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Synthesis and Structure of a Stable Selenodiimide Complex

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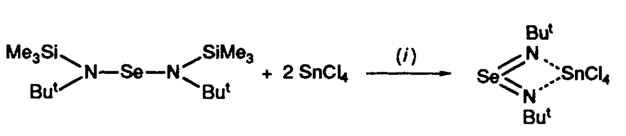
The stable selenodiimide complex $SnCl_4[(Bu^tN{=})_2Se]$ **1** has been prepared from $Se[NBu^t(SiMe_3)]_2$ and $SnCl_4$, and also by treating the unstable $(Bu^tN{=})_2Se$ (obtained from NBu^tH_2 and $SeCl_4$) with $SnCl_4$; the crystal structure of **1**·2thf indicates appreciable Se=N double-bond character [171.0(3) pm] but also shows that the selenium atom is unexpectedly co-ordinated by the two tetrahydrofuran (thf) oxygens.

The syntheses and properties of sulfodiimides have been investigated intensively in recent decades. These compounds proved to be versatile precursors for the synthesis of heterocyclics and preparation of metal complexes.[1–5] In contrast, little is known about the analogous selenium compounds,[6–9] the majority of which decompose at room temperature (selenodiimides with perfluorinated substituents are stable to higher temperatures). The thermolabile $(Me_3SiN{=})_2Se$[7] was used in the synthesis of the cyclophosphazaselenene $N(Ph_2P)_2N_2SeCl$.[10,11] Sharpless *et al.*[12] reported on selenodiimides as precursors in organic synthesis. To our knowledge there have been no structural investigations of selenodiimides or use of them as ligands in metal complexes. We have now found that $SnCl_4$ reacts with $Se[NBu^t(SiMe_3)]_2$[13] to yield $SnCl_4[(Bu^tN{=})_2Se]$ **1** (Scheme 1), which could be obtained as a yellow crystalline adduct **1**·2thf after recrystallisation from tetrahydrofuran (thf).* An alternative route to **1** is the preparation of the less-stable $(Bu^tN{=})_2Se$ from NBu^tH_2 and $SeCl_4$, followed immediately by the addition of $SnCl_4$ in CH_2Cl_2.*

Fig. 1 shows the structure of **1**·2thf.† It has a crystallographic two-fold axis passing through Se and Sn. The atoms Se, N(1), C(1), Sn, N(1′) and C(1′) are coplanar within 3 pm. The Se–N distance indicates appreciable double-bond character when compared with Pauling's Se–N single bond distance of 186 pm[16] or the prediction of 185 pm based on a recent version[17] of the Schomaker–Stevenson equation; a true Se=N double bond should be about 20 pm shorter,[16] *i.e. ca.* 165 pm. The much longer Se–N distances of 181.5(12)[18] in **2** and 179.1(4) pm[19] in **3** indicate that the selenodiimide resonance extreme only makes a minor contribution to these structures.



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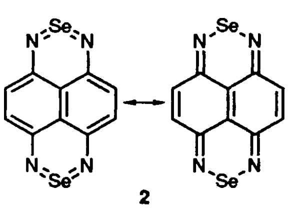
Scheme 1 (*i*) CH_2Cl_2, $-SnCl_2$, $-2SiMe_3Cl$



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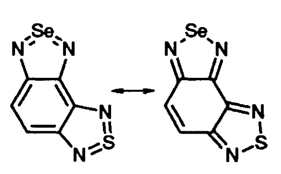

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A closer approximation to a N=Se=N description may apply when the selenium is bonded to an additional electronegative atom, *e.g.* as in $N(Ph_2P)_2N_2SeCl$ (average 173 pm)[10] or $[N(Ph_2P)(PhC)N_2Se]_2$ (174 pm).[11] Compound **1** may also be compared with the analogous sulfodiimide adduct $SnCl_4[(Me_3SiN{=})_2S]$[20] **4**, which crystallised from liquid SO_2 without solvent molecules. Compounds **1** and **4** show a symmetric (C_{2v}) distortion of the co-ordination octahedron at tin, with N–Sn–N angles of 66.5(2) and 62.6(2)°, respectively. The unusual interaction of the thf oxygens with selenium in **1**·2thf [266.8(3)

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* (*a*) To a solution of $Se[NBu^t(SiMe_3)]_2$ (2.16 g, 5.8 mmol) in CH_2Cl_2 (20 cm^3) was added $SnCl_4$ (3.03 g, 11.6 mmol) in CH_2Cl_2 (10 cm^3) at room temperature. After stirring for 3 d at room temperature a green solid (1.42 g) separated. It was dissolved in thf (500 cm^3) and the insoluble by-products filtered off. The solvent of the yellow solution was removed *in vacuo*. Yellow solid **1** (0.87 g, 31%) remained. The compound decomposes at 142 °C. (*b*) The compound $SeCl_4$ (0.55 g, 2.5 mmol) in diethyl ether (20 cm^3) was allowed to react with *tert*-butylamine (1.58 cm^3, 15 mmol) according to the literature method.[8] The solvent was removed *in vacuo* and the residue dissolved in CH_2Cl_2 (8 cm^3). To this solution was added dropwise $SnCl_4$ (0.65 g, 2.5 mmol) in CH_2Cl_2 (10 cm^3) at room temperature. Immediately a yellow solid was formed. It was filtered off, dissolved in thf (200 cm^3) and red by-products removed by filtration. After removing the solvent, 0.35 g (29%) of **1** remained, decomp. 141 °C. The NMR measurements were performed in $(CD_3)_2SO$, although rapid decomposition was observed: ^1H (reference $SiMe_4$), δ 1.57 (s); ^{119}Sn ($SnMe_4$), δ −501.6 (s); ^{77}Se ($SeMe_2$), δ 1392.0 (s). (Found: C, 20.1; H, 3.8; Cl, 29.3; N, 5.7; Se, 16.4. Calc. for $C_8H_{18}Cl_4N_2SeSn$: C, 19.95; H, 3.75; Cl, 29.5; N, 5.80; Se, 16.40%).

† *Crystal data.* $C_{16}H_{34}Cl_4N_2O_2SeSn$, $M = 625.8$, orthorhombic, space group *Pbcn*, $a = 1596.5(2)$, $b = 894.7(1)$, $c = 1743.2(2)$ pm, $U = 2.490$ nm^3, $Z = 4$, $D_c = 1.670$ Mg m^{-3}, $F(000) = 1248$; crystal dimensions, 0.35 × 0.31 × 0.27 mm. Data were collected at 153 K on a Stoe-Siemens-AED four-circle diffractometer using Mo-Kα radiation ($\lambda = 71.073$ pm). 2202 Reflections ($2\theta = 8$–50°) were measured, and a semiempirical absorption correction based on 349 ψ-scan data employed [μ(Mo-Kα) = 2.930 mm^{-1}, transmission 0.75–0.94]. The structure was solved by direct methods (SHELXS 90)[14] and refined by full-matrix least squares against F^2 (SHELXL 92)[15] to $R = 0.027$ [for 1776 $F > 4\sigma(F)$] and $wR_2 = \Sigma w(F_o^2 - F_c^2)^2/\Sigma wF_o^4 = 0.065$ (for all 2190 unique data). Weighting scheme used, $w = [\sigma^2(F_o^2) + (0.022p)^2 + 3.99p]^{-1}$ where $p = (F_o^2 + 2F_c^2)$ 13. Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

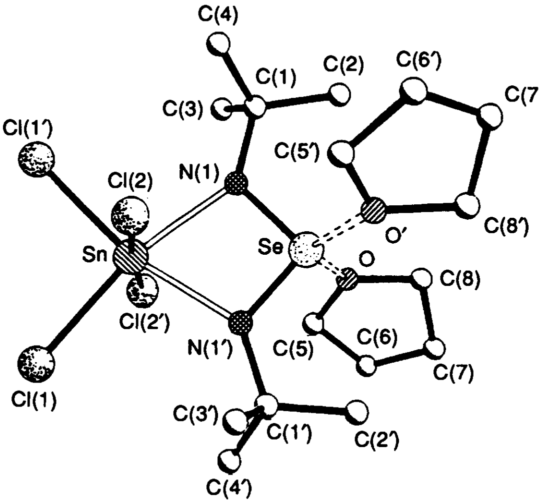

Fig. 1 Molecular structure of $SnCl_4[(Bu^tN=)_2Se]\cdot 2thf$ at 153 K in the crystal. Atoms generated by the crystallographic two-fold axis are indicated by primes; hydrogen atoms have been omitted for clarity. Selected bond lengths (pm) and angles (°): Se–N(1) 171.0(3), Sn–N(1) 225.8(3), Sn–Cl(1) 237.8(2), Sn–Cl(2) 240.0(2), N(1)–C(1) 150.0(4), Se···O 266.8(3); N(1)–Sn–N(1') 66.5(2), N(1)–Se–N(1') 92.8(2), O–Se–O' 139.7(2)

pm] suggests that the selenium is positively charged. The large O–Se–O' angle [139.7(2)°] indicates some stereochemical activity of the lone pair on selenium. The smaller N–Sn distances in **1** [225.8(3) pm] than in **4** [232.6(4) pm] also suggest that the $Se^+–N^-$ or $S^+–N^-$ resonance extreme is more important for the Se=N as opposed to the S=N bond. The appreciably smaller N(1)–Se–N(1') angle of **1** [92.8(2)°] than N–S–N in **4** [103.7(2)°] may be correlated with the thf adduct formation.

Acknowledgements

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