Synthesis and Structures of Host Molecules containing an Se–Se Bond. Intramolecular Hypervalent Nature of Selenium Atoms in the Crystal State

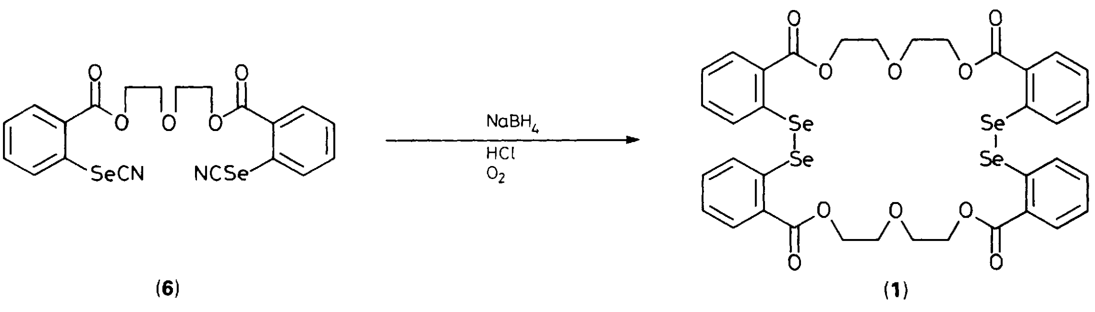
Shuji Tomoda* and Michio Iwaoka

Department of Chemistry, College of Arts and Sciences, The University of Tokyo, Komaba, Meguro-ku, Tokyo 153, Japan

The first host molecules containing an Se–Se bond, 5,13,20,28-tetraoxo-3,4 : 14,15 : 18,19 : 29,30-tetrabenzo-6,9,12,21,24,27-hexaoxa-1,2,16,17-tetraselenacyclotriaconta-3,14,18,29-tetraene (**1**) and 2,9-dioxo-3,4 : 7,8-dibenzo-13,15,21,24-tetraoxa-5,6-diselena-1,10-diazabicyclo[8.8.8]hexacosa-3,7-diene (**2**), have been synthesized and their structures have been determined by *X*-ray analysis.

Organoselenium compounds containing an Se–Se bond are of particular interest firstly, because they are useful reagents for selective organic synthesis,[1] secondly, because the Se–Se bond undergoes facile homolytic cleavage under thermal or photochemical conditions,[2] and thirdly, because they are suggested to be intermediates in a biologically important process involving glutathione peroxidase, a selenium-containing enzyme.[3] Incorporation of this bond into crown-ether type host molecules might provide a unique opportunity for a new molecular device, which would undergo selective membrane transport of specific metal ions under light irradiation[4] or act as a catalyst in a photochemically induced redox cycle,[5] if appropriate metal ions are present in the cavity. We report here the first synthesis of this class of host molecules (**1**) and (**2**) and their molecular structures determined by *X*-ray analysis.

Since crown-like molecules of the form ($-CH_2CH_2E-)_n$ have seen extensive use as model systems in host–guest chemistry, chelating parts for specific metal ions have been constructed by using diethylene glycol (**3**) for (**1**) and 1,4,10,13-tetraoxa-7,16-diazacyclo-octadecane (**4**) for (**2**), both of which are commercially available. Introduction of selenium into these materials presented a cumbersome problem. Obviously, benzeneselenyl derivatives were the first choice because the reactivity of the Se–Se bond can be controlled by the substituent(s) on the benzene ring. After a number of unsuccessful attempts, we found 2-selenocyanatobenzoyl chloride (**5**)[6] to be the best reagent for the incorpora-



Scheme 1

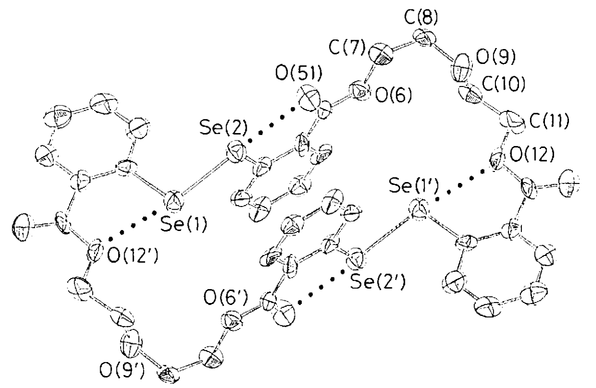


Figure 1. ORTEP drawing of (1). Selected bond lengths: Se(1)–Se(2) 2.317(3), Se(2)–C(3) 1.93(2), C(15)–Se(1′) 1.93(2) Å. Bond angles: Se(1)–Se(2)–C(3) 102.2(5), C(15)–Se(1′)–Se(2′) 102.9(4)°. Dihedral angles: Se(1)–Se(2) 86.4(6), O(6)–C(7) 177(1), C(7)–C(8) 77(2), C(8)–O(9) 105(2), O(9)–C(10) 175(1), C(10)–C(11) 77(2), C(11)–O(12) 179(1)°. Interatomic distances: O(12′)–Se(1) 2.71(1), Se(2)–O(51) 2.65(1) Å.

tion of the selenium unit. Host molecules, (**1**) and (**2**),† were synthesized by the inter- and intra-molecular cyclization of the selenium-containing units, (**6**) and (**7**), which were obtained by the reaction between (**5**) and the diol (**3**) or the diamine (**4**) in 89 and 75% yields, respectively (Schemes 1 and 2). Low overall yields in the cyclization of (**6**) and (**7**) [5% for (**1**) and 33% for (**2**)] may be due to complex oligomerization of the diselenolate intermediate generated by the reaction of (**6**) and (**7**) with sodium borohydride followed by treatment with hydrochloric acid, although highly dilute conditions were employed.

Single crystal X-ray analysis was performed for (**1**) and (**2**)‡ which were recrystallized from dichloromethane and carbon tetrachloride, respectively. As shown in Figure 1, (**1**) has a centre of inversion at the centre of mass. The shape of the host cavity does not seem round, but rectangular, which is divided into two segments; one is surrounded by O(6), O(9), O(12), and Se(1′) and the other by O(6′), O(9′), O(12′), and Se(1). This indicates that (**1**) can accommodate two metal ions simultaneously. The dihedral angle around the Se(1)–Se(2) or Se(1′)–Se(2′) bond (86.4°) is as expected for diphenyl diselenide.[7] The most interesting feature of the molecular structure is the unusual proximity between Se(2) and O(51)

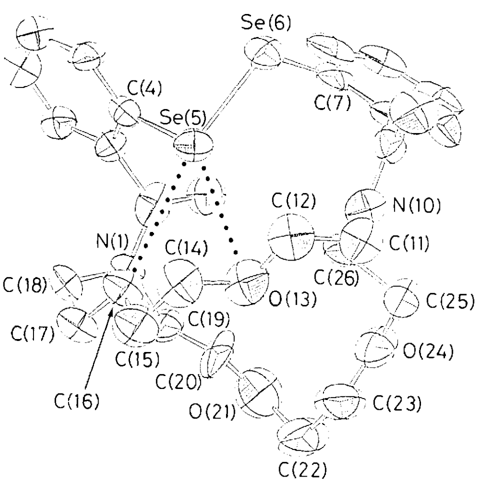


Figure 2. ORTEP drawing of (2) without CCl$_4$. Selected bond lengths: C(4)–Se(5) 1.90(1), Se(5)–Se(6) 2.313(2), Se(6)–C(7) 1.92(2) Å. Bond angles: C(4)–Se(5)–Se(6) 100.0(4), Se(5)–Se(6)–C(7) 101.9(4)°. Dihedral angles: Se(5)–Se(6) 99.7(6), C(11)–C(12) 71(2), C(12)—O(13) 179(1), O(13)–C(14) 174(1), C(14)–C(15) 75(2), C(15)–O(16) 176(1), O(16)–C(17) 180(1), C(17)–C(18) 60(2), C(19)–C(20) 166(1), C(20)–O(21) 166(1), O(21)–C(22) 49(2), C(22)–C(23) 55(2), C(23)–O(24) 166(1), O(24)–C(25) 82(2), C(25)–C(26) 170(1)°. Interatomic distances: Se(5)–O(13) 3.44(1), Se(5)–O(16) 3.14(1) Å.

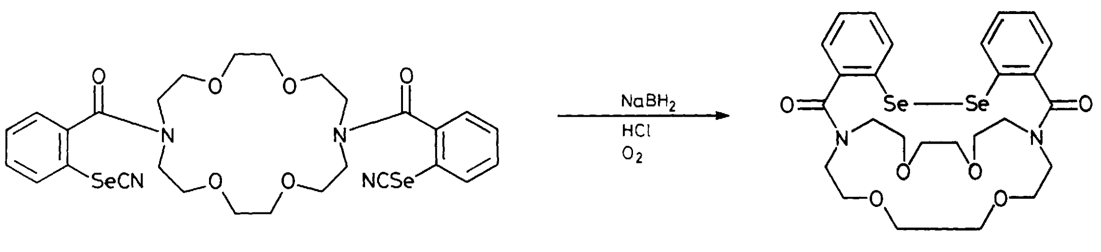
(2.65 Å) and that between O(12′) and Se(1) (2.71 Å). These apparently short interatomic distances may suggest the existence of strong attractive interactions between these atoms. Almost linear alignment of these four atoms, O(12′)–Se(1)–Se(2)–O(51), clearly shows that these interactions are due to the hypervalent property of selenium atoms.[8] This may contribute to the conformational stability of the macrocyclic system. Furthermore, the π-electron conjugation between the benzene ring and the carbonyl group seems guaranteed by coplanarity of these π-electron systems. While the combined effects, the hypervalent interactions and the π-electron conjugation, add some stabilization to the large ring system, strains are generated to a certain extent by the rigid nature of the linear O(12′)–Se(1)–Se(2)–O(51) unit. It is highly likely that the linear alignment of this unit may cause some deviation in the peripheral conformation of the cavity from the ordinary one. It has been found that this is indeed the case. As for the type of crown molecules having the general formula $(-CH_2CH_2O-)_n$, conformational analysis has been thoroughly studied[9] and the most stable conformations are assigned to be the *anti* (*a*) for the C–C–O–C bond and the *gauche* (*g*) for the O–C–C–O bond. This assignment is directly applicable to the linkage, O(6)–C(7)–C(8)–O(9)–C(10)–C(11)–O(12), of (**1**) except for C(8)–O(9); conformational assignments for these bonds are *a*–*g*–*e*(eclipse)–*a*–*g*–*a*. Apparently conformational irregularity occurs to a minimum extent in the third bond [C(8)–O(9)] presumably due to the linear alignment of O(12′)–Se(1)–Se(2)–O(51).

The molecular structure of (**2**) is shown in Figure 2. Carbon tetrachloride, which is included per one molecule of (**2**) as the crystal solvent, is omitted. The dihedral angle around the Se(5)–Se(6) bond (99.7°) is not significantly deviated from the ordinary Se–Se bond. There are again short intramolecular atomic distances between Se(5) and O(13) (3.44 Å) and between Se(5) and O(16) (3.14 Å), suggesting strong attractive interactions between these atoms. The interactions are ascribed to the hypervalent nature of Se(5) since the alignment of Se(6)–Se(5)–O(16) (167°) is almost linear. It should be noted that the two bridge-head nitrogen atoms [N(1) and

---

† *Selected data* for (**1**): m.p. 194—197 °C; m/z 472 ($M^+/2$); ^{77}Se NMR δ 452.7 p.p.m.; UV $\lambda_{max.}$ 233, 257, 321 nm; IR 1715, 1690 (C=O), 1290, 1270 cm^{-1} (C–O). For (**2**): m.p. 136—138 °C; m/z 628 (M^+); ^{77}Se NMR δ 432.7 p.p.m.; UV $\lambda_{max.}$ 233, 251, 330 nm; IR 1640 cm^{-1} (C=O).

‡ *Crystal data* for (**1**): $C_{36}H_{32}O_{10}Se_4$, M = 940.5, monoclinic, a = 21.093(5), b = 8.194(3), c = 10.193(7) Å, β = 91.66(6)°, U = 1761.0 Å^3, space group $P2_1/n$, Z = 2, D_c = 1.77 g cm^{-3}. A Rigaku automated 4-circle diffractometer was employed with Mo-K_α radiation monochromatized by graphite. The structure was solved by the heavy atom method and was refined by the full-matrix least-squares method neglecting hydrogen atoms. R-value was reduced to 0.078 for 1729 non-zero reflections. For (**2**): $C_{26}H_{32}N_2O_6Se_2 \cdot CCl_4$, M = 780.3, triclinic, a = 12.806(5), b = 10.276(4), c = 12.485(4) Å, α = 88.86(3), β = 106.64(3), γ = 91.03(3)°, U = 1573.7 Å^3, space group $P\bar{1}$, Z = 2, D_c = 1.65 g cm^{-}. The structure was solved by the direct method and was refined by the full-matrix least-squares method neglecting hydrogen atoms. R-value was reduced to 0.076 for 2892 non-zero reflections. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Crystallographic Data Centre. See Notice to Authors, Issue No. 1.



(7) **(2)**

Scheme 2

N(10)] are sp^2-hybridized, which assures amido conjugation with the neighbouring carbonyl groups, but that they are not in conjugation with the benzene rings. The hypervalent interactions involving one of the selenium atoms and the amido conjugation are important factors for the stabilization of this bicyclic system, but due to these factors the molecule is forced to be unsymmetrical and the two crown bridges, C(11) through C(18) and C(19) through C(26), are no longer conformationally equivalent. The hypervalent interactions may be the major factor which is responsible for such a large conformational difference between the two bridges. Conformation of the C(11)–C(12)–O(13)–C(14)–C(15)–O(16)–C(17)–C(18) bridge, which interacts with Se(5), is designated as *g–a–a–g–a–a–g*, in complete agreement with previous conformational analysis on a similar system.[9] However, the conformation of the C(19)–C(20)–O(21)–C(22)–C(23)–O(24)–C(25)–C(26) bridge, which does not interact with Se(5), is shown as *a–a–g–g–a–g–a*. Four bonds, C(19)–C(20), O(21)–C(22), O(24)–C(25), and C(25)–C(26), have irregular dihedral angles. This probably implies that both the hypervalent interactions and the amido conjugation may be responsible for the conformational deviation in the crown bridge which is free from the interaction with selenium. Thus the molecular structures of (**1**) and (**2**) obtained by *X*-ray analysis suggest that the hypervalent property of the selenium atom greatly affects the shape of the host cavity in the solid state.

Synthesis of other host molecules having Se–Se bond(s) and complexation of these molecules with various metal and non-metal substrates are now examined. The results will be reported in due course.

This work is partially supported by Grants-in-Aid sponsored by the Ministry of Education, Science and Culture (Nos. 01540413, 01648507, and 01644003).

Received, 5th September 1989; 9/03785C

References

1 C. Paulmier, 'Selenium Reagents and Intermediates in Organic Synthesis,' Pergamon Press, 1986; K. C. Nicolaou and N. A. Petasis, 'Selenium in Natural Products Synthesis,' CIS, 1984; D. L. J. Clive, *Tetrahedron*, 1978, **34**, 1049; H. J. Reich, *Acc. Chem. Res.*, 1979, **12**, 22; D. Liotta, *ibid.*, 1984, **17**, 28.
2 D. L. Klayman and W. H. H. Gunter, 'Organic Selenium Compounds: their Chemistry and Biology,' Wiley-Interscience, New York, 1973, p. 941; D. H. Brown, R. J. Cross, and D. Millington, *J. Chem. Soc., Dalton Trans.*, 1977, 159.
3 K.-S. Tan, A. P. Arnold, and D. L. Rabenstein, *Can. J. Chem.*, 1988, **66**, 54; R. C. Dickson and A. L. Tappel, *Arch. Biochem. Biophys.*, 1969, **130**, 547; R. J. Shamberger, 'Biochemistry of Selenium,' Plenum Press, 1983; Leopold Flohé, 'Glutathione Peroxidaze Brought into Focus,' in 'Free Radicals in Biology,' ed. W. A. Pryor, Academic Press, 1982.
4 S. Shinkai, M. Ishihara, K. Ueda, and O. Manabe, *J. Chem. Soc., Chem. Commun.*, 1984, 727.
5 G. Pandey, V. Jayathirtha Rao, and U. T. Bhalerao, *J. Chem. Soc., Chem. Commun.*, 1989, 416.
6 R. Lesser and R. Weiss, *Ber.*, 1913, **46**, 2640.
7 R. E. Marsh, *Acta Crystallogr.*, 1952, **5**, 458.
8 S. Tomoda, M. Iwaoka, K. Yakushi, A. Kawamoto, and J. Tanaka, *J. Phys. Org. Chem.*, 1988, **1**, 179; I. Hargittai and B. Rozsondai, 'Structural chemistry of organic compounds containing selenium or tellurium,' in 'The Chemistry of Organic Selenium and Tellurium Compounds, Volume 1,' eds. S. Patai and Z. Rappoport, Wiley, 1986.
9 J. Dale, *Tetrahedron*, 1974, **30**, 1683.