Preparation of $\overline{\mathrm{SeNSNSe}}(\mathrm{AsF_6})_2$ and Structural Characterisation of the 6π 'Electron-rich Aromatic' $\overline{\mathrm{SeNSNSe}}^{2+}$ [‡]

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Highly crystalline $\overline{\mathrm{SeNSNSe}}(\mathrm{AsF_6})_2$ was prepared by the oxidation of $(\overline{\mathrm{SeNSNSe}})_2(\mathrm{AsF_6})_2$ with $\mathrm{AsF_5}$ in liquid $\mathrm{SO_2}$. The X-ray crystal structure was determined which consists of discrete planar $\overline{\mathrm{SeNSNSe}}^{2+}$ cations and $\mathrm{AsF_6}^-$ anions with significant cation–anion interactions. The average Se–N [1.70(2)], S–N [1.59(1)] and Se–Se [2.310(2) Å] bond distances are consistent with the removal of the unpaired electron from the π^* singly occupied molecular orbital of the 7π $\overline{\mathrm{SeNSNSe}}^{\bullet +}$. The ^{77}Se [−70 °C, $\delta(\mathrm{Me_2Se}) = 2411.7$, $v_{\frac{1}{2}} = 10.2$ Hz] and ^{14}N NMR [r.t., $\delta(\mathrm{MeNO_2}) = -72.5$, $v_{\frac{1}{2}} = 690$ Hz] and Raman spectrum in $\mathrm{AsF_3}$ solution are all consistent with retention of the ring structure in solution. The reaction of $\mathrm{Se_4(AsF_6)_2}$ and $\mathrm{S_4N_4}$ was reinvestigated and found to give appreciable amounts of $(\overline{\mathrm{SNSNS}})_2(\mathrm{AsF_6})_2$ and $(\overline{\mathrm{SeNSNS}})_2(\mathrm{AsF_6})_2$ as well as the reported $(\overline{\mathrm{SeNSNSe}})_2(\mathrm{AsF_6})_2$. A pure sample of $(\overline{\mathrm{SeNSNSe}})_2(\mathrm{AsF_6})_2$ was prepared by reduction of $\overline{\mathrm{SeNSNSe}}(\mathrm{AsF_6})_2$ with $\mathrm{CsN_3}$.

Several early attempts to prepare mixed S–N–Se compounds led to irreproducible results and to products that were not characterised with certainty.[1–5] The first structurally characterised example of this class was $(\overline{\mathrm{SeNSNSe}})_2(\mathrm{AsF_6})_2$.[6] Table 1 lists other reactions in which S–N–Se compounds were either formed or designated as synthetic targets.

The compound $(\overline{\mathrm{SeNSNSe}})_2(\mathrm{AsF_6})_2$ was prepared by the reaction of $\mathrm{S_4N_4}$ and $\mathrm{Se}_n(\mathrm{AsF_6})_2$ (n = 4 or 8) (1:1 ratio) in liquid $\mathrm{SO_2}$ and characterised by X-ray crystallography.[6] The difficulties encountered in obtaining a pure sample by this route motivated us to reinvestigate this reaction, a full account of which is included below.

We have shown that $(\overline{\mathrm{SNSNS}})_2(\mathrm{AsF_6})_2$ is oxidised by $\mathrm{AsF_5}$ in the presence of a trace of $\mathrm{Br_2}$ in $\mathrm{SO_2}$ solution according to equation (1).[11,12] In solution $\mathrm{SN^+}$ and $\mathrm{SNS^+}$ were identified from their ^{14}N NMR spectra.[12] In the solid state $\overline{\mathrm{SNSNS}}(\mathrm{AsF_6})_2$ containing the 6π $\overline{\mathrm{SNSNS}}^{2+}$ cation was formed by the lattice-enforced cycloaddition of $\mathrm{SN^+}$ and $\mathrm{SNS^+}$.[13] It was therefore of interest to explore the analogous oxidation of $(\overline{\mathrm{SeNSNSe}})_2(\mathrm{AsF_6})_2$ by $\mathrm{AsF_5}$ with traces of $\mathrm{Br_2}$ and to determine the nature of the products in solution and in the solid state. A preliminary disclosure of the X-ray crystal structure of $\overline{\mathrm{SeNSNSe}}(\mathrm{AsF_6})_2$ was included in an earlier publication.[14] At about the same time, Haas and Kasprowski[8,§] reported another preparative route to $\overline{\mathrm{SeNSNSe}}(\mathrm{AsF_6})_2$ (see Table 1, reactions 10 and 11) and stated that its X-ray crystal structure had been determined, but structural and crystallographic details were not given.

$$(\overline{\mathrm{SNSNS}})_2(\mathrm{AsF_6})_2 + 3\mathrm{AsF_5} \xrightarrow[\text{trace } \mathrm{Br_2}]{\mathrm{SO_2}} 2\mathrm{SNSAsF_6} + 2\mathrm{SNAsF_6} + \mathrm{AsF_3} \quad (1)$$

We have also prepared and characterised in solution and in the solid state (X-ray) the first stable binary selenium–nitrogen containing species, $(\overline{\mathrm{SeNSeNSe}})_2(\mathrm{AsF_6})_2$ and $\overline{\mathrm{SeNSeNSe}}(\mathrm{AsF_6})_2$.[15] We have determined the X-ray crystal structures of the related $\overline{\mathrm{Se/SNSNSe/S}}(\mathrm{AsF_6})_2$, $(\overline{\mathrm{Se/SNSNSe}})_2(\mathrm{AsF_6})_2$ and $(\overline{\mathrm{Se/SNSNSe/S}})_2(\mathrm{AsF_6})_2$ which will be reported elsewhere.[16] Thus all possible 7π $\mathrm{Se}_x\mathrm{S}_{3-x}\mathrm{N_2}^{\bullet +}$ and 6π $\mathrm{Se}_x\mathrm{S}_{3-x}\mathrm{N_2}^{2+}$ (x = 0–3) cations have now been characterised in the solid state and in solution, except $\overline{\mathrm{SNSNS}}^{2+}$ which only exists as such in the solid state in $\overline{\mathrm{SNSNS}}(\mathrm{MF_6})_2$ (M = As or Sb).[11–15]

Experimental

General Procedures and Reagents.—General techniques and apparatus, unless specified, were as described in refs.17–19. Moisture-sensitive materials and crystals suitable for X-ray analysis and all solid products were manipulated inside a vacuum atmosphere Dri-Lab. Infrared spectra were recorded as Nujol mulls between KBr or CsI plates in the 4000–200 cm^{-1} range on a Perkin-Elmer 683 spectrometer, Raman spectra on a Spex-Ramalab spectrometer and a Spectra Physics 164-W argon-ion laser (5145 Å) at 190 mW using a slit width of 4 cm^{-1}. Solid samples were mounted in sealed glass melting point tubes and solutions were prepared in liquid $\mathrm{AsF_3}$ in sealed Pyrex glass tubes (outside diameter 5 mm). Low-temperature spectra were obtained at −196 °C with the m.p. tubes immersed

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

[§] *Note added at proof.* Very recently a full paper[8b] on the preparation of $\overline{\mathrm{SeNSNSe}}(\mathrm{AsF_6})_2$ using $\mathrm{Se(NSO)_2}$ starting material, and related compounds have been reported which included full details of the X-ray crystal structures of $\mathrm{Cl}\overline{\mathrm{SeNSNS}}^+\mathrm{X}^-$ (X = $\mathrm{NbF_6}$, $\mathrm{SbCl_6}$ or Cl). The reported route affords purer $\overline{\mathrm{SeNSNSe}}(\mathrm{AsF_6})_2$, the properties and vibrational spectra of which were essentially the same as those obtained in this work. However, the ^{77}Se NMR chemical shift of the $\overline{\mathrm{SeNSNSe}}^{2+}$ cation (δ 2434; temperature and $v_{\frac{1}{2}}$ not specified) reported in ref. 8(*b*) is different from the value we obtained (δ 2411.7 $v_{\frac{1}{2}}$ = 10.2 Hz). It is possible that the difference in chemical shifts arises from the presence of hydrolysis products (*e.g.* $\overline{\mathrm{SeNSNSe}}^{\bullet +}$ see above) in the reported material[8b] which may undergo rapid exchange with the dication.

Table 1 Summary of reported work in mixed S–N–Se chemistry

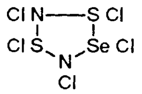
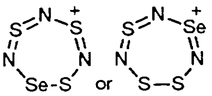
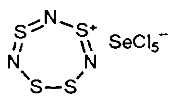
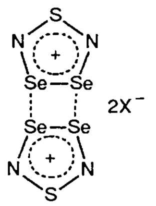
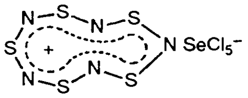
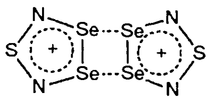
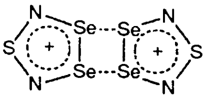
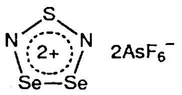
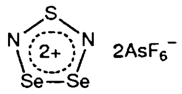
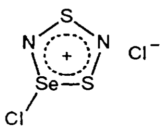
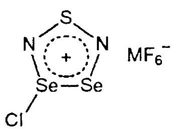
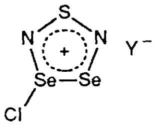
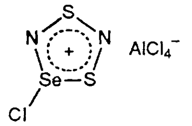
No.	Reaction	Solvent	Proposed (P) or determined (D)[a] identity of products	Mode of characterisation (comments)	Ref.
1	$Se_2Cl_2 + S_4N_4$	$SOCl_2$	(P) 	Chemical analyses	1
2	$Se_2Cl_2 + S_4N_4$	$SOCl_2$, 40 °C	(P) 	IR and chemical analyses[b]	2
3	$Se_2Cl_2 + S_4N_4$	$SOCl_2$, 40 °C	(D) 	X-ray[c]	10
4(a)	$[(Me_3Si)_2N]_2S$ **1** + $SeCl_4 + Se_2Cl_2$ (*ca.* 1:1:0.5 ratio)	CH_2Cl_2	(P)  X = Cl or Br	Chemical analyses	3
4(b)	**1** + $SeBr_4$ (1:1 ratio)	CH_2Cl_2		Chemical analyses, IR[d] and mass spectra	
5	$S_4N_4 + SeCl_4$ (1:1 ratio)	Benzene	(P) $S_4N_4SeCl_3^+Cl^-$	Conductance measurement, chemical analyses	4
6	$S_4N_4 + SeCl_4$ (1:1 ratio)	Benzene–Toluene	(P) $S_4N_4{\cdot}SeCl_4$	Chemical analyses[e]	5
7	$S_4N_4 + SeCl_4$ (1:1 ratio)	SO_2	(D) 	X-Ray, Raman, IR	7
8	$S_4N_4 + Se_4(X^-)_2$ (1:1 ratio) X = AsF_6 or Sb_2F_{11}	SO_2	(D)  $2MF_6^-$(M = As or Sb)	X-Ray, IR[g]	6
9	$Se(NSO)_2 + MF_5$ (1:1 ratio) M = As, Sb, or Nb	SO_2	 $2MF_6^-$(M = As, Sb or Nb)	Chemical analyses, IR, X-ray (M = As)[h]	8
10	$Se(NSO)_2 + AsF_5$	SO_2		*h*	8
11	$ClSeNSNSe^+Cl^-$ + $AgAsF_6$	SO_2		*h*	8
12	$S_3N_3Cl_3 + Se_2Cl_2$ (1:1 ratio)	SO_2	(D) 	IR, Raman, ^{77}Se, ^{15}N NMR, X-ray[i]	7
13	$S_4N_4 + Se_2Cl_2$–$SbCl_5$ or $SeCl_4$–$SbCl_5$ mixtures	SO_2	(D) Disordered $Se_xS_{3-x}N_2Cl^+SbCl_6^-$ Cations (x = 0–3)	X-Ray	7
14	$SeNSNSe^+MF_6^-$ + Cl_2 (M = As or Nb)	SO_2	 M = Nb or As	*h*, *j*	8

Table 1 (*continued*)

No.	Reaction	Solvent	Proposed (P) or determined (D)[a] identity of products	Mode of characterisation (comments)	Ref.
15	$Se(NSO)_2 + XCl_5$ (X = P or Sb)	CH_2Cl_2	 Y = Cl or $SbCl_6$	h	8
16	$NSAlCl_4$ + EtSeCl (or Se) (1:1 ratio)	CH_2Cl_2	(D) 	IR, ^{14}N, ^{15}N, ^{77}Se NMR, X-ray	9

[a] It is possible that other species were also formed in addition to the compound whose X-ray structure was determined (*e.g.* see footnote *g*). [b] Reinvestigation of reaction (1); Se_2Cl_2 in $SOCl_2$ was added to S_4N_3Cl prepared *in situ* from the reaction of S_4N_4 and $SOCl_2$. Structure was proposed on the basis of the similarity of the IR spectrum of the product to that of S_4N_3Cl. [c] Reinvestigation of reaction (2). The reaction procedure and weights of reagents were identical to those used in reaction (2). [d] Structure was proposed on the basis of the similarity of the IR spectrum of the product to that of $(S_3N_2{}^+)_22Cl^-$. [e] Chemical analyses was consistent with $S_4N_4{\cdot}SeCl_4$ but the IR spectrum was similar to that of $S_5N_5{}^+$ in $S_5N_5{}^+AlCl_4{}^-$. [f] Chemical analyses were consistent with $S_4N_4{\cdot}SeCl_4$. The discrepancy between the $S_5N_5{}^+SeCl_5{}^-$ stoichiometry and the results of chemical analyses was ascribed to some sample decomposition during the analyses. [g] In this paper we describe our reinvestigation of this reaction and show that $(SeNSNS)_2(AsF_6)_2$ and $(SNSNS)_2(AsF_6)_2$ are also formed as minor products. We have also prepared pure $(SeNSNSe)_2(AsF_6)_2$ for the first time. [h] The compound was characterised by IR, Raman and ^{77}Se NMR spectroscopy (see *Note added at proof*). [i] $SeS_2N_2Cl_2$ contains both neutral $Cl_2SeNSNS$ and the ion pair $ClSeNSNS^+\ Cl^-$ in the same crystal lattice. [j] Bond distances given for $ClSeNSNSNbF_6$ (see *Note added at proof*).

in liquid nitrogen contained in a transparent glass Dewar flask. Fourier-transform Raman spectra were recorded at Bruker Spectrospin (Canada), Milton, Ontario, on a Bruker FRA 106 FT-Raman spectrometer. Mass spectra were recorded from solids in sealed m.p. tubes on a Kratos MS50TC mass spectrometer at an ionising voltage of 70 eV (*ca.* 1.12×10^{-17} J) using the direct-inlet method. The ESR spectra of SO_2 solutions at room temperature (r.t.) and frozen powders (−160 °C) were recorded on a locally modified version of a Varian E-4 spectrometer equipped with a variable-temperature control unit using diphenylpicrylhydrazyl (dpph) as field marker. A quartz ESR tube (outside diameter 3 mm) was used in order to minimise absorption of the microwave power by liquid SO_2. The NMR samples were prepared in thick-walled precision NMR tubes (Wilmad Glass, Buena, NJ; outside diameter 10 mm) fitted with J. Young O-ringette type valves (PTFE stopcock, Model BST/2) in SO_2. In oxidation reactions with AsF_5 the solvent was an SO_2–AsF_3 or an SO_2–AsF_3–AsF_5 (unreacted) mixture which changed the solubilities of products relative to that in pure SO_2. The NMR spectra were recorded at r.t. (^{14}N) or at −70 °C (^{77}Se) on a Varian Associates X-L 200 spectrometer operating at 14.45 (^{14}N) and 38.164 MHz (^{77}Se). Chemical shifts were externally referenced at r.t. to neat $MeNO_2$ (^{14}N) or neat Me_2Se (^{77}Se) with the high-frequency direction positive. No line-broadening functions were applied. Nitrogen-14 NMR acquisition parameters were as described in ref. 12. The ^{77}Se NMR spectra were acquired in 16 K data points with a spectral width of 50 KHz, pulse repetition time of 0.16 s and a pulse width of 20 μs. For each sample, three spectra were obtained over the chemical shift ranges of δ −308 to 1002, 923–2233 and 2233–3543 by adjusting the transmitter offset at a constant spectral width of 50 KHz. Good spectra could usually be obtained with 3000 scans from *ca.* 0.5 mol dm^{-3} solution. Chemical analysis were performed by Beller Mikroanalytisches Laboratorium, Göttingen.

The SO_2 (Matheson) and AsF_3 (Ozark-Mahoning) were vacuum distilled onto and stored over CaH_2 and NaF, respectively, CsN_3 (Eastman Kodak) was vacuum dried, AsF_5 (Ozark-Mahoning) was used without further purification, S_4N_4[20] (m.p. 176–178 °C; lit.,[21] 187–187.5 °C) and $Se_4(AsF_6)_2$[22] were prepared by our published methods.

Preparation of $(SeNSNSe)_2(AsF_6)_2$.—The compounds $Se_4(AsF_6)_2$ (2.57 g, 3.70 mmol) and S_4N_4 (0.618 g, 3.70 mmol) in liquid SO_2 (7.25 g) were stirred for 12 h producing a red-brown solution over a black solid. The solvent was removed and the resulting black solid (3.145 g) was finely ground and continuously washed by SO_2 in a modified extraction vessel[23] with three collection bulbs, one at the centre and two joined at about 45°. Continuous refluxing with SO_2 for 3 h produced a red-brown solution over black crystals (0.75 g), a further 18 h gave 0.89 g, and finally extraction for 2 d led to a red-brown solution over black crystals in the 'least' soluble fraction (1.02 g). The first and second fractions were transferred into the side bulbs which will be referred to as the 'most' soluble and 'middle' fractions, respectively. At this time, the solvent from the frit was colourless indicative of complete extractions of SO_2-soluble products. An insoluble black powder on the frit (0.483 g) was identified as selenium (mass and IR spectra; chemical analysis S, 4.75; Se, 95.30%). Chemical analyses of the 'least' soluble fraction [Found (Calc.) for $(SeNSNSe)_2(AsF_6)_2$]: As, 18.45 (18.40); F, 27.8 (28.0); N, 6.95 (6.90); S, 7.95 (7.90); Se, 39.10 (38.80)%.

The infrared spectrum of the 'most' soluble portion showed mainly the presence of $(SNSNS)_2(AsF_6)_2$ with a strong band at 990 cm^{-1} attributable to $(SeNSNSe)_2(AsF_6)_2$. The band due to $(SeNSNS)_2(AsF_6)_2$ overlapped with a strong peak due to $(SNSNS)_2(AsF_6)_2$ at 970 cm^{-1}. The infrared spectra of the 'middle' and 'least' soluble fractions were identical to that of pure $(SeNSNSe)_2(AsF_6)_2$ (see below, Fig. 4, and Table 3) which implied that $(SeNSNS)_2(AsF_6)_2$ and $(SNSNS)_2(AsF_6)_2$ impurities are not readily detected by their infrared spectra. The ESR results are given in Table 2. A portion of each fraction was separately oxidised by AsF_5 with traces of Br_2 to the corresponding dications. The ^{77}Se (−70 °C) and ^{14}N (r.t.) NMR spectra of each fraction showed the presence of $SeNSNSe^{2+}$, $SeNSNS^{2+}$, SN^+ and SNS^+ (see Table 2) implying that the unoxidised fractions contained $(SeNSNSe)_2(AsF_6)_2$, $(SeNSNS)_2(AsF_6)_2$ and $(SNSNS)_2(AsF_6)_2$ (which on oxidation gives SN^+ and SNS^+ in solution).[12]

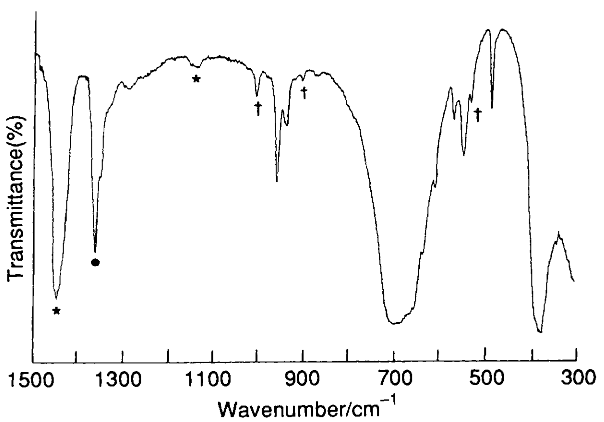


Fig. 1 Infrared spectrum of SeNSNSe$(AsF_6)_2$. Nujol peaks indicated by asterisks, peaks due to SeNSNS$(AsF_6)_2$ (ref. 16) indicated by daggers

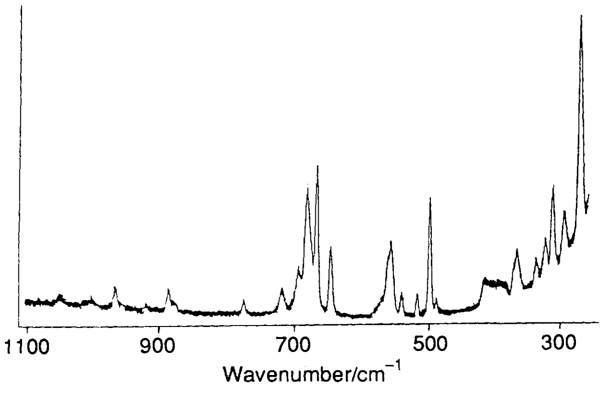


Fig. 2 Raman spectrum of crystalline SeNSNSe$(AsF_6)_2$ at -196 °C. Scan range 150–1500 cm^{-1}; power 115 mW; slit width 4 cm^{-1}; period 0.5 s; photon counting 3×10^4 counts per second; scan speed 124 cm min^{-1}

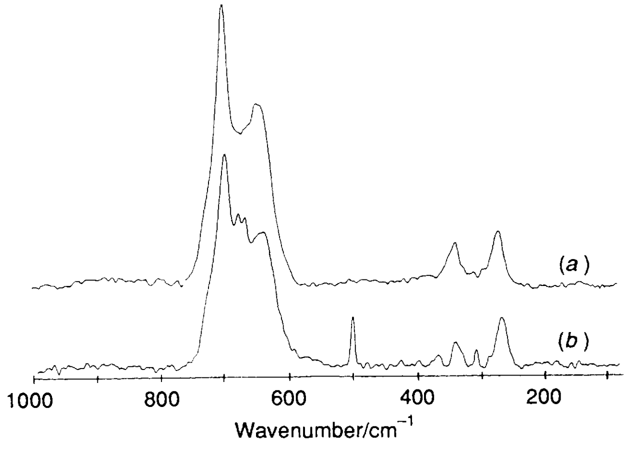


Fig. 3 Fourier-transform Raman spectrum of AsF_3 (l) (*a*) and SeNSNSe$(AsF_6)_2$ in AsF_3(l) (*b*) at r.t.

Preparation and Characterisation of SeNSNSe$(AsF_6)_2$.—An excess of AsF_5 (0.74 g, 4.35 mmol) relative to the amount required by equation (3) (see below) was treated with impure $(SeNSNSe)_2(AsF_6)_2$ (0.83 g, 1.02 mmol from the 'least' soluble fraction) in liquid SO_2 (6.25 g) with traces of Br_2 in a two-bulb vessel, giving a transparent yellow solution above a highly crystalline light yellow solid after 45 min at r.t. The solution was filtered into the second bulb and the crystals were washed five times with SO_2 (*ca.* 1 cm^3). The volatile materials were removed giving pure highly crystalline materials (0.85 g), 70% recovered yield based on equation (3) from the less-soluble fraction, and a less-pure yellow solid (0.52 g) from the more soluble product [Found (Calc.) for SeNSNSe$(AsF_6)_2$]: As, 27.70 (25.15); F, 37.30 (38.25); N, 4.80 (4.70); S, 5.60 (5.35); Se, 24.70 (26.50)%. NMR: ^{14}N (r.t. SO_2 solvent), δ -72.5, $\nu_{\frac{1}{2}} = 690$ Hz; ^{77}Se [-70 °C, SO_2 (3.5 g) and AsF_5 (1.1 g) solvent], δ 2411.7, $\nu_{\frac{1}{2}} = 10.2$ Hz; (r.t., SO_2–AsF_5 solvent, freshly prepared *in situ*), δ 2412.1, $\nu_{\frac{1}{2}} = 25.6$ Hz. The vibrational data for SeNSNSe$(AsF_6)_2$ are given in Table 3. The infrared and Raman spectra are shown in Figs. 1 and 2 respectively, and the Raman spectrum in liquid AsF_3 is included in Fig. 3. The identity of SeNSNSe$(AsF_6)_2$ was confirmed by single-crystal X-ray analysis (see below).

Crystals of SeNSNSe$(AsF_6)_2$ are yellow and black in reflected and transmitted lights, respectively. The compound decomposes at 150 °C to give a greenish yellow solid (brown when cold) which melts at 212–215 °C. It is moderately soluble in liquid SO_2 (*ca.* 20% w/w), but dissolves readily in a SO_2 (3.5 g)–AsF_5 (1.1 g) mixture at *ca.* -40 °C, increasing in solubility as the temperature is lowered, and is soluble in liquid AsF_3 (*ca.* 40% w/w) at r.t. When prepared *in situ* with an excess of AsF_5 under rigorously dry conditions it does not give an ESR spectrum. However, on removal of the volatile materials and addition of fresh and dry SO_2, a spectrum of the SeNSNSe$^{\bullet +}$ radical was obtained which implies that SeNSNSe$(AsF_6)_2$ is very readily reduced, presumably by traces of water. The compound is very sensitive to traces of moist air and rapidly acquires a brown coating. The ^{77}Se NMR spectrum of a fresh solution of SeNSNSe$(AsF_6)_2$ prepared *in situ* with excess of AsF_5 showed a peak at r.t. (δ 2412.1) with essentially the same chemical shift as that obtained at -70 °C (δ 2411.7). However, if the compound is manipulated inside the dry-box and then redissolved in liquid SO_2 a peak is not observed at r.t. in the ^{77}Se NMR spectrum but only at a low temperature (*e.g.* at -70 °C). The infrared spectrum of the compound does not change on prolonged grinding, or on subjection to a dynamic vacuum for a long period. These results show that, in contrast to SNSNS^{2+} in SNSNS$(AsF_6)_2$,[13] the SeNSNSe^{2+} cation does not readily abstract a fluoride ion from AsF_6^-. However, SeNSNSe^{2+} readily reacts with CCl_3F* in liquid SO_2 to give ClSeNSNSe$^+$.

Reduction of Purified SeNSNSe$(AsF_6)_2$ *with* CsN_3 (1 : 1 *ratio*) *leading to Pure* $(SeNSNSe)_2(AsF_6)_2$.—A sample of the purified (^{77}Se, ^{14}N NMR) SeNSNSe$(AsF_6)_2$ (0.512 g, 0.86 mmol) in SO_2 (4.52 g) was treated with vacuum-dried CsN_3 (0.150 g, 0.86 mmol) in a two-bulb vessel, producing a red-brown solution over a brown precipitate after stirring for 12 h. Volatile materials were removed and the resulting brown solid (0.625 g) was finely ground and subjected to continuous extraction[23] with liquid SO_2 for 2 d. The soluble black crystals (0.348 g, 100% yield) were identified as $(SeNSNSe)_2(AsF_6)_2$ (IR and ESR spectra, see below), and the white solid (0.275 g) as $CsAsF_6$ (IR). The infrared spectrum of pure $(SeNSNSe)_2(AsF_6)_2$ in Nujol is shown in Fig. 4: 1000s, 955vs, 710vs [$\nu_3(AsF_6^-)$], 690m [$\nu_1(AsF_6^-)$], 670vs, 628 (sh), 623vs, 587w [$\nu_2(AsF_6^-)$], 550m, 397vs [$\nu_4(AsF_6^-)$], and 355w [$\nu_5(AsF_6^-)$] cm^{-1}.

A partially dissolved sample of $(SeNSNSe)_2(AsF_6)_2$ (0.31 g) in SO_2 (*ca.* 0.25 g) was agitated for 1 min in an ultrasonic bath at 30 °C. The solution (*ca.* 7.2×10^{-3} mol dm^{-3}) was then filtered into a quartz ESR tube (outside diameter 3 mm). The ESR

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* The reaction with CCl_3F was carried out with slightly impure SeNSNSe$(AsF_6)_2$ containing small amounts of SeNSNS$(AsF_6)_2$ (IR). The infrared spectrum of the resulting yellow solid did not show bands attributable to either SeNSNSe^{2+} or SeNSNS^{2+} which implied that both cations reacted with CCl_3F.

Table 2 ESR data for material washed out of impure $(SeNSNSe)_2(AsF_6)_2$, and corresponding NMR data for the oxidised products

No.	Fraction	^{77}Se NMR[a] at −70 °C Mole ratio of SeNSNSe^{2+}; SeNSNS^{2+}	^{14}N at r.t.[a,b,c] Mole ratio of SeNSNSe^{2+} : SeNSNS^{2+} : SNS$^+$: SN$^+$	ESR in SO_2 solution[d] at r.t. of unoxidised products
1	'Least' soluble: 0.363 g in SO_2 (3.71 g) and AsF_5 (0.637 g, 3.75 mmol)	2:1	15:0:1.5:1	SeNSNS$^{\bullet +}$ (g = 2.026)[e] SNSNS$^{\bullet +}$ (qnt., g = 2.011)[f] (trace)
2	'Middle' portion: 0.300 g in SO_2 (5.0 g) and AsF_5 (0.746 g, 4.39 mmol)	2.25:1	17:0:1:1	SeNSNS$^{\bullet +}$ SNSNS$^{\bullet +}$ (qnt., *ca.* 5%)
	'Most' soluble: 0.441 g in SO_2 (3.99 g) and AsF_5 (1.28 g, 7.5 mmol)	1:2	6:6.7:1:1	SeNSNS$^{\bullet +}$ SNSNS$^{\bullet +}$ *ca.* 50:50 mixture

[a] SeNSNSe^{2+} and SeNSNS^{2+} were identified by comparison of their observed resonances (δ and $\nu_{\frac{1}{2}}$) with the values obtained in this work and ref. 16, respectively: SeNSNS^{2+}, δ(^{77}Se) 2422.5, $\nu_{\frac{1}{2}}$ = 14.5 Hz, δ(^{14}N) 68.9. [b] SNS$^+$ and SN$^+$ were identified by comparison of their observed resonances (δ and $\nu_{\frac{1}{2}}$) with our published data in ref. 12. [c] The dications have large $\nu_{\frac{1}{2}}$ values for the ^{14}N NMR peaks and the errors in the integrated peak area estimation are therefore large. Note that although SeNSNS^{2+} is undoubtedly present (^{77}Se NMR spectrum), none was detected in fractions 1 and 2 by ^{14}N NMR spectroscopy. [d] *ca.* 3 × 10^{-3} mol dm^{-3}. [e] Ref. 14. [f] Ref. 24.

spectrum of the fresh solution (*ca.* 15 min after dissolution) at r.t. consisted of a broad signal (g = 2.046).[14] In order to prevent precipitation (rather than decomposition as stated in ref. 14) of $(SeNSNSe)_2(AsF_6)_2$, the solution was frozen rapidly in liquid N_2 (−196 °C) prior to transfer into the ESR cavity which was already cooled to −160 °C. The powder ESR spectrum in frozen SO_2 at −160 °C and some ESR parameters were reported earlier.[14,15] The solution was left at r.t. for 5 d, and another ESR spectrum was obtained which was identical (g = 2.046) to that obtained from the fresh solution. The radical ions SeNSNS$^{\bullet +}$ and SNSNS$^{\bullet +}$ were not observed over the whole range (4000 G, 0.4 T) of the spectrum.

X-Ray Crystallographic Analysis of $SeNSNSe(AsF_6)_2$.—Diffraction intensities were measured at 293 K on an Enraf–Nonius CAD-4 diffractometer equipped with graphite-monochromated Mo-Kα radiation (λ = 0.710 73 Å) running the NRCCAD[25] control program. An ω–2θ scan was used at a speed of 4° (2θ) min^{-1} and backgrounds were estimated by extending the scan by 25% on either side of the scan limits. The limits of the peak were then ascertained by profile analysis to provide an improved background correction. Unit-cell parameters were obtained by least-squares refinement using the coordinates of 25 reflections, centred using the TRUANG option of NRCCAD, thereby minimising the effects of instrumental and crystal-alignment errors. Lorentz and polarisation factors were applied and absorption corrections were made using the empirical routine of Walker and Stuart.[26]

The structure was solved by direct-methods techniques and subsequent difference syntheses. Crystal data are summarised in Table 4. Refinement was by full-matrix least squares with weights based on counter statistics. All atoms were refined with anisotropic thermal parameters. On inspection some of the final atomic coordinates seem to indicate the presence of unaccounted for symmetry. However, the routine MISSYM with relatively loose tolerances showed this not to be the case. Computations were performed using the NRCVAX suite of crystal structure programs.[27] Scattering factors were taken from ref. 28 and were corrected for anomalous dispersion. The final atomic coordinates are given in Table 5.

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters and remaining bond lengths and angles.

Results and Discussion

A Reinvestigation of the Reaction of S_4N_4 *and* $Se_4(AsF_6)_2$.—The course of the reaction was essentially identical to that described in ref. 6 and was complete within 24 h (colour changes and precipitation of a black solid) with no evidence for nitrogen elimination. The bulk product was washed with continuous refluxing liquid SO_2 leading to an insoluble product (95% Se, 5% S w/w) and three slightly soluble fractions. In the previous work[6] the insoluble product was identified as a sulfur–selenium mixture. It is possible that in this work, most of the sulfur, which has a slight solubility in SO_2, was extracted into the soluble products.

The ESR spectrum of all three soluble fractions in SO_2 solution at r.t. showed SeNSNS$^{\bullet +}$ [14] and SNSNS$^{\bullet +}$ [29] but not SeNSNSe$^{\bullet +}$,[14] presumably due to line broadening (see Table 2). However, all three radicals were observed by Preston and co-workers[14] in the powder ESR spectra of a frozen solution of impure $(SeNSNSe)_2(AsF_6)_2$. The difficulty of characterising these products is further illustrated by the chemical analysis for all elements of the 'least' soluble fraction which was consistent with $(SeNSNSe)_2(AsF_6)_2$, and by its infrared spectrum which was identical to that of the pure product. However, the mass spectrum indicated a mixture, with parent ions attributable to SNSNS$^+$ (m/z = 124, 2%), SeNSNS$^+$ (m/z = 172, 1.5%) and SeNSNSe$^+$ (m/z = 220, 11.5%) as well as their fragmentation peaks and peaks attributable to AsF_5 (*i.e.* AsF_4^+ to As^+). The distribution of products was most reliably established from the ^{77}Se NMR spectra of the dications given on reaction of the monocations with AsF_5. These showed (see Table 2) that all three oxidised fractions contained SeNSNSe^{2+}, SeNSNS^{2+}, SN$^+$ and SNS$^+$ (the last two from dissociation of SNSNS^{2+} [12]). We estimated from the NMR data that the 'least' soluble fraction contained about 60% SeNSNSe$^{\bullet +}$, 30% SeNSNS$^{\bullet +}$ and 10% SNSNS$^{\bullet +}$ (in mmol %). The relative amount of SeNSNS$^{\bullet +}$ is even greater in the 'most' soluble fraction (60%). The overall reaction can reasonably be described by equation (2), for

$$Se_4(AsF_6)_2 + S_4N_4 \xrightarrow{SO_2} (Se_xS_{3-x}N_2)_2(AsF_6)_2 + (4-2x)Se + (2x-2)S \quad (2)$$

$2 \geqslant x \geqslant 1$. The amount of selenium produced implies that x is

Table 3 Vibrational data for $\mathrm{SeNSNSe(AsF_6)_2}$ and tentative assignments[a]

IR (Nujol) (Fig. 1)	Raman: Solid[b] (Fig. 2) −196 °C, 5145 Å, Δν	Raman: Fourier transform in $\mathrm{AsF_3(l)}$[c] (Fig. 3)	Tentative assignments
	1050 (7)		?
1018vw			*d*
973s	965 (10)		ν_{sym}(SN)[e]
958 (sh)	960 (< 5)		?
918(vw)	920 (< 5)		*d*
	886 (10)		ν_{asym}(SeN)[e]
	776 (7)		?
	718 (12)		*d*
698vs (br)	694 (20)		$\nu_3(\mathrm{AsF_6^-})$[f]
	682 (59)	680w *	$\nu_1(\mathrm{AsF_6^-})$[f]
668w (sh)	668 (67)	669w *	?
648 (sh)	649 (31)		ν_{sym}(SeN)[e]
619w (sh)			?
		592vw	?
583w	572 (< 5)		$\nu_2(\mathrm{AsF_6^-})$[f]
560m	558 (34)		
548vw			*d*
	543 (5)		?
503m	500 (55)	500m	ν_{asym}(SN)[e]
491w (sh)	484 (< 5)		?
	410 (5)		?
393s			$\nu_4(\mathrm{AsF_6^-})$[f]
	366 (23)	369w	$\nu_5(\mathrm{AsF_6^-})$[f]
	336 (7)[g]		?
316w	321 (9)		?
	310 (37)	310w	ν_{sym}(Se–Se)
	292 (20)[g]		Bend
	267 (100)	270m (br)[h]	Bend

v = Very, s = strong, m = medium, w = weak, sh = shoulder and br = broad; asterisk indicates overlapping with strong and broad $\mathrm{AsF_3}$ bands. [a] The assignments given here are based on a normal coordinate analysis which will be reported elsewhere.[13b] The symmetric and asymmetric stretching vibrations transform into A_1 and B_2, respectively. [b] Relative areas are given in parentheses. [c] Relative areas could not be obtained because some of the peaks overlapped with $\mathrm{AsF_3}$ bands (see Fig. 3); $\mathrm{AsF_3}$ peaks are not included. [d] $\mathrm{SeNSNSe^{2+}}$ impurity, see ref. 16. [e] These vibrations are heavily mixed; assignments show major contribution only, ref. 13*b*. [f] By comparison with $\mathrm{AsF_6^-}$ salts, ref. 24. [g] Intensity varies with the laser power. [h] Peak overlaps with a moderately intense $\mathrm{AsF_3}$ band.

about 1.2 and a value of about $x = 1.5$ was estimated from the NMR data assuming the weight of sulfur could be ignored.

The structures of $\mathrm{(Se/SNSNSe/S)_2(AsF_6)_2}$,[16] $\mathrm{(Se/SNSNSe)_2(AsF_6)_2}$[16] and $\mathrm{(SeNSNSe)_2(AsF_6)_2}$[6] are all isomorphous (space group $P2_1/n$) and isostructural: $\mathrm{(Se/SNSNSe/S)_2(AsF_6)_2}$ contains disordered $\mathrm{SeNSNS^{\bullet+}}$ and $\mathrm{(Se/SNSNSe)_2(AsF_6)_2}$ disordered $\mathrm{SeNSNSe^{\bullet+}}$ and $\mathrm{SeNSNS^{\bullet+}}$ radical cations linked into loosely bound dimer dications. Therefore it is possible to envisage the formation of a large number of disordered solid-state phases all of which are isomorphous containing various combinations of $\mathrm{SNSNS^{\bullet+}}$, $\mathrm{SNSNSe^{\bullet+}}$ and $\mathrm{SeNSNSe^{\bullet+}}$ radical cations in the dimer units and a wide range of average stoichiometries. This may explain the difficulty of separating pure $\mathrm{(SeNSNSe)_2(AsF_6)_2}$ from the reaction mixture which may consist of a number of $\mathrm{(Se_xS_{3-x}N_2)_2(AsF_6)_2}$ (x = 1–3) disordered phases all with similar low solubility in $\mathrm{SO_2}$.

Preparation of Pure $\mathrm{(SeNSNSe)_2(AsF_6)_2}$.—Pure black crystalline $\mathrm{(SeNSNSe)_2(AsF_6)_2}$, devoid of detectable amounts (ESR) of $\mathrm{SNSNS^{\bullet+}}$ and $\mathrm{SeNSNS^{\bullet+}}$, was obtained by reduction of a purified sample of $\mathrm{SeNSNSe(AsF_6)_2}$ (see below) by $\mathrm{CsN_3}$ (isolated yield *ca.* 100%). The ESR spectrum of a fresh solution of pure $\mathrm{(SeNSNSe)_2(AsF_6)_2}$ in $\mathrm{SO_2}$ at r.t. showed only $\mathrm{SeNSNSe^{\bullet+}}$ (g = 2.046).[14] The spectrum obtained from the same sample left at r.t. for 5 d was identical to that of the fresh solution, and $\mathrm{SNSNS^{\bullet+}}$ and $\mathrm{SeNSNS^{\bullet+}}$ were not observed indicating that the $\mathrm{SeNSNSe^{\bullet+}}$ radical did not scramble in solution. This implies that the formation of $\mathrm{SNSNS^{\bullet+}}$ and $\mathrm{SeNSNS^{\bullet+}}$ does not arise from some inter-radical scrambling process, [*e.g.* the related $\mathrm{2RCNSNS^{\bullet} \longrightarrow 2RCNSSN^{\bullet}}$ (R = $\mathrm{CF_3}$, $\mathrm{CH_3}$, I, $\mathrm{NMe_2}$, or $\mathrm{Bu^t}$)],[30] but directly from the reaction of $\mathrm{S_4N_4}$ with $\mathrm{Se_4(AsF_6)_2}$. The solution and powder ESR spectra and parameters of $\mathrm{SeNSNSe^{\bullet+}}$ have been reported.[14] The infrared spectrum of pure $\mathrm{(SeNSNSe)_2(AsF_6)_2}$ is shown in Fig. 4 and the data are listed in the experimental section.

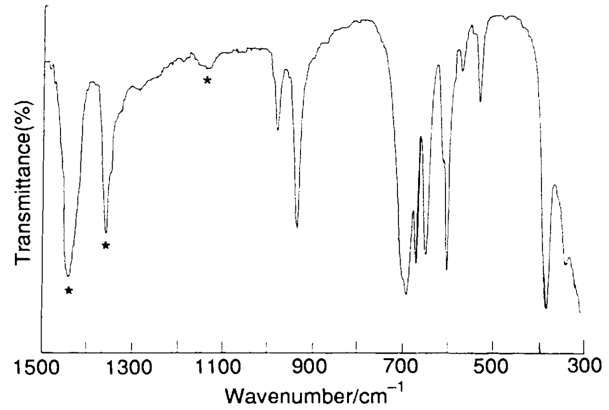

Fig. 4 Infrared spectrum of purified $\mathrm{(SeNSNSe)_2(AsF_6)_2}$. Nujol peaks indicated by asterisks.

Preparation and Characterisation of $\mathrm{SeNSNSe(AsF_6)_2}$.—Impure $\mathrm{(SeNSNSe)_2(AsF_6)_2}$ from the 'least' soluble fraction was oxidised by $\mathrm{AsF_5}$ with traces of $\mathrm{Br_2}$ in liquid $\mathrm{SO_2}$ according to equation (3). The reaction was fast even in the absence of

$$\mathrm{(SeNSNSe)_2(AsF_6)_2 + 3AsF_5 \xrightarrow[\text{trace Br}_2]{SO_2} 2SeNSNSe(AsF_6)_2 + AsF_3} \quad (3)$$

traces of $\mathrm{Br_2}$ and essentially complete in 1 h as indicated by the colour changes and the formation of a crystalline material. The product contained small amounts of $\mathrm{SNAsF_6}$, $\mathrm{SNSAsF_6}$ (^{14}N NMR spectroscopy) and $\mathrm{SeNSNS(AsF_6)_2}$ (^{77}Se NMR spectroscopy, −70 °C) which are the oxidised products of $\mathrm{(SNSNS)_2(AsF_6)_2}$ and $\mathrm{(SeNSNS)_2(AsF_6)_2}$ impurities in the starting material. Purification was effected by fractional crystallisation, the less-soluble fraction gave yellow highly crystalline $\mathrm{SeNSNSe(AsF_6)_2}$ (0.85 g, *ca.* 70% isolated yield). The weight (1.37 g) of bulk solid product (expected 1.22 g) indicated that the reaction proceeded essentially according to equation (3). It was difficult to prepare $\mathrm{SeNSNSe(AsF_6)_2}$ completely devoid of traces of $\mathrm{SeNSNSe^{\bullet+}}$ (ESR spectrum) unless the reaction was carried out under thoroughly anhydrous conditions.

The purity of $\mathrm{SeNSNSe(AsF_6)_2}$ was established by ^{77}Se, ^{14}N NMR and vibrational spectroscopy; the spectra obtained did not indicate the presence of detectable amounts of other species, although the IR spectrum showed the presence of small amounts of $\mathrm{SeNSNS(AsF_6)_2}$[16] impurities (see Fig. 1). In some similar experiments, $\mathrm{SeNSNSe(AsF_6)_2}$ contained small amounts

Table 4 Crystallographic data for SeNSNSe$(AsF_6)_2$

Formula	$As_2F_{12}N_2SSe_2$
M	595.82
Crystal size/mm	0.47 × 0.35 × 0.24
System	Monoclinic
Space group	*C*2
a/Å	12.700(2)
b/Å	8.6764(7)
c/Å	10.655(1)
β/°	93.489(9)
U/Å^3	1171.8(2)
Z (molecules per cell)	4
D_c/Mg m^{-3}	3.38
F(000)	1088
No. Reflections	4365
No. Unique reflections	2040
Observed reflections ($I_{net} > 2.5\sigma I_{net}$)	1845
μ(Mo-Kα)/m^{-1}	12.16
R_f[a] obs.(all)	0.031(0.038)
R'[b] obs.(all)	0.044(0.046)

[a] $\Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $[\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|]^{\frac{1}{2}}$, where $w = 1/\sigma^2(I)$.

Table 5 Fractional atomic positional parameters for SeNSNSe$(AsF_6)_2$ with estimated standard deviations (e.s.d.s) in parentheses

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Se(1)	0.205 36(9)	0.636 36	0.143 0(1)
Se(2)	0.214 89(9)	0.641 4(2)	0.360 1(1)
N(1)	0.167 6(7)	0.450(1)	0.133 8(8)
N(2)	0.177 4(7)	0.454(1)	0.374 3(8)
S	0.150 3(2)	0.349 3(4)	0.256 1(3)
As(1)	0.864 09(8)	0.520 1(2)	0.252 04(9)
F(11)	0.808 0(6)	0.639(1)	0.140 3(6)
F(12)	0.916 5(7)	0.398(1)	0.361 4(8)
F(13)	0.975 8(6)	0.620(2)	0.256(1)
F(14)	0.814 6(6)	0.637(2)	0.362 4(6)
F(15)	0.750 0(8)	0.420(2)	0.249(1)
F(16)	0.906 6(9)	0.402(2)	0.143 7(8)
As(2)	1/2	0.502 6(2)	1/2
F(21)	0.581 3(6)	0.639(1)	0.445 2(7)
F(22)	0.577 9(7)	0.360(1)	0.442 0(8)
F(23)	0.423 8(6)	0.505(2)	0.361 2(7)
As(3)	1/2	0.496 5(2)	0
F(31)	0.554(1)	0.631(2)	0.095(1)
F(32)	0.388 9(7)	0.488(2)	0.077 0(9)
F(33)	0.553 6(8)	0.359(2)	0.093(1)

of SeNSNS$(AsF_6)_2$[16] (*ca.* 3–10%, ^{77}Se NMR spectrum) as an impurity which was more readily separated in large-scale reactions. Chemical analyses for all elements showed good agreement with those calculated for SeNSNSe$(AsF_6)_2$ and the assignment of its vibrational spectra based on normal co-ordinate analyses[13] (see Table 3) were consistent with the given structure. The identity of SeNSNSe$(AsF_6)_2$ was confirmed by X-ray crystal structure analyses (see below). The ^{14}N NMR spectrum (r.t.) of SeNSNSe$(AsF_6)_2$ in SO_2 solution showed a broad peak (δ −72.5, $v_{\frac{1}{2}}$ = 690 Hz) consistent with a ring structure rather than simple cations such as SeN^+ or $SeNS^+$ both of which would be expected to have relatively sharp peaks. The ^{77}Se NMR (−70 °C) resonance was observed at high frequency (δ 2411.7, $v_{\frac{1}{2}}$ = 10.2 Hz) indicating that the selenium nuclei are strongly deshielded consistent with the di-positive charge and the delocalised 6π ring system. The related 6π SeNSNS^{2+} [16] (δ = 2422.4, $v_{\frac{1}{2}}$ = 14.5 Hz) and SeNSeNSe^{2+} [15] (δ 2434.0, $v_{\frac{1}{2}}$ = 9.2 Hz) as AsF_6^- salts also showed resonances at high frequency. The presence of one peak in the ^{77}Se NMR spectrum (−70 °C) assignable to SeNSNSe^{2+}, rather than two peaks, implies that dissociation of the ring does not occur in solution. The ^{77}Se NMR chemical shift at r.t. was essentially identical to that observed at −70 °C which shows that if SeNSNSe^{2+} dissociates in solution to SeN^+ and $SeNS^+$ the extent is very small. In addition, the strong peaks in the Raman spectrum of a crystalline sample of SeNSNSe$(AsF_6)_2$ were also observed in that obtained from an AsF_3 solution of the compound (see Fig. 3) with no evidence for the presence of other species demonstrating that significant dissociation does not occur in solution at r.t.

Thus the ^{77}Se, ^{14}N NMR and Raman spectra show that the SeNSNSe^{2+} cation retains its ring structure in solution in contrast to SNSNS^{2+} in SNSNS$(AsF_6)_2$[13] which completely dissociates to SN^+ and SNS^+ in SO_2. This behaviour is consistent with the tendency for selenium compounds to be

Table 6 Bond distances (Å) and angles (°) for SeNSNSe$(AsF_6)_2$ with e.s.d.s in parentheses

SeNSNSe^{2+}			
Se(1)–Se(2)	2.310(2)	Se(2)–Se(1)–N(1)	94.2(3)
Se(1)–N(1)	1.69(1)	Se(1)–Se(2)–N(2)	94.2(3)
Se(2)–N(2)	1.71(1)	Se(1)–N(1)–S	122.1(5)
S–N(1)	1.60(1)	Se(2)–N(2)–S	121.8(5)
S–N(2)	1.57(1)	N(1)–S–N(2)	107.7(5)
AsF_6^-			
As(1)–F(11)	1.696(8)	F(11)–As(1)–F(12)	177.9(5)
As(1)–F(12)	1.684(9)	F(11)–As(1)–F(13)	91.2(5)
As(1)–F(13)	1.663(9)	F(11)–As(1)–F(14)	88.1(4)
As(1)–F(14)	1.703(9)	F(11)–As(1)–F(15)	88.6(5)
As(1)–F(15)	1.69(1)	F(11)–As(1)–F(16)	91.5(5)
As(1)–F(16)	1.66(1)		
As(2)–F(21)	1.699(9)	F(12)–As(1)–F(13)	90.7(5)
As(2)–F(22)	1.723(9)	F(12)–As(1)–F(14)	92.7(5)
As(2)–F(23)	1.718(6)	F(12)–As(1)–F(15)	89.5(5)
		F(12)–As(1)–F(16)	87.7(5)
As(3)–F(31)	1.67(1)	F(13)–As(1)–F(14)	91.2(6)
As(3)–F(32)	1.676(8)	F(13)–As(1)–F(15)	179.5(6)
As(3)–F(33)	1.67(1)	F(13)–As(1)–F(16)	91.5(6)
		F(14)–As(1)–F(15)	88.3(5)
		F(14)–As(1)–F(16)	177.2(6)
		F(15)–As(1)–F(16)	89.0(6)
F(21)–As(2)–F(22)	90.2(5)	F(31)–As(3)–F(32)	90.4(8)
F(21)–As(2)–F(23)	91.0(5)	F(31)–As(3)–F(33)	90.1(7)
F(21d)–As(2)–F(22)	177.6(5)	F(31a)–As(3)–F(32)	90.3(8)
F(21d)–As(2)–F(23)	87.9(5)	F(31a)–As(3)–F(33)	178.7(8)
F(22)–As(2)–F(23)	90.4(5)	F(32)–As(3)–F(32a)	174.7(9)
F(22d)–As(2)–F(23)	90.7(5)	F(32)–As(3)–F(33)	90.1(7)
F(23)–As(2)–F(23d)	178.5(7)	F(33)–As(3)–F(33a)	88.7(7)

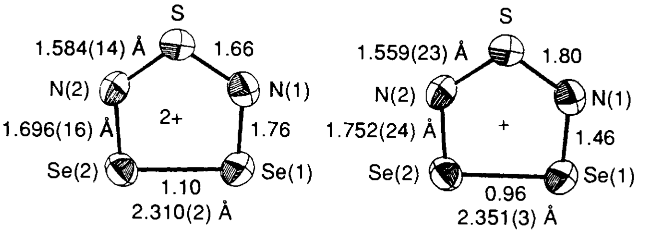

Fig. 5 An ORTEP plot of the SeNSNSe^{2+} cation and calculated π-bond orders and average bond lengths in SeNSNSe^{2+} and SeNSNSe$^{\bullet +}$. The bond order (*N*) was calculated by the Pauling equation $N = 10^{(D_1 - R)/0.71}$, where *R* is the observed bond length (Å) and D_1 the sum of the appropriate covalent radii (Å) for a single bond. D_1 = 2.34, 1.87 and 1.74 for Se–Se, Se–N and S–N, respectively (see ref. 33)

Table 7 Interionic contacts * (Å) and selected angles (°) for SeNSNSe$(AsF_6)_2$ with e.s.d.s in parentheses

Se(1)···F(13)	3.223(9)	F(13b)···Se(1)···F(15c)	93.1(3)	Se(1)···Se(2)···F(13b)	70.0(2)	F(13b)···S···F(14e)	157.2(3)
Se(1)···F(15c)	2.75(1)	F(13b)···Se(1)···F(32)	149.5(4)	Se(1)···Se(2)···F(14d)	169.7(2)	F(13b)···S···F(21e)	102.8(3)
Se(1)···F(32)	2.79(1)	F(15c)···Se(1)···F(32)	111.2(4)	Se(1)···Se(2)···F(15c)	65.3(2)	F(13b)···S···F(14e)	102.6(3)
Se(1)···F(33c)	2.76(1)	F(32)···Se(1)···F(33c)	149.3(4)	Se(1)···Se(2)···F(21d)	129.6(1)	F(14e)···S···F(31e)	94.9(4)
Se(1)···F(11a)	3.012(7)	F(13b)···Se(2)···F(14d)	99.8(2)	Se(1)···Se(2)···F(22c)	109.6(2)	F(21e)···S···F(31e)	81.9(4)
Se(2)···F(13b)	3.174(8)	F(13b)···Se(2)···F(15c)	94.4(3)	Se(1)···Se(2)···F(23)	89.3(2)	N(1)···Se(1)···F(11a)	87.1(4)
Se(2)···F(14d)	3.003(7)	F(13b)···Se(2)···F(21d)	160.1(2)	Se(2)···Se(1)···F(11a)	178.51(2)	N(1)···Se(1)···F(13b)	73.7(4)
Se(2)···F(15c)	2.74(1)	F(13b)···Se(2)···F(23)	146.3(3)	Se(2)···Se(1)···F(13b)	67.7(2)	N(1)···Se(1)···F(15c)	158.6(4)
Se(2)···F(21d)	3.216(8)	F(15c)···Se(2)···F(22c)	69.7(3)	Se(2)···Se(1)···F(15c)	64.9(2)	N(1)···Se(1)···F(32)	77.4(5)
Se(2)···F(22c)	2.751(9)	F(15c)···Se(2)···F(21d)	98.0(3)	Se(2)···Se(1)···F(32)	105.5(2)	N(1)···Se(1)···F(33c)	117.8(4)
Se(2)···F(23)	2.903(9)	F(15c)···Se(2)···F(23)	100.8(3)	Se(2)···Se(1)···F(33c)	100.0(3)	N(1)···S···F(11e)	82.6(9)
S···F(11e)	3.030(9)	F(14d)···Se(2)···F(15c)	118.1(3)	N(2)···Se(2)···F(13b)	73.1(4)	N(1)···S···F(13b)	74.2(4)
S···F(13b)	3.23(1)	F(14d)···Se(2)···F(23)	99.2(2)	N(2)···Se(2)···F(14d)	81.3(4)	N(1)···S···F(14e)	121.7(4)
S···F(14e)	2.96(1)	F(21d)···Se(2)···F(22c)	107.4(3)	N(2)···Se(2)···F(15c)	159.0(3)	N(1)···S···F(21e)	167.7(4)
S···F(21e)	2.892(9)	F(22c)···Se(2)···F(23)	151.0(3)	N(2)···Se(2)···F(21d)	98.9(3)	N(1)···S···F(31e)	87.1(5)
S···F(31e)	2.79(1)	F(11e)···S···F(13b)	155.4(3)	N(2)···Se(2)···F(22c)	116.4(4)	N(2)···S···F(11e)	123.8(4)
		F(11e)···S···F(21e)	98.0(3)	N(2)···Se(2)···F(23)	82.6(4)	N(2)···S···F(13b)	72.4(4)
						N(2)···S···F(14e)	86.3(4)
						N(2)···S···F(21e)	82.2(4)
						N(2)···S···F(31e)	161.8(5)

* Includes all contacts less than the isotropic van der Waals radii (Se··· F 3.37, S··· F 3.27 Å), ref. 37.

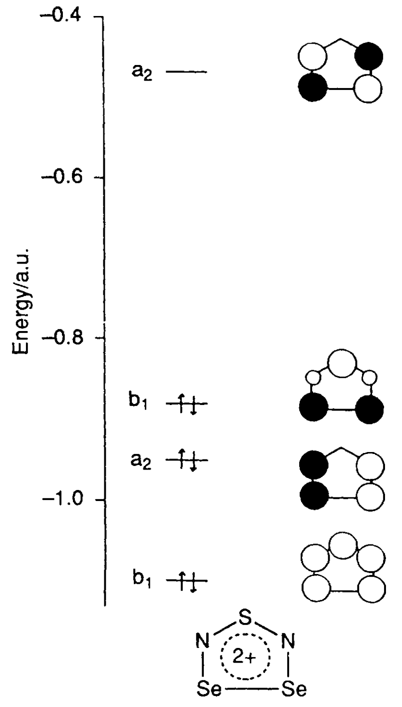

Fig. 6 Qualitative π molecular orbitals of SeNSNSe^{2+} derived from that of SNSNS^{2+} (ref. 13). 1 a.u. = 4.539×10^{-18} J

polymeric and have higher co-ordination than the monomeric sulfur analogues [*e.g.* monomeric SO_2, polymeric $(SeO_2)_x$;[31] OSF_4, $(OSeF_4)_2$[32]].

The X-Ray Crystal Structure of SeNSNSe$(AsF_6)_2$.—The X-ray crystal structure of SeNSNSe$(AsF_6)_2$ consists of discrete, planar SeNSNSe^{2+} cations and distorted AsF_6^- ions with strong interionic interactions. The SeNSNSe^{2+} cation is shown in Fig. 5 which also includes average bond distances in SeNSNSe^{2+} and SeNSNSe$^{\cdot +}$ and calculated π-bond orders. The bond distances and angles within the cation and the anion are listed in Table 6.

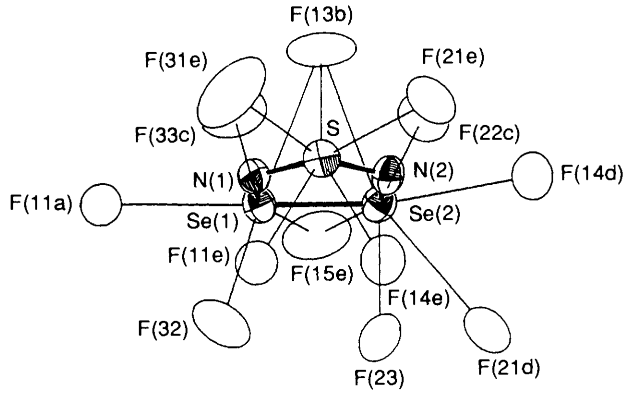

Fig. 7 Cation–anion contacts in SeNSNSe$(AsF_6)_2$

The Se–Se bond [2.310(2) Å] in SeNSNSe^{2+} is significantly (3σ test) shorter than that in SeNSNSe$^{\cdot +}$ [2.351(3) Å], but the Se–N and S–N bonds in the two cations are not significantly different. However, the Se–Se and the average Se–N distances in SeNSNSe^{2+} are shorter than the corresponding bonds in SeNSNSe$^{\cdot +}$ consistent with the removal of the unpaired electron from the π* SOMO (singly occupied molecular orbital) of SeNSNSe$^{\cdot +}$, assuming that it is the same as that of SNSNS$^{\cdot +}$ [refs. 24, 29(*a*) and 34] (see Fig. 6).

The bonding in SeNSNSe^{2+} may be described by a simple MO model derived from that of SNSNS^{2+} (Fig. 6) (which is also similar to that of SNSNS$^{\cdot +}$ [24,29a,34]) according to which all the bonds in SeNSNSe^{2+} are expected to have some π-bonding character. Thus the calculated π-bond orders for the Se–N (1.76) and S–N (1.66) are consistent with the MO model and imply the presence of thermodynamically stable[35] delocalised $4p_\pi$(Se)–$2p_\pi$(N) and $3p_\pi$(S)–$2p_\pi$(N) bonds. The calculated Se–Se π-bond order (1.10) is somewhat lower than that expected from the simple MO treatment which indicates a substantial $4p_\pi$– $4p_\pi$ contribution from the totally symmetric bonding MO in the Se–Se region. Similar effects are present in the related SeNSeNSe^{2+} (ref. 15) and SNSNS^{2+} (ref. 13) (as the AsF_6^- salts) in which the calculated π-bond orders indicate negligible π bonding in the Se–Se (bond order 1.02) and S–S (bond order

0.96) bonds, although there is substantial π bonding in the Se–N and S–N regions. This may result in part from some lengthening of the chalcogen–chalcogen bond due to repulsion of the two adjacent positively charged chalcogen atoms. The average S–N distances in $\overline{\mathrm{SeNSNSe}}^{2+}$ (1.584 Å) and $\overline{\mathrm{SeNSNSe}}^{\bullet +}$ (1.559 Å) provide calculated* NSN bond angles of 111.2 [observed 107.7(5)] and 117.5° (observed 111.8°, average), respectively. The small differences between the calculated and observed values imply that both cations are not strained.

Cation–Anion Interactions in $\overline{\mathrm{SeNSNSe}}(\mathrm{AsF_6})_2$.—There are significant interionic interactions between the $\overline{\mathrm{SeNSNSe}}^{2+}$ cation and the fluorine atoms of the $\mathrm{AsF_6}^-$ anions. These are illustrated in Fig. 7 with the corresponding cation–anion contacts less than the sum of the appropriate isotropic van der Waals radii (Se $\cdots$ F 3.37, S $\cdots$ F 3.27 Å)[37] given in Table 7. There are short fluorine contacts to Se(1), Se(2) and S(1) which indicates that the dipositive charge is distributed over the selenium and the sulfur centres. There are no N $\cdots$ F contacts implying zero or negative charge on the nitrogen atoms. The number of significant Se $\cdots$ F and S $\cdots$ F contacts in the $\overline{\mathrm{SeNSNSe}}^{2+}$ cation are essentially the same as those in $(\overline{\mathrm{SeNSNSe}}^{\bullet +})_2$ but the contacts are shorter in the $\overline{\mathrm{SeNSNSe}}^{2+}$ cation consistent with its dipositive charge. The sum of the bond valences† for the M $\cdots$ F (M = Se or S) contacts for $\overline{\mathrm{SeNSNSe}}^{2+}$ are 0.62 [Se(1)], 0.69 [Se(2)], and 0.43 [S(1)], and the values for $\overline{\mathrm{SeNSNSe}}^{\bullet +}$ are 0.46 [Se(1)], 0.30 [Se(2)] and 0.29 [S(1)]. The bond valences are consistently higher in $\overline{\mathrm{SeNSNSe}}^{2+}$ than in $\overline{\mathrm{SeNSNSe}}^{\bullet +}$. The higher value for Se relative to S in both cations indicates that the positive charge is more localised on Se than on S, although the number and length of S $\cdots$ F contacts are similar.

The pattern of the cation–anion contacts in the $\overline{\mathrm{SeNSNSe}}^{2+}$ cation is very similar to those observed in $(\overline{\mathrm{SeNSNSe}})_2(\mathrm{AsF_6})_2$,[6] $\overline{\mathrm{SNSNS}}(\mathrm{AsF_6})_2$,[13] $\overline{\mathrm{SeNSeNSe}}(\mathrm{AsF_6})_2$,[15] and various salts of the dimeric $(\overline{\mathrm{SNSNS}}^{\bullet +})_2$ cation.[24] Most of the contacts in $\overline{\mathrm{SeNSNSe}}(\mathrm{AsF_6})_2$ are approximately perpendicular to or in the plane of the $\overline{\mathrm{SeNSNSe}}^{2+}$ ring as observed in the related compounds mentioned above (see Table 7). A discussion of this type of contacts has been given by Gillespie *et al.*[6,24] and a more detailed discussion of the related contacts in $\overline{\mathrm{SNSNS}}(\mathrm{AsF_6})_2$ will be given elsewhere.[13]

The $\mathrm{AsF_6}^-$ anions (see Table 6) are distorted and essentially of octahedral symmetry. There is no direct correlation between the strength of the interionic contacts and the relative As–F distances as was observed in $(\overline{\mathrm{SeNSNSe}})_2(\mathrm{AsF_6})_2$.[6]

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* The NSN bond angle (*S*) in degrees was calculated by the Banister equation[36] for cations [derived for $-\mathrm{S^{II}}-$ and $=\mathrm{S^{IV}}=$ compounds; $d(\mathrm{SN}) = 213.00 - 0.4861S$, where d(SN) is the observed bond distance in pm.

† The relative magnitudes of the bond valences[38] can be used to assess the strength of the M $\cdots$ F (M = Se or S) contacts. Bond valence (BV) in valence units (v.u.) is given by BV = $(R/R_0)^{-n}$, where R is the observed bond distance (Å), R_0 = 1.550, n = 3.8 for $\mathrm{S^{IV}}$–F; R_0 = 1.17, n = 4.0 for $\mathrm{Se^{IV}}$–F. The actual formal oxidation state of the S and Se is in fact not IV but between II and IV.

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