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A monomeric selenium(IV) diimide and a dimeric seleninylamine

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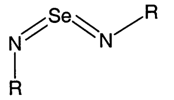
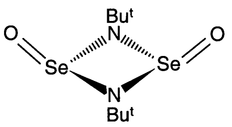
The selenium(IV) diimide AdN=Se=NAd (Ad = 1-adamantyl) adopts a monomeric structure with a *Z,E* configuration in the solid state whereas the seleninylamine OSe(μ-NBu^t)$_2$SeO crystallizes as the *cis*-dimer.

Selenium diimides RN=Se=NR, the aza analogues of SeO$_2$, are efficient *in situ* reagents for allylic amination of olefins and 1,2-diamination of 1,3-dienes.[1] Although the first example, Bu^{t}N=Se=NBu^t (**1a**) was reported more than 25 years ago[1] and the hybrid imido–oxo system Bu^{t}NSeO (**2**) has been known since 1986,[2] their solid-state structures have not been determined. Both of these imidoselenium(IV) compounds are thermally unstable oils. For example, Bu^{t}N=Se=NBu^t decomposes at room temperature to give the six-membered ring (SeNBu^t)$_3$ as the major product.[3] Multinuclear NMR studies of **1a** indicate a monomeric structure with a *Z,E* configuration in solution.[4] An *N,N′*-chelated adduct SnCl$_4$[(Bu^{t}N)$_2$Se] (THF)$_2$ has been structurally characterized.[5]



1a, R = Bu^t
1b, R = Ad



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Tellurium(IV) diimides adopt dimeric structures, *e.g.* Bu^{t}N-Te(μ-NBu^t)$_2$TeNBu^t,[6] whereas the extensively studied sulfur(IV) diimides RN=S=NR are invariably monomeric in the solid state, as well as in solution or in the gas phase.[7,8] DFT calculations on the model systems MeN=E=NMe (E = S, Se, Te) predict that the dimerization is highly exothermic for E = Te and endothermic for E = S, in agreement with experimental observations, but approximately thermoneutral for E = Se.[9] Consequently, it is not clear whether a monomeric or a dimeric structure will be preferred for selenium(IV) diimides. We describe here the syntheses † and X-ray structures ‡ of AdN=Se=NAd (**1b**, Ad = 1-adamantyl) and **2** representing the first solid-state structure determinations of (a) a selenium(IV) diimide and (b) a seleninylamine.

The new selenium(IV) diimide AdN=Se=NAd (**1b**) was obtained in 95% yield by the reaction of 1-adamantylamine with SeCl$_4$ in THF.† The adamantyl derivative **1b** is a moisture-sensitive, yellow crystalline solid, which decomposes at *ca.* 125 °C. An X-ray crystal structure analysis of **1b**§ revealed a monomeric structure with a *Z,E* configuration (Fig. 1), consistent with the conclusions from NMR studies of **1a**.[2] Furthermore the NMR parameters for THF solutions of **1b**, δ(^{14}N) = +110 and +1, δ(^{77}Se) = 1651 are in excellent agreement with those reported for **1a**, δ(^{14}N, THF) = +106.4 and +1.5, δ(^{77}Se, toluene) = 1654,[4] indicating that these two Se(IV) diimides have the same structure in solution. The Se=N bond lengths in **1b** are significantly different, 1.679(8) and 1.732(7) Å [*cf.* the predicted double bond value of *ca.* 1.65 Å[10] and *d*(SeN) = 1.710(3) Å in SnCl$_4$[(^{t}BuN)$_2$Se](THF)$_2$].[5] The longer bond is associated with a wider bond angle at nitrogen ∠ C(1)–N(1)–Se(1) = 125.0(6)° [*cf.* ∠ C(11)–N(2)–Se(1) = 117.6(5)°] suggesting that steric effects are responsible for this structural feature.

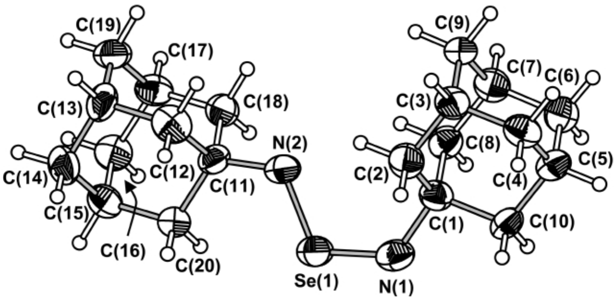

Fig. 1 Structure of AdN=Se=NAd (**1b**). Selected bond distances [Å] and bond angles [°]: Se(1)–N(1) 1.679(8), Se(1)–N(2) 1.732(7), N(1)–Se(1)–N(2) 113.0(3), C(1)–N(1)–Se(1) 125.0(6), C(11)–N(2)–Se(1) 117.6(5).

In contrast to the structure of **1b**, the seleninylamine **2** adopts a dimeric structure O=Se(μ-NBu^t)$_2$Se=O in which the two exocyclic oxo substituents are in a *cis* configuration (Fig. 2).§ The Se=O bond length of 1.621(2) Å is comparable to the value of 1.628(4) Å found for the unsymmetrical imido–oxo system *cis*-Bu^{t}NSe(μ-NBu^t)$_2$SeO.[3] The bridging Se–N bond lengths of 1.881(2) and 1.888(2) Å are slightly longer than the value of 1.86 Å predicted for Se(IV)–N single bonds,[10] but they are consistent with the bridging Se–N bonds of 1.862(4)–1.943(4) Å in *cis*-Bu^{t}NSe(μ-NBu^t)$_2$SeO.[3]

These results complete the solid-state structural characterization of the isoelectronic series SeO$_2$, Se(O)NR and Se(NR)$_2$. In contrast to the polymeric chain structure of SeO$_2$ (**3**),[11] the selenium(IV) diimides **1a** and **1b** are monomeric in the solid state and in solution, whereas the hybrid imido–oxo system **2** is dimeric.

Interestingly, the dimer *trans*-OSe(μ-O)$_2$SeO (**4**) has been identified in the vapour of selenium dioxide by a matrix IR study.[12] The sulfur analogues of **1**, **2** and **3** are all monomeric,[13]

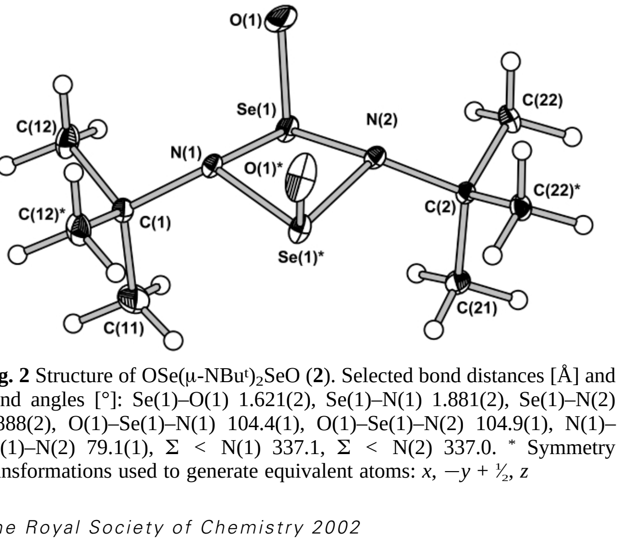

Fig. 2 Structure of OSe(μ-NBu^t)$_2$SeO (**2**). Selected bond distances [Å] and bond angles [°]: Se(1)–O(1) 1.621(2), Se(1)–N(1) 1.881(2), Se(1)–N(2) 1.888(2), O(1)–Se(1)–N(1) 104.4(1), O(1)–Se(1)–N(2) 104.9(1), N(1)–Se(1)–N(2) 79.1(1), Σ < N(1) 337.1, Σ < N(2) 337.0. * Symmetry transformations used to generate equivalent atoms: x, $-y + \frac{1}{2}$, z

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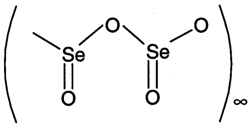

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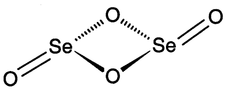

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whereas tellurium(IV) diimides are dimeric[6] and tellurium(IV) oxide is a three-dimensional polymer.[14]

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Notes and references

† All manipulations were carried out under anaerobic and anhydrous conditions. The seleninylamine **2** was prepared by the literature procedure[2] and recrystallized from THF at −20 °C. THF was dried and distilled under a nitrogen atmosphere over Na–benzophenone. 1-Adamantylamine (Aldrich) and $SeCl_4$ (Aldrich) were used without further purification.

The selenium diimide **1b** was obtained by adding dropwise a solution of 1-adamantylamine (2.723 g, 18.0 mmol) in THF (15 mL) to a solution of $SeCl_4$ (0.662 g, 3.0 mmol) in THF (30 mL) at −80 °C. The reaction mixture was stirred at −78 °C for 45 min and then allowed to warm up to room temperature. After 30 min the white precipitate of $[C_{10}H_{15}NH_3]Cl$ was removed by filtration and the solvent was removed under vacuum to give yellow microcrystalline **1b** (1.076 g, 2.85 mmol, 95%) [mp 125 °C (dec.) with sublimation]. X-Ray quality crystals were grown from THF solution at −24 °C. ^{14}N NMR (d_8-THF, 25 °C): δ = +110 and 1 ppm; ^{77}Se NMR (toluene, 25 °C): δ = 1651 ppm. ^{14}N and ^{77}Se NMR spectra were recorded on a Bruker DPX-400 spectrometer operating at 28.915 and 76.311 MHz, respectively. The spectral widths were 14.49 and 90.09 kHz, yielding the respective resolutions of 14.15 and 1.37 Hz/data point. The ^{14}N pulse width was 12 µs and the ^{77}Se pulse width was 6.7 µs, corresponding to nuclear tip angles of 21 and 46°. The ^{14}N chemical shifts are reported relative to CH_3NO_2(l) at 25 °C. The ^{77}Se NMR spectrum is referenced externally to a saturated aqueous solution of SeO_2 and the chemical shifts are reported relative to neat Me_2Se(l) at 25 °C [$\delta(Me_2Se) = \delta(SeO_2) + 1302.6$].

‡ Diffraction data of **1b** and **2** were collected on a Nonius Kappa CCD diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) and recording 360 frames *via* φ-rotation ($\Delta\varphi$ = 1°; two times 40 s per frame). The data were corrected for Lorentz and polarization effects, and an empirical absorption correction was applied to the net intensities. The structure was solved by direct methods[15a] and refined on F^2.[15b] The calculated hydrogen atoms were included in the final refinement (methyl groups: C–H = 0.98 Å; methylene groups: C–H = 0.99 Å; tertiary carbon: C–H = 1.00 Å). The scattering factors for the neutral atoms were those incorporated with the programs.

§ Crystal data for **1b**: $C_{20}H_{30}N_2Se$, M = 377.42, yellow plates (0.20 × 0.20 × 0.12 mm³), monoclinic, space group $P2_1/c$, a = 10.986(2), b = 6.624(1), c = 25.059(5) Å, β = 99.69(3)°, V = 1797.6(6) Å³, Z = 4, ρ calc. = 1.395 g cm^{-3}, $\mu(MoK_\alpha)$ = 2.091 mm^{-1}, $\lambda(MoK_\alpha)$ = 0.71073 Å, T = −100(2) °C, $F(000)$ = 792. Total no. of reflections was 14846 (2321 unique). R_1 = 0.0765 and wR_2 = 0.1669 [1735 reflections with $F_o > 4\sigma(F_o)$] (R_1 = 0.1076 and wR_2 = 0.1839 all data); $w = [\sigma(F_o^2) + (0.0504P)^2 + 11.65P]^{-1}$, where $P = \max[(F_o^2, 0) + 2F_c^2]/3$. S = 1.167 for 209 parameters. Maximum and minimum values in the final difference Fourier synthesis are 0.710 and −0.648 e Å^{-3}.

Crystal data for **2**: C_4H_9NOSe, M = 166.08, yellow block (0.30 × 0.15 × 0.10 mm), orthorhombic, space group $Pnma$, a = 19.517(4), b = 11.499(2), c = 5.672(1) Å, V = 1273.0(4) Å³, Z = 8, ρ calc. = 1.733 g cm^{-3}, $\mu(MoK_\alpha)$ = 5.790 mm^{-1}, $\lambda(MoK_\alpha)$ = 0.71073 Å, T = −153(2) °C, $F(000)$ = 656. Total no. of reflections was 15441 (1608 unique). R_1 = 0.0360, wR_2 = 0.0826 [1404 reflections with $F_o > 4\sigma(F_o)$] (R_1 = 0.0439 and wR_2 = 0.0861 all data); $w = [\sigma(F_o^2) + (0.0395P)^2 + 1.82P]^{-1}$, where $P = \max[(F_o^2, 0) + 2F_c^2]/3$. S = 1.102 for 78 parameters. Maximum and minimum values in the final difference Fourier synthesis are 0.666 and −0.904 e Å^{-3}.

CCDC reference numbers 189238 (**1b**) and 189239 (**2**). See http://www.rsc.org/suppdata/cc/b2/b205011k/ for crystallographic data in CIF or other electronic format.

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