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## Reactivity of extended chalcogen–nitrogen π-systems: compounds Ar–Se–N=S=N–Se–Ar

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The reactions of Ar–Se–N=S=N–Se–Ar with SO<sub>2</sub>Cl<sub>2</sub> (as well as with ArSeCl and *p*-TolICl<sub>2</sub>) and H<sub>2</sub>O gave Ar–SeCl<sub>2</sub>–N=S=N–Se–Ar and  $[NH_4]^+[ArSeSO_3]^-$  (Se-Bunte salts), respectively, whose structures were confirmed by X-ray diffraction.

Currently, the electronic and molecular structures of oligomeric analogues of polymeric sulfur nitride  $(SN)_x$  (a molecular metal and low-temperature superconductor),<sup>1</sup> particularly Ar–X–N=S=N–X–Ar (X = S, Se),<sup>2</sup> receive much attention. The heteroatom reactivity of these extended chalcogen–nitrogen  $\pi$ -systems, expected to be high and varied, is less studied. For Ar–S–N=S=N–S–Ar, it is only known that they react with ArSCl to give [ArSNSNSN–Ar]+Cl<sup>-</sup> salts.<sup>3</sup>

We found that, in contrast to S congeners, compounds Ph–Se–N=S=N–Se–Ph 1 and PhSeCl afford Ph–SeCl<sub>2</sub>–N=S=N–Se–Ph 2 and PhSeSePh (Scheme 1).<sup>†</sup> The structure of 2 was elucidated by X-ray diffraction (XRD) as the *E*,*Z* configuration (Figure 1).<sup>‡</sup> The same product was also obtained with other

Thermal analysis in the range of 30-300 °C was performed in a helium atmosphere with a Hetzsch 409 PC/PG instrument equipped with a platinum pan; the heating rate was 10 °C min<sup>-1</sup>.

The IR spectra were measured in KBr pellets on a Bruker Vector 22 spectrometer; and the <sup>1</sup>H and <sup>19</sup>F NMR spectra, on Bruker AV-400 and Bruker AV-300 spectrometers, respectively, at frequencies of 400.13 and 282.4 MHz, respectively; the standards were TMS and  $C_6F_6$ .

Interaction between Ph-Se-N=S=N-Se-Ph 1 and  $SO_2Cl_2$ , p-TolICl<sub>2</sub> or PhSeCl. Compound Ph-SeCl<sub>2</sub>-N=S=N-Se-Ph 2:

(a) At 0 °C and under argon, a solution of SO<sub>2</sub>Cl<sub>2</sub> (120 mg, 0.8 mmol) in 5 ml of toluene was added dropwise to a stirred solution of  $1^2$  (315 mg, 0.8 mmol) in a mixture of 10 ml of hexane and 5 ml of toluene. The reaction mixture was stirred for additional 3 h at ambient temperature, and the precipitate was filtered off, washed twice with both solvents and dried *in vacuo*. Compound **2** was obtained in the form of yellow crystals in a yield of 262 mg (74%).

(b) At 0 °C and under argon, a solution of p-TolICl<sub>2</sub> (251 mg, 0.9 mmol) in 20 ml of toluene was added dropwise to a stirred solution of **1** (324 mg, 0.9 mmol) in a mixture of 20 ml of hexane and 2 ml of toluene. The reaction mixture was stirred overnight at ambient temperature, and the precipitate was filtered off, washed with hexane and dried *in vacuo*. Compound **2** was obtained in a yield of 152 mg (38%).



Scheme 1



**Figure 1** XRD (*a*) molecular and (*b*) crystal structures of compound **2**. Selected bond lengths (Å), bond and torsion angles (°): C–Se(*E*) 1.937(5), Se–Cl 2.3124(17) and 2.5177(17), Se–N 1.814(5), N–S 1.570(5), S–N 1.526(5), N–Se(*Z*) 1.863(5), Se(*Z*)–C 1.915(6); C–Se(*E*)–N 96.7(2), C–Se–Cl 91.10(17) and 89.41(16), Cl–Se–Cl 176.70(6), N–Se–Cl 91.21(17) and 91.97(17), Se–N–S 118.5(3), N–S–N 108.2(3), S–N–Se(*Z*) 117.7(3), N–Se–C 94.0(2); C–C–Se(*E*)–N 169.0(4), C–C–Se–Cl 77.6(4) and –99.1(4), Cl–Se–N–S 125.5(3) and –53.7(3), C–Se–N–S –143.3(3), Se–N–S–N –174.9(3), N–S–N–Se(*Z*) –2.6(4), S–N–Se–C –171.2(3), N–Se–C–C –113.4(5).

(c) At -10 °C and under argon, a solution of PhSeCl (300 mg, 1.6 mmol) in a mixture of 10 ml of hexane and 1 ml of toluene was added dropwise to a stirred solution of **1** (292 mg, 0.8 mmol) in a mixture of 20 ml of hexane and 2 ml of toluene. The precipitate was filtered off and recrystallized from toluene at low temperature. Compound **2** was obtained in a yield of 71 mg (16%).

For **2**:  $T_{decomp.}$  70 °C. <sup>1</sup>H NMR (toluene- $d_8$ )  $\delta$ : 7.47 (m, 2 H), 6.89 (m, 3 H). Found (%): Cl, 15.95; N, 6.40; S, 6.85. Calc. for C<sub>12</sub>H<sub>10</sub>Cl<sub>2</sub>N<sub>2</sub>SSe<sub>2</sub> (%): Cl, 16.00; N, 6.32; S, 7.24. The single crystals suitable to XRD were obtained by low-temperature crystallization from toluene.

*Hydrolysis of Ar–Se–N=S=N–Se–Ar. Typical procedure.* A solution of 0.1 mmol of Ar–Se–N=S=N–Se–Ar<sup>2</sup> in 2 ml of hexane was placed in one tube of an H-shaped Schlenk vessel, and 10 ml of water into another.

<sup>&</sup>lt;sup>†</sup> The ESI mass spectra were obtained with a Bruker Daltonik micrOTOF-Q hybrid quadrupole time-of-flight mass-spectrometer equipped with an electrospray ionization (ESI) source, for MeCN solutions with nitrogen as drying gas. ESI-MS conditions: negative scan in the range m/z 100–3000;  $V_{\rm cap} = 4000$  V; drying gas flow, 4 dm<sup>3</sup> min<sup>-1</sup> and temperature, 220 °C; nebylizer pressure, 1.0 bar. A small syringe pump was used for the introduction of solutions samples directly to spray chamber of the mass-spectrometer, flow rate was 3 µl min<sup>-1</sup>. In all cases, isotopic distributions in the experimental mass-spectra were in a good agreement with theoretical simulations.

chlorinating agents such as  $SO_2Cl_2$  and *p*-ToIICl<sub>2</sub>.<sup>†</sup> The highest isolated yield of **2**, 74% was achieved with  $SO_2Cl_2$ .

The Se(*E*) center of **2** possesses the geometry of a distorted trigonal bipyramid with the chlorine atoms in axial positions, which is typical of  $R_2$ SeHal<sub>2</sub> compounds.<sup>6</sup> In the crystal, the Se–Cl bonds have different lengths, and the Cl atom of the longer bond (2.518 Å) is involved in three shortened intermolecular contacts with one S and two Se atoms, whereas that of the shorter bond (2.312 Å) does not reveal such contacts (Figure 1).

Compound **2** is thermally unstable and produces PhSeCl upon heating in an individual state above  $70 \,^{\circ}$ C or boiling its toluene solution (Scheme 1).

In both hydrocarbon and fluorocarbon series, the hydrolysis of Ar–Se–N=S=N–Se–Ar in a hexane solution by water vapor at ambient temperature led to ammonium Se-arylselenosulfates  $[NH_4]^+[ArSeSO_3]^-$ **3–6** (Scheme 2),<sup>†</sup> whose structures were confirmed by XRD (Figure 2).<sup>‡</sup> In the IR spectra of the salts, bands at 1243–1234 and 1037–2025 cm<sup>-1</sup> can be assigned to the stretching modes of the SO<sub>3</sub> moiety, and those at 628–617 and 520–519 cm<sup>-1</sup>, to the deformation modes.<sup>7</sup>

S-Organylthiosulfates or Bunte salts,  $[Cat]^+[RSSO_3]^-$  (R = Alk, Ar), have found numerous applications in fundamental and applied chemistry.<sup>8</sup> Their Se-organyl congeners are much less studied,

 $[NH_4]^+[3-ClC_6H_4SeSO_3]^- 4$  was obtained in the form of white powder, yield 20%,  $T_{decomp.}$  140 °C. IR ( $\nu/cm^{-1}$ ): 3441 (m), 3179 (s), 3082 (s), 2912 (m), 1636 (w), 1566 (m), 1458 (m), 1398 (s), 1221 (vs), 1184 (vs), 1159 (s), 1105 (w), 1082 (w), 1065 (w), 1026 (vs), 993 (m), 891 (w), 795 (s), 756 (m), 685 (m), 638 (vs), 542 (w), 521 (m), 430 (w). Found (%): C, 24.94; H, 2.80; Cl, 12.25; N, 5.32; S, 11.34. Calc. for C<sub>6</sub>H<sub>8</sub>ClNO<sub>3</sub>SSe (%): C, 24.97; H, 2.79; Cl, 12.28; N, 4.85; S, 11.11.

 $[NH_4]^+[C_6F_5SeSO_3]^-$  **5** was obtained in the form of white needles suitable to XRD, yield 15%,  $T_{decomp}$  160 °C. MS, m/z: 326.863 (calc. for  $[C_6F_5O_3SSe]^-$ , 326.866). IR ( $\nu/cm^{-1}$ ): 3223 (s), 3102 (m), 2929 (w), 2879 (w), 2855 (w), 1634 (m), 1514 (s), 1486 (vs), 1428 (s), 1237 (s), 1195 (s), 1107 (m), 1088 (s), 1027 (vs), 974 (s), 825 (m), 628 (s), 520 (w). Found (%): C, 20.78; H, 1.24; F, 27.91; N, 4.29; S, 9.65. Calc. for  $C_6H_4F_5NO_3SE$  (%): C, 20.94; H, 1.17; F, 27.60; N, 4.07; S, 9.32.

[NH<sub>4</sub>]<sup>+</sup>[3-ClC<sub>6</sub>F<sub>4</sub>SeSO<sub>3</sub>]<sup>−</sup> **6** was obtained in the form of transparent colorless needles suitable to XRD, yield 28%,  $T_{decomp}$ . 160 °C. MS, m/z: 342.828 (calc. for [C<sub>6</sub>ClF<sub>4</sub>O<sub>3</sub>SSe]<sup>−</sup>, 342.836). <sup>1</sup>H NMR,  $\delta$ : 5.93. <sup>19</sup>F NMR,  $\delta$ : 60.2 (d, J 9.5 Hz), 43.6 (dd, J 25.1 and 6.1 Hz), 31.3 (dd, J 20.1 and 6.4 Hz), 1.3 (ddd, J 25.0, 20.2 ad 9.3 Hz). IR ( $\nu$ /cm<sup>-1</sup>): 3202 (s), 3096 (m), 3060 (m), 2877 (w), 2840 (w), 1615 (m), 1487 (vs), 1447 (vs), 1424 (s), 1234 (vs), 1198 (vs), 1079 (s), 1025 (vs), 909 (s), 761 (m), 719 (w), 627 (vs), 519 (w). Found (%): C, 19.98; H, 1.12; N, 3.84; Cl, 9.90; F, 20.76; S, 8.85. Calc. for C<sub>6</sub>H<sub>4</sub>ClF<sub>4</sub>NO<sub>3</sub>SSe (%): C, 19.99; H, 1.12; N, 3.88; Cl, 9.83; F, 21.08; S, 8.89.

Synthesis of salt 5. At 0 °C, a solution of  $(NH_4)_2SO_3 \cdot H_2O$  (445 mg, 3.3 mmol) in 5 ml of water was added to a stirred solution of  $C_6F_5SeBr^4$  (978 mg, 3 mmol) in 10 ml of CHCl<sub>3</sub>. After 15 min, the reaction system was filtered, and the white solid was washed with CHCl<sub>3</sub> (3×10 ml) on the filter and extracted with acetone (3×10 ml). The acetone solution was evaporated to dryness, and the residue was combined with that from evaporation of water part of the filtrate under reduced pressure. The combined crude product was extracted with MeCN (3×5 ml), the extract was filtered, and the mixture of 15 ml of toluene and 15 ml of hexane was added to the filtrate. The precipitate was filtered off, washed subsequently with toluene and hexane and dried *in vacuo*. Salt **5** was obtained in the form of shiny white crystals, 395 mg (40%).



Figure 2 XRD structures of salts (*a*) **5** and (*b*) **6** (disorder of the Cl atom over two positions<sup>‡</sup> is omitted). Selected bond lengths (Å) and bond angles (°): **5**: C–Se 1.913(9), Se–S 2.270(2), S–O 1.441(6), 1.458(6) and 1.464(6); C–Se–S 94.5(3), Se–S–O 102.6(3), 104.1(3) and 106.4(3), O–S–O 113.7(4), 114.1(4) and 114.5(4); **6**: C–Se 1.901(5), Se–S 2.2634(11), S–O 1.443(3), 1.453(3) and 1.455(3); C–Se–S 94.73(16), Se–S–O 102.31(14), 104.21(14) and 107.18(14), O–S–O 113.4(2), 113.8(2) and 114.6(2).

and for R = Ar only a few derivatives are described.<sup>9</sup> To the best of our knowledge, any polyfluorinated selenosulfate salts  $[Cat]^+[RSeSO_3]^-$  were unknown.

As compared with Se congeners, Ar–S–N=S=N–S–Ar derivatives<sup>2</sup> revealed enhanced stability toward water vapor under employed conditions<sup>†</sup> and were quantitatively recovered after eight weeks of exposing to the vapor. However, note that a few  $[NH_4]^+[ArSSO_3]^-$  salts together with Ar–S–N=S=N–S–Ar derivatives were isolated earlier as minor by-products after the aqueous acid decomposition of reaction mixtures produced by  $(SN)_4$  and ArMgHal, the main products were ArSSAr.<sup>10</sup> Taking into account that the hydrolysis conditions were very different, we believe that the discussed  $[NH_4]^+[ArSSO_3]^-$  salts<sup>10</sup> came from the hydrolysis of Ar–S–N=S=N–S–Ar during the workup of reaction mixtures.

For comparison, salt **5** was also prepared from  $C_6F_5SeBr$  and aqueous  $(NH_4)_2SO_3^{\dagger}$  by a modified approach,<sup>9(c)</sup> and its properties were identical to those of the salt obtained from the hydrolysis.

The salts  $[NH_4]^+[ArSeSO_3]^-$  are thermally unstable. For example, according to thermal analysis data, salt **5** decomposes

For **2**:  $C_{12}H_{10}Cl_2N_2SSe_2$ , M = 443.11, orthorhombic, space group *Pbca*, a = 8.4475(6), b = 8.5870(7) and c = 41.614(4) Å, V = 3018.6(4) Å<sup>3</sup>, Z = 8,  $d_{calc} = 1.950$  g cm<sup>-3</sup>,  $\mu = 5.378$  mm<sup>-1</sup>, F(000) = 1712, crystal dimensions  $0.01 \times 0.07 \times 0.30$  mm, 20101 reflections collected with  $1.0 < \theta < 28.8^{\circ}$ , 2806 [ $I > 2\sigma(I)$ ] used in structural analysis,  $R_1 = 0.0574$ ,  $wR_2 = 0.1135$ , S = 1.15.

For **5**: C<sub>6</sub>H<sub>4</sub>F<sub>5</sub>NO<sub>3</sub>SSe, M = 344.13, monoclinic, space group  $P_{2_1/c}$ , a = 4.8854(3), b = 31.846(2) and c = 6.6899(4) Å,  $\beta = 102.402(4)^\circ$ , V = 1016.53(11) Å<sup>3</sup>, Z = 4,  $d_{calc} = 2.249$  g cm<sup>-3</sup>,  $\mu = 3.970$  mm<sup>-1</sup>, F(000) = 664, crystal dimensions  $0.20 \times 0.20 \times 0.20$  mm, 4623 reflections collected with  $2.6 < \theta < 27.5^\circ$ , 2123 [ $I > 2\sigma(I)$ ] used in structural analysis,  $R_1 = 0.0722$ ,  $wR_2 = 0.1840$ , S = 1.03.

For **6**: C<sub>6</sub>H<sub>4</sub>CIF<sub>4</sub>NO<sub>3</sub>SSe, M = 360.58, monoclinic, space group  $P_{2_1}/c$ , a = 4.9135(2), b = 33.2112(14) and c = 6.7559(3) Å,  $\beta = 100.372(2)^\circ$ , V = 1084.44(8) Å<sup>3</sup>, Z = 4,  $d_{calc} = 2.209$  g cm<sup>-3</sup>,  $\mu = 3.952$  mm<sup>-1</sup>, F(000) = 696, crystal dimensions  $0.10 \times 0.10 \times 0.90$  mm, 19894 reflections collected with  $1.2 < \theta < 30.1^\circ$ , 2919 [ $I > 2\sigma(I)$ ] reflections used in structural analysis,  $R_1 = 0.0584$ ,  $wR_2 = 0.1205$ , S = 1.02. The Cl atom is disordered over the positions 3 and 5 of the ring with the occupation ratio 0.52:0.48. The disorder leads to enlarged thermal ellipsoids because of which the F atoms (when in one of these positions) can be refined only isotropically.

The data were collected on a Bruker Kappa Apex-II diffractometer using MoK $\alpha$  radiation ( $\lambda = 71.073$  pm) at 150 K. The structures were solved by direct methods using the SHELXL-97 program,<sup>5</sup> all non-hydrogen atoms were refined unisotropically unless otherwise indicated.

CCDC 835104–835106 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data\_request/cif. For details, see 'Notice to Authors', *Mendeleev Commun.*, Issue 1, 2011.

After 4 weeks at ambient temperature, crystals of  $[NH_4]^+[ArSeSO_3]^-$  appeared in the first tube were separated from solvent and dried *in vacuo*.

<sup>[</sup>NH<sub>4</sub>]<sup>+</sup>[C<sub>6</sub>H<sub>5</sub>SeSO<sub>3</sub>]<sup>−</sup> **3** was obtained in the form of small white scales not suitable to XRD, yield 75%,  $T_{decomp.}$  120 °C. MS, m/z: 236.901 (calc. for [C<sub>6</sub>H<sub>5</sub>O<sub>3</sub>SSe]<sup>−</sup>: 236.913). IR ( $\nu$ /cm<sup>−1</sup>): 3431 (s), 3177 (s), 3065 (s), 2928 (m), 2855 (m), 1630 (w), 1574 (w), 1476 (m), 1435 (s), 1304 (w), 1196 (vs), 1184 (vs), 1173 (vs), 1065 (w), 1028 (vs), 1016 (vs), 999 (m), 748 (s), 694 (m), 631 (vs), 528 (m), 469 (w). Found (%): C, 27.94; H, 3.53; N, 5.57; S, 12.57. Calc. for C<sub>6</sub>H<sub>9</sub>NO<sub>3</sub>SSe (%): C, 28.35; H, 3.57; N, 5.51; S, 12.62.

*X-ray diffraction data.* 

above 160 °C with the quantitative formation of  $C_6F_5SeSeC_6F_5$ , whose identity was confirmed by <sup>19</sup>F NMR spectroscopy. The salts are also unstable in solution at ambient temperature. For instance, an initially colorless solution of **6** in MeCN became yellow and released a precipitate of NH<sub>4</sub>HSO<sub>4</sub> (IR) after 20 h at ambient temperature; <sup>19</sup>F NMR spectroscopy revealed that the solution contained a 3:7 mixture of **6** and corresponding ArSeSeAr.

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