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Acyclic imidoselenium(II) dihalides: synthesis and X-ray structures of $ClSe[N(Bu^t)Se]_nCl$ (n = 1, 2)

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The reaction of $SeCl_2$ with *tert*-butylamine in THF yields the acyclic imidoselenium(II) dichlorides $ClSeN(Bu^t)NSeCl$ and $ClSeN(Bu^t)SeN(Bu^t)SeCl$, in addition to the six-membered ring $Se_3(NBu^t)_3$.

Numerous selenium–nitrogen (Se–N) compounds have been discovered in the past decade.[1–3] These include a number of nitride halides of Se(III) and Se(IV), *e.g.* the cyclic system $Se_3N_2Cl^+$,[4] the acyclic cations $N(SeCl)_2{}^+$ and $N(SeCl_2)_2{}^+$,[5,6] and the anion $N(SeCl_3)_2{}^-$.[7] Transient selenonitroso derivatives ArN=Se (Ar = 4-XC_6H_4, X = Br, Me; Ar = 2-XC_6H_4, X = SMe, SeMe) have been trapped as Diels–Alder adducts with dimethylbutadiene,[8] but oligomers of this unit [cyclic Se(II) imides] have not been described. The only known cyclic Se(II) imides, $Se_6(NBu^t)_2$ and $Se_9(NBu^t)_6$, contain Se–Se linkages.[9] We report here, the preparation and X-ray structures of $ClSe[N(Bu^t)Se]_nCl$ (**1**, n = 1; **2**, n = 2), the first two members of a homologous series of imidoselenium(II) dihalides, which represent a new class of SeN compounds, and $Se_3(NBu^t)_3$ **3**, the first cyclic oligomer of an SeNR unit. There are no sulfur or tellurium analogues of **1** and **2**.

The reaction of $SeCl_2$[10] with Bu^tNH_2 in a 2 : 3 molar ratio in THF at −80 °C yields a mixture of **1** and **2**,† in addition to the cyclic Se(II) imide **3**. The lower solubility of the imidoselenium(II) dihalides allows them to be isolated as red crystals by fractional crystallization. Both **1** and **2** are extremely moisture-sensitive and the crystals of **1** melt below room temperature. Compound **2** can be isolated in 34% yield when the reaction of $SeCl_2$ with Bu^tNH_2 is conducted in a 1 : 2 molar ratio. The identities of **1** and **2** were established by X-ray crystallography.

The X-ray analysis of **1**‡ revealed an acyclic ClSeNSeCl arrangement with planar geometry at the nitrogen atom [$\Sigma <$ N(1) = 359.7°] (Fig. 1). The two Cl substituents are in similar orientations above the SeNSe plane as indicated by the ClSeNSe torsion angles of 84.8(4) and −92.9(4)°. By contrast, the related Se(III) system $[ClSeNSeCl]^+$ is planar and both *cis,cis* and *cis,trans* isomers have been observed in the solid state.[5] Presumably the rotation of the Se–Cl bonds away from planarity in **1** minimises lone pair–lone pair repulsions between Se and N. The mean Se–N bond distance of 1.810 Å in **1** is slightly shorter than the value of 1.869 Å found for $Se[N(SiMe_3)_2]$[11] and the predicted Se(II)–N single bond value of 1.86 Å.[12] The mean Se–Cl bond length of 2.219 Å is, as expected, somewhat longer than the corresponding value of *ca.* 2.15 Å found for the cation $[ClSeNSeCl]^+$.[5]

An X-ray structural determination‡ showed that **2** consists of a U-shaped SeNSeNSe unit terminated by Cl atoms, which adopt very different orientations (Fig. 2). The torsion angles Cl(1)–Se(1)–N(1)–Se(3) and Cl(2)–Se(2)–N(2)–Se(3) are 83.0(2) and −116.5(1)°, respectively. The SeNSeNSe unit is distinctly non-planar with torsion angles of 40.8(2) and -69.4(2)° for Se(1)–N(1)–Se(3)–N(2) and N(1)–Se(3)–N(2)–Se(2), respectively. The marked difference in torsion angles is apparently reflected in a variation in the Se–N bond lengths. Those involving N(2) are almost equal, 1.803(3) and 1.822(3) Å, while the values for the two Se–N(1) bonds differ by 0.19 Å. The geometry at the nitrogen atoms is approximately planar [$\Sigma <$ N(1) = 355.2°, $\Sigma <$ N(2) = 357.0°]. The Se–Cl bond distances are 2.269(1) and 2.312(1) Å in **2** *cf.* 2.219 Å for **1**. Negative hyperconjugation [lp(N) $\rightarrow$ σ*(Se–Cl)] may contribute to a lengthening of the Se–Cl bonds.[5b]

The NMR data for **1** and **2** are consistent with their solid-state structures.† Single NBu^t environments are observed in both the ^1H and ^{13}C NMR spectra. The ^{77}Se NMR spectrum of **1** in toluene exhibits a singlet at δ 1854 and that of **2** shows two resonances at δ 1620 and 1613, which are assigned to NSeCl and NSeN, respectively, on the basis of their relative intensities.

The formation of **1** and **2** can be envisaged to occur *via* the intermediate $[Bu^tN(H)SeCl]$ **4** (Scheme 1). When the molar ratio $SeCl_2$:Bu^tNH_2 is increased to 1:3 a complex mixture of selenium(II) imides is produced, including the known cyclic systems $Se_6(NBu^t)_2$ and $Se_9(NBu^t)_6$[9] and a new SeN heterocycle $Se_3(NBu^t)_3$, **3**, which was isolated in *ca.* 10% yield as yellow crystals by fractional crystallization from *n*-hexane. An X-ray structural determination showed that **3** is a six-membered ring [|d(Se–N)| = 1.833 Å] in a chair conformation analogous

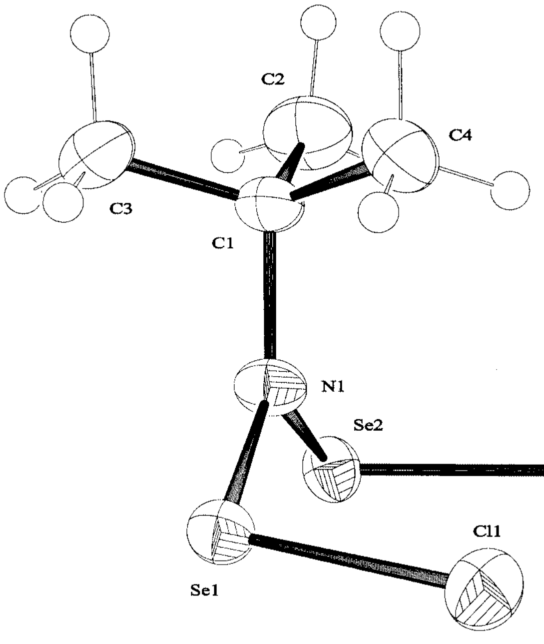

Fig. 1 ORTEP view (50% probability ellipsoids) of $ClSeN(Bu^t)SeCl$ **1**. Selected bond lengths (Å) and angles (°): Se(1)–N(1) 1.804(6), Se(2)–N(1) 1.816(7), Se(1)–Cl(1) 2.223(2), Se(2)–Cl(2) 2.215(2), N(1)–Se(1)–Cl(1) 103.9(2), N(1)–Se(2)–Cl(2) 103.8(2); C(1)–N(1)–Se(1) 119.9(5), C(1)–N(1)–Se(2) 123.1(5), Se(1)–N(1)–Se(2) 116.7(4).

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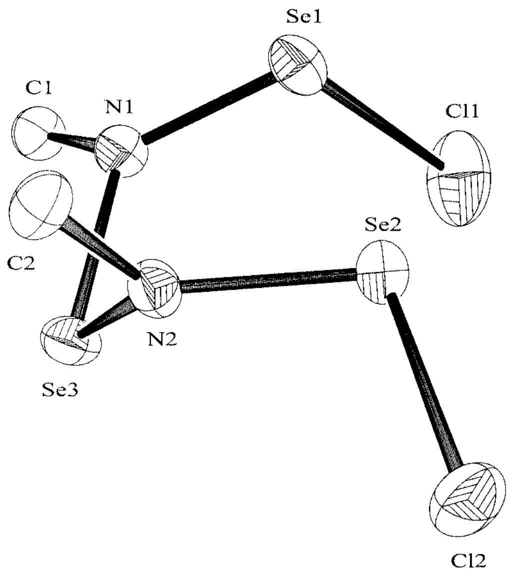
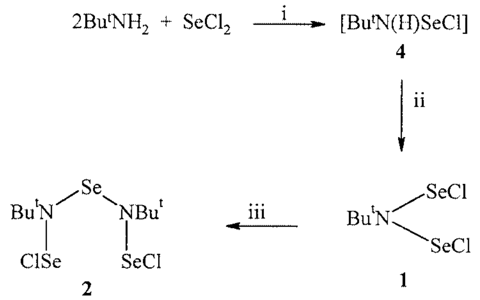


Fig. 2 ORTEP view (50% probability ellipsoids) of $ClSeN(Bu^t)SeN=(Bu^t)SeCl$ **2**. For clarity, only α-carbon atoms of Bu^t groups are shown. Selected bond lengths (Å) and angles (°): Se(1)–N(1) 1.758(3), Se(2)–N(2) 1.822(3), Se(3)–N(1) 1.948(3), Se(3)–N(2) 1.803(3), Se(1)–Cl(1) 2.269(1), Se(2)–Cl(2) 2.312(1); Cl(1)–Se(1)–N(1) 109.24(10), Cl(2)–Se(2)–N(2) 98.93(8), Se(1)–N(1)–Se(3) 118.03(14), Se(2)–N(2)–Se(3) 112.97(16), N(1)–Se(3)–N(2) 96.54(12).



Scheme 1 *Reagents and conditions*: i, $-[Bu^tNH_3]Cl$, THF, −80 °C; ii, $SeCl_2$, Bu^tNH_2, $-[Bu^tNH_3]Cl$, THF, −80 °C; iii, $3Bu^tNH_2$, $SeCl_2$, $-2[Bu^tNH_3]Cl$, THF, −80 °C.

to that of the tellurium analogue.[13] Details of this structure and our ^{77}Se NMR investigations of these systems will be given in a full account of this work.

In summary, we have isolated and structurally characterized the first two members of a novel class of Se(II)–N compound, the imidoselenium(II) dihalides, **1** and **2**, as well as the first example of a cyclic oligomer of a selenonitroso compound, **3**. The acyclic systems are potentially versatile reagents for the synthesis of Se(II)–N macrocycles, while **3** can be viewed as a tridentate Se(II) ligand.

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Notes and references

† A solution of $SeCl_2$ (15 mmol)[10] in THF (10 mL) was added to a solution of Bu^tNH_2 (2.2 mL, 22.5 mmol) in THF (40 mL) at −80 °C. The reaction mixture was stirred for 1 h at −80 °C and then for a further 1 h at 23 °C. The precipitate of $[Bu^tNH_3]Cl$ was removed by filtration and solvent was evaporated under vacuum to give a dark red oil. A hexane solution of this oil at −22 °C deposited X-ray quality dark red crystals of **1** and red crystals of **2**, which were separated manually. The total yield of **1** and **2** was estimated to be *ca.* 50% from the ^{77}Se NMR spectrum of the reaction mixture.

NMR characterization data: **1** δ (^{1}H) (C_7D_8, 25 °C) 1.10 [*s*, $C(CH_3)_3$]; δ (^{13}C) (C_7H_8, 25 °C) 74.1 $[\mathit{C}(CH_3)_3]$, 31.4 $[C(\mathit{C}H_3)_3]$; δ (^{77}Se) (C_7D_8, 25 °C) 1857 (NSeCl) (referenced to an external saturated solution of SeO_2 at 25 °C); chemical shifts are reported relative to Me_2Se(l) at 25 °C [δ(Me_2Se) = δ(SeO_2) + 1302.6].

2 δ (^{1}H) (C_7D_8, 25 °C) 1.16 [*s*, $C(CH_3)_3$]; δ (^{13}C) (C_7H_8, 25 °C) 26.8 $[C(\mathit{C}H_3)_3]$, not observed $[\mathit{C}(CH_3)_3]$; δ (^{77}Se) (C_7H_8, −30 °C) 1620 (NSeCl), 1613 (N*Se*N).

3 δ (^{1}H) (C_7D_8, 25 °C) 1.23 [*s*, $C(CH_3)_3$]; δ (^{13}C) [C_7H_8–C_7D_8 (4:1), 25 °C] 64.8 $[\mathit{C}(CH_3)_3]$, 30.7 $[C(\mathit{C}H_3)_3]$; δ (^{77}Se) [C_7H_8–C_7D_8 (4:1), 25 °C] 1396 (NSeN).

‡ *Crystal data*: for **1**: $C_4H_9Cl_2NSe_2$, M = 299.94, monoclinic, space group $P2_1/c$, a = 7.263(1), b = 10.282(1), c = 12.312(1) Å, β = 92.06(1)°, V = 918.8(2) Å^3, Z = 4, D_c = 2.168 g cm^{-3}, $F(000)$ = 568, μ = 8.553 mm^{-1}, T = 173 K, crystal dimensions 0.30 × 0.25 × 0.15 mm. Data were collected on a Nonius Kappa CCD diffractometer using graphite monochromated radiation (λ = 0.71073 Å). Total no. of reflections was 4419 of which 2076 had $I > 2.00\sigma(I)$. The structure was solved by direct methods[14a] and refined on F^2, R_1 = 0.0753, wR_2 = 0.1947.

For **2**: $C_8H_{18}Cl_2N_2Se_3$, M = 450.02, monoclinic, space group $P2_1/c$, a = 9.989(2), b = 9.643(2), c = 16.124(3) Å, β = 101.81(3)°, V = 1520.2(5) Å^3, Z = 4, D_c = 1.966 g cm^{-3}, $F(000)$ = 864, μ = 7.586 mm^{-1}, T = 173 K, crystal dimensions 0.20 × 0.10 × 0.10 mm. Data were collected on a Nonius Kappa CCD diffractometer using graphite monochromated Mo-Kα radiation (λ = 0.71073 Å). Total no. of reflections was 10 567 of which 2629 had $I > 2.00\sigma(I)$. The structure was solved by direct methods[14a] and refined on F^2,[14b] R_1 = 0.0262, wR_2 = 0.0792.

CCDC 182/1587. See http://www.rsc.org/suppdata/cc/b0/b001002m/ for crystallographic files in .cif format.

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