MOLECULAR STRUCTURE DETERMINATION AND STUDIES ON CHEMICAL AND ELECTROCHEMICAL REDOX REACTIONS OF A CYCLIC TRISELENIDE COMPOUND, 4,7-DIMETHOXYBENZOTRISELENOLE

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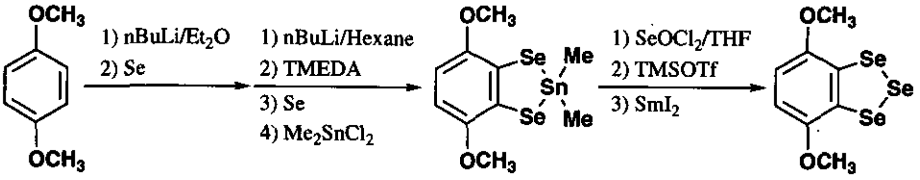
Abstract - Crystalline triselenide compound, 4,7-dimethoxybenzotriselenole, was prepared and characterized by single-crystal X-ray analysis; in the unit cell the two molecules stack each other with distorted triselenide rings sticking out from the benzene column. Interconversion accompanying one-electron transfer steps between the triselenole and the corresponding triselenolium radical cation salt has been constructed by chemical and electrochemical treatments.

Although several cyclic trisulfide compounds, trithioles, have been reported,[1] much less is known of triselenoles due to their synthetic limitation.[2] Recently, we reported the construction of reversible one-electron redox systems by using 4,7-diisopropylbenzotriselenole and found that its radical cation salt obtained on treatment with one-electron oxidant has an unusual 7π electron framework.[3,4] However, unfortunately, the triselenole had been obtained as an oily material at room temperature. Therefore, to date the solid-state structure of triselenole has not been clear. We report here the synthesis and the characterization of the crystal structure by X-ray crystallographic analysis of new crystalline 4,7-dimethoxybenzotriselenole, and the chemical and electrochemical one-electron redox reactions between the triselenole and the corresponding stable radical cation salt.

The triselenole (**2**) was synthesized from commercially available 1,4-dimethoxybenzene by following modified methods previously reported.[5] The 4,7-dimethoxy-2,2-dimethyl-1,3,2-benzodiselenastannole (**1**)[6] was prepared by a sequence of tandem ortho lithiation and selenation, and followed by dimethyltin protection. Then, sequential treatment of the stannole (**1**) (89 mg, 0.20 mmol) in tetrahydrofuran (THF) (15 ml) under an Ar atmosphere at -78 °C with selenyl chloride (0.014 ml, 0.20 mmol) in THF (5 ml), trimethylsilyl trifluoromethanesulfonate (TMSOTf) (0.036 ml, 0.20 mmol) in THF (4 ml), 0.1 M THF solution of samarium(II) iodide (4.0 ml, 0.40 mmol), followed by usual work-up, purification by column chromatography (silica gel, eluent, carbon tetrachloride), and further purification by recrystallization from chloroform gave 56 mg (75%) of 4,7-dimethoxybenzotriselenole (**2**)[7] (Scheme 1).



1 (28%) **2** (75%)

Scheme 1

The crystal structure of the triselenole (**2**) was determined by X-ray crystallography (Figure 1).[8] The planar diselenobenzene moiety has a selenium at 2-position displaced from the plane (Se-Se-Se-C torsion angles are 39.0 and 37.2°). A unique distorted geometry of the 5-membered triselenole ring indicates the presence of lone pair-lone pair repulsion of the divalent selenium atoms neighboring each other. The angles around the seleniums are slightly narrow to those in literature, whereas the selenium-selenium bond lengths, selenium-carbon(sp^2) bond lengths are similar to those of acyclic selenium compounds previously reported.[9] Interestingly, in the unit cell the two similar molecules stack each other with distorted triselenide rings sticking out from the benzene column along b-axis.

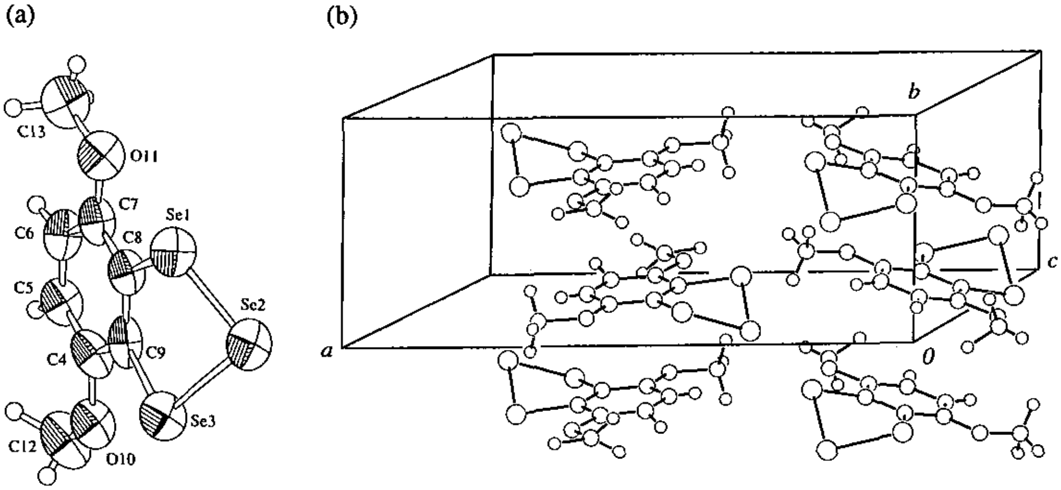
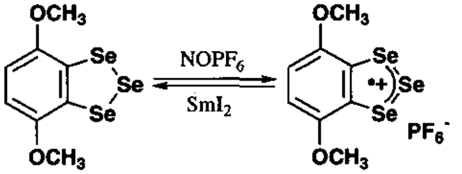


Figure 1. ORTEP drawing (a) and packing diagram (b) of **2**. Selected bond lengths (Å), bond angles (°), and torsion angles (°) are as follows: Se(1)-Se(2) 2.340(3), Se(2)-Se(3) 2.339(3), Se(1)-C(8) 1.91(1), Se(3)-C(9) 1.89(1), C(8)-C(9) 1.44(2); Se(1)-Se(2)-Se(3) 91.88(9), Se(2)-Se(1)-C(8) 93.6(5), Se(2)-Se(3)-C(9) 92.9(5), Se(1)-C(8)-C(9) 119(1), Se(3)-C(9)-C(8) 120.7(9); Se(1)-Se(2)-Se(3)-C(9) 39.0(4), Se(3)-Se(2)-Se(1)-C(8) -37.2(5), Se(1)-C(8)-C(9)-Se(3) 5(1), Se(1)-C(8)-C(7)-C(6) -179(1), Se(1)-C(8)-C(9)-C(4) -179(1), Se(3)-C(9)-C(8)-C(7) -177(1), Se(3)-C(9)-C(4)-C(5) 176(1).

The electrochemical redox property of the selenole (**2**) was examined by cyclic voltammetric technique.[10] Cyclic voltammograms of the selenole (**2**) (scan rate 50-500 mV/sec) exhibited sets of reversible oxidation and reduction waves with low oxidation potential[11] at E_{pa}=0.47 V, E_{pc}=0.39 V, $E_{1/2}$=0.43 V vs. Ag/Ag$^+$ (Figure 2). The new stable triselenolium radical cation salt (**3**)[12] was obtained by chemical one-electron oxidation of **2** with 1 equiv of $NOPF_6$ in THF/CH_3CN in 92% yield (Scheme 2). The dark purple salt (**3**) dissolved readily in THF to give a red-purple solution and the X-band esr spectrum of the solution at 10

°C showed the presence of a peak (g=2.057) attributable to radical character. The salt (**3**) undergoes chemical one-electron reduction to give **2** by treatment with 1 equiv. of samarium(II) iodide in THF in 94% yield (Scheme 2). In addition, the cyclic voltammetry of the isolated radical cation salt (**3**) also displayed reversible redox profiles with the same redox potentials observed in triselenole (**2**) (Figure 3). Therefore, the redox interconversion accompanying one-electron transfer steps between the triselenole (**2**) and the triselenolium radical cation salt (**3**) has been established by both chemical and electrochemical methods. Further studies on syntheses, crystal structures, and redox reactions of mixed chalcogen ring systems are in progress.



2 (94%) **3** (92%)

Scheme 2

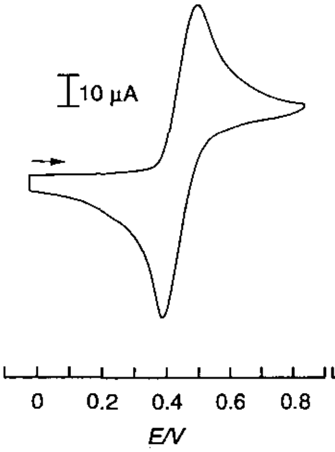


Figure 2.
Cyclic voltammogram of triselenole (**2**), scan rate 100 mV/s.

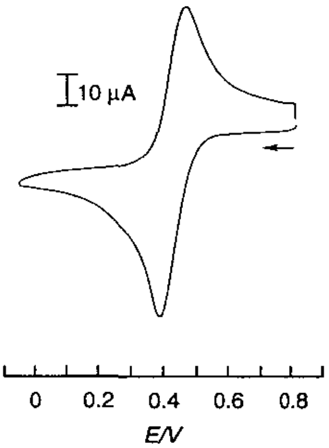


Figure 3.
Cyclic voltammogram of triselenolium radical cation salt (**3**), scan rate 100 mV/s.

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6. Stannole (**1**): colorless needles; mp 205.0-206.5 °C (decomp.); ^1H nmr (400 MHz, $CDCl_3$) δ 1.06 (s, 6H, Me_2Sn), 3.85 (s, 6H, MeO), 6.63 (s, 2H, ArH); $\{^1H\}^{13}C$ nmr (101 MHz, $CDCl_3$) δ 1.7, 56.7, 108.0, 128.6, 153.8; $\{^1H\}^{77}Se$ nmr (76 MHz, $CDCl_3$, relative to Me_2Se) δ 72.0 ($J_{Se\text{-}117Sn}$=1017, $J_{Se\text{-}119Sn}$=1064 Hz); $\{^1H\}^{119}Sn$ nmr (149 MHz, $CDCl_3$, relative to Me_4Sn) δ 90.7 ($J_{Sn\text{-}77Se}$=1064 Hz); ms (m/z) 446 (M^+, ^{80}Se, ^{120}Sn). Anal. Calcd for $C_{10}H_{14}O_2Se_2Sn$: C, 27.12; H, 3.19. Found: C, 27.13; H, 3.40.
7. Triselenole (**2**): Dark red prisms; mp 122.5-124.0 °C; ^1H nmr (400 MHz, $CDCl_3$) δ 3.80 (s, 6H, MeO), 6.63 (s, 2H, ArH); $\{^1H\}^{13}C$ nmr (101 MHz, $CDCl_3$) δ 55.6, 110.9, 130.9, 152.4; $\{^1H\}^{77}Se$ nmr (76 MHz, $CDCl_3$, relative to Me_2Se) δ 434.7, 532.9 ($J_{Se\text{-}Se}$=296 Hz); MS (m/z) 374 (M^+, ^{78}Se, ^{80}Se x 2). Anal. Calcd for $C_8H_8O_2Se_3$: C, 25.76; H, 2.16. Found: C, 25.94; H, 2.14.
8. Crystal data for **2**: A dark red prismatic crystal of $C_8H_8O_2Se_3$, M=373.03, crystal size 0.20 x 0.14 x 0.48 mm, monoclinic space group $P2_1/c$, a=17.453(3)Å, b=6.923(3)Å, c=18.767(2)Å, β=114.172(8)°, V=2068.6(7)$Å^3$, Z=8, D_c=2.395gcm^{-3}. The intensity data ($2\theta_{max}$=120.1°) were collected on a Rigaku AFC7R diffractometer at 20 °C with ω-2θ scan technique, scan speed=8.0 °min^{-1} (in ω), scan width=(1.42 + 0.30 tanθ)°, and CuKα radiation (λ=1.54178Å). The structure was solved by heavy-atom Patterson methods (PATTY) and expanded using Fourier techniques (DIRDIF92). All calculations were performed using the teXsan crystallographic software package. The final cycle of full-matrix least-square refinement was based on 2095 observed reflections (I>3.00σ(I)) and 300 variable parameters with R=0.066, Rw=0.076.
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10. Cyclic voltamograms of **2** (2.0 mM) and **3** (2.0 mM) were measured in MeCN at 20 °C containing 0.1M $n\text{-}Bu_4N^+ClO_4^-$ as a supporting electrolyte using a glassy-carbon working electrode and Ag/0.01M $AgNO_3$ as a reference electrode, scan rate 50-500 mV/s.
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12. Radical cation salt (**3**): Dark purple powder; mp 208.0-212.0 (decomp); $\{^1H\}^{31}P$ nmr (161 MHz, CD_3CN, relative to H_3PO_4) δ -143.7 (sept., $J_{P\text{-}F}$=707 Hz). Anal. Calcd for $C_8H_8O_2F_6PSe_3$: C, 18.55; H, 1.56. Found: C, 18.84; H,1.51.

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