A STRUCTURAL COMPARISON OF ORGANOTERMINATED SELENIDE, DISELENIDE, AND TRISELENIDE

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GRAPHICAL ABSTRACT

Abstract A series of organosubstituted mono-, di-, and triselenides has been prepared and structurally characterized. In this series, a novel modification of 1,2,3-triseleno-[3]ferrocenophane has been obtained in which intermolecular contacts between the central selenium atoms are below the sum of the van der Waals radii. Moreover, dimesitylselenide has been structurally characterized.

Keywords Selenium; ferrocenophane; closed shell interaction; crystal structure

INTRODUCTION

During the Xerox process, light-induced charge separation in amorphous Se/Te alloys takes place. However, undesired residual charges may persist after exposure to light which
may be due to formation of chalcogenonium cations and chalcogenolate anions in the solid state (valence-alternation-model).\textsuperscript{1,2} In an alternative model, the collapse of such polar defects in Se/Te alloys has been proposed, which involves the interaction of persistent “onium” and “ate” functionalities in a nonclassical way.\textsuperscript{3} Also in the solid state structures of the elemental forms of $\alpha$-selenium and $\alpha$-tellurium, short contacts between atoms of different spiral chains are observed, which are well below the van der Waals radii of the atoms involved and may suggest closed shell interactions. Based on our previous work in organoselenium chemistry,\textsuperscript{4–7} we encountered structures of some organic and organometallic selenides in which similar interactions may or may not take place depending on the substituents and the geometry imposed by the latter. Here, we would like to report the solid state structures of a new modification of 1,2,3-triseleno[3]-ferrocenophane in comparison to that of dimesitylselenide co-crystallized with dimesitylselenide.

**RESULTS AND DISCUSSION**

1,2,3-Triseleno-[3]ferrocenophane I has been prepared by oxidation of dilithioferrocene with gray selenium following a published procedure.\textsuperscript{8} The analytical and spectroscopic data are in good agreement with the literature. Crystals of I have been obtained by slow evaporation of a heptane solution at room temperature. According to single crystal X-ray diffraction studies at 92 K, 1,2,3-triseleno[3]ferrocenophane I crystallizes in the monoclinic space group $P2_1/c$. A crystal structure of the same compound has been previously described in an orthorhombic modification (I$_{\text{ort}}$), which in fact shows a markedly different packing in the unit cell.\textsuperscript{9,10} In the molecular structure of I (Fig. 1), the Se–Se distance is close to 2.33 Å (Table 1) while the Se–C contacts differ slightly (Se(1)–C(11) 1.888(6) and Se(3)–C(31) 1.904(6) Å). The corresponding Se–Se–Se and C–Se–Se angles are close to 100° while the dihedral angles characterizing the folding of the bridging

![Figure 1](image-url) ORTEP plot of the molecular structure of I. Thermal ellipsoids are drawn at 50% probability level. The H atoms are drawn with arbitrary radii.
Table 1 Relevant distances [Å] and angles [°] in the crystal structures of 1 and I_{ort} for comparison

|                  | 1     | I_{ort} |
|------------------|-------|---------|
| Se(1)–C(11)     | 1.888 (6) | 1.907 (7) |
| Se(1)–Se(2)     | 2.3289 (10) | 2.3220 (14) |
| Se(2)–Se(3)     | 2.3347 (11) | 2.3323 (13) |
| Se(3)–C(31)     | 1.904 (6) | 1.893 (7) |
| C(11)–Se(1)–Se(2) | 99.08 (19) | 98.9 (2) |
| Se(1)–Se(2)–Se(3) | 100.06 (4) | 100.68 (4) |
| C(31)–Se(3)–Se(2) | 98.9 (2) | 99.0 (23) |
| C(11)–Se(1)–Se(2)–Se(3) | 73.6 (2) | 75.3 (2) |
| Se(1)–Se(2)–Se(3)–C(31) | −74.0 (2) | −72.7 (2) |

triselenane-unit approach ±74° (Table 1). These geometric parameters are slightly different compared to open chain triselenanes but quite similar to those obtained for the orthorhombic modification (I_{ort}) of the same compound (Table 1). A substantial difference in the crystal structures of 1 and I_{ort} is, however, the short intermolecular Se2...Se2 distance in 1 (Fig. 2), which is as low as 3.6348(13) Å and compares to 5.0816(21) Å in orthorhombic I_{ort}. The Se2...Se2 distances in 1 are well below the sum of the van der Waals radii of the respective atoms, which is 3.8 Å but longer than the interchain distances of 3.44 Å in α-selenium. A similar intermolecular Se...Se contact has been observed for [Fe(C5H4S)2Se] with 3.639(1) Å, which also crystallizes in the monoclinic space group P2_1/c.8 Obviously the different crystal symmetry allows a closer intermolecular contact between the respective functionalities. Even more pronounced structural effects have been observed for intermolecular Se...Te and Te...Te contacts.12,13 Such structural peculiarities have been interpreted as indicators for secondary bonding interactions,14,15 but even without closed shell interaction, the proximity of intermolecular Se-chains may affect the tendency for interaction or charge separation upon irradiation related to those occurring in the Xerox process.

When monofunctional organometallic compounds of the type R–M (M = Li, MgBr) are allowed to react with elemental selenium, related organoselenides of the type R₂Seₙ can
be expected besides R–SeM. We have performed this reaction starting from MesMgBr (Mes = 2,4,6-trimethylphenyl) and elemental selenium. Besides the primary insertion product, Mes–SeMgBr, the corresponding neutral mono- and diselenides 2 and 3 have been obtained. Although both compounds have been described in the literature before, monoselenide 3 has not been structurally characterized so far. Upon extraction of the reaction products with unpolar solvents, 2 and 3 can be separated from magnesium selenides. Protonation of the crude reaction mixture with aqueous hydrochloric acid reveals the formation of Mes₂Se₂ (2), Mes₂Se (3), and MesSeH (4) in the relative ratio 1:1:2 according to ⁷⁷Se NMR. Recrystallization from toluene gave crystals of co-crystallized 2 and 3 (Fig. 3). According to single crystal X-ray diffraction studies at 100 K, the 1:1 combination of 2 and 3 crystallizes in the monoclinic space group P2₁/n (Table 2). The geometrical parameters

Figure 3 Crystal structure of 2 and 3. Thermal ellipsoids are drawn at 50% probability level. The disordered methyl group is plotted with open bonds. Selected bond lengths and angles: Se(1)–Se(2) 2.34482(19)Å, Se(1)–C(11) 1.9265(12)Å, Se(2)–C(21) 1.9260(12)Å, Se(3)–C(31) 1.9322(14)Å, Se(3)–C(41) 1.9288(14)Å, C(11)–Se(1)–Se(2) 100.79(4)°, C(21)–Se(2)–Se(1) 101.57(4)°, C(41)–Se(3)–C(31) 101.96(6)°, C(11)–Se(1)–Se(2)–C(21) −81.63(6)°.
Table 2 Crystal data and structure refinement for 1 and the 1:1 co-crystallisate of 2 and 3

|       | 1                  | 2                  |
|-------|--------------------|--------------------|
| Formula  | C_{10}H_{8}FeSe_{3} | C_{18}H_{22}Se_{3}C_{18}H_{22}Se_{2} |
| Formular weight [g/mol] | 420.89             | 713.59             |
| Temperature [K] | 92                 | 100                |
| Wavelength [Å] | 0.71073            | 0.71073            |
| Crystal system | monoclinic         | monoclinic         |
| Space group | P2_{1}/c            | P2_{1}/n            |
| Unit cell dimensions |                   |                    |
| a [Å]      | 9.670(2)           | 12.9804(4)         |
| b [Å]      | 9.528(2)           | 7.9408(2)          |
| c [Å]      | 11.615(3)          | 31.5704(10)        |
| β [°]      | 94.33(2)           | 96.1070(10)        |
| Volume [Å³] | 1067.1(4)          | 3235.64(16)        |
| Z         | 4                  | 4                  |
| Calcd. density [mg/m³] | 2.620             | 1.465              |
| μ [mm⁻¹]  | 11.598             | 3.433              |
| Θ-range for data collected [°] | 2.77–25.99        | 1.64–30.00         |
| Goodness of fit on F² | 1.054             | 1.046              |
| R₁ (obsd. data) | 0.0484            | 0.0211             |
| wR₂ (all data) | 0.1283            | 0.0528             |

for 2 are in the expected region and are comparable to previously reported structures of this compound. The diselenide unit shows an Se–Se distance of 2.34482(19) Å, which is slightly longer than those in the other two published polymorphs (2.328 and 2.334 Å) while the Se–C distances (1.9265(12) and 1.9260(12) Å), the C–Se–Se angles (100.79(4) and 101.57(4)°), and the dihedral angle C11–Se1–Se2–C21 (–81.63(6)°) are very similar. For dimesitylselenide 3 however, it is the first time that structural data have been obtained outside the coordination sphere of a metal. The Se–C distances are close to 1.93 Å and therefore slightly longer than in 1. The C–Se–C angle is 102° and slightly larger than the C–Se–Se angles in 1 and 2. Intermolecular Se...Se contacts are well beyond the sum of the van der Waals radii and bonding interactions therefore can be excluded.

SUMMARY AND CONCLUSION

In conclusion, we have reported a novel modification of triselena-[3]ferrocenophane 1 in which intermolecular contacts between the central selenium atoms below the sum of the van der Waals radii are evident. Moreover, the structural characterization of dimesitylselenide 3 has been presented. While there are several structural reports on coordination compounds involving 3, this is the first report on the structure of the noncoordinated ligand.

EXPERIMENTAL

All manipulations were carried out under inert argon atmosphere using standard Schlenk technique, if not otherwise stated. ¹H and ¹³C NMR spectra have been recorded with a Bruker AMX 360 spectrometer (Bruker Biospin GmbH; Rheinstetten, Germany) operating at 360 MHz (¹H) and 91 MHz (¹³C) and with a Varian Unity 400 spectrometer.
(Varian, Inc., Palo Alto, USA) operating at 400 MHz (1H) and 101 MHz (13C). Residual solvent signals have been used as internal reference for 1H and 13C spectra. 77Se NMR spectra have been recorded with a Bruker AMX 360 spectrometer operating at 69 MHz and are externally referenced to Me2Se. CCDC reference numbers 970114 and 970115 contain the supplementary crystallographic data for derivatives 1 and 2·3. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (international) + 44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk.

Synthesis of Compound 1

1,1’-Dilithioferrocene24 (1.82 g, 9.2 mmol) is dissolved in 30 mL of a mixture (1:1) of tetrahydrofuran (THF)/toluene and cooled to –80°C. Gray selenium (1.45 g, 18.4 mmol) was added in portions at that temperature. The reaction mixture is slowly warmed to room temperature with continued stirring. After 10 h the orange precipitate is collected (0.96 g) and recrystallized from chloroform (mp 169°C). 1HN M R(CDC13): δ = 3.8 (m, 2H, Hα), 4.3 (m, 4H, Hβ, β’), 4.5 (m, 2H, Hα’). 13CN M R(CDC13): δ = 69.7 (Cα), 71.3 (Cβ), 71.8 (Cα’), 78.8 (Cβ’), 89.1 (Cq).

Synthesis of Compounds 2 and 3

Magnesium powder (4.87 g, 0.2 mol) was immersed in 40 mL of THF in an argon atmosphere. To this mixture, MesBr (29.13 mL, 0.190 mol) diluted with 20 mL of THF were added dropwise via an additional funnel. Upon complete addition, the mixture was refluxed for 2 h. The mixture was then slowly cooled to room temperature and gray selenium (15 g, 0.190 mol) was added in small portions. Upon complete addition, the mixture was heated to reflux for an additional 2 h. Without heating, stirring was continued for further 10 h. The resulting solid gray mixture was then quenched with 70 mL of aqueous HCl (4 M) under ice cooling. The resulting orange solution was extracted twice with 100 mL of diethyl ether. The ether phase was evaporated to dryness under vacuum and the resulting product was recrystallized from toluene. Spectral data before recrystallization: 77Se NMR (C6D6): δ = 145 (d, 1JSeH = 59 Hz, MesSeH), 350 (s, Mes2Se), 487 (s, Mes–Se–Se–Mes); 1H NMR (C6D6): δ = 0.97 (s, 1JHSe = 59 Hz, SeH), 1.98 (s, p-CH3), 2.06 (s, o-CH3), 2.16 (s, p-CH3), 2.19 (s, o-CH3), 2.26 (s, p-CH3), 2.29 (s, o-CH3), 2.67 (s, m-CH).

X-Ray Diffraction Studies on Compound 1

The measurements were performed with a STOE four-circle diffractometer (STOE & Cie Gmbh, Darmstadt, Germany) using graphite-monochromatized Mo Kα radiation at 92 K on a red block shaped crystal (0.22 × 0.22 × 0.18 mm): C10H8FeSe3, Mr = 420.89, monoclinic, space group P21/c, a = 9.670(2) Å, b = 9.528(2) Å, c = 11.615(3) Å, β = 94.33(2)°, V = 1067.1(4) Å³, Z = 4, dcalc = 2.620 g cm⁻³, μ = 11.598 mm⁻¹. A total of 2781 reflections were collected (θmax = 26.0°), from which 2080 were unique (Rint = 0.0568), with 1820 having I > 2σ(I). The structure was solved by direct methods (SHELXS-97) and refined by full-matrix least-square techniques against F² (SHELXL-97).25 The nonhydrogen atoms were refined with anisotropic displacement parameters without any constraints. The H atoms of the cyclopentadienyl rings were put at the external bisectors of the C–C–C angles at C–H.
distance of 0.95 Å and one common isotropic displacement parameter was refined for the H atoms of the same ring. For 129 parameters, final R indices of $R_1 = 0.0484$ and $wR_2 = 0.1283$ (GOF = 1.054) were obtained. An empirical absorption correction has been applied. The largest peak in a difference Fourier map was 1.628 eÅ$^{-3}$.

**X-Ray Diffraction Studies on Compound 2-3**

The measurements were performed with a Bruker APEX-II CCD using graphite-monochromatized Mo K$_\alpha$ radiation at 100 K on a yellow needle shaped crystal (0.23 × 0.10 × 0.08 mm): C$_{18}$H$_{22}$SeC$_{18}$H$_{22}$Se$_2$, $M_r$ 713.59, monoclinic, space group $P2_1/n$, $a = 12.9804(4)$ Å, $b = 7.9408(2)$ Å, $c = 31.5704(10)$ Å, $\beta = 96.1070(10)^\circ$, $V = 3235.64(16)$ Å$^3$, $Z = 4$, $d_{\text{calc}} = 1.465$ g cm$^{-3}$, $\mu = 3.433$ mm$^{-1}$. A total of 46,598 reflections were collected ($\theta_{\text{max}} = 30.0^\circ$), from which 9395 were unique ($R_{\text{int}} = 0.0263$), with 8345 having $I > 2\sigma(I)$. The structure was solved by direct methods (SHELXS-97) and refined by full-matrix least-square techniques against $F^2$ (SHELXL-97). The nonhydrogen atoms were refined with anisotropic displacement parameters without any constraints. The H atoms of the phenyl rings were put at the external bisector of the C–C–C angle at a C–H distance of 0.95 Å and common isotropic displacement parameters were refined for the H atoms of the same phenyl group. The H atoms of the methyl group C48 are disordered over two orientations and were refined with site occupation factors of 0.5 at two positions rotated from each other by 60$^\circ$ with common isotropic displacement parameters for the H atoms and idealized geometry with tetrahedral angles, enabling rotation around the C–C bond and C–H distances of 0.98 Å. The H atoms of the other methyl groups were refined with common isotropic displacement parameters for the H atoms of the same group and idealized geometry with tetrahedral angles, enabling rotation around the C–C bond, and C–H distances of 0.98 Å. For 380 parameters, final R indices of $R_1 = 0.0211$ and $wR_2 = 0.0528$ (GOF = 1.046) were obtained. A multiscan-type absorption correction has been applied (Bruker SADABS). The largest peak in a difference Fourier map was 0.447 eÅ$^{-3}$.

**SUPPLEMENTAL MATERIAL**

Supplementary data for this article can be accessed on the publisher’s website, www.tandfonline.com/gpss

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