

Preparation and crystal structure of a new tetracoordinated cyclic selenurane with two unsymmetrical apical ligands of oxygen and selenium: transannular hypercoordination between oxy- and diseleno-groups

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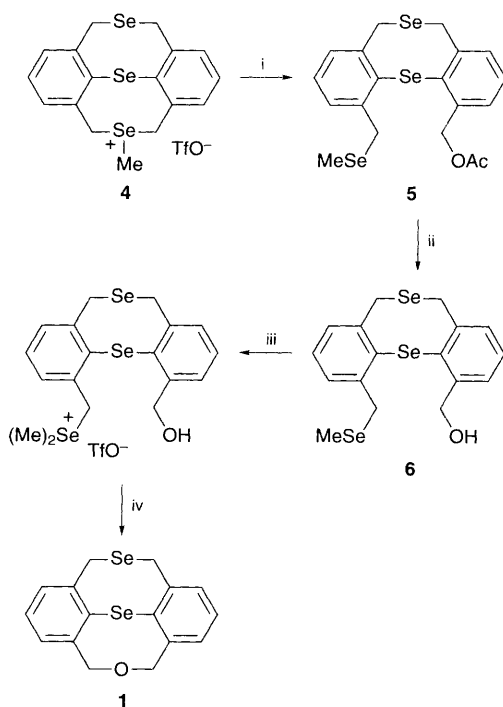
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The reaction of a selenoxide **2** of 1,11-(methanoxomethano)-5*H*,7*H*-dibenzo[*b,g*][1,5]-diselenocine **1** with triflic anhydride gives a new selenurane dication salt **3** with two unsymmetrical apical oxy- and seleno-ligands, *i.e.* the chair form of **2** is changed to the boat form of **3** by the three centre transannular interaction between the oxygen and the two selenium atoms.

Although we have reported that the transannular interaction between two heteroatoms of selenium heterocycles provides a hypervalent species, such behaviour by fourth-row elements and multiheteroatoms has not received much attention.¹ We have now found that the three centre transannular interaction between the oxygen and the two selenium atoms of a new oxidiselenocine, 1,11-(methanoxomethano)-5*H*,7*H*-dibenzo[*b,g*][1,5]diselenocine **1**, produced an isolable selenurane dication **3** which consists of two unsymmetrical apical chalcogeno ligands of oxy- and seleno-groups. Generally, hypervalent selenuranes have two symmetrical electronegative groups such as halogen atoms or hydroxy or carboxyl groups at the apical positions.² Here we report the preparation and crystal structure of a new cyclic selenurane dication **3**.

The new oxidiselenocine **1** was prepared from selenonium salt **4**³ (Scheme 1).[†]

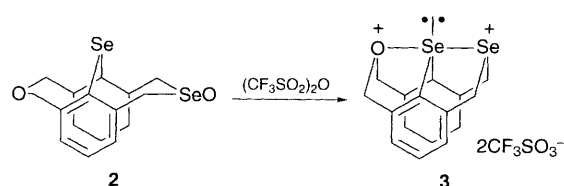


Scheme 1 Reagents: i, AcONa; ii, aq. KOH; iii, MeOTf, iv, aq. KOH

With regard to the conformational properties of **1**, for eight-membered rings two different conformers, (chair- and boat-forms) exist.⁴ The conformers can be assigned by the ¹H NMR spectral data of the benzylic methylene protons of the eight-membered ring. The ¹H NMR spectrum of **1** in CDCl₃ at 25 °C exhibits the benzylic methylene protons as an AB quartet absorptions at δ 3.81, 5.52 (*J* = 13.0 Hz) and δ 4.87, 5.79 (*J* = 12.3 Hz), which were assigned to the twin-chair form. The ¹H NMR spectra of **1** do not change over the temperature range from –50 (in CDCl₃) to +180 °C in Me₂SO-²H₆ indicating that **1** is conformationally rigid. Analogously, the conformation of the selenoxide **2** obtained from oxidation of **1** with MCPBA is a twin-chair form as evidenced from the ¹H NMR spectral data.[†]

Treatment of the selenoxide **2** with triflic anhydride [(CF₃SO₂)₂O, Tf₂O] (1 equiv.) in anhydrous CHCl₃ under an Ar atmosphere at room temperature resulted in the formation of the selenurane dication salt **3** (98%) (Scheme 2).[†] This reaction may proceed through the initial formation of the trifloxy-selenonium cation, which subsequently would be converted into **3** by a stepwise transannular substitution of each seleno- and oxy-group. The conformation of **3** in CD₃CN is a twin-boat form, *i.e.* the benzylic methylene protons appear at δ 5.11, 5.73 (ABq, *J* = 15.9 Hz) and δ 5.27, 5.57 (ABq, *J* = 16.1 Hz). The ¹H-coupled ⁷⁷Se NMR spectrum of **3** in CD₃CN shows two resonances at δ 636.6 (t, *J*_{SeH} = 34.3 Hz, SeCH₂) and at δ 890.7 (s, SeAr); the former resonance is assigned to the selenonium cation and the latter peak to the selenurane structure.^{2,5}

The crystal structure of the new selenurane dication **3** was determined by X-ray diffraction (Fig. 1).[‡] The X-ray analysis clearly revealed that the conformation of **3** was fixed as a twin-boat form by a three-centre transannular bond between the oxygen and the two selenium atoms, although normally the chair conformer has been shown to be more stable and rigid than the boat conformer.⁴ The bond length of Se(1)–Se(2) is 2.3865(7) Å which is only slightly longer than the normal Se–Se single bond (2.34 Å) in diselenides.² The transannular O...Se(1) contact is 2.427(4) Å which is remarkably shorter than the sum of the van der Waals radii (3.4 Å) of the two elements. The O–Se(1)–Se(2) bond angle of 164.97(9)° is roughly collinear, and the Ceq–Se(1)–Ceq bond angle is 96.8(2)°. Thus, the configuration about the selenium atom is distorted trigonal bipyramidal with two apical O–Se and Se–Se bonds, two equatorial Se–C bonds, and the lone-pair electrons considered to occupy the third equatorial position. These structural features are consistent



Scheme 2

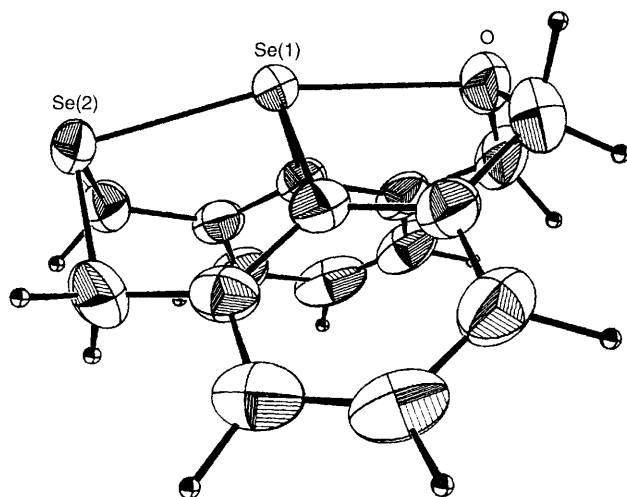


Fig. 1 The crystal structure of selenurane **3**. For clarity, the triflate anions are omitted.

with a selenurane structure. This is the first example of transannular hypercoordination between oxy- and diseleno-groups.

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Footnotes

† Selected physical and spectroscopic data for **1**: mp 209.5–210.5 °C; ^1H NMR (CDCl_3) δ 3.81, 5.52 (ABq, $J = 13.0$ Hz, 4 H, CH_2Se), 4.87, 5.79 (ABq, $J = 12.3$ Hz, 4 H, CH_2O) and 7.06–7.17 (m, 6 H, ArH); ^{13}C NMR (CDCl_3) δ 32.3, 79.7, 128.3, 128.9, 129.9, 136.0, 145.9 and 148.4; ^{77}Se

NMR (CDCl_3) δ 200.6 (SeAr) and 372.4 (t, $J_{\text{SeH}} = 33.0$ Hz, SeCH_2Ar); MS m/z 382 (M^+). For **2**: mp 174–175 °C (decomp); ^1H NMR (CDCl_3) δ 4.16, 6.11 (ABq, $J = 11.3$ Hz, 4 H, CH_2Se), 4.90, 5.77 (ABq, $J = 12.6$ Hz, 4 H, CH_2O), 7.20 (d, $J = 7.4$ Hz, 2 H, ArH), 7.27 (t, $J = 7.4$ Hz, 2 H, ArH) and 7.36 (d, $J = 7.4$ Hz, 2 H, ArH); ^{13}C NMR (CDCl_3) δ 61.1, 79.4, 130.5, 130.6, 130.9, 136.4, 138.3 and 146.6; ^{77}Se NMR (CDCl_3) δ 223.0 (SeAr) and 943.9 (Se CH_2Ar). For **3**: mp 240 °C (decomp); ^1H NMR (CD_3CN) δ 5.11, 5.73 (ABq, $J = 15.9$ Hz, 4 H, CH_2O), 5.27, 5.57 (ABq, $J = 16.1$ Hz, 4 H, CH_2Se), 7.41 (d, $J = 7.7$ Hz, 2 H, ArH), 7.56 (d, $J = 7.7$ Hz, 2 H, ArH) and 7.72 (t, $J = 7.7$ Hz, 2 H, ArH); ^{13}C NMR (CD_3CN) δ 50.7, 76.9, 128.0, 130.2, 130.5, 134.6, 139.7 and 141.0; ^{77}Se NMR (CD_3CN) δ 636.6 (t, $J_{\text{SeH}} = 34.3$ Hz, SeCH_2Ar) and 890.7 (s, SeAr).

‡ Crystal data for the selenurane dication salt **3**: $\text{C}_{18}\text{H}_{14}\text{Se}_2\text{F}_6\text{O}_7\text{S}_2$, monoclinic, space group $P2_1/a$, $a = 8.752(1)$, $b = 12.402(1)$, $c = 21.227(2)$ Å, $\beta = 96.10(1)^\circ$, $V = 2291.1$ Å 3 , $Z = 4$, $D = 1.97$ g cm $^{-3}$, Mo-K α radiation ($\lambda = 0.71073$ Å), CAD4 diffractometer, 3759 with $I > 3\sigma(I)$. The structure was solved by direct methods and refined anisotropically by full-matrix least-squares using the MolEN program package. The final R value was 0.043. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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