A General Route to $N(SCl)_2^+$ and SNS^+ Salts†

Bryan Ayres,[a] Arthur J. Banister,*[a] Philip D. Coates,[a] Michael I. Hansford,[a] Jeremy M. Rawson,[a] Clifton E. F. Rickard,[b] Michael B. Hursthouse,[c] K. M. Abdul Malik[c] and Majid Motevalli[d]
[a] *Chemistry Department, University of Durham, South Road, Durham DH1 3LE, UK*
[b] *Chemistry Department, University of Auckland, Private Bag, Auckland, New Zealand*
[c] *School of Chemistry and Applied Chemistry, University of Wales, Cardiff, P.O. Box 912, Cardiff CF1 3TB, UK*
[d] *Chemistry Department, Queen Mary and Westfield College, Mile End Road, London E1 4NJ, UK*

A 1:3 mixture of $(NSCl)_3$ and AgX (where X is a 'hard' anion) in liquid SO_2 act as a convenient source of [SN]X. The reactivity of salts of this SN^+ cation towards sulfur and SCl_2 has been examined. Reaction of $(NSCl)_3$ with AgX (X = AsF_6, SbF_6 or CF_3SO_3) and SCl_2 in liquid SO_2 gave $[N(SCl)_2]X$ in high yield (>75%). Reduction of these salts with $SnCl_2$ provides a convenient route to the corresponding [SNS]X salts. Replacement of SCl_2 by sulfur in the $(NSCl)_3$ + $AgCF_3SO_3$ reaction yields only *ca.* 30% $[SNS][CF_3SO_3]$. The other main product is $[S_6N_4][CF_3SO_3]_2$ which crystallises in the space group $P2_1/n$ [$Z = 2$, $a = 8.632(4)$, $b = 10.614(8)$, $c = 8.387(6)$ Å, $\beta = 90.79(5)°$, $R = 0.025$] and shows similar intermolecular S···O contacts to $[S_6N_4][ClS_2O_6]_2$ [$P\bar{1}$, $Z = 1$, $a = 7.689(1)$, $b = 10.726(1)$, $c = 6.614(1)$ Å, $\alpha = 101.00(2)$, $\beta = 114.42(2)$, $\gamma = 90.35(2)°$, $R = 0.031$]. The relative reactivities of the different SNS^+ salts with PhCN lie in the order $AsF_6^- > SbCl_6^- > CF_3SO_3^- > SbF_6^- > AlCl_4^-$. The structure of $[PhCNSNS][AsF]_6$ has been determined: space group $P2_1/a$, $Z = 4$, $a = 10.824(5)$, $b = 8.287(2)$, $c = 13.599(3)$ Å, $\beta = 106.32(4)°$, $R = 0.055$.

The reactivity of SNS^+ with alkenes,[1] alkynes[2,3] and nitriles[3,4] (and to a lesser extent S=N and halogens) is well documented. Reactions of $[SNS][AsF_6]$ with such unsaturated species typically proceed in high yield (>80%) through a dipolar cycloaddition involving the lowest unoccupied molecular orbital (LUMO) of SNS^+ and the highest occupied molecular orbital (HOMO) of the dienophile. The compound $[SNS][AsF_6]$ can be formed by the reaction[5] of $[S_8][AsF_6]_2$ with NaN_3 or of $[SN][AsF_6]$ with sulfur in liquid SO_2.[6a] However it is more cleanly prepared[5] in excess of 90% yield by the reaction of S_4N_4 with AsF_5 and sulfur in liquid SO_2 [equation (1)]. This

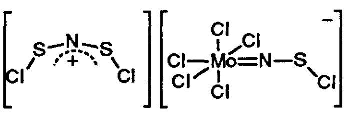
$$S_4N_4 + \tfrac{1}{2}S_8 + 6AsF_5 \longrightarrow 4[SNS][AsF_6] + 2AsF_3 \quad (1)$$

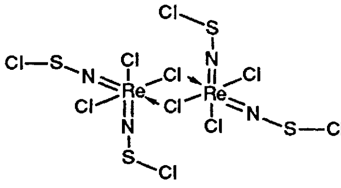
reaction must be carried out with some care as it is potentially hazardous (involving explosive S_4N_4[7] and toxic AsF_5[8]). Other alternative and convenient high-yield routes to SNS^+ salts, especially $[SNS][AsF_6]$, are therefore needed and such a method is described below.

We have recently reported[9] that reduction of $N(SCl)_2^+$ salts with $SnCl_2$ provides a high-yield route to the SNS^+ cation, the $SbCl_6^-$ and $AlCl_4^-$ salts being isolated in 70 and 86% yields respectively [equation (2)]. Since reduction of $[N(SCl)_2]X$ with

$$[N(SCl)_2][AlCl_4] + SnCl_2 \longrightarrow [SNS][AlCl_4] + SnCl_4 \quad (2)$$

$SnCl_2$ would appear to be a convenient route to [SNS]X, we have investigated synthetic routes to other $N(SCl)_2^+$ salts as precursors to the SNS^+ reagent. In most routes to $N(SCl)_2^+$ salts the reactions proceed *via* the formation of NSCl–metal halide adducts.[10–13] In some cases these intermediates are well characterised and are usually monomeric or dimeric in nature (*e.g.* **I** and **II**). Subsequent reaction with SCl_2 provides the required $N(SCl)_2^+$ cation, frequently in high yield.


I


II

In comparison, the preparation of $N(SCl)_2^+$ salts with anions which are not of the type $M_xCl_y^{z-}$ (such as AsF_6^-, BF_4^- and $CF_3CO_2^-$) has not been achieved through convenient routes. Instead these have been formed by reaction[14] of the corresponding SN^+ salt with SCl_2 (or, in the case of $[SNS][AsF_6]$, by direct chlorination[15] of SNS^+). However such routes have not been fully investigated since the preparation of the intermediate thionitrosyl cation is arduous, for instance $[SN][MF_6]$ (M = As or Sb) may be prepared by the potentially dangerous reaction[16] of NSF with MF_5 whilst the alternative route[6] to $[SN][AsF_6]$ involves the use of a large excess of expensive $AgAsF_6$. Moreover these salts are extremely susceptible to nucleophilic attack (particularly hydrolysis) and purification, isolation and storage must be carried out under the most rigorous of conditions.

The salt $[SN][PF_6]$ has previously been prepared[17] *in situ*

---

† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

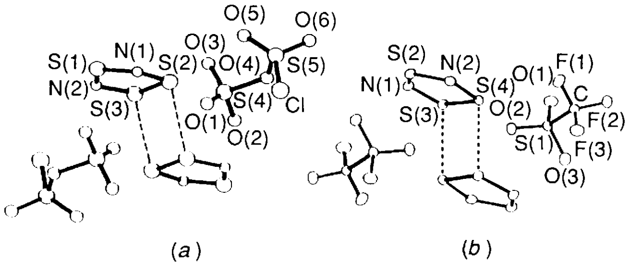
Table 1 Preparation of [SNS]X from [N(SCl)$_2$]X

Anion X	Recovered yield (%)		Total yield (%) of [SNS]X based on (NSCl)$_3$
	[N(SCl)$_2$]X	[SNS]X	
AsF$_6$	96[a]	94	90
SbCl$_6$	90[b]	90	81
AlCl$_4$	82[b]	86	71
FeCl$_4$	85[b]	72	61
SbF$_6$	80[a]	75	60
CF$_3$SO$_3$	75[a]	70	53
SeCl$_6$	84[b]	0[c]	0

[a] Prepared from the silver salt. [b] Prepared from (NSCl)$_3$ and the corresponding Lewis acid. [c] Formed [S$_3$N$_2$Cl]$_2$[SeCl$_6$].

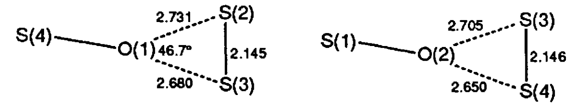
Table 2 Intermolecular S···O contacts < 3.35 Å in [S$_6$N$_4$][ClS$_2$O$_6$]$_2$ (*a*) and [S$_6$N$_4$][CF$_3$SO$_3$]$_2$ (*b*)

(*a*)			
O(1)···S(1)	2.980(3)	O(1)···S(2)	2.731(3)
O(1)···S(3)	2.680(3)	O(2)···S(1)	3.251(3)
O(2)···S(2)	3.043(4)	O(3)···S(1)	3.030(3)
O(3)···S(3)	3.071(3)	O(5)···S(1)	2.996(3)
O(6)···S(1)	2.917(3)		
(*b*)			
O(1)···S(3)	2.966	O(1)···S(2)	3.173
O(2)···S(3)	2.705	O(2)···S(4)	3.302
O(2)···S(4)	2.650	O(2)···S(2)	3.045
O(2)···S(3)	3.268	O(3)···S(4)	2.871
O(3)···S(2)	2.956		



(*a*) (*b*)

Fig. 1 Crystal structures of (*a*) [S$_6$N$_4$][ClS$_2$O$_6$]$_2$ and (*b*) [S$_6$N$_4$][CF$_3$SO$_3$]$_2$



(*a*) (*b*)

Fig. 2 Close intermolecular S···O contacts in (*a*) [S$_6$N$_4$][ClS$_2$O$_6$]$_2$ and (*b*) [S$_6$N$_4$][CF$_3$SO$_3$]$_2$

from (NSCl)$_3$ and AgPF$_6$, and we were interested in examining the general application of this initial step with a view to the synthesis of N(SCl)$_2{}^+$ and hence SNS$^+$ salts.

Results and Discussion

On addition of SCl$_2$ to a mixture of AgX (X = AsF$_6$, SbF$_6$ or CF$_3$SO$_3$) and (NSCl)$_3$ in liquid SO$_2$ a thick, olive-green precipitate rapidly formed which on stirring for 12–24 h yielded an orange-yellow solution over a white precipitate of AgCl. The product in all cases [equation (3)] was readily isolated by

$$(NSCl)_3 + 3SCl_2 + 3AgAsF_6 \longrightarrow 3AgCl + 3[N(SCl)_2][AsF_6] \quad (3)$$

filtration and removal of the SO$_2$. The crude yellow solid isolated in this manner was then stirred in CH$_2$Cl$_2$ for several hours (to allow solvation of any unreacted SCl$_2$) followed by filtration and then dried *in vacuo*. The products were readily characterised by their infrared spectra, which showed only the characteristic N(SCl)$_2{}^+$ absorption bands[18] (ν_{max} 1127s, 720s, 662m, 526s, 508ms, 447m and 360s cm^{-1}) and the bands for the anion (although in some cases there was evidence for the presence of trace quantities of the corresponding SNS$^+$ salt.[5] Generation of small quantities of SNS$^+$ by this route is not surprising since SO$_2$ has previously been shown to act as a dechlorinating agent for S/N species[19]).

In comparison, no reaction occurred between LiAsF$_6$ (or NaSbF$_6$) and the (NSCl)$_3$–SCl$_2$ mixture under similar conditions. This is presumably partly due to the higher lattice energy of AgCl (864 kJ mol^{-1}) compared with LiCl and NaCl (834 and 769 kJ mol^{-1} respectively[20]).

Reduction of these N(SCl)$_2{}^+$ salts with SnCl$_2$ in liquid SO$_2$ readily provided the corresponding SNS$^+$ cation, in a similar manner to that observed for the AlCl$_4{}^-$ and SbCl$_6{}^-$ salts.[9] In this way not only was [SNS][AsF$_6$] synthesised in 90% recovered yield but the new SNS$^+$ reagents [SNS][CF$_3$SO$_3$] and [SNS][FeCl$_4$] have also been prepared. The slightly lower yields observed in the case of triflate salts (see Table 1) arises from their extreme air-sensitivity; both [N(SCl)$_2$][CF$_3$SO$_3$] and [SNS][CF$_3$SO$_3$] are readily hydrolysed and apparatus was rigorously flame-dried before use in order to improve the yields. Despite this air-sensitivity, the evident ability to prepare SNS$^+$ salts with 'organic' anions should improve solubility in organic media and facilitate further solution studies.

We have previously shown[6a] that reaction of [SN][AsF$_6$] with sulfur in liquid SO$_2$ also provides [SNS][AsF$_6$] in *ca.* 50% isolable yield, whilst Awere and Passmore[6b] have recently achieved quantitative yields of [SNS][AsF$_6$] under similar conditions. We have now found that when [SN][AsF$_6$] [prepared *in situ* from equimolar amounts of AgAsF$_6$ and (NSCl)$_3$] is added to sulfur [SNS][AsF$_6$] is formed in high yield (80% recovered). However, when the reaction was not allowed to continue to completion or in the absence of a stoichiometric amount of sulfur, the [SNS][AsF$_6$] was sometimes contaminated with traces of the known compound[21] [S$_3$N$_2$][AsF$_6$]$_2$ (it has already been established[21] that S$_3$N$_2{}^{2+}$ dissociates into SNS$^+$ and SN$^+$ in liquid SO$_2$). In comparison, reaction of (NSCl)$_3$ and AgCF$_3$SO$_3$ (acting as a source of [SN][CF$_3$SO$_3$]) with sulfur provided [SNS][CF$_3$SO$_3$] in only 35% isolated yield, the desired product being contaminated with [S$_6$N$_4$][CF$_3$SO$_3$]$_2$. Crystals of [S$_6$N$_4$][CF$_3$SO$_3$]$_2$, readily grown by slow evaporation of the SO$_2$ reaction mixture, were picked and mounted in Lindemann capillaries under a nitrogen atmosphere.

Structure of [S$_6$N$_4$][CF$_3$SO$_3$]$_2$.—This was first determined in 1980 by Roesky and co-workers,[22] the salt being prepared from the reaction of triflic anhydride with S$_4$N$_4$. However this structure contained CH$_3$CN of crystallisation and refined with an *R* value of 0.056. Redetermination of the unsolvated structure at 208 K has led to significant improvement in the accuracy (*R* = 0.025).

The molecular packing of [S$_6$N$_4$][CF$_3$SO$_3$]$_2$ shows a strong similarity to that observed in the first S$_6$N$_4{}^{2+}$ salt[23] characterised by X-ray crystallography, [S$_6$N$_4$][ClS$_2$O$_6$]$_2$ (the full structure details of which we report here). Fig. 1 shows the atom numbering in the two salts. The S$_6$N$_4{}^{2+}$ cation in [S$_6$N$_4$][CF$_3$SO$_3$]$_2$ is centrosymmetric and is built up of two S$_3$N$_2{}^{\bullet+}$ monomers held together through strong S···S interactions (2.971 Å), a common feature of all S$_6$N$_4{}^{2+}$ salts.[23,24] The structures of both [S$_6$N$_4$][CF$_3$SO$_3$]$_2$ and [S$_6$N$_4$][ClS$_2$O$_6$]$_2$ are characterised by many short S···O intermolecular con-

Table 3 Preparation of [PhCNSNS]X from the reaction of [SNS]X with PhCN

SNS Reagent	Conditions	Time	T/°C	Yield (%)
[SNS][AsF$_6$]	Neat	5 min	20	90
	Liquid SO$_2$	1 h	20	95
[SNS][SbCl$_6$]	Neat	7 d	20	0^a
	Neat	3 h	110	75
	CH$_2$Cl$_2$	1 d	40	0^a
	Liquid SO$_2$	7 d	20	0^a
[SNS][CF$_3$SO$_3$]	Neat	1 h	20	70
	Liquid SO$_2$	2 h	20	74
	CH$_2$Cl$_2$	2 h	40	30
[SNS][SbF$_6$]	Neat	1 h	20	35
	Liquid SO$_2$	3 h	20	50
[SNS][AlCl$_4$]	Neat	1 h	20	0^b
	CH$_2$Cl$_2$	2 h	20	0^b
	Liquid SO$_2$	1 h	20	0^b

[a] Did not react. [b] Decomposed.

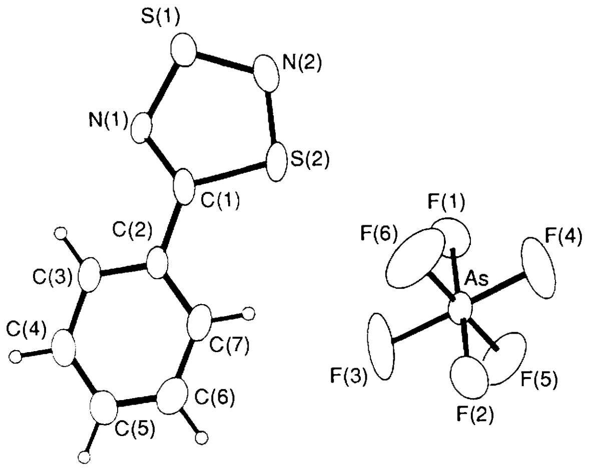


Fig. 3 Crystal structure of [PhCNSNS][AsF$_6$]

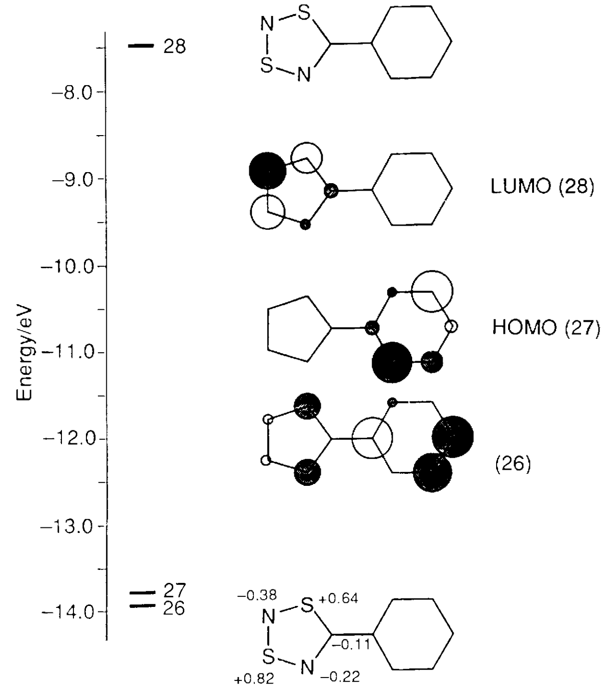


Fig. 4 Charge distribution in [PhCNSNS][AsF$_6$] and molecular orbital energies: eV ≈ 1.60 × 10^{-19} J

tacts (Table 2), the shortest of which involve O(1) {O(2) in the case of [S$_6$N$_4$][CF$_3$SO$_3$]$_2$} and the basal sulfurs of the S$_3$N$_2$ ring (Fig. 2). It is significant that the oxygen atom lies only *ca.* 0.06 Å away from the S$_3$N$_2$ ring plane in both [S$_6$N$_4$][ClS$_2$O$_6$]$_2$ and [S$_6$N$_4$][CF$_3$SO$_3$]$_2$, allowing an in-plane interaction involving the overlap of the lone-pair orbital on oxygen with a vacant orbital based on the disulfide linkage. This type of in-plane interaction is common in other materials where the disulfide link carries a positive charge, *e.g.* S$_4$N$_3$Cl,[25] [PhCNSSN]Cl[26] and [(PhCNSSN)$_2$Cl][S$_3$N$_3$].[27] The other S···O contacts are less directional and may be considered to be predominantly ionic in nature.

Reactivity.—A comparison of the reactivity of these SNS$^+$ salts was carried out through their reactions with benzonitrile. A summary of the conditions employed and the maximised yields is shown in Table 3. Reaction of PhCN with [SNS][AlCl$_4$] failed to provide pure samples of [PhCNSNS][AlCl$_4$] despite the use of a variety of solvents: the major products were identified from the infrared spectra as [S$_6$N$_4$][AlCl$_4$]$_2$ and [S$_6$N$_4$]Cl$_2$. Although [SNS][SbF$_6$] provided the [PhCNSNS]$^+$ salt in reasonable yield, it simultaneously decomposed to the S$_3$N$_2{}^{\bullet+}$ cation, although not as extensively as [SNS][AlCl$_4$]. Both [SNS][AsF$_6$] and [SNS][CF$_3$SO$_3$] react at room temperature with PhCN, either neat or in liquid SO$_2$, to provide the corresponding dithiadiazolylium salt, [PhCNSNS]X. However the extremely air-sensitive nature of [SNS][CF$_3$SO$_3$] incurs a lower yield than [SNS][AsF$_6$], and its reactions are slower due to a lower solubility in liquid SO$_2$. The highest yield of [PhCNSNS]$^+$ was for the AsF$_6{}^-$ salt, the reaction proceeding smoothly in excess of 90% recovered yield; trace quantities of coloured impurities were readily removed by washing with CH$_2$Cl$_2$ and the material was recrystallised by exhaustive extraction with CH$_2$Cl$_2$ in a sealed extractor.[19] The salt [SNS][SbCl$_6$] did not decompose or react with PhCN, MeCN or C$_6$F$_5$CN at room temperature but did react under refluxing conditions (with an excess of nitrile) to provide the required dithiadiazolylium cations in high yield (> 70%). It is to be anticipated that [SNS][SbCl$_6$] will also react with multicyano organics such as C$_6$H$_4$(CN)$_2$ in a melt.

Structure of [PhCNSNS][AsF$_6$].—This structure (Fig. 3) consists of discrete [PhCNSNS]$^+$ cations and AsF$_6{}^-$ anions held together through a variety of weak S···F and H···F interactions. The strongest of these interactions involve S(1) [S(1)···F(5) 3.002, S(1)···F(1) 3.019, S(1)···F(1′) 3.077, S(1)···F(6) 3.157 and S(1)···F(4) 3.3224 Å] which on the basis of PM3 molecular orbital calculations[28] has most of the positive charge (+0.82) centred on it (Fig. 4). However the S(2) centre (+0.64) is also involved in secondary bonding with two weaker sulfur–fluorine interactions [S(2)···F(2) 3.130, S(2)···F(5) 3.262 Å]. The strongest H···F interactions are at 2.59 [H(4)···F(2)] and 2.64 Å [H(5)···F(2)]. Similar short interactions have also been observed in the methyl analogue,[3a] [MeCNSNS][AsF$_6$], and in [C(CNSNS)$_3$][AsF$_6$]$_2$·SO$_2$.[4b] It may also be noted that although the two ring systems in the [PhCNSNS]$^+$ cation are both planar, they are mutually rotated by 23° about the C(1)–C(2) bond [dihedral angle N(1)–C(1)–C(2)–C(3) 23.1(9)°].

Conclusion

The reaction of silver salts with (NSCl)$_3$ and SCl$_2$ has provided a convenient, safe, high-yield route to a variety of both N(SCl)$_2{}^+$ and SNS$^+$ salts. Initial studies show that, with nitriles, [SNS][AsF$_6$] provides the cleanest cycloaddition reactions under the mildest conditions. The salt [SNS][CF$_3$SO$_3$] also reacts under mild conditions in high yields, but the extreme air-sensitivity of this reagent is likely to hinder its applications. However high yields are also achieved under more forcing conditions with [SNS][$\mathrm{SbCl_6}$] and, in some cases, this salt may prove to be an alternative reagent to [SNS][$\mathrm{AsF_6}$].

Experimental

All reactions and manipulations were carried out under an atmosphere of dry nitrogen and solvents were dried before use. Infrared spectra were recorded as Nujol mulls between KBr or CsI plates using a Perkin Elmer 577 or 457 grating spectrophotometer, mass spectra by a VG Analytical 7070E spectrometer and ^{1}H NMR spectra at 250 MHz on a Brüker AM 250 spectrometer. Carbon, H and N analyses were carried out on a Carlo Erba 1106 elemental analyser.

Materials.—The compounds $\mathrm{AgAsF_6}$, $\mathrm{AgSbF_6}$, $\mathrm{SeCl_4}$, $\mathrm{C_6F_5CN}$ (Aldrich), $\mathrm{AgCF_3SO_3}$, $\mathrm{SCl_2}$, $\mathrm{SO_2Cl_2}$ (Fluka) and $\mathrm{SnCl_2}$ (BDH) were used without further purification, PhCN was distilled and stored under a nitrogen atmosphere, $\mathrm{(NSCl)_3}$ was prepared by chlorination of $\mathrm{S_3N_2Cl_2}$ [29] with $\mathrm{SO_2Cl_2}$ [30] and [SNS][$\mathrm{AlCl_4}$], [SNS][$\mathrm{SbCl_6}$], [$\mathrm{N(SCl)_2}$][$\mathrm{SbCl_6}$], [$\mathrm{N(SCl)_2}$][$\mathrm{AlCl_4}$] and [$\mathrm{N(SCl)_2}$][$\mathrm{FeCl_4}$] were prepared according to the literature method.[9,10,31]

Preparations.—[$\mathrm{N(SCl)_2}$]$_2$[$\mathrm{SeCl_6}$].—The compounds $\mathrm{(NSCl)_3}$ (0.543 g, 6.6 mmol) and $\mathrm{SeCl_4}$ (2.21 g, 10 mmol) were stirred in $\mathrm{SOCl_2}$ (30 cm^3) in a round bottomed flask (250 cm^3) and $\mathrm{SCl_2}$ added. The mixture was heated to reflux for 6 h before allowing to cool. A lemon-yellow powder was formed which was filtered off and washed with small quantities of ice-cold $\mathrm{SOCl_2}$. Yield 4.956 g, 84%. IR: ν_{max} 1136m, 730s, 720m, 660s, 650m, 524s, 510s and 495s cm^{-1} (Found: N, 4.8. Calc.: N, 4.7%).

[$\mathrm{N(SCl)_2}$]X (X = $\mathrm{AsF_6}$, $\mathrm{CF_3SO_3}$ *or* $\mathrm{SbF_6}$). The compounds $\mathrm{(NSCl)_3}$ and AgX (3 equivalents) were stirred in liquid $\mathrm{SO_2}$ in one limb of a two-limbed reaction vessel, then $\mathrm{SCl_2}$ (a slight molar excess) was added to give an immediate olive-green colouration. The mixture was stirred for 18 h to provide an orange-yellow solution over a white precipitate (AgCl). After filtration, the white solid was washed three times with back-condensed $\mathrm{SO_2}$. Removal of the solvent left a yellow solid which was then pumped to dryness: [$\mathrm{N(SCl)_2}$][$\mathrm{AsF_6}$] [5.6 mmol scale, based on $\mathrm{(NSCl)_3}$], yield 5.45 g (96%), IR ν_{max} 1125s 700vs (br), 525s, 505s, 385vs and 360s (sh) cm^{-1} (Found: N, 4.2. Calc.: N, 4.1%); [$\mathrm{N(SCl)_2}$][$\mathrm{CF_3SO_3}$] [0.33 mmol scale, based on $\mathrm{(NSCl)_3}$], yield 0.22 g (75%), IR ν_{max} 1400w, 1250s (br), 1175s, 1022vs, 940m, 750m, 720m, 635vs, 615m, 572m, 515m, 500w, 470w and 422m cm^{-1} (Found: C, 4.4; N, 4.9. Calc.: C, 4.0; N, 4.7%); [$\mathrm{N(SCl)_2}$][$\mathrm{SbF_6}$] [0.33 mmol scale, based on $\mathrm{(NSCl)_3}$], yield 0.308 g (80%), IR ν_{max} 1122s, 750m (sh), 715m (sh), 692s (sh), 640vs (br), 505ms, 360m and 280vs cm^{-1} (Found: N, 3.5; Sb, 31.8. Calc.: N, 3.6; Sb, 31.6%).

[SNS]X (X = $\mathrm{AsF_6}$, $\mathrm{SbF_6}$, $\mathrm{FeCl_4}$ *or* $\mathrm{CF_3SO_3}$). The compounds [$\mathrm{N(SCl)_2}$]X and $\mathrm{SnCl_2}$ (molar equivalents) were stirred in liquid $\mathrm{SO_2}$ in one limb of a two-limbed reaction vessel for 18 h, to provide a cream-yellow precipitate of [SNS]X and a solvent bilayer ($\mathrm{SnCl_4}$ and $\mathrm{SO_2}$). The solvent was then removed and the system pumped to dryness. The product was then washed with ice-cold $\mathrm{CH_2Cl_2}$ to provide pure [SNS]X: [SNS][$\mathrm{AsF_6}$] (10 mmol scale), yield 2.51 g (94%), IR ν_{max} 1495vs, 820w, 700vs (br) and 395vs cm^{-1} (Found: As, 28.05; N, 5.20. Calc.: As, 28.10; N, 5.25%); [SNS][$\mathrm{SbF_6}$] (1 mmol scale), yield 0.234 g (75%), IR ν_{max} 1500s, 805w, 650vs (br), 392vs and 285vs cm^{-1} (Found: N, 4.65. Calc.: N, 4.45%); [SNS][$\mathrm{FeCl_4}$] (2 mmol scale), yield 397 mg (72%), IR ν_{max} 1480s, 802w, 380vs and 345m cm^{-1} (Found: Fe, 19.65; N, 4.90. Calc.: Fe, 20.25; N, 5.10%); [SNS][$\mathrm{CF_3SO_3}$] (1 mmol scale), yield 0.159 g (70%), IR and analytical data similar to those below.

[SNS][$\mathrm{CF_3SO_3}$]. The compounds $\mathrm{(NSCl)_3}$ (0.634 g, 2.6 mmol) and $\mathrm{AgCF_3SO_3}$ (2.0 g, 7.78 mmol) were stirred in liquid $\mathrm{SO_2}$ in one limb of a two-limbed reaction vessel for 0.5 h. The system was then cooled to −70 °C and S (0.0311 g, 7.78 mmol) added against a counterflow of dry nitrogen. The mixture was then allowed to warm to room temperature producing an olive-green solution which was then stirred for 4 h at room temperature during which time the solution gradually turned bright yellow. The solution was carefully filtered into the second limb and the volume reduced to yield small thin yellow platelets of [SNS][$\mathrm{CF_3SO_3}$]. The bulb was then cooled to −15 °C and the supernatant decanted off. Removal of the solvent from the soluble materials produced a mixture of [$\mathrm{S_6N_4}$][$\mathrm{CF_3SO_3}$]$_2$, [SNS][$\mathrm{CF_3SO_3}$] and a small quantity of unidentified red oil. Yield of [SNS][$\mathrm{CF_3SO_3}$] 0.65 g, 37%. IR ν_{max} 1250s (br), 1220s (br), 1180s (br), 1030s (br), 760s, 635vs, 580m, 520m, 440s and 380s cm^{-1} (Found: C, 5.3; N, 6.0; S, 41.5. Calc.: C, 5.3; N, 6.2; S, 42.3%). Mass spectrum [chemical ionisation (CI)]: *m/z* 227 ($\mathrm{SNS{\cdot}CF_3SO_3^+}$, 8), 149 ($\mathrm{CF_3SO_3^+}$, 8) and 78 ($\mathrm{SNS^+}$, 53%).

Reduction of [$\mathrm{N(SCl)_2}$]$_2$[$\mathrm{SeCl_6}$]. The salt [$\mathrm{N(SCl)_2}$]$_2$[$\mathrm{SeCl_6}$] (0.295 g, 0.5 mmol) and $\mathrm{SnCl_2}$ (0.190 g, 1 mmol) were placed in one limb of a two-limbed reaction vessel and $\mathrm{CH_2Cl_2}$ (5 cm^3) syringed in. The reaction mixture was stirred for 24 h at room temperature to give a yellow precipitate. The product was washed with $\mathrm{CH_2Cl_2}$ (3 × 3 cm^3) to remove any traces of $\mathrm{SnCl_4}$ and minor side-products (mostly [$\mathrm{S_6N_4}$][$\mathrm{SeCl_6}$]) and was identified by IR spectroscopy as [$\mathrm{S_3N_2Cl}$]$_2$[$\mathrm{SeCl_6}$]. IR ν_{max} 1125m, 1032s, 1020s, 675s, 570ms, 564m and 517m cm^{-1}.

[$\mathrm{R\overline{CNSNS}}$][$\mathrm{AsF_6}$] (R = aryl). The salt [SNS][$\mathrm{AsF_6}$] (0.267 g, 1 mmol) was placed in one limb of a two-limbed reaction vessel and RCN (0.5 cm^3) was syringed in to give an immediate brown solution. The mixture was stirred for 3 h at room temperature before washing with $\mathrm{CH_2Cl_2}$ to yield microcrystalline [$\mathrm{R\overline{CNSNS}}$][$\mathrm{AsF_6}$]: [$\mathrm{Ph\overline{CNSNS}}$][$\mathrm{AsF_6}$], yield 0.33 g (90%), IR ν_{max} 1595m, 1405s, 1345w, 1325w, 1297w, 1260w, 1215w, 1190m, 1170w, 1100m, 1070w, 1000m, 985s, 913m, 888m, 840w, 797s, 772vs, 697vs (br), 670s, 645m, 635m, 610w, 583w, 440s and 400vs cm^{-1} (Found: C, 22.5; H, 1.4; N, 7.5. Calc.: C, 22.7; H, 1.4; N, 7.6%) (larger crystals suitable for X-ray analysis were grown by exhaustive $\mathrm{CH_2Cl_2}$ extraction, then picked and mounted in the open air in glass Lindemann capillaries); [$\mathrm{C_6F_5\overline{CNSNS}}$][$\mathrm{AsF_6}$], yield 0.433 g (94%), IR ν_{max} 1655s, 1620w, 1530s, 1500s, 1390m, 1295w, 1173m, 1162ms, 1048m, 1000s, 956ms, 900m, 815s, 777m, 700vs (br), 652m, 581w, 447w and 400s cm^{-1} (Found: C, 18.0; N, 6.3. Calc.: C, 18.3; N, 6.1%).

[$\mathrm{R\overline{CNSNS}}$][$\mathrm{SbCl_6}$] (R = aryl). The salt [SNS][$\mathrm{SbCl_6}$] (0.415 g, 1 mmol) was placed in one limb of a two-limbed reaction vessel and RCN (2 cm^3) syringed in. The solution was heated at *ca.* 100 °C for 4 h during which time the solution turned olive-green. Once no more solid material was observable in the reaction vessel, heating was continued for 30 min before allowing to cool. The dark green microcrystalline precipitate which formed was isolated as a lime-green solid by washing with cold $\mathrm{CH_2Cl_2}$: [$\mathrm{Ph\overline{CNSNS}}$][$\mathrm{SbCl_6}$], yield 0.385 g (75%), IR ν_{max} 1597m, 1410s, 1168m, 982w, 932w, 905w, 890w, 795m, 765s, 720w, 680s, 647w, 630s, 585w and 533 cm^{-1} (Found: C, 16.4; H, 1.0; Cl, 39.9; N, 5.7; S, 12.1; Sb, 21.1. Calc.: C, 16.3; H, 1.0; Cl, 41.3; N, 5.4; S, 12.4; Sb, 23.6%), ^{1}H NMR ($\mathrm{CD_3CN}$) δ 8.97 (d, 1 H), 8.61 (m, 2 H) and 8.45 (m, 2 H), m.p. 179.5 °C (decomp.), mass spectrum [electron impact (EI)]: *m/z* 181.1 ($\mathrm{PhCNSNS^+}$, 40), 135.1 ($\mathrm{PhCNS^+}$, 4), 121.0 ($\mathrm{PhCS^+}$, 9), 104.1 ($\mathrm{CNSNS^+}$, 16), 103.1 ($\mathrm{PhCN^+}$, 100), 92.0 ($\mathrm{SNSN^+}$, 2), 78.0 ($\mathrm{SNS^+}$, 55), 77.1 ($\mathrm{Ph^+}$, 6) and 45.9 ($\mathrm{SN^+}$, 34%); [$\mathrm{C_6F_5\overline{CNSNS}}$][$\mathrm{SbCl_6}$], yield 0.460 g (76%), IR ν_{max} 1657s, 1620m, 1530m, 1510s, 1320w, 1300w, 1170m, 1160m, 1050m, 1010s, 953s, 900s, 813s, 777m, 742m, 650m, 580m and 440s cm^{-1} (Found: C, 13.8; N, 4.4; Sb, 19.8. Calc.: C, 13.9; N, 4.6; Sb, 20.1%), ^{19}F NMR ($\mathrm{CD_3CN}$) δ −132.19 (s, 2 F), −140.24 (s, 1 F) and −159.68 (s, 2 F), m.p. 179.0 °C (decomp.), mass spectrum (EI):

Table 4 Crystal data and details of intensity data collection and refinement

Formula	$[S_6N_4][ClS_2O_6]_2$	$[S_6N_4][CF_3SO_3]_2$	$[\mathrm{Ph}\overline{\mathrm{CNSNS}}][AsF_6]$
M	639.56	546.56	370.17
Crystal size (mm)	0.60 × 0.40 × 0.25	0.40 × 0.30 × 0.15	0.30 × 0.30 × 0.20
Crystal form	Dark green plates	Lustrous green plates	Lime-green needles
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/n$	$P2_1/a$
a/Å	7.689(1)	8.632(4)	10.824(5)
b/Å	10.726(1)	10.614(8)	8.287(2)
c/Å	6.614(1)	8.387(6)	13.599(3)
α/°	101.00(2)	90	90
β/°	114.42(2)	90.79(5)	106.32(4)
γ/°	90.35(2)	90	90
U/Å^3	485.38	768.34	1170.66
θ range for cell/°	0–25	10–13	1.5–25
Z	1	2	4
D_c/g cm^{-3}	2.19	2.36	2.10
F(000)	318	540	720
μ/cm^{-1}	14.3	12.2	32.9
T/K	298	208	291
θ range for data/°	0–25	1.5–25	1.5–28
Total data measured	3500	1553	7011
Total unique	1707	1340	2108
Total observed $[F_o > 3\sigma(F_o)]$	1336	1180	1850
No. of parameters	127	118	164
ρ_{min}, ρ_{max}/e Å^{-3}	−1.1, 0.3	0.37, 0.31	0.45, 0.85
Weighting scheme	$\sigma(F_o)^{-2}$	$[\sigma^2(F_o) + 0.0002F_o^2]^{-1}$	Unit
R	0.031	0.025	0.055
R'	0.030	0.036	0.054

Table 5 Fractional atomic coordinates (× 10^4) for $[S_6N_4][ClS_2O_6]_2$

Atom	*x*	*y*	*z*
Cl	1631(2)	−4050(1)	−1139(2)
S(1)	3056(1)	2330(1)	309(2)
S(2)	1836(1)	989(1)	2686(2)
S(3)	2414(1)	−218(1)	94(2)
S(4)	1697(1)	−2126(1)	4272(2)
S(5)	3610(1)	−3809(1)	2039(2)
O(1)	1139(4)	−1564(2)	2313(4)
O(2)	138(4)	−2552(3)	4676(5)
O(3)	3364(4)	−1542(3)	6178(5)
O(4)	2371(4)	−3583(2)	3401(4)
O(5)	4809(4)	−2707(3)	2460(5)
O(6)	4364(5)	−4978(3)	2315(5)
N(1)	2403(4)	2325(3)	2271(5)
N(2)	3067(4)	910(3)	−809(5)

Table 6 Fractional atomic coordinates (× 10^4) for $[S_6N_4][CF_3SO_3]_2$

Atom	*x*	*y*	*z*
S(1)	7694.5(7)	6352.4(6)	−1582.1(8)
O(1)	8382(2)	7100(2)	−340(2)
O(2)	8745(2)	5998(2)	−2843(2)
O(3)	6202(2)	6756(2)	−2166(2)
C	7294(3)	4851(3)	−604(3)
F(1)	8596(2)	4280(2)	−166(2)
F(2)	6461(2)	5028(2)	694(2)
F(3)	6515(2)	4078(2)	−1566(2)
S(2)	8518.5(7)	1314.8(6)	630.3(8)
N(1)	8292(2)	−151(2)	541(3)
S(3)	6650.4(7)	−751.3(6)	1029.6(8)
S(4)	5557.1(7)	981.1(6)	1703.7(8)
N(2)	7002(3)	1894(2)	1326(3)

Table 7 Fractional atomic coordinates (× 10^4) for $[\mathrm{Ph}\overline{\mathrm{CNSNS}}]$-$[AsF_6]$

Atom	*x*	*y*	*z*
As	4 377.2(6)	5 817.0(8)	6 749.4(5)
F(1)	3 432(5)	4 377(6)	6 004(4)
F(2)	5 285(5)	7 269(6)	7 494(4)
F(3)	4 082(7)	4 968(7)	7 784(4)
F(4)	4 636(7)	6 669(7)	5 709(4)
F(5)	5 638(5)	4 588(7)	6 913(6)
F(6)	3 102(6)	7 014(8)	6 606(7)
S(1)	−2 082(2)	4 267(3)	6 082(1)
S(2)	451(2)	4 309(3)	6 566(1)
N(1)	−1 485(5)	3 993(6)	7 267(4)
N(2)	−872(6)	4 453(8)	5 679(4)
C(1)	−204(6)	4 007(7)	7 578(4)
C(2)	556(6)	3 829(7)	8 632(4)
C(3)	−5(6)	3 062(8)	9 306(5)
C(4)	692(7)	2 927(9)	10 320(5)
C(5)	1 905(7)	3 544(9)	10 670(5)
C(6)	2 479(8)	4 277(10)	9 998(6)
C(7)	1 783(6)	4 436(9)	8 962(5)

m/*z* 271.1 ($C_6F_5CNSNS^+$, 3), 238.9 ($C_6F_5CNSN^+$, 2), 225.1 ($C_6F_5CNS^+$, 8), 193.1 ($C_6F_5CN^+$, 25), 78.0 (SNS^+, 4) and 46.0 (SN^+, 36%).

$[\mathrm{Ph}\overline{\mathrm{CNSNS}}][CF_3SO_3]$. The salt $[SNS][CF_3SO_3]$ (0.35 g, 1.6 mmol) was placed in one limb of a two-limbed reaction vessel and PhCN (0.17 g, 1.6 mmol) syringed into the other. Sulfur dioxide (10 cm^3) was condensed into both limbs and allowed to warm to room temperature. The two solutions were brought together and stirred for 2 h to yield a red-brown solution. Removal of the solvent and light washing with SO_2 yielded a yellow-brown solid. Yield 0.38 g, 74% (Found: C, 29.2; H, 1.5; F, 17.1; N, 8.6; S, 30.0. Calc.: C, 29.1; H, 1.5; F, 17.3; N, 8.5; S, 29.1%).

Reaction of PhCN *with* $[SNS][AlCl_4]$. The salt $[SNS]$-$[AlCl_4]$ (0.247 g, 1 mmol) was placed in one limb of a two-limbed reaction vessel and PhCN (1 cm^3) syringed into the other. Dichloromethane (10 cm^3) was added to the PhCN, and the resulting mixture transferred onto the $[SNS][AlCl_4]$. Over a period of several minutes the yellow $[SNS][AlCl_4]$ gave way to a deep green solid. Stirring was continued for 2 h. The solubles were filtered off and pumped to dryness to leave a green-brown oil. The IR spectrum of the insolubles showed them to be a mixture of $[S_6N_4][AlCl_4]_2$ and $[S_6N_4]Cl_2$. That of the soluble component showed this to be predominantly PhCN with some $[S_6N_4][AlCl_4]_2$. IR ν_{max} 988m, 964m, 955s, 933s,

Table 8 Bond lengths (Å) and angles (°) for [S_6N_4][ClS_2O_6]$_2$

S(1)–N(1)	1.574(3)	S(1)–N(2)	1.563(3)
S(2)–S(3)	2.145(1)	S(2)–S(3′)	3.027(1)
S(2)–N(1)	1.601(3)	S(3)–N(2)	1.609(3)
S(4)–O(1)	1.438(3)	S(4)–O(2)	1.423(4)
S(4)–O(3)	1.405(3)	S(4)–O(4)	1.718(3)
S(5)–Cl	1.986(2)	S(5)–O(4)	1.552(3)
S(5)–O(5)	1.405(3)	S(5)–O(6)	1.396(3)
N(1)–S(1)–N(2)	107.6(2)	S(3)–S(2)–N(1)	97.2(1)
S(2)–S(3)–N(2)	96.6(1)	O(1)–S(4)–O(2)	114.2(2)
O(1)–S(4)–O(3)	116.2(2)	O(1)–S(4)–O(4)	103.4(2)
O(2)–S(4)–O(3)	117.2(2)	O(2)–S(4)–O(4)	99.0(2)
O(3)–S(4)–O(4)	103.3(2)	Cl–S(5)–O(4)	101.7(1)
Cl–S(5)–O(5)	107.0(1)	Cl–S(5)–O(6)	107.4(2)
O(4)–S(5)–O(5)	111.1(2)	O(4)–S(5)–O(6)	107.1(2)
O(5)–S(5)–O(6)	120.8(2)	S(1)–N(1)–S(2)	119.1(2)
S(1)–N(2)–S(3)	119.6(2)	S(4)–O(4)–S(5)	124.9(2)

Table 9 Bond lengths (Å) and angles (°) for [S_6N_4][CF_3SO_3]$_2$

O(1)–S(1)	1.432(3)	O(2)–S(1)	1.452(3)
O(3)–S(1)	1.437(3)	C–S(1)	1.828(5)
F(1)–C	1.325(4)	F(2)–C	1.326(4)
F(3)–C	1.327(4)	N(1)–S(2)	1.569(4)
N(2)–S(2)	1.566(4)	S(3)–N(1)	1.612(4)
S(4)–S(3)	2.146(3)	N(2)–S(4)	1.614(4)
S(3)–S(4)	2.971(3)		
O(2)–S(1)–O(1)	114.6(2)	O(3)–S(1)–O(1)	116.3(2)
O(3)–S(1)–O(2)	113.3(2)	C–S(1)–O(1)	103.6(2)
C–S(1)–O(2)	103.0(2)	C–S(1)–O(3)	103.8(2)
F(1)–C–S(1)	111.0(3)	F(2)–C–S(1)	110.7(3)
F(2)–C–F(1)	107.7(3)	F(3)–C–S(1)	113.3(3)
F(3)–C–F(1)	107.9(3)	F(3)–C–F(2)	108.1(3)
N(2)–S(2)–N(1)	107.6(2)	S(3)–N(1)–S(2)	119.3(2)
S(4)–S(3)–N(1)	96.9(2)	N(2)–S(4)–S(3)	96.8(2)
S(4)–N(2)–S(2)	119.3(2)		

Table 10 Bond lengths (Å) and angles (°) for [PhCNSNS][AsF_6]

F(1)–As	1.708(6)	F(2)–As	1.697(6)
F(3)–As	1.682(7)	F(4)–As	1.674(7)
F(5)–As	1.667(7)	F(6)–As	1.667(8)
N(1)–S(1)	1.576(7)	N(2)–S(1)	1.563(8)
N(2)–S(2)	1.596(8)	C(1)–S(2)	1.735(8)
C(1)–N(1)	1.332(9)	C(2)–C(1)	1.446(9)
C(3)–C(2)	1.387(9)	C(7)–C(2)	1.373(10)
C(4)–C(3)	1.378(10)	C(5)–C(4)	1.364(11)
C(6)–C(5)	1.381(12)	C(7)–C(6)	1.405(11)
F(2)–As–F(1)	178.7(3)	F(3)–As–F(1)	88.9(4)
F(3)–As–F(2)	90.6(4)	F(4)–As–F(1)	90.4(4)
F(4)–As–F(2)	90.0(4)	F(4)–As–F(3)	178.7(4)
F(5)–As–F(1)	89.0(4)	F(5)–As–F(2)	92.2(4)
F(5)–As–F(3)	88.5(4)	F(5)–As–F(4)	92.6(5)
F(6)–As–F(1)	90.5(4)	F(6)–As–F(2)	88.3(4)
F(6)–As–F(3)	90.1(5)	F(6)–As–F(4)	88.9(5)
F(6)–As–F(5)	178.5(4)		
N(2)–S(1)–N(1)	103.3(4)	C(1)–S(2)–N(2)	97.5(4)
C(1)–N(1)–S(1)	114.4(5)	S(2)–N(2)–S(1)	112.9(4)
N(1)–C(1)–S(2)	111.8(5)	C(2)–C(1)–S(2)	123.8(6)
C(2)–C(1)–N(1)	124.4(6)	C(3)–C(2)–C(1)	118.0(7)
C(7)–C(2)–C(1)	121.0(7)	C(7)–C(2)–C(3)	121.0(7)
C(4)–C(3)–C(2)	118.7(7)	C(5)–C(4)–C(3)	121.4(8)
C(6)–C(5)–C(4)	120.2(8)	C(7)–C(6)–C(5)	119.4(8)
C(6)–C(7)–C(2)	119.3(8)		

853w, 740 (sh), 725m, 707s, 705vs, 702vs, 582w, 572m, 444w, 437m, 380s and 370vs cm^{-1}.

[PhCNSNS][SbF_6]. The salt [SNS][SbF_6] (0.313 g, 1 mmol) was placed in one limb of a two-limbed reaction vessel and PhCN (1 cm^3) syringed into the second limb. Sulfur dioxide was condensed onto the PhCN and the mixture added to the [SNS][SbF_6]. The mixture was stirred for 5 h, yielding a yellow solution. On removal of the solvent a yellow solid formed which contained some small green crystallites. The material was briefly washed with CH_2Cl_2 to remove unreacted PhCN and pumped to dryness. The solid product was washed with CH_3CN–CH_2Cl_2 (2:1) at 0 °C to provide predominantly [PhCNSNS]-[SbF_6]. Yield 0.208 g, 50%. IR ν_{max} 1590w, 1400m, 1325w, 1260w, 1212w, 1180m, 1165w, 1085m, 1062w, 1002m, 983s, 922m, 888m, 840w, 792m, 770s, 670 (sh), 650vs (br), 648m, 630m, 583w, 442m and 290s (br) cm^{-1}.

Crystal Structure Determinations.—Crystal data and details of the structure determinations and refinements are given in Table 4. Data for [S_6N_4][ClS_2O_6]$_2$ were collected from a crystal sealed in a quartz capillary using a Hilger and Watts Y290 diffractometer with zirconium-filtered Mo-Kα radiation (λ 0.710 69 Å) and a ω–2θ scan mode. Data for [S_6N_4]-[CF_3SO_3]$_2$ were collected using an Enraf-Nonius CAD4 diffractometer with graphite-monochromated Mo-Kα radiation and an ω–2θ scan mode, whilst data for [PhCNSNS][AsF_6] were recorded using an Enraf-Nonius FAST TV area detector diffractometer and graphite-monochromated Mo-Kα radiation from a rotating-anode generator. In each case crystals were sealed in thin-walled glass capillaries. Experimental procedures used with each instrument have been previously described in detail.[32–34]

The structures were solved routinely using direct methods or the Patterson method, developed and refined using difference syntheses and full-matrix least squares. All non-hydrogen atoms were refined with anisotropic thermal parameters. The phenyl hydrogens in [PhCNSNS][AsF_6] were included in calculated positions with a common U_{iso} being refined for all. Final atomic fractional coordinates are listed in Tables 5–7, bond lengths and angles in Tables 8–10. The calculations were performed using the SHELX[35] program systems.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Acknowledgements

We thank the Isle of Man Board of Education for a studentship (to J. M. R.) and the SERC for two studentships (to B. A. and M. I. H.), financial support (to M. B. H.) and continued funding to J. M. R. as a post-doctoral research associate. We would also like to thank the microanalytical section of Durham University Chemistry Department for analyses and Dr. R. Matthews for NMR spectra.

References

1 N. Burford, J. P. Johnson, J. Passmore, M. J. Schriver and P. S. White, *J. Chem. Soc., Chem. Commun.*, 1986, 966.

2 E. G. Awere, N. Burford, C. Mailer, J. Passmore, M. J. Schriver, P. S. White, A. J. Banister, H. Oberhammer and L. H. Sutcliffe, *J. Chem. Soc., Chem. Commun.*, 1987, 66

3 (*a*) G. K. MacLean, J. Passmore, M. N. S. Rao, M. J. Schriver, P. S. White, D. Bethell, R. S. Pilkington and L. H. Sutcliffe, *J. Chem. Soc., Dalton Trans.*, 1985, 1405; (*b*) W. V. F. Brooks, N. Burford, J. Passmore, M. J. Schriver and L. H. Sutcliffe, *J. Chem. Soc., Chem. Commun.*, 1987, 69; (*c*) N. Burford, J. Passmore and M. J. Schriver, *J. Chem. Soc., Chem. Commun.*, 1986, 140; (*d*) S. Parsons, J. Passmore, M. J. Schriver and P. S. White, *J. Chem. Soc., Chem. Commun.*, 1991, 369; (*e*) S. Parsons, J. Passmore, M. J. Schriver and X. Sun, *Inorg. Chem.*, 1991, 3342; (*f*) G. K. MacLean, J. Passmore, M. J. Schriver, P. S. White, D. Bethell, R. S. Pilkington and L. H. Sutcliffe, *J. Chem. Soc., Chem. Commun.*, 1983, 808.

4 (*a*) A. J. Banister, J. M. Rawson, S. L. Birkby and W. Clegg, *J. Chem. Soc., Dalton Trans.*, 1991, 1099; (*b*) A. J. Banister, I. Lavender,

J. M. Rawson and W. Clegg, *J. Chem. Soc., Dalton Trans.*, 1992, 859; (*c*) C. Aherne, A. J. Banister, A. W. Luke, J. M. Rawson and R. J. Whitehead, *J. Chem. Soc., Dalton Trans.*, 1992, 1277; (*d*) A. J. Banister, I. Lavender, J. M. Rawson and R. J. Whitehead, *J. Chem. Soc., Dalton Trans.*, 1992, 1449; (*e*) A. J. Banister and A. W. Luke, *J. Polym. Sci. Part A, Polym. Chem.*, 1992, in the press.

5 A. J. Banister, R. G. Hey, G. K. MacLean and J. Passmore, *Inorg. Chem.*, 1982, **21**, 1679.

6 (*a*) A. Apblett, A. J. Banister, D. Biron, A. G. Kendrick, J. Passmore, M. J. Schriver and M. Stojanac, *Inorg. Chem.*, 1986, **25**, 4451; (*b*) E. G. Awere and J. Passmore, *J. Chem. Soc., Dalton Trans.*, 1992, 1343.

7 A. J. Banister, *Inorg. Synth.*, 1977, **17**, 197.

8 W. Braker, A. L. Mossman and D. Siegel, *Effects of Exposure to Toxic Gases – First Aid and Medical Treatment*, 2nd edn., Matheson, Lyndhurst, NJ, 1977.

9 A. J. Banister and J. M. Rawson, *J. Chem. Soc., Dalton Trans.*, 1990, 1517.

10 A. J. Banister and A. G. Kendrick, *J. Chem. Soc., Dalton Trans.*, 1987, 1565.

11 H. G. Hauck, P. Klingelhöfer, U. Müller and K. Dehnicke, *Z. Anorg. Allg. Chem.*, 1984, **510**, 180.

12 U. Kynast, P. Klingelhöfer, U. Müller and K. Dehnicke, *Z. Anorg. Allg. Chem.*, 1984, **515**, 61.

13 U. Müller, P. Klingelhöfer, U. Kynast and K. Dehnicke, *Z. Anorg. Allg. Chem.*, 1985, **520**, 18.

14 O. Glemser, E. Kindler, B. Krebs, R. Mews, F.-M. Schnepel and J. Wegener, *Z. Naturforsch., Teil B*, 1980, **35**, 657.

15 W. V. F. Brooks, G. K. MacLean, J. Passmore, P. S. White and C. M. Wong, *J. Chem. Soc., Dalton Trans.*, 1983, 1961.

16 O. Glemser and W. Kock, *Angew. Chem., Int. Ed. Engl.*, 1971, **10**, 127.

17 M. Herberhold and L. Haummaier, *Z. Naturforsch., Teil B*, 1980, **35**, 1277.

18 F.-M. Schnepel, *Spectrochim. Acta, Part A*, 1980, **36**, 895.

19 R. W. H. Small, A. J. Banister and Z. V. Hauptman, *J. Chem. Soc., Dalton Trans.*, 1984, 1377.

20 *Handbook of Chemistry and Physics*, 70th edn., ed. R. C. Weast, CRC Press, Boca Raton, FL, 1989.

21 J. Passmore and M. J. Schriver, *Inorg. Chem.*, 1988, **27**, 2749.

22 B. Krebs, G. Henkel, S. Pohl and H. W. Roesky, *Chem. Ber.*, 1980, **113**, 226.

23 A. J. Banister, H. G. Clarke, I. Rayment and H. M. M. Shearer, *Inorg. Nucl. Chem. Lett.*, 1974, **10**, 647.

24 R. J. Gillespie, J. P. Kent and J. F. Sawyer, *Inorg. Chem.*, 1981, **20**, 3784; R. J. Gillespie, P. R. Ireland and J. E. Vekris, *Can. J. Chem.*, 1975, **53**, 3147; H. W. Roesky, M. Witt, J. Schimkowiak, M. Schmidt, M. Noltemeyer and G. M. Sheldrick, *Angew. Chem.*, 1962, **94**, 541; U. Thewalt and M. Burger, *Z. Naturforsch., Teil B*, 1981, **36**, 293; R. Gleiter, R. Bartetzko and P. Hoffmann, *Z. Naturforsch., Teil B*, 1980, **35**, 1166.

25 A. Hazell and R. G. Hazell, unpublished work.

26 A. Hazell and R. G. Hazell, *Acta Crystallogr., Sect. B*, 1985, **41**, 274.

27 A. J. Banister, M. I. Hansford, Z. V. Hauptman, S. T. Wait, W. Clegg, A. W. Luke and K. A. Jørgensen, *J. Chem. Soc., Dalton Trans.*, 1990, 2793.

28 (*a*) M. J. S. Dewar and W. J. Thiel, *J. Am. Chem. Soc.*, 1977, **99**, 4899; (*b*) J. J. P. Stewart, Quantum Chemistry Program Exchange, No. 455 (MOPAC), 1984.

29 W. L. Jolly and K. D. Maguire, *Inorg. Synth.*, 1967, **9**, 102.

30 G. G. Alange, A. J. Banister and B. Bell, *J. Chem. Soc., Dalton Trans.*, 1972, 2399.

31 G. G. Alange, A. J. Banister and P. J. Dainty, *Inorg. Nucl. Chem. Lett.*, 1979, **15**, 175.

32 H. M. M. Shearer, A. J. Banister, J. Halfpenny and G. Whitehead, *Polyhedron*, 1983, **2**, 149.

33 R. A. Jones, M. B. Hursthouse, K. M. A. Malik and G. Wilkinson, *J. Am. Chem. Soc.*, 1979, **101**, 4128.

34 A. A. Danopoulos, G. Wilkinson, B. Hussain-Bates and M. B. Hursthouse, *J. Chem. Soc., Dalton Trans.*, 1991, 1855.

35 G. M. Sheldrick, SHELXS 86, Program for Crystal Structure Determination, University of Göttingen, 1986; SHELX 76, Program for Crystal Structure Determination, University of Cambridge, 1976.

Received 18*th May* 1992; *Paper* 2/02558B