The Preparation, Characterization in Solution of the 7π Radical 1,2,4-Triseleno-3,5-diazolylium and the 6π (1,2,4-Triseleno-3,5-diazolium)$^{2+}$ Cations, and the *X*-Ray Crystal Structures of $(\overline{\text{SeNSeNSe}})_2(\text{AsF}_6)_2$ and $\overline{\text{SeNSeNSe}}(\text{AsF}_6)_2$ containing the First Stable Binary Selenium–Nitrogen Species

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$(\overline{\text{SeNSeNSe}})_n(\text{AsF}_6)_2$ (n = 1,2) containing the first stable binary selenium–nitrogen species, have been prepared by the reaction of stoicheiometric quantities of $\text{Se}_4(\text{AsF}_6)_2$ (n = 2) or AsF_5 (n = 1 and 2) with Se_4N_4 in liquid SO_2, and their structures determined by *X*-ray crystallography; in solution $(\overline{\text{SeNSeNSe}})_2(\text{AsF}_6)_2$ gives the indefinitely stable 7π radical $\overline{\text{SeNSeNSe}}^{+\bullet}$ (e.s.r. spectrum of frozen powder), and $\overline{\text{SeNSeNSe}}(\text{AsF}_6)_2$ the 6π $\overline{\text{SeNSeNSe}}^{2+}$ (Raman and ^{14}N n.m.r. spectra).

Numerous binary sulphur–nitrogen species have been prepared and structurally characterised[1] including NS^+,[2] SNS^+,[3] $(\overline{\text{SNSNS}})_2\text{N}^+$,[4] $\overline{\text{SNSNS}}^{+\bullet}$, $(\text{SNSNS}^{+\bullet})_2$, S_4N_3^+, $\text{S}_4\text{N}_4^{2+}$, S_4N_5^+, S_5N_5^+, S_2N_2, S_4N_2, S_4N_4, $(\text{SN})_x$, SSNS^-, SSSNS^-, S_3N_3^-, and S_4N_5^-. Analogous selenium–nitrogen compounds are restricted to Se_4N_4, which is even more thermodynamically and kinetically[5] unstable than S_4N_4 [$\Delta H_f^\circ(\text{S}_4\text{N}_4)$ 460 ± 8 kJ mol^{-1}; ΔH_f° (Se_4N_4) 682 ± 13 kJ mol^{-1}]. In contrast to neutral and anionic sulphur–nitrogen compounds, sulphur–nitrogen cations do not undergo explosive nitrogen elimination reactions (except S_4N_5^+). We therefore anticipated that selenium–nitrogen cations would also be thermally stable. The mixed sulphur–selenium–nitrogen cation $(\overline{\text{SeNSNSe}})_2(\text{AsF}_6)_2$ is known,[6] and on reaction with AsF_5 gives $\overline{\text{SeNSNSe}}(\text{AsF}_6)_2$.[7] Very surprisingly, we were able[7a] to assign e.s.r. powder spectra of frozen solutions of $\overline{\text{SeNSNSe}}(\text{AsF}_6)_2$ in liquid SO_2 or D_2SO_4 to $\overline{\text{SeNSNSe}}^{+\bullet}$ and $\overline{\text{SeNSeNSe}}^{+\bullet}$, as well as lesser amounts of $\overline{\text{SNSNS}}^{+\bullet}$! This motivated us to synthesise selenium–nitrogen cations on a preparative scale directly, including the radical cation $\overline{\text{SeNSeNSe}}^{+\bullet}$, $(\mathbf{3})^{+\bullet}$, and to clarify the e.s.r. results. The first selenium–nitrogen cation containing salts $(\overline{\text{SeNSeNSe}})_2(\text{AsF}_6)_2$ (**1**) and $\overline{\text{SeNSeNSe}}(\text{AsF}_6)_2$ (**2**) were subsequently prepared in high yield in liquid SO_2 solutions according to equations 1—4.

$$\text{Se}_4\text{N}_4 + \text{Se}_4(\text{AsF}_6)_2 \rightarrow \underset{(\mathbf{1})}{(\overline{\text{SeNSeNSe}})_2(\text{AsF}_6)_2} + 2\text{Se} \quad (1)$$

$$3\text{Se}_4\text{N}_4 + 6\text{AsF}_5 \rightarrow 2(\mathbf{1}) + 2\text{N}_2 + 2\text{AsF}_3 \quad (2)$$

$$(\mathbf{1}) + 3\text{AsF}_5 \rightarrow \underset{(\mathbf{2})}{2\overline{\text{SeNSeNSe}}(\text{AsF}_6)_2} + \text{AsF}_3 \quad (3)$$

$$3\text{Se}_4\text{N}_4 + 12\text{AsF}_5 \rightarrow 4(\mathbf{2}) + 2\text{N}_2 + 4\text{AsF}_3 \quad (4)$$

Highly crystalline (**1**) and (**2**) are both stable on grinding, on manipulation with a nickel spatula, and on heating during attempted melting point determinations. A solution of (**2**) in liquid AsF_3 maintained at 55 °C for 1 h did not lose N_2, and a solid sample maintained at 140 °C for 4 days *in vacuo* in a sealed tube, still contained some of the original compound (i.r.). These salts contain the first examples of stable binary selenium–nitrogen species and open up this area for exploration. Compound (**1**) also contains the indefinitely stable 7π

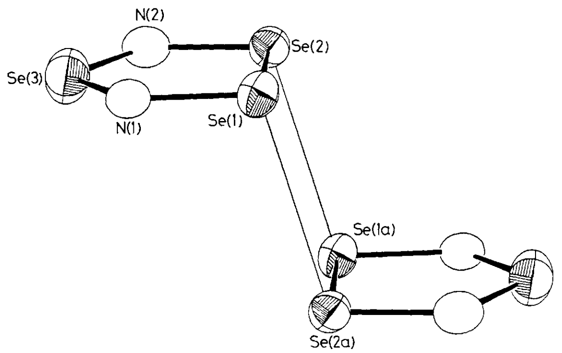


Figure 1. The structure of the two crystallographically unique centrosymmetric $[(\mathbf{3})^{+\cdot}]_2$ dimers in (**1**). Bond distances (Å) and angles (°) in $[(\mathbf{3})^{+\cdot}]_2$: the second value given in each case corresponds to that for the other independent dimer. Se(1)–Se(2) 2.398(3), 2.395(3); Se(1)–N(1) 1.761(15), 1.739(14); Se(3)–N(1) 1.691(15), 1.724(14); Se(3)–N(2) 1.688(14), 1.703(14); Se(2)–N(2) 1.759(14), 1.769(14); Se(1)–Se(2a) 3.123(3), 3.149(3). Se(1)–N(1)–Se(3) 120.8(8), 120.9(8); Se(2)–N(2)–Se(3) 120.6(8), 120.8(8); Se(1)–Se(2)–N(2) 95.6(5), 95.5(4); Se(2)–Se(1)–N(1) 95.2(5), 96.1(4); N(1)–Se(3)–N(2) 107.7(7), 106.7(7); N(1)–Se(1)–Se(2a) 106.6(5), 105.1(5); N(2)–Se(2)–Se(1a) 107.7(5), 105.6(5); Se(1)–Se(2)–Se(1a) 89.31(8), 89.13(8); Se(2)–Se(1)–Se(2a) 90.69(8), 90.87(8).

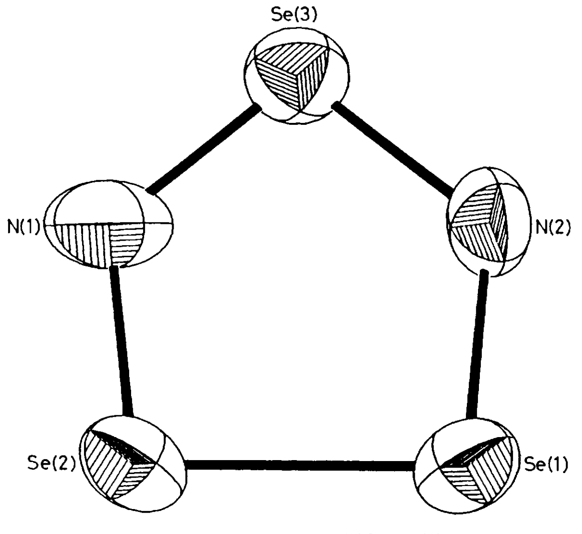
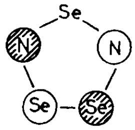


Figure 2. The structure of the 6π cation $(\mathbf{3})^{2+}$ in (**2**). Bond distances (Å) and angles (°) in $(\mathbf{3})^{2+}$: Se(1)–Se(2) 2.334(3), Se(1)–N(2) 1.734(21), Se(3)–N(2) 1.698(21), Se(3)–N(1) 1.689(18), Se(2)–N(1) 1.744(20); Se(1)–N(2)–Se(3) 122.3 (12), N(2)–Se(3)–N(1) 103.8(9), Se(3)–N(1)–Se(2) 122.7(10), N(1)–Se(2)–Se(1) 95.2(5), Se(2)–Se(1)–N(2) 95.8(7).

radical, $(\mathbf{3})^{+\cdot}$. However their synthesis depends on prior preparation of the potentially explosive Se_4N_4. This we have found to be accessible† in small amounts (*ca.* 1 g) in a slightly impure, rather than pure, state as the tendency to explode seems to increase with purity (*cf.* S_4N_4).[8]

The identities of (**1**) and (**2**) were confirmed by the determination of their *X*-ray crystal structures.‡ The $[(\mathbf{3})^{+\cdot}]_2$ and $(\mathbf{3})^{2+}$ cations are illustrated in Figures 1 and 2, respectively. The $[(\mathbf{3})^{+\cdot}]_2$ dication is very similar to those of the related $(\text{SeNSNSe}^{+\cdot})_2$ (ref. 6) and $(\text{SNSNS}^{+\cdot})_2$.[9] In both crystallographically different $[(\mathbf{3})^{+\cdot}]_2$ dimers, the 7π $(\mathbf{3})^{+\cdot}$ monomers are weakly linked, in a centrosymmetric *trans* arrangement, through the diselenium portions of each of the rings [2 × 3.123(3), 2 × 3.149(3) Å] by overlap of the selenium portions of the two singly occupied molecular orbitals (SOMO)(**A**), [by comparison with the SOMO of $\text{SNSNS}^{+\cdot}$ (refs. 7a, 10, 11)]. The bond distances within the 6π $(\mathbf{3})^{2+}$ cation are consistent with the removal of an electron from the 7π $(\mathbf{3})^{+\cdot}$ SOMO, (**A**). Thus the selenium–selenium distance and the adjacent selenium–nitrogen distances are all shorter in the dication [by 0.0625, and 0.018 Å (averages), respectively]. The Se–N bond distances in both cations are indicative[6] of significant 2pπ–4pπ bonding which is more pronounced in the dication.



(A)

The Raman spectrum of a solution of (**2**) in liquid AsF_3 at −10 °C was similar to that of the solid and only one resonance was present in the ^{14}N n.m.r. spectrum of an SO_2 solution at room temperature [$\delta(NO_2Me)$ −67.6 p.p.m., $\nu_{1/2}$ 200 Hz]. Thus $(\mathbf{3})^{2+}$ retains its ring structure in solution, in contrast to SNSNS^{2+}, which dissociates to NS^+ and SNS^+.[12]

The e.s.r. powder spectrum of frozen solutions of (**1**) and $(\text{SeNSNSe})_2(AsF_6)_2$ in liquid SO_2 show the presence of peaks attributable to $(\mathbf{3})^{+\cdot}$ and $\text{SeNSNSe}^{+\cdot}$, respectively (Figure 3). The spectra are similar, but not identical, as their SOMOs are very similar [see (**A**)]. These data agree with our reported[7a] results for $\text{SeNSNSe}^{+\cdot}$, but not $(\mathbf{3})^{+\cdot}$. We previously[7a] obtained e.s.r. spectra of frozen solutions of $(\text{SeNSNSe})_2(AsF_6)_2$, and assigned the spectrum to a mixture of $(\mathbf{3})^{+\cdot}$ and $\text{SeNSNSe}^{+\cdot}$ because of the splittings of the peaks in the low

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† Se_4N_4 was prepared by a slight modification of the published procedure.[14] $SeBr_4$ was prepared from Se (99%) (containing some sulphur) and Br_2 in CS_2. This was reacted with a large excess of liquid NH_3 in a Parr bomb. The resulting Se_4N_4 was dried with anhydrous EtOH and stored under dry CCl_4 in plastic containers. All the precautions outlined in refs. 14 and 15 were strictly observed. The resulting products consistently contained some $\text{SeNSNSe}^{+\cdot}$ or SeNSNSe^{2+} [$\delta(Me_2Se)$ 2412 p.p.m., $\nu_{1/2}$ = 11.8 Hz, −70 °C]. The relative amount decreased when 99.999% Se was used but the tendency for the purer Se_4N_4 to explode increased.

‡ *Crystal data* for (**1**): $(\text{SeNSeNSe})_2(AsF_6)_2$, M = 907.29, triclinic, space group $P\bar{1}$, a = 8.2132(15), b = 10.3249(15), c = 10.4519(13) Å, α = 82.384(11), β = 82.439(13), γ = 70.542(14)°, U = 824.7 Å^3, Z = 2, D_c = 3.66 Mg m^{-3}, $\mu(\text{Mo-}K_\alpha)$ = 8.64 mm^{-1}, crystal size 0.30 × 0.30 × 0.20 mm. Data were collected on an Enraf–Nonius CAD-4 automated diffractometer with graphite monochromated Mo-K_α radiation (λ = 0.71073 Å) using ω–2θ scans (2$\theta_{\text{max.}}$ of 50°), and were corrected for absorption.[16] The structure was solved by direct methods and refined by full-matrix least-squares[17] to residuals of R = 0.051, R_w = 0.064 (0.096, 0.076 including unobserved) for 1860 reflections [$I \geqslant 2.5\sigma(I)$] (2876 total) and 218 parameters. All atoms were assigned anisotropic thermal parameters. Scattering factors were taken from the International Tables for Crystallography[18] and corrected for anomalous dispersion.

For (**2**): $\text{SeNSeNSe}(AsF_6)_2$, M = 642.49, monoclinic, space group $C2$, a = 12.7989(15), b = 8.6837(9), c = 10.8132(10) Å, β = 91.467(9)°, U = 1201.4 Å^3, Z = 4, D_c = 3.55 Mg m^{-3}, $\mu(\text{Mo-}K_\alpha)$ = 14.69 mm^{-1}, crystal size 0.69 × 0.46 × 0.35 mm. Data collection, structural solutions, and refinement were carried out as described above. Residuals of R = 0.052, R_w = 0.062 (0.064, 0.065 including unobserved) for 935 reflections [$I \geqslant 2.5\sigma(I)$] (1125 total) and 173 parameters were obtained. All atoms were assigned anisotropic thermal parameters. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the University of Bonn. See Notice to Authors, Issue No. 1.

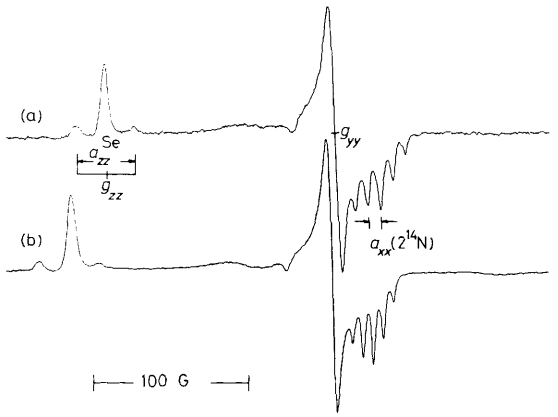

Figure 3. The *X*-band e.s.r. powder spectra, at −160 °C, of frozen solutions of (a) (**1**) and (b) ($\overline{\text{SeNSNSe}}$)$_2$(AsF$_6$)$_2$ in anhydrous liquid SO$_2$; *g* and hyperfine tensors for (**3**)$^{+\bullet}$, a_{xx} (2^{14}N) 9 (±0.2) G, g_{yy} 2.011 (±0.001), g_{zz} 2.123 (±0.001), a_{zz} (^{77}Se) 43 (±0.2) G, g_{iso} (22 °C) 2.043 (±0.001); for $\overline{\text{SeNSNSe}}^{+\bullet}$, a_{xx} (2^{14}N) 7.25 (±0.2) G, g_{yy} 2.011 (±0.001), g_{zz} 2.136 (±0.001), a_{zz} (^{77}Se) 43 (±0.2) G, g_{iso} (22 °C) 2.046 (±0.001).

field region. These results arose from the non-rigorously anhydrous conditions, and the assignments for (**3**)$^{+\bullet}$ (but not $\overline{\text{SeNSNSe}}^{+\bullet}$) were therefore erroneous.

Compound (**1**) was prepared as follows. SO$_2$ (7.05 g) was condensed onto a mixture of Se$_4$N$_4$ (0.60 g, 1.60 mmol) and Se$_4$(AsF$_6$)$_2$ (1.06 g, 1.53 mmol) at −78 °C.§ The mixture was stirred for 6 h, producing a red–brown solution over a dark brown solid. The solvent was removed, and the brown solid (1.63 g) finely ground in the Dri-lab, and placed on the glass frit of an extraction vessel[9b] joined to a two bulbed vessel incorporating a medium sintered glass frit. Continuous refluxing with liquid SO$_2$ for 3 days, followed by purification and removal of the solvent, led to a crystalline black extracted product (1.08 g) having a dark green appearance in reflected light, and a black powder (0.317 g, selenium) remaining on the frit. Elemental analysis for all elements fitted very well with the given formulation [recovered yield of (**1**) 78% based on Se$_4$(AsF$_6$)$_2$ and equation 1]. Compound (**1**) (0.494 g) was also prepared in high yield by the reaction of Se$_4$N$_4$ (0.28 g, 0.75 mmol) and AsF$_5$ (0.25 g, 1.45 mmol) in SO$_2$ (2.6 g) according to equation 2.

Compound (**2**) was prepared as follows. An excess of AsF$_5$ (1.58 g, 9.23 mmol) relative to that indicated in equation 4 was condensed onto Se$_4$N$_4$ (0.48 g, 1.3 mmol) in SO$_2$ (4.4 g) at −78 °C§ in a two bulbed vessel, producing a red-brown solution above yellow crystals after stirring for 6 h. The solution was transferred into the second bulb and the yellow crystals were washed twice with about 1 ml of SO$_2$. 0.73 g of highly crystalline yellow material were obtained from the less soluble fraction, and 0.62 g of yellow-brown solid from the more soluble fraction. Subsequent elemental analyses for all elements on the crystals fitted very well for (**2**). The ^{77}Se n.m.r. spectrum in SO$_2$ solution at −70 °C showed only one peak at δ (Me$_2$Se) 2434 p.p.m., $\nu_{1/2}$ 10.05 Hz. This is the highest ^{77}Se chemical shift so far recorded,[13] consistent with the depositive charge, and an aromatic 6π ring system. The presence of one, rather than the expected two, resonances for (**3**)$^{2+}$, and the absence of satellite peaks due to ^{77}Se–^{77}Se spin coupling suggest a rapid equilibrium as shown in equation 5. However, the Raman spectrum in AsF$_3$ at −10 °C showed only (**3**)$^{2+}$, and one resonance in the ^{14}N n.m.r. in SO$_2$ at room temperature. Therefore if equilibrium (5) does occur at room temperature and below, it must be very far to the left. Compound (**2**) (0.452 g) was also prepared by the oxidation of (**1**) (0.319 g, 0.70 mmol) by AsF$_5$ (0.42 g, 2.47 mmol) in SO$_2$ (2.88 g) as described in equation 3.

$$\overline{\text{SeNSeNSe}}^{2+} \rightleftharpoons \text{NSe}^{+} + \text{SeNSe}^{+} \qquad (5)$$

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References

1 H. G. Heal, 'The Inorganic Heterocyclic Chemistry of Sulphur, Nitrogen, and Phosphorus,' Academic Press Inc., London, 1980, and references therein; T. Chivers and R. T. Oakley, *Top. Curr. Chem.*, 1982, **102**, 117, and references therein; T. Chivers, *Acc. Chem. Res.*, 1984, **17**, 166, and references therein; R. Gleiter, *Angew. Chem., Int. Ed. Engl.*, 1981, 20, 444.
2 A. Apblett, A. J. Banister, D. Biron, A. G. Kendrick, J. Passmore, M. Schriver, and M. Stojanac, *Inorg. Chem.*, 1986, **25**, 4451, and references therein.
3 P. Johnson, J. Passmore, P. S. White, A. J. Banister, and A. G. Kendrick, *Acta Crystallogr., Sect. C*, 1987, **43**, 1651, and references therein.
4 G. K. MacLean, J. Passmore, and P. S. White, *J. Chem. Soc., Dalton Trans.*, 1984, 211.
5 W. Behrendt and U. W. Gerwarth, 'Gmelin Handbook of Inorganic Chemistry,' Se Suppl. vol. Bl, Springer-Verlag, 1981, p. 321, and references therein; C. K. Barker, A. W. Cordes, and J. L. Margrave, *J. Phys. Chem.*, 1965, **69**, 334.
6 R. J. Gillespie, J. P. Kent, and J. F. Sawyer, *Inorg. Chem.*, 1981, **20**, 4053, and references therein.
7 (a) E. Awere, J. Passmore, K. F. Preston, and L. H. Sutcliffe, *Can. J. Chem.*, 1988, **66**, 1776; (b) E. G. Awere, J. Passmore, and P. S. White, manuscript in preparation.
8 M. Villena-Blanco and W. L. Jolly, *Inorg. Synth.*, 1967, **9**, 98.
9 (a) A. J. Banister, H. G. Clarke, I. Rayment, and H. M. M. Shearer, *Inorg. Nucl. Chem. Lett.*, 1974, **10**, 647; (b) R. W. H. Small, A. J. Banister, and Z. V. Hauptman, *J. Chem. Soc., Dalton Trans.*, 1984, 1377; (c) R. J. Gillespie, J. P. Kent, and J. F. Sawyer, *Inorg. Chem.*, 1981, **20**, 3784, and references therein.
10 R. G. Gleiter, R. Bartetzko, and P. Hofmann, *Z. Naturforsch., Teil B*, 1980, **35**, 1166.
11 S. H. Fairhurst, K. F. Preston, and L. H. Sutcliffe, *Can. J. Chem.*, 1984, **62**, 1124.
12 J. Passmore and M. J. Schriver, *Inorg. Chem.*, 1988, **27**, 2749.
13 R. K. Harris and B. E. Mann, 'NMR and the Periodic Table,' Academic Press Inc., London, 1978, p. 402; M. J. Collins, R. J. Gillespie, J. F. Sawyer, and G. J. Schrobilgen, *Inorg. Chem.*, 1986, **25**, 2053, and references therein.
14 J. Jander and V. Doetsch, *Chem. Ber.*, 1960, **93**, 561,
15 H. Garcia-Fernandez, *Bull. Soc. Chim. Fr.*, 1973, 1210.
16 N. Walker and D. Stuart, *Acta Crystallogr., Sect. A*, 1983, **39**, 158.
17 E. J. Gabe, F. L. Lee, and Y. Le Page, 'The NRCVAX Crystal Structure System. In Crystallographic Computing 3: Data Collection, Structure Determination, Proteins and Databases,' eds. G. M. Sheldrick, C. Kruger, and R. Goddard, Clarendon Press, Oxford, 1985, pp. 167—174.
18 'International Tables for Crystallography,' vol. IV, Kynoch Press, Birmingham, 1974.

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§ We found that Se$_4$N$_4$ explodes violently on cooling with liquid nitrogen. Therefore, transfer of volatile materials was always carried out at −78 °C.