

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

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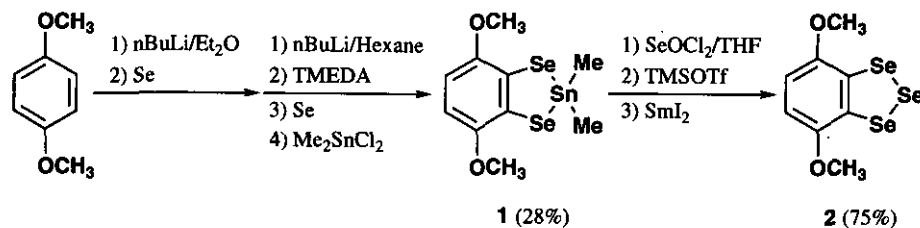
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**Abstract** - Crystalline triselenide compound, 4,7-dimethoxybenzotriselenole, was prepared and characterized by single-crystal X-ray analysis; in the unit cell the two molecules stack each other with distorted triselenide rings sticking out from 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.

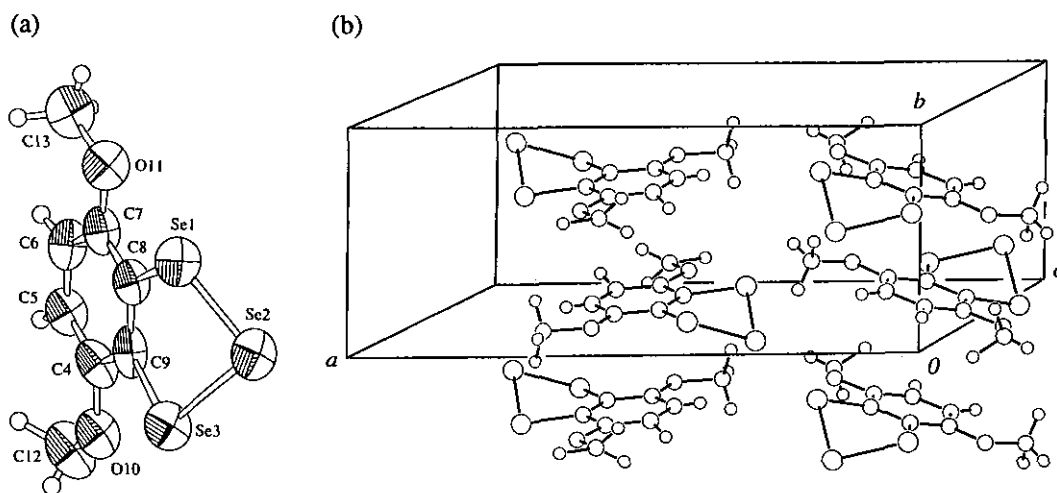
Although several cyclic trisulfide compounds, trithioles, have been reported,<sup>1</sup> much less is known of triselenoles due to their synthetic limitation.<sup>2</sup> Recently, we reported the construction of reversible one-electron redox systems by using 4,7-diisopropylbenzotriselenole and found that its radical cation salt obtained on treatment with one-electron oxidant has an unusual  $7\pi$  electron framework.<sup>3,4</sup> 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.<sup>5</sup> The 4,7-dimethoxy-2,2-dimethyl-1,3,2-benzodiselenastannole (**1**)<sup>6</sup> 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**)<sup>7</sup> (Scheme 1).



Scheme 1

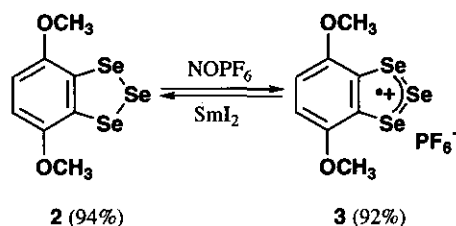
The crystal structure of the triselenole (**2**) was determined by X-ray crystallography (Figure 1).<sup>8</sup> The planar diselenobenzene moiety has a selenium at 2-position displaced from the plane (Se-Se-Se-C torsion angles are 39.0 and 37.2°). A unique distorted geometry of the 5-membered triselenole 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<sup>2</sup>) bond lengths are similar to those of acyclic selenium compounds previously reported.<sup>9</sup> 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.



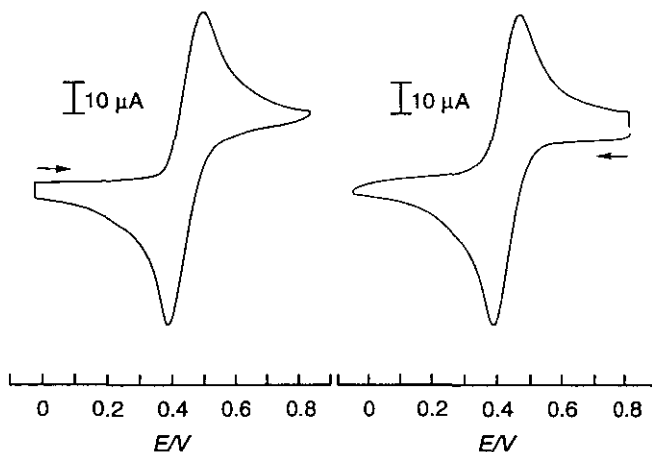
**Figure 1.** ORTEP drawing (a) and packing diagram (b) of **2**. Selected bond lengths (Å), bond angles (°), and torsion angles (°) are as follows: Se(1)-Se(2) 2.340(3), Se(2)-Se(3) 2.339(3), Se(1)-C(8) 1.91(1), Se(3)-C(9) 1.89(1), C(8)-C(9) 1.44(2); Se(1)-Se(2)-Se(3) 91.88(9), Se(2)-Se(1)-C(8) 93.6(5), 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.<sup>10</sup> Cyclic voltammograms of the selenole (**2**) (scan rate 50-500 mV/sec) exhibited sets of reversible oxidation and reduction waves with low oxidation potential<sup>11</sup> at  $E_{pa}=0.47$  V,  $E_{pc}=0.39$  V,  $E_{1/2}=0.43$  V vs. Ag/Ag<sup>+</sup> (Figure 2). The new stable triselenolium radical cation salt (**3**)<sup>12</sup> was obtained by chemical one-electron oxidation of **2** with 1 equiv of NOPF<sub>6</sub> in THF/CH<sub>3</sub>CN 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.



**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.

## ACKNOWLEDGEMENTS

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## REFERENCES AND NOTES

- For example, see; S. Ogawa, N. Yomoji, S. Chida, and R. Sato, *Chem. Lett.*, 1994, 507; M. J. Plater and C. W. Rees, *J. Chem. Soc., Perkin Trans. 1*, 1991, 317; N. Tokitoh, H. Ishizuka, A. Yabe, and W. Ando, *Tetrahedron Lett.*, 1989, **30**, 2955; B. L. Chenard, R. L. Harlow, A. L. Johnson, and S. A. Vladuchick, *J. Am. Chem. Soc.*, 1985, **107**, 3871; K. Rasheed and J. D. Warkentin, *J. Org. Chem.*, 1980, **45**, 4806.
- M. J. Earle, K. R. Griffiths, and A. G. Massey, *Polyhedron*, 1992, **11**, 395; R. E. Humphries and A. G. Massey, *Phosphorus and Sulfur*, 1988, **36**, 135; N. Tokitoh, H. Ishizuka, and W. Ando, *Chem. Lett.*, 1988, 657.
- S. Ogawa, T. Kikuchi, S. Niizuma, and R. Sato, *J. Chem. Soc., Chem. Comm.*, 1994, 1593. Two other trichalcogenolium radical cations have been reported. See; G. Wolmershäuser and G. Heckmann, *Angew. Chem., Int. Ed. Engl.*, 1992, **31**, 779; T. S. Cameron, R. C. Haddon, S. M. Mattar, S. Parsons, J. Passmore, and A. P. Ramirez, *J. Chem. Soc., Dalton Trans.*, 1992, 1563.

4. Other type 5-membered  $7\pi$  radical cations have been reported. See; T. S. Cameron, R. C. Haddon, S. M. Mattar, S. Parsons, J. Passmore, and A. P. Ramirez, *Inorg. Chem.*, 1992, **31**, 2274; E. G. Awere, J. Passmore, P. S. White, and T. Klapötke, *J. Chem. Soc., Chem. Comm.*, 1989, 1415; E. G. Awere, J. Passmore, K. F. Preston, and L. H. Sutcliffe, *Can. J. Chem.*, 1988, **66**, 1776.
5. S. Ogawa, T. Kikuchi, A. Sasaki, S. Chida, and R. Sato, *Tetrahedron Lett.*, 1994, **35**, 5469.
6. Stannole (**1**): colorless needles; mp 205.0-206.5 °C (decomp.);  $^1\text{H}$  nmr (400 MHz,  $\text{CDCl}_3$ )  $\delta$  1.06 (s, 6H,  $\text{Me}_2\text{Sn}$ ), 3.85 (s, 6H, MeO), 6.63 (s, 2H, ArH);  $\{^1\text{H}\}^{13}\text{C}$  nmr (101 MHz,  $\text{CDCl}_3$ )  $\delta$  1.7, 56.7, 108.0, 128.6, 153.8;  $\{^1\text{H}\}^{77}\text{Se}$  nmr (76 MHz,  $\text{CDCl}_3$ , relative to  $\text{Me}_2\text{Se}$ )  $\delta$  72.0 ( $J_{\text{Se-}^{117}\text{Sn}}=1017$ ,  $J_{\text{Se-}^{119}\text{Sn}}=1064$  Hz);  $\{^1\text{H}\}^{119}\text{Sn}$  nmr (149 MHz,  $\text{CDCl}_3$ , relative to  $\text{Me}_4\text{Sn}$ )  $\delta$  90.7 ( $J_{\text{Sn-}^{77}\text{Se}}=1064$  Hz); ms (m/z) 446 ( $\text{M}^+$ ,  $^{80}\text{Se}$ ,  $^{120}\text{Sn}$ ). Anal. Calcd for  $\text{C}_{10}\text{H}_{14}\text{O}_2\text{Se}_2\text{Sn}$ : 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;  $^1\text{H}$  nmr (400 MHz,  $\text{CDCl}_3$ )  $\delta$  3.80 (s, 6H, MeO), 6.63 (s, 2H, ArH);  $\{^1\text{H}\}^{13}\text{C}$  nmr (101 MHz,  $\text{CDCl}_3$ )  $\delta$  55.6, 110.9, 130.9, 152.4;  $\{^1\text{H}\}^{77}\text{Se}$  nmr (76 MHz,  $\text{CDCl}_3$ , relative to  $\text{Me}_2\text{Se}$ )  $\delta$  434.7, 532.9 ( $J_{\text{Se-Se}}=296$  Hz); MS (m/z) 374 ( $\text{M}^+$ ,  $^{78}\text{Se}$ ,  $^{80}\text{Se} \times 2$ ). Anal. Calcd for  $\text{C}_8\text{H}_8\text{O}_2\text{Se}_3$ : C, 25.76; H, 2.16. Found: C, 25.94; H, 2.14.
8. Crystal data for **2**: A dark red prismatic crystal of  $\text{C}_8\text{H}_8\text{O}_2\text{Se}_3$ ,  $M=373.03$ , crystal size 0.20 x 0.14 x 0.48 mm, monoclinic space group  $\text{P}2_1/c$ ,  $a=17.453(3)\text{Å}$ ,  $b=6.923(3)\text{Å}$ ,  $c=18.767(2)\text{Å}$ ,  $\beta=114.172(8)^\circ$ ,  $V=2068.6(7)\text{Å}^3$ ,  $Z=8$ ,  $D_c=2.395\text{gcm}^{-3}$ . The intensity data ( $2\theta_{\text{max}}=120.1^\circ$ ) were collected on a Rigaku AFC7R diffractometer at 20 °C with  $\omega$ - $2\theta$  scan technique, scan speed= $8.0^\circ\text{min}^{-1}$  (in  $\omega$ ), scan width= $(1.42 + 0.30 \tan\theta)^\circ$ , and  $\text{CuK}\alpha$  radiation ( $\lambda=1.54178\text{Å}$ ). 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 ( $I>3.00\sigma(I)$ ) and 300 variable parameters with  $R=0.066$ ,  $R_w=0.076$ .
9. M. J. Potrzebowski, M. Michalska, J. Blaszczyk, M. W. Wiczorek, W. Ciesielski, S. Kazmierski, and J. Pluskowski, *J. Org. Chem.*, 1995, **60**, 3139; P. J. Barrie and R. J. H. Clark, *Inorg. Chem.*, 1995, **34**, 4299; J. J. Ellison, K. Ruhlandt-Senge, H. H. Hope, and P. P. Power, *ibid.*, 1995, **34**, 49; M. Iwaoka and S. Tomoda, *Phosphorus, Sulfur, and Silicon*, 1992, **67**, 125.
10. Cyclic voltamograms of **2** (2.0 mM) and **3** (2.0 mM) were measured in MeCN at 20 °C containing 0.1M n-Bu $_4\text{N}^+\text{ClO}_4^-$  as a supporting electrolyte using a glassy-carbon working electrode and Ag/0.01M  $\text{AgNO}_3$  as a reference electrode, scan rate 50-500 mV/s.
11. H. Fujihara, Y. Higuchi, H. Mima, and N. Furukawa, *Chem. Lett.*, 1994, 619; H. Fujihara, M. Yabe, M. Ikemori, and N. Furukawa, *J. Chem. Soc., Perkin Trans. 1*, 1993, 2145; H. Fujihara, Y. Ueno, J. J. Chiu, and N. Furukawa, *Chem. Lett.*, 1991, 1649; H. Fujihara, R. Akaishi, and N. Furukawa, *ibid.*, 1990, 549.
12. Radical cation salt (**3**): Dark purple powder; mp 208.0-212.0 (decomp);  $\{^1\text{H}\}^{31}\text{P}$  nmr (161 MHz,  $\text{CD}_3\text{CN}$ , relative to  $\text{H}_3\text{PO}_4$ )  $\delta$  -143.7 (sept.,  $J_{\text{P-F}}=707$  Hz). Anal. Calcd for  $\text{C}_8\text{H}_8\text{O}_2\text{F}_6\text{PSe}_3$ : C, 18.55; H, 1.56. Found: C, 18.84; H, 1.51.