive yellow crystalline powder composed of $I{-}N{=}S{=}N{-}I$ molecules in *syn-anti* configuration:[274]
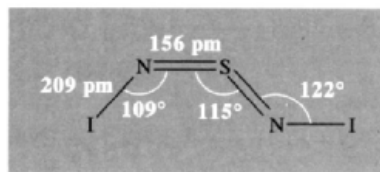
(vi) Sulfur–nitrogen–oxygen compounds [207]

This is a classic area of inorganic chemistry dating back to the middle of the last century and only a brief outline will be possible. It will be convenient first to treat the sulfur nitrogen oxides and then the amides, imides and nitrides of sulfuric acid. Hydrazides and hydroxylamides of sulfuric acid will also be considered. Some of these compounds have remarkable properties and some are implicated in the lead-chamber process for the manufacture of H_2SO_4 (p. 708). The field is closely associated with the names of the great German chemists E. Frémy ($\sim$1845), A. Claus ($\sim$1870), F. Raschig ($\sim$1885–1925), W. Traube ($\sim$1890–1920), F. Ephraim ($\sim$1910), P. Baumgarten ($\sim$1925) and, in more recent years, M. Becke-Goehring ($\sim$1955) and F. Seel ($\sim$1955–65).

(a) *Sulfur–nitrogen oxides.* Trisulfur dinitrogen dioxide, $S_3N_2O_2$, is best made by treating S_4N_4 with boiling $OSCl_2$ under a stream of SO_2:

$$S_4N_4 + 2OSCl_2 \longrightarrow S_3N_2O_2 + 2Cl_2 + S_2N_2 + S$$

It is a yellow solid with an acyclic structure (Fig. 15.49a), cf N_2O_5 (p. 458). Moist air converts $S_3N_2O_2$ to SO_2 and S_4N_4 whereas SO_3

[272] H. W. ROESKY, C. GRAF, M. N. S. RAO, B. KREBS and G. HENKEL, *Angew. Chem. Int. Edn. Engl.* **18**, 780–1 (1979)), and references therein. H. W. ROESKY, M. N. S. RAO, C. GRAF, A. GIEREN and E. HADICKE, *Angew. Chem. Int. Edn. Engl.* **20**, 592–3 (1981).

[273] G. WOLMERSHÄUSER, G. B. STREET and R. D. SMITH, $CS_3N_2Br_2$, *Inorg. Chem.* **18**, 383–5 (1979).

[274] M. ROCK, P. BRAVIN and K. SEPPELT, *Z. anorg. allg. Chem.* **618**, 89–92 (1992).
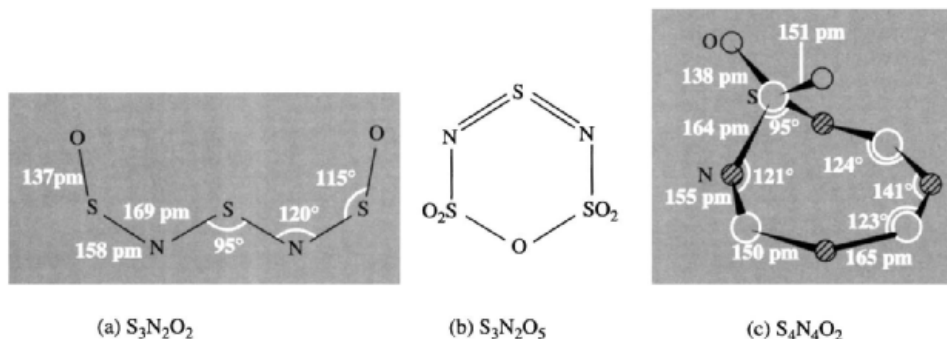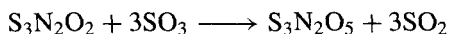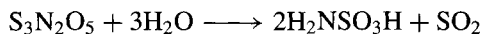
Figure 15.49   Structures of sulfur–nitrogen oxides.

oxidizes it smoothly to $S_3N_2O_5$:

$$S_3N_2O_2 + 3SO_3 \longrightarrow S_3N_2O_5 + 3SO_2$$

The pentoxide $S_3N_2O_5$ can also be made directly from S_4N_4 and SO_3. It forms colourless, strongly refracting crystals which readily hydrolyse to sulfamic acid:

$$S_3N_2O_5 + 3H_2O \longrightarrow 2H_2NSO_3H + SO_2$$

It has a cyclic structure and may be regarded as a substituted diamide of disulfuric acid, $H_2S_2O_7$ (Fig. 15.49b).

An alternative synthetic strategy for sulfur-nitrogen oxides is exemplified by the more recent reaction:[275]

$$S_3N_2Cl_2 + SO_2(NH_2)_2 \xrightarrow[\text{reflux}]{CCl_4} S_4N_4O_2$$
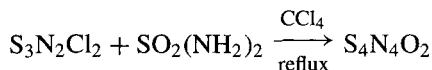
The product forms orange-yellow crystals, mp 166 (d), having a structure in which 1 S atom of an S_4N_4 ring carries both O atoms. X-ray diffractometry shows substantial deviation from the parent S_4N_4 structure, a notable feature being the coplanarity of the S_3N_2 moiety furthest removed from the SO_2 group (Fig. 15.49c). If $S_4N_4O_2$ is allowed to react with 2 mols of SO_3 in liquid SO_2, two further compounds are formed: the known $S_3N_2O_5$ (Fig. 15.49b) and the novel greenish-black $S_6N_5O_4$, which is composed of separately stacked tricyclic radical cation dimers
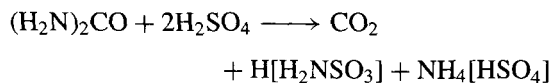
$[\{S_3N_2^{\bullet}\}_2]^{2+}$ (Fig. 15.39b)) and the cyclic anion $S_3N_3O_4^-$, i.e. $[O_2\overline{SNSNS(O)_2O}]^-$.[276] Numerous other *cyclic-* and *polycyclic-*N/S/O species have recently been prepared and structurally characterized.[277]

(b) *Amides of sulfuric acid.* Amidosulfuric acid (better known as sulfamic acid, $H[H_2NSO_3]$), is a classical inorganic compound and an important industrial chemical. Formal replacement of both hydroxyl groups in sulfuric acid leads to sulfamide $(H_2N)_2SO_2$ (p. 742) which is also clearly related structurally to the sulfuryl halides X_2SO_2 (p. 694).

Sulfamic acid can be made by many routes, including addition of hydroxylamine to SO_2 and addition of NH_3 to SO_3:

$$H_2NOH + SO_2 \longrightarrow H[H_2NSO_3]$$

$$NH_3 + SO_3 \longrightarrow H[H_2NSO_3]$$
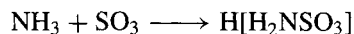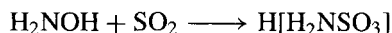
The industrial synthesis uses the strongly exothermic reaction between urea and anhydrous H_2SO_4 (or dilute oleum):

$$(H_2N)_2CO + 2H_2SO_4 \longrightarrow CO_2$$
$$+ H[H_2NSO_3] + NH_4[HSO_4]$$

[275] H. W. ROESKY,   W. SCHAPER,   O. PETERSEN   and T. MÜLLER, *Chem. Ber.* **110**, 2695–8 (1977).

[276] H. ROESKY, M. WITT, J. SCHIMKOWIAK, M. SCHMIDT, M. NOLTEMEYER and G. M. SHELDRICK, *Angew. Chem. Int. Edn. Engl.* **21**, 538–9 (1982).

[277] T. CHIVERS,   R. T. OAKLEY,   A. W. CORDES   and W. T. PENNINGTON, *J. Chem. Soc., Chem. Commun.*, 1214–5 (1981). T. CHIVERS, A. W. CORDES, R. T. OAKLEY and W. T. PENNINGTON, *Inorg. Chem.* **22**, 2429–35 (1983). T. CHIVERS and M. HOJO, *Inorg. Chem.* **23**, 4088–93 (1984).

(a) $^+H_3NSO_3^-$ sulfamic acid   (b) $[H_2NSO_3]^-$ sulfamate ion   (c) $(H_2N)_2SO_2$ sulfamide
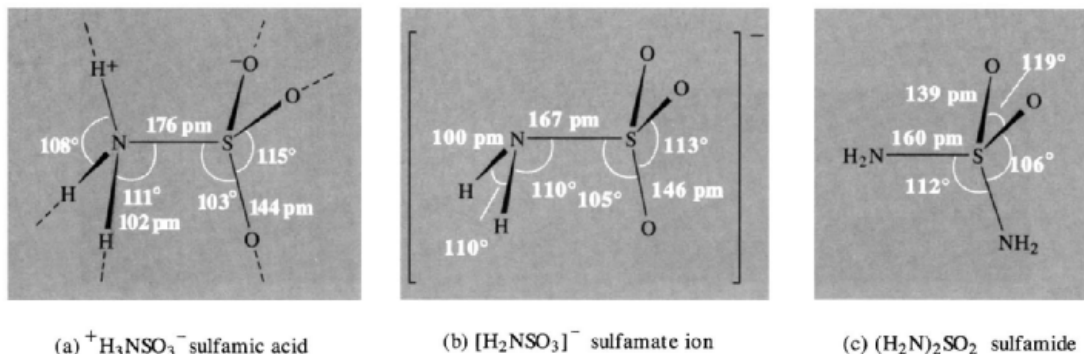
Figure 15.50   The structures of (a) sulfamic acid, (b) the sulfamate ion, and (c) sulfamide.

Salts are obtained by direct neutralization of the acid with appropriate oxides, hydroxides, or carbonates. Sulfamic acid is a dry, non-volatile, non-hygroscopic, colourless, white, crystalline solid of considerable stability. It melts at 205°, begins to decompose at 210°, and at 260° rapidly gives a mixture of SO_2, SO_3, N_2, H_2O, etc. It is a strong acid (dissociation constant 1.01×10^{-1} at 25° solubility ~25 g per 100 g H_2O) and, because of its physical form and stability, is a convenient standard for acidimetry. Over 50 000 tonnes are manufactured annually and its principal applications are in formulations for metal cleaners, scale removers, detergents and stabilizers for chlorine in aqueous solution.[278] Its salts are used in flame retardants, weed killers and for electroplating.
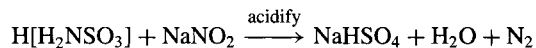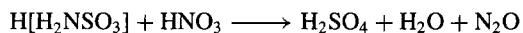
In the solid state sulfamic acid forms a strongly H-bonded network which is best described in terms of zwitterion units $^+H_3NSO_3^-$ rather than the more obvious formulation as aminosulfuric acid, $H_2NSO_2(OH)$. The zwitterion has the staggered configuration shown in Fig. 15.50a and the S–N distance is notably longer than in the sulfamate ion or sulfamide.

Dilute aqueous solutions of sulfamic acid are stable for many months at room temperature but at higher temperatures hydrolysis to $NH_4[HSO_4]$ sets in. Alkali metal salts are stable in neutral and
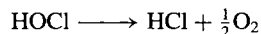
alkaline solutions even at the bp. Sulfamic acid is a monobasic acid in water (see Fig. 15.50b for structure of the sulfamate ion). In liquid ammonia solutions it is dibasic and, with Na for example, it forms $NaNH.SO_3Na$. Sulfamic acid is oxidized to nitrogen and sulfate by Cl_2, Br_2 and ClO_3^-, e.g.:

$$2H[H_2NSO_3] + KClO_3 \longrightarrow N_2 + 2H_2SO_4$$
$$+ KCl + H_2O$$
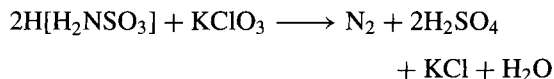
Concentrated HNO_3 yields pure N_2O whilst aqueous HNO_2 reacts quantitatively to give N_2:

$$H[H_2NSO_3] + HNO_3 \longrightarrow H_2SO_4 + H_2O + N_2O$$

$$H[H_2NSO_3] + NaNO_2 \xrightarrow{\text{acidify}} NaHSO_4 + H_2O + N_2$$

This last reaction finds use in volumetric analysis. The use of sulfamic acid to stabilize chlorinated water depends on the equilibrium formation of N-chlorosulfamic acid, which reduces loss of chlorine by evaporation, and slowly re-releases hypochlorous acid by the reverse hydrolysis:
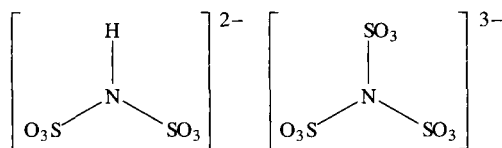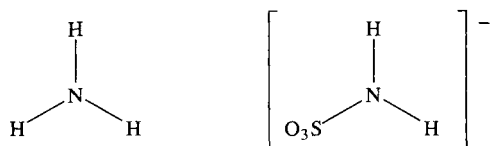
$$Cl_2 + H_2O \rightleftharpoons HOCl + HCl$$
$$H[H_2NSO_3] + HOCl \rightleftharpoons HN(Cl)SO_3H + H_2O$$
$$HOCl \longrightarrow HCl + \tfrac{1}{2}O_2$$

Sulfamide, $(H_2N)_2SO_2$, can be made by ammonolysis of SO_3 or O_2SCl_2. It is a colourless crystalline material, mp 93°, which begins to decompose above this temperature. It is soluble in water to give a neutral non-electrolytic solution but in boiling water it decomposes to ammonia and sulfuric acid. The structure (Fig. 15.50c)

278 E. B. BELL, Sulfamic acid and sulfamates, *Kirk–Othmer Encyclopedia of Chemical Technology*, 3rd edn., Vol. 21, pp. 940–60, Wiley, New York, 1983.

can be compared with those of sulfuric acid, $(HO)_2SO_2$ (p. 710) and the sulfuryl halides X_2SO_2 (p. 694).

(c) *Imido and nitrido derivatives of sulfuric acid.* In the preceding section the sulfamate ion and related species were regarded as being formed by replacement of an OH group in $(HO)SO_3^-$ or $(HO)_2SO_3$ by an NH_2 group. They could equally well be regarded as sulfonates of ammonia in which each H atom is successively replaced by SO_3^- (or SO_3H):

H
|
N
/ \
H   H

Ammonia

$$\left[\begin{array}{c} H \\ | \\ N \\ O_3S \quad \diagdown \quad H \end{array} \right]^-$$

(Sulfamate)
Amidosulfate
Aminosulfonate

$$\left[\begin{array}{c} H \\ | \\ N \\ O_3S \quad \diagdown \quad SO_3 \end{array} \right]^{2-}$$

Imidodisulfate
Imidodisufonate

$$\left[\begin{array}{c} SO_3 \\ | \\ N \\ O_3S \quad \diagdown \quad SO_3 \end{array} \right]^{3-}$$

Nitridotrisulfate
Nitrilotrisulfonate

Both sets of names are used in the literature. Free imidodisulfuric acid $HN(SO_3H)_2$ (which is isoelectronic with disulfuric acid $H_2S_2O_7$, p. 705) and free nitridotrisulfuric acid $N(SO_3H)_3$ are unstable, but their salts are well characterized and have been extensively studied.

Imidodisulfuric acid derivatives can be prepared from urea by using less sulfuric acid than required for sulfamic acid (p. 741):

$$4(H_2N)_2CO + 5H_2SO_4 \xrightarrow{\text{warm}} 4CO_2$$
$$+ 2HN(SO_3NH_4)_2 + (NH_4)_2SO_4$$
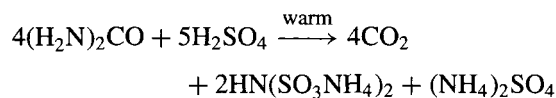
Addition of aqueous KOH liberates NH_3 and affords crystalline $HN(SO_3K)_2$ on evaporation. All 3 H atoms in $HN(SO_3H)_2$ can be replaced by NH_4 or M^I, e.g. the direct reaction of NH_3 and SO_3 yields the triammonium salt:

$$4NH_3 + 2SO_3 \longrightarrow NH_4[N(SO_3NH_4)_2]$$
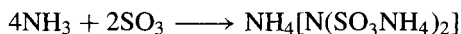
Imidodisulfates can also be obtained by hydrolysis of nitridotrisulfates (see below). Figure 15.51 compares the structure of the imidodisulfate and parent disulfate ions, as determined from the potassium salts. Comparison with the hydroxylamine derivative $K[HN(OH)SO_3]$ (below) is also instructive.
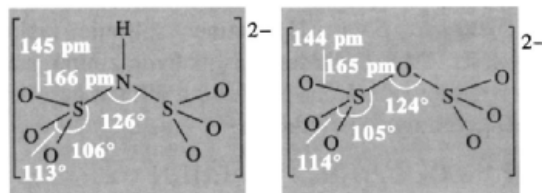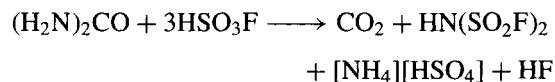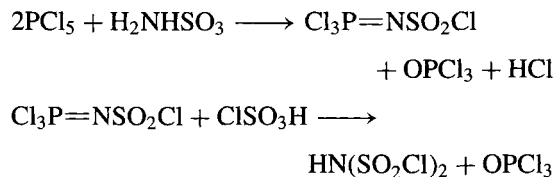

**Figure 15.51** Comparison of the structures of the imidodisulfate and disulfate ions in their potassium salts.

Fluoro and chloro derivatives of imidodisulfuric acid can be made by reacting HSO_3F or HSO_3Cl (rather than H_2SO_4) with urea:

$$(H_2N)_2CO + 3HSO_3F \longrightarrow CO_2 + HN(SO_2F)_2$$
$$+ [NH_4][HSO_4] + HF$$

$HN(SO_2F)_2$ melts at 17°, boils at 170° and can be further fluorinated with elemental F_2 at room temperature to give $FN(SO_2F)_2$, mp −79.9°, bp 60°. The chloro derivative $HN(SO_2Cl)_2$ is a white crystalline compound, mp 37°: it is made in better yield from sulfamic acid by the following reaction sequence:

$$2PCl_5 + H_2NHSO_3 \longrightarrow Cl_3P{=}NSO_2Cl$$
$$+ OPCl_3 + HCl$$

$$Cl_3P{=}NSO_2Cl + ClSO_3H \longrightarrow$$
$$HN(SO_2Cl)_2 + OPCl_3$$

Salts of nitridotrisulfuric acid, $N(SO_3M^I)_3$, are readily obtained by the exothermic reaction of nitrites with sulfites or hydrogen sulfites in hot aqueous solution:

$$KNO_2 + 4KHSO_3 \longrightarrow N(SO_3K)_3$$
$$+ K_2SO_3 + 2H_2O$$
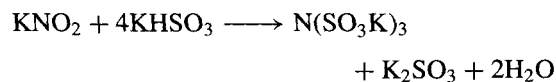
The dihydrate crystallizes as the solution cools. Such salts are stable in alkaline solution but hydrolyse in acid solution to imidodisulfate (and then more slowly to sulfamic acid):

$$[N(SO_3)_3]^{3-} + H_3O^+ \longrightarrow$$
$$[HN(SO_3)_2]^{2-} + H_2SO_4$$
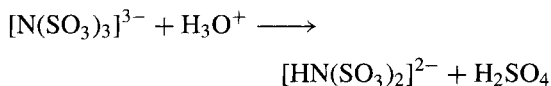
(d) *Hydrazine and hydroxylamine derivatives of sulfuric acid.* Hydrazine sulfonic acid, $H_2NNH.HSO_3$ is obtained as its hydrazinium salt by reacting anhydrous N_2H_4 with diluted gaseous SO_3 or its pyridine adduct:

$$C_5H_5NSO_3 + 2N_2H_4 \longrightarrow C_5H_5N$$
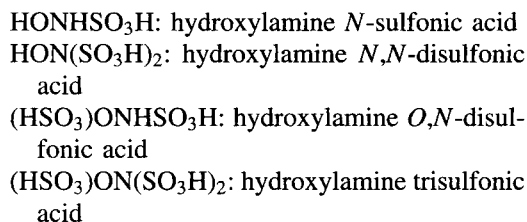$$+ [N_2H_5]^+[H_2NNHSO_3]^-$$
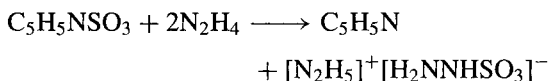
The free acid is monobasic, pK 3.85; it is much more easily hydrolysed than sulfamic acid and has reducing properties comparable with those of hydrazine. Like sulfamic acid it exists as a zwitterion in the solid state: $^+H_3NNHSO_3^-$.

Symmetrical hydrazine disulfonic acid can be made by reacting a hydrazine sulfonate with a chlorosulfate:

$$H_2NNHSO_3^- + ClSO_3^- \longrightarrow HCl$$
$$+ [O_3SNHNHSO_3]^{2-}$$
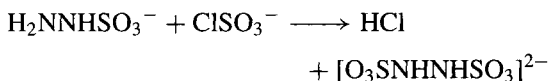
Oxidation of the dipotassium salt with HOCl yields the azodisulfonate $KO_3SN{=}NSO_3K$. Numerous other symmetrical and unsymmetrical hydrazine polysulfonate derivatives are known.

With hydroxylamine, $HONH_2$, 4 of the 5 possible sulfonate derivatives have been prepared as anions of the following acids:

$HONHSO_3H$: hydroxylamine N-sulfonic acid
$HON(SO_3H)_2$: hydroxylamine N,N-disulfonic acid
$(HSO_3)ONHSO_3H$: hydroxylamine O,N-disulfonic acid
$(HSO_3)ON(SO_3H)_2$: hydroxylamine trisulfonic acid

The first of these can be made by careful hydrolysis of the N,N-disulfonate which is itself made by the reaction of SO_2 and a nitrite in cold alkaline solution:

$$KNO_2 + KHSO_3 + SO_2 \longrightarrow HON(SO_3K)_2$$
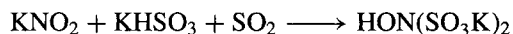
The potassium salt readily crystallizes from the cold solution thus preventing further reaction with the hydrogen sulfate to give nitridotrisulfate (p. 743). The structure of the hydroxylamine N-sulfonate ion is shown in Fig. 15.52a. The closely related N-nitrosohydroxylamine N-sulfonate ion (Fig. 15.52b) can be made directly by absorbing NO in alkaline K_2SO_3 solution: the 6 atoms ONN(O)SO all lie in one plane and the interatomic distances suggest an S–N single bond but considerable additional π bonding in the N–N bond.

Oxidation of hydroxylamine N,N-disulfonate with permanganate or PbO_2 yields the intriguing

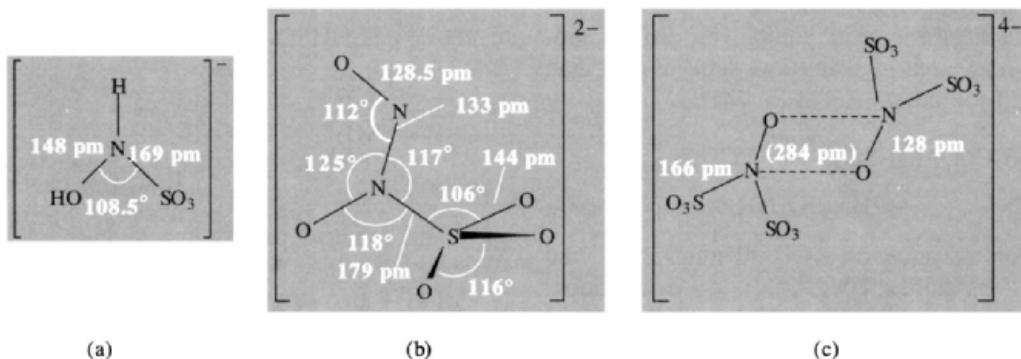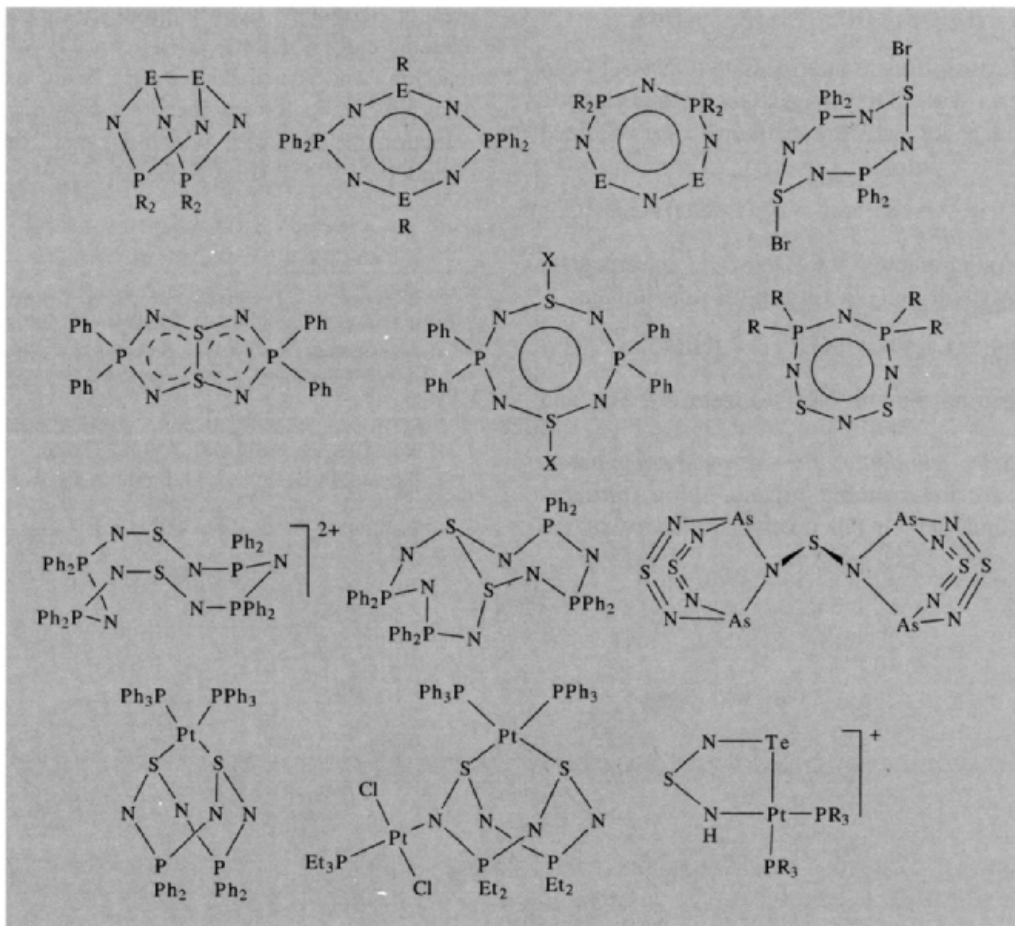**Figure 15.52** Structures of various S–N oxoanions: (a) hydroxylamine-N-sulfonate, (b) N-nitrosohydroxylamine N-sulfonate and (c) the dimeric anion in Frémy's salt $\{K_2[ON(SO_3)_2]\}_2$.

nitrosodisulfonate $K_2[ON(SO_3)_2]$: this was first isolated by Frémy as a yellow solid which was subsequently shown to be dimeric and diamagnetic due to the formation of long $N\cdots O$ bonds in the crystal (Fig. 15.52c). However, in aqueous solution the anion dissociates reversibly into the deep violet, paramagnetic monomer $[ON(SO_3)_2]^{2-}$.
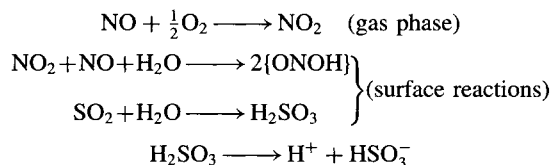
Hydroxylamine trisulfonates, e.g. $(KO_3S)ON(SO_3K)_2$ are made by the reaction of K_2SO_3 with potassium nitrosodisulfonate (Frémy's salt). Acidification of the product results in rapid hydrolysis to the *O,N*-disulfonate which can be isolated as the exclusive product:

$$(KO_3S)ON(SO_3K)_2 + H_2O \longrightarrow$$

$$(KO_3S)ONH(SO_3K) + KHSO_4$$
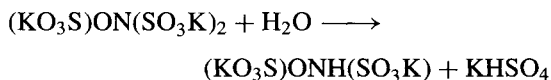
Sulfonic acids containing nitrogen have long been implicated as essential intermediates in the synthesis of H_2SO_4 by the lead-chamber process (p. 708) and, as shown by F. Seel and his group, the crucial stage is the oxidation of sulfite ions by the nitrosyl ion NO^+:

$$SO_3^{2-} + NO^+ \longrightarrow [ONSO_3]^- \xrightarrow{\ NO^+\ } 2NO + SO_3$$

The NO^+ ions are thought to be generated by the following sequence of reactions:

$$NO + \tfrac{1}{2}O_2 \longrightarrow NO_2 \quad \text{(gas phase)}$$

$$\left.\begin{array}{l} NO_2 + NO + H_2O \longrightarrow 2\{ONOH\} \\ SO_2 + H_2O \longrightarrow H_2SO_3 \end{array}\right\} \text{(surface reactions)}$$

$$H_2SO_3 \longrightarrow H^+ + HSO_3^-$$
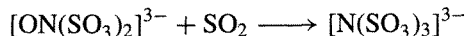
$${ONOH} + H^+ \longrightarrow NO^+ + H_2O$$

The nitrososulfonate intermediate $[ONSO_3]^-$ can also react with $SO_3{}^{2-}$ to give the hydroxylamine disulfonate ion which can likewise be oxidized by NO^+:

$$[ON(SO_3)_2]^{3-} + NO^+ \longrightarrow N_2O + SO_3 + SO_4{}^{2-}$$

In a parallel reaction the $[ONSO_3]^-$ intermediate can react with SO_2 to form nitrilotrisulfonate:

$$[ON(SO_3)_2]^{3-} + SO_2 \longrightarrow [N(SO_3)_3]^{3-}$$

This then reacts with NO^+ to form N_2, SO_3 and $SO_4{}^{2-}$.

(e) *Selected other sulfur–nitrogen compounds.* There are innumerable organo–sulfur–nitrogen compounds which fall outside the scope of the present treatment. Even without the presence of skeletal carbon atoms, a rich variety of novel reactions and structural types is being explored as briefly indicated on the preceding page by a selection of examples which is itself far from complete:[279–282] (E = S, Se).

[279] N. Burford,   T. Chivers,   M. N. S. Rao   and J. F. Richardson, *Inorg. Chem.* **23**, 1946–52 (1984).

[280] M. Heberhold, K. Guldar, A. Gieren, C. Ruiz-Perez and T. Hübner, *Angew. Chem. Int. Edn. Engl.* **26**, 82–3 (1987).

[281] P. F. Kelly,   A. M. Z. Slawin,   D. J. Williams   and J. D. Woollins, *Polyhedron* **9**, 2659–62 (1990).

[282] T. Chivers, D. D. Doxsee, M. Edwards and R. W. Hilts, in R. Steudel (ed.), *The Chemistry of Inorganic Ring Systems*, Elsevier, Amsterdam, 1992, Chap. 15, pp. 271–94.