Bull. Chem. Soc. Jpn., ***63***, *249—251 (1990)*

Crystal and Molecular Structure of the Crystalline Host-Guest Complex between (*R*)-(+)-2,2′-Dihydroxy-1,1′-binaphthyl and (*S*)-(−)-(Ethyl *m*-Tolyl Selenoxide)

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(Received July 7, 1989)

Synopsis. The crystal and molecular structure of the title complex was determined by X-ray method. The absolute configuration of the host (+)-2,2′-dihydroxy-1,1′-binaphthyl (**1**) was determined to be *R* and the guest (−)-(ethyl *m*-tolyl selenoxide) (**2**) to be *S*. Two Se–C and one S–O bond lengths are 1.926(7), 1.970(8), and 1.677(5) Å, respectively, and the arrangement around Se atom is roughly tetrahedral. There are O(guest)···HO(host)OH···O(guest) hydrogen bonds between the host and the guest molecules.

Previously, we reported that some selenoxides were efficiently resolved by complexation with (*R*)-(+)-**1**.[1] In order to elucidate the mechanism of the chiral recognition by **1**, systematic structural studies about the complexes of **1** and many guest compounds with different sizes, chiralities, and functional groups seem to be necessary. We report here the structure of a 1 : 1 crystalline complex **3** of (+)-**1** and (−)-**2**.

Table 1. Final Atomic Coordinates with Estimated Standard Deviations in Parentheses, and Their Equivalent Isotropic Thermal Parameters $B_{eq}=(4/3)\sum_i\sum_j B_{ij}a_i\cdot a_j$

Atom	*x*	*y*	*z*	B_{eq}/Å^2
O1	0.3213(2)	0.0656(4)	0.6053(4)	4.51
C2	0.2073(3)	0.0907(5)	0.6867(5)	2.74
C3	0.2647(3)	0.1405(6)	0.6300(5)	3.39
C4	0.2635(4)	0.2713(6)	0.5970(6)	4.19
C5	0.2070(4)	0.3449(6)	0.6191(6)	4.27
C6	0.1479(4)	0.2998(6)	0.6777(5)	3.64
C7	0.0867(4)	0.3721(7)	0.7014(6)	4.49
C8	0.0294(4)	0.3278(7)	0.7540(6)	4.88
C9	0.0285(3)	0.1976(7)	0.7875(6)	4.52
C10	0.0872(4)	0.1241(6)	0.7684(5)	3.44
C11	0.1475(3)	0.1686(6)	0.7130(4)	2.87
O12	0.1228(2)	−0.0966(4)	0.5873(4)	3.86
C13	0.2081(3)	−0.0476(5)	0.7238(5)	2.84
C14	0.1649(3)	−0.1346(6)	0.6714(5)	3.15
C15	0.1649(4)	−0.2634(6)	0.7051(5)	3.62
C16	0.2056(4)	−0.2988(6)	0.7930(5)	3.90
C17	0.2477(4)	−0.2127(6)	0.8530(5)	3.46
C18	0.2871(4)	−0.2475(7)	0.9464(5)	4.70
C19	0.3275(4)	−0.1634(9)	1.0023(6)	5.35
C20	0.3314(4)	−0.0347(8)	0.9651(5)	4.68
C21	0.2936(4)	0.0028(8)	0.8742(5)	3.59
C22	0.2506(3)	−0.0832(6)	0.8143(5)	2.96
SE23	0.01102(4)	0.32054(7)	0.41879(6)	3.79
O24	−0.0663(2)	0.3047(5)	0.4871(3)	4.10
C25	−0.0166(4)	0.2801(6)	0.2709(5)	4.34
C26	0.0184(5)	0.3358(10)	0.1850(6)	6.84
C27	−0.0054(6)	0.3071(13)	0.0802(6)	9.17
C28	−0.0609(5)	0.2264(11)	0.0618(6)	7.18
C29	−0.0943(4)	0.1664(9)	0.1486(6)	5.53
C30	−0.0712(4)	0.1950(8)	0.2540(6)	4.93
C31	−0.1540(6)	0.0752(11)	0.1268(8)	9.32
C32	0.0616(4)	0.1605(7)	0.4501(6)	4.88
C33	0.1302(4)	0.1555(10)	0.3888(7)	6.72

Experimental

A large crystal with metallic luster of **3** was cut into the size of 0.10×0.20×0.35 mm^3 and used for the X-ray diffraction experimental. The unit cell parameters and reflection intensities were measured on a Rigaku automatic four-circle diffractometer AFC-5 with graphite-monochromated Cu $K\alpha$ (λ=1.5418 Å) radiation. Unit cell constants were obtained by the least-squares fit using 20 refrections with range of $40\leq 2\theta \leq 60°$. Intensity data were collected up to 2θ=125°, including Bijvoet pair reflections: $0\leq h\leq 21$, $0\leq k\leq 12$, $-14\leq l\leq 14$, by ω–2θ scan technique. The scan width, scan rate, and background counting time at both ends of a scan were $\Delta\omega=(1.10+0.17\tan\theta)°$, 4° min^{-1} in ω, and 5 s respectively. Three standard reflections were monitored after every 100 reflections, and they showed no decay during the intensity measurement. The Lorentz and polarization effects were corrected, but no corrections for absorption and extinction were applied. 4219 reflections were observed, in which 3488 with $F_o > 3\sigma(F_o)$ were used for the analysis. The structure was solved by the direct method MULTAN78[2] using reflections with *h*, *k*, and $l\geq 0$. The refinement was carried out by the block-diagonal least-squares method[3] with the function minimizing of $\sum\omega(|F_o|-|F_c|)^2$ where a unit weight was used throughout the refinement. All the hydrogen atoms were found in the difference Fourier map. The absolute structure was determined by Bijvoet pair reflections with $f'_{Se}=0.879$, $f''_{Se}=1.139$ as follows: the least-squares refinements were done on enantio sets independently with anisotropic temperature factors for non-hydrogen atoms, and isotropic ones for hydrogen atoms. The final *R* value were converged to *R*=0.053, *wR*=0.055 for the former set and 0.059, 0.060 for the latter one, respectively, and the former set showed good relations in magnitudes of F_o and F_c between Bijvoet pair reflections. Therefore, the former set was decided to show the absolute structure. The final atomic parameters are listed in Table 1.[4] The atomic-scattering factors were taken from International Tables for X-ray Crystallography.[5] All the computations were done on an IBM 3081-GX3 at the Information Processing Center of Shimane University.

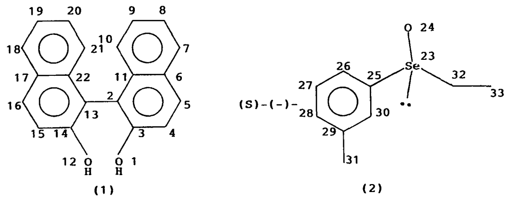
Crystal data: $C_9H_{12}OSe\cdot C_{20}H_{14}O_2$, F.W.=501.48, Orthorhombic, $P2_12_12$, a=18.709(2), b=10.526(1), c=12.211(1) Å, V=2404.6(4) Å^3, Z=4, D_x=1.385, D_m=1.356(6) Mg m^{-3} (flotation with citric acid aqueous solution), μ=2.59 mm^{-1}, F(000)=1032.

Results and Discussion

The atomic numbering and a part of the crystal structure of the complex **3** are in Scheme 1 and in Fig. 1, respectively. The absolute configuration of (−)-**2** is determined to *S* and that of (+)-**1** is confirmed to be *R*.[6] Each two naphthalene rings in (*R*)-(+)-**1** is planar

Table 2. Bond Lengths and Angles with Estimated Standard Deviations in Parentheses

(a) Bond lengths (l/Å)					
O1-C3	1.354(8)	C2-C3	1.381(9)	C2-C11	1.424(9)
C2-C13	1.525(9)	C3-C4	1.435(10)	C4-C5	1.338(10)
C5-C6	1.400(10)	C6-C7	1.405(10)	C6-C11	1.447(9)
C7-C8	1.334(11)	C8-C9	1.430(11)	C9-C10	1.363(10)
C10-C11	1.397(9)	O12-C14	1.355(8)	C13-C14	1.379(9)
C13-C22	1.413(9)	C14-C15	1.417(9)	C15-C16	1.368(10)
C16-C17	1.407(10)	C17-C18	1.407(10)	C17-C22	1.444(9)
C18-C19	1.350(12)	C19-C20	1.431(12)	C20-C21	1.375(12)
C21-C22	1.415(11)	Se23-O24	1.678(5)	Se23-C25	1.927(7)
Se23-C32	1.970(8)	C25-C26	1.369(13)	C25-C30	1.374(11)
C26-C27	1.389(17)	C27-C28	1.360(17)	C28-C29	1.384(15)
C29-C30	1.392(13)	C29-C31	1.497(15)	C32-C33	1.487(13)
(b) Bond angles (ϕ/°)					
C3-C2-C11	120.4(4)	C3-C2-C13	120.3(4)	C11-C2-C13	119.4(3)
O1-C3-C2	119.9(4)	O1-C3-C4	120.5(5)	C2-C3-C4	119.5(4)
C3-C4-C5	120.7(6)	C4-C5-C6	122.1(7)	C5-C6-C7	124.4(5)
C5-C6-C11	118.7(4)	C7-C6-C11	116.8(6)	C6-C7-C8	124.4(6)
C7-C8-C9	118.8(5)	C8-C9-C10	119.0(4)	C9-C10-C11	122.9(7)
C2-C11-C6	118.6(4)	C2-C11-C10	123.4(6)	C6-C11-C10	118.0(5)
C2-C13-C14	119.3(4)	C2-C13-C22	119.4(3)	C14-C13-C22	121.1(5)
O12-C14-C13	119.8(3)	O12-C14-C15	120.2(4)	C13-C14-C15	120.0(4)
C14-C15-C16	119.3(4)	C15-C16-C17	123.0(7)	C16-C17-C18	123.3(7)
C16-C17-C22	117.3(6)	C18-C17-C22	119.5(4)	C17-C18-C19	122.2(8)
C18-C19-C20	119.3(5)	C19-C20-C21	120.2(6)	C20-C21-C22	121.8(8)
C13-C22-C17	119.1(4)	C13-C22-C21	123.7(6)	C17-C22-C21	117.1(6)
O24-Se23-C25	102.3(3)	O24-Se23-C32	103.4(3)	C25-Se23-C32	97.0(3)
Se23-C25-C26	119.7(5)	Se23-C25-C30	119.0(4)	C26-C25-C30	121.3(8)
C25-C26-C27	117.4(10)	C26-C27-C28	122.2(13)	C27-C28-C29	120.2(8)
C28-C29-C30	118.1(7)	C28-C29-C31	119.6(7)	C30-C29-C31	122.4(9)
C25-C30-C29	120.7(7)	Se23-C32-C33	110.3(6)		



Scheme 1.

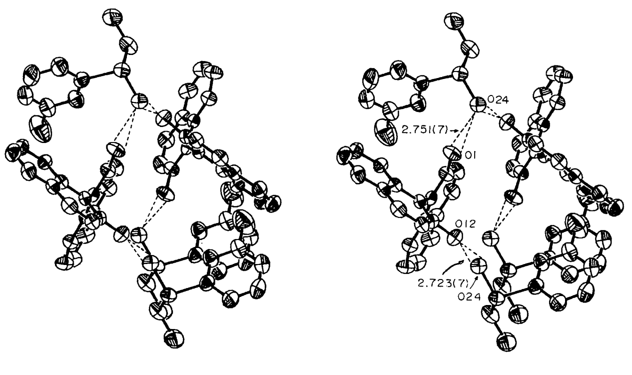


Fig. 1. Stereoscopic drawing of a part of the crystal structure. Hydrogen bonds are indicated by the dotted lines.

and their dihedral angle is 75.4°, and the overall shape of **1** is like a character T. Bond lengths and angles are listed in Table 2. The C-C bond connecting two naphthalene rings is in a length of 1.525(9) Å. Bond lengths and angles in the naphthalene rings show typical conjugated double bond character. The deviations of the hydroxyl oxygen atoms from each plane of the naphthalene ring are −0.04 Å(O1) and 0.14 Å(O2), and the C-O bond lengths are 1.354(8) Å and 1.355(8) Å for C2-O1 and C12-O2 respectively, whose values are in a middle of C-O single (1.43 Å) and double bond (1.22 Å). On the other hand, the atoms in *m*-tolyl moiety and Se atom of **2** are in a plane and their maximum deviations from the plane are 0.02 Å (C24) and −0.08 Å (Se), respectively. A conformation around the Se atom is roughly tetrahedral, and two Se-C and the Se-O bond lengths are 1.926(7), 1.970(8), and 1.677(5) Å respectively. The Se=O and Se-ethyl group are both gauche conformation to the *m*-tolyl moiety (the torsion angles: O24-Se23-C25-C26=149(1)°, C32-Se23-C25-C26=−105(2)°). The host (*R*)-(+)-**1** and the guest (*S*)-(−)-**2** is connected by O(guest)···HO(host)OH···O(guest) hydrogen bonds (the distances: O24 ($1/2+x$, $1/2-y$, $1-z$)···O1=2.751(7) Å, O12···O24($-x$, $-y$, z)=2.723(7) Å). The crystal structure along *b*-axis is shown in Fig. 2. There are two right-handed hydrogen bonded helical chains along *b*-axis which run to the opposite direction along *b*-axis each other. As illustrated in Fig. 3, if the above

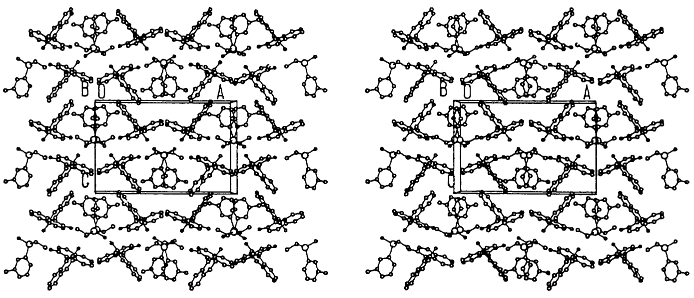


Fig. 2. Crystal structure of the host-guest complex along *b*-axis.

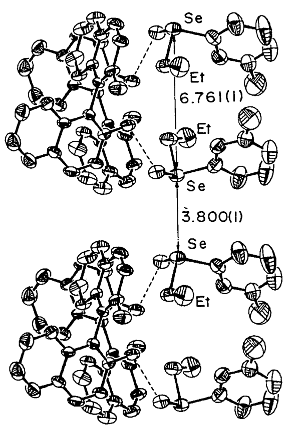


Fig. 3. A partial look about (*S*)-(−)-**2** in **3**.

mentioned hydrogen bonds and van der Waals contacts are neccessary to maintain the crystal structure, it is impossible to replace (*S*)-(−)-**2** by (*R*)-(+)-**2**, because the distance between Se atoms facing each other at the lone-paired electrons is 3.800(1) Å, whereas the corresponding distance facing each other at the ethyl groups is 6.761(1) Å. Therefore, the replacement of the lone-pair electrons by the bulky ethyl group is unattainable. But the selective inclusion of the (*S*)-(−)-**2** with (*R*)-(+)-**1** contrasts with that of *R*-enantiomer of methyl *m*-tolyl sulfoxide with (*R*)-(+)-**1**,[6] and further studies are needed to elucidate the enantioselective mechanism.

The authers wish to thank for the Ministry of Education, Science and Culture for Grant-in-Aid for Scientific Research on Priority Areas, No. 6328005.

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