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Synthesis and Mercurophilic Properties of Sulfur-Containing Troponoid Crown Ethers

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Condensation of 2,7-dibromotropone and 7-bromo-4-isopropyl-2-(4-tolysulfonyloxy)tropone with oligoethylene glycol bis(2-mercaptoethyl) ethers gave sulfur-containing crown ether derivatives. Among these mercurophilic derivatives, triethylene glycol bis(2-mercaptoethyl) derivatives transport and extract mercury ion excellently.

Previously, we have reported selective transportation and reversible extraction of mercury ion by means of troponoid-annexed dithio-crown ether derivatives.[1,2] We have also prepared polymer-supported derivatives.[3] However, preparations of these crown compounds required several steps. Therefore, it is desirable to develop a simple route to the derivatives having these interesting properties. At the same time, the observed reversibility of the complexation was explained in terms of Coulomb repulsion between the mercury (II) ion and hydroxytropylium ion formed upon acidification. Should this be the case, the sulfur atoms directly attached on the troponoid rings should be more sensitive towards acidification. Previously-prepared derivatives had at least one mercaptomethyl group being connected to the tropone ring.

Herein, we describe an easy synthesis of mercurophilic troponoids having sulfur substituents at 2- and 7-positions.

Results and Discussion

Preparation of the Dithio-Crown Ethers. At first, 2,7-dibromotropone (**1**)[4,5] was condensed, mediated by sodium hydride, with bis(2-mercaptoethyl) ether (**2a**) and its mono-, di-, tri-, and tetra-ethylene glycol homologues (**2b**, **2c**, **2d**, and **2e**) to give the 1:1-condensates (**3a** to **3e**) and 2:2-condensates (**4a** to **4c**). With longer bis(bromoethyl) ethers, 2:2-condensates were not formed due to a disadvantage in an entropy factor. Structures of new compounds were clarified by NMR spectroscopy as depicted in Scheme 1; in the ^{1}H NMR spectra all of these **3a** to **3e** had A_2B_2-type aromatic proton multiplets, and their overlapped ^{13}C NMR singals showed them to be symmetric compounds. These fundamental features were also observed in the NMR spectra of **4a** to **4c**.

In addition, the reaction of 7-bromo-4-isopropyl-2-(*p*-tolysulfonyloxy)tropone (**5**), prepared from 7-bromohinokitiol and *p*-tolysulfonyl chloride, with **2a**, **2b**, **2c**, **2d**, and **2e** afforded the corresponding 1:1- and 2:2-condensates (**6a**—**6e** and **7a**—**7c**). The ^{1}H NMR spectra of **6a** to **6e** showed ABX-systems in the aromatic proton regions. Although the isopropyl group on the seven-membered ring made them unsymmetrical, chemical shifts closely resembling with each other in the ^{13}C NMR spectra ascertained their structures. In this respect, it is clear from the ^{1}H and ^{13}C NMR spectra that **7a** to **7c** are chromatographically inseparable regioisomeric 1:1-mixtures. The yields of the condensates are included in Scheme 1.

Throughout the reactions, the yields of **3** and **4** were lower than those of **6** and **7**, but, one-step formation of the dithio-crown derivatives was satisfactory.

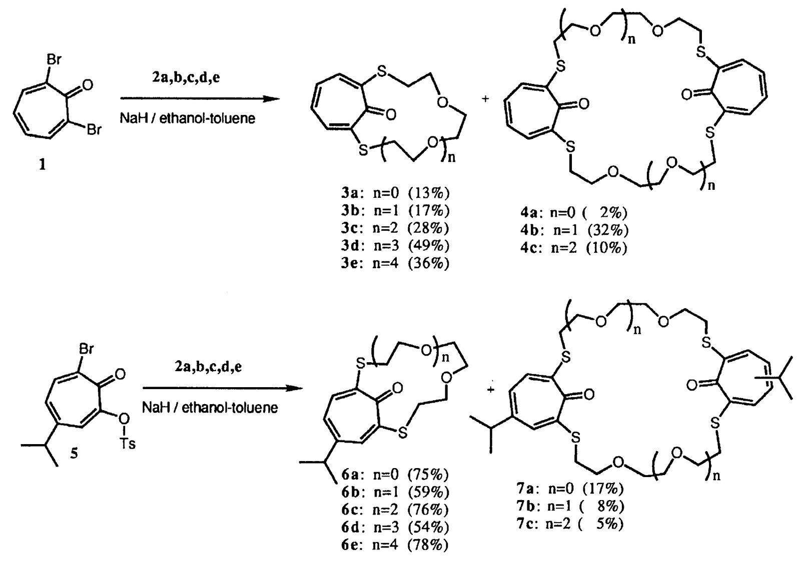
Complex Formation with Mercury Salt. In parallel to the previously examined compounds, these dithio-crown ethers capture mercury ion in neutral conditions, and liberate it upon acidification with hydrochloric acid as detected in the ^{1}H and ^{13}C NMR spectroscopy (Fig. 1). Surprisingly, the cavity size of **3a** or **6a** is not large enough to include mercury ion, but they did form the complexes with mercury ion. This was quite unpredicted.

Attempted complex formation with various metal ions, i. e., among alkali metals, alkaline earth metals, and some transition metal ions, lithium, sodium, magnesium, calcium, barium, cobalt, nickel, iron, copper, zinc, cadmium, and silver ions showed no indication of ^{1}H NMR spectral change.

In respects of the chemical shift differences, $\Delta\delta$, between **3d** and its mercury complex, which was measured in chloroform-*d* solution obtained by extraction from an aqueous mercury solution [^{1}H NMR δ=3.25 (4H, t, J=6.4 Hz), 3.61 (12H, m), 3.68 (4H, t, J=6.4 Hz), 6.95 (2H, m), and 7.41 (2H, m), and ^{13}C NMR δ=31.2 (2C), 68.7 (2C), 69.9 (4C), 70.5 (2C), 130.1 (2C), 133.2 (2C), 148.1 (2C), and 180.2], the complexation caused a very little but clear change for all the carbons; e. g., the carbonyl carbon ($\Delta\delta$=−0.7)[6] and the carbon bearing the thioether group ($\Delta\delta$=+1.4).

In the series of **3**, the molar ratios of the extracted mercury ion were compared with each other (Fig. 2), **3d** showed the highest value, 0.98, and others showed inferior figures, 0.29 for **3a**, 0.35 for **3b**, 0.24 for **3c**, and 0.71 for **3e**.

Thus, there is a size dependency for the complex formation, among the homologues, **3d** was most effective in respects of both extraction and transportation, and significant difference between **3d** and others, like **3e**, is noticed. This should be attributable to an appropriate size of the cavity in **3d**. In parallel, **6d** was most effec-



Scheme 1. Synthesis of dithio-crown ethers.

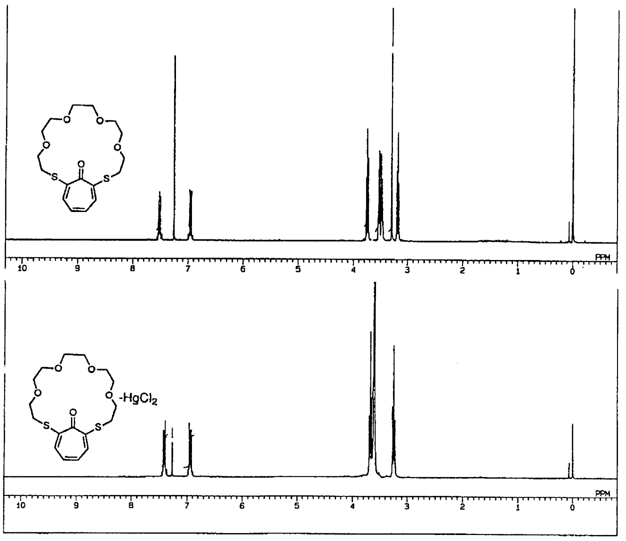


Fig. 1. The ^{1}H NMR spectra of **3d** and its Hg^{2+} complex.

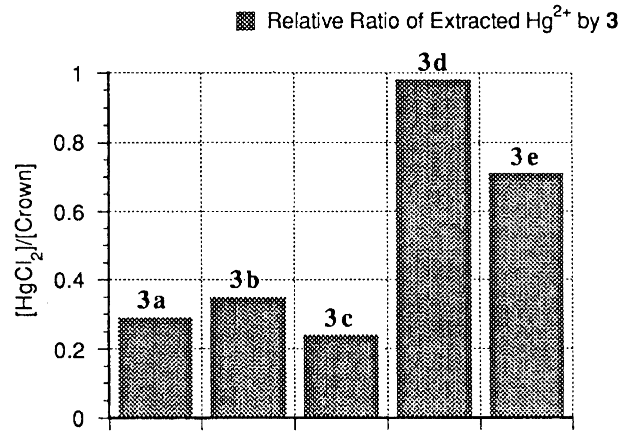


Fig. 2. Molar ratio of extracted Hg^{2+} to various **3** in a single extractive operation.

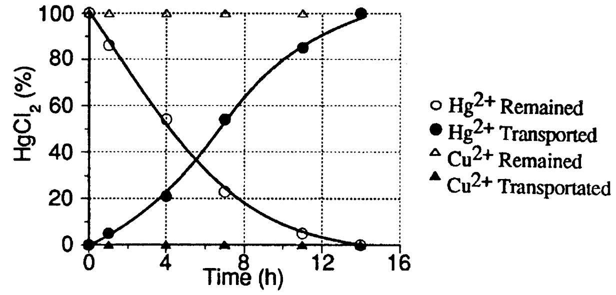


Fig. 3. Selective transportation of Hg ion from equimolar mixture of $HgCl_2$ and $CuCl_2$ with **3d**.

tive among its homologues. At the same time, the rates of the liberation step of mercury ion are very much improved, reflecting a marked decrease of basicity of the sulfur atoms, which are directly connected to the aromatic ring; the previous examples show complete liberation required almost twice the complexation period.[1,3] Figure 3 shows representative results of the transportation of mercury ion; e. g., by means of **3d**, mercury ion is selectively transferred smoothly, while coexisting copper ion remained in the original solution (Table 1).[1,3]

It is worthy of note that **3d** is the most effective mercurophilic troponoid among those prepared to date. Therefore, further studies, such as introductions of functional groups into **3d** or **6d** will be desirable, and the results will be reported in future.

Stereostructure of Mercurophilic Dithio-Crown Derivatives. Fortunately, some of the **3a** and its mercury complexes crystallized nicely. According to the X-ray diffraction structural analysis,[7] the mercury complex of **3a**, monoclinic crystal with cell dimensions $a=11.693(1)$, $b=15.083(3)$, $c=10.349(1)$ Å, and $\beta=98.000(8)°$ with $P2_1/a$, showed at the stage of the final R factor$=0.046$, its structure contains two mercury atoms per one **3a**. A discrepancy with the

Table 1. Relative Rate of Transportations of Hg^{2+} by Various Dithio-Crown Derivatives

Compounds	t_1/h[a)]	t_2/h[b)]	Compounds	t_1/h[a)]	t_2/h[b)]
3a	70	75	**6a**	90	110
3b	36	60	**6b**	78	110
3c	50	74	**6c**	40	88
3d	10	12	**6d**	22	75
3e	36	39	**6e**	90	110

a) t_1: Time required to become Hg ion undetectable in aq I. b) t_2: Time required to complete the transfer of Hg ion to aq II.

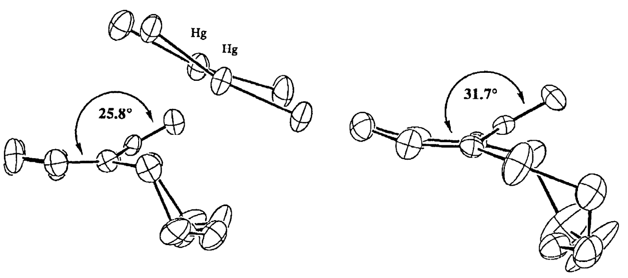


Fig. 4. ORTEP diagrams of **3a** and its Hg^{2+} complex.

result of extraction to the organic layer is not surprising, but the noteworthy thing is that two mercury ions are coordinated with one carbonyl oxygen assisted by two sulfur atoms. The stereoview of **3a** is depicted in Fig. 4. As predicted, the mercury-free **3a**, the cell dimensions of which were a=13.400(2), b=28.764(4), and c=12.035(2) Å with *Pbca*, had a non planar seven-membered ring, particularly, the carbonyl group deviated from the plane set by adjacent C=C bonds by as much as 31.7°, while that of the mercury complex with **3a** was 25.8°.

In conclusion, there is a fitting size of dithio-crown ethers for mercury ion, but the smaller ring derivatives still extract and transport the mercury ion. It is now suggested that mercury ion does not penetrate deep into the dithio-crown rings, and this geometry plays a positive role to facilitate the reversible complexation.

Experimental

The elemental analyses were done by Mrs. M. Miyazawa of the Institute of Advanced Material Study, Kyushu University. The melting points were measured with a Yanagimoto Micro Melting Point Apparatus and are uncorrected. The NMR spectra were measured with JEOL FX 100 Model and GSX 270H Model spectrometers in $CDCl_3$; the chemical shifts are expressed in unit of δ. The mass spectra were measured with a JEOL 01SG-2 spectrometer. The IR spectra were taken as KBr disks for crystalline compounds or as liquid films inserted between NaCl plates for oily compounds, using a JASCO IR-A102 spectrometer. The UV spectra were measured using Hitachi U-3200 and U-3410 spectrophotometers. The stationary phase for column chromatography was Wakogel C-300 and the eluent was a mixture of ethyl acetate, chloroform, and hexane.

Preparation of 7-Bromo-4-isopropyl-2-(4-tolysulfonyloxy)tropone (5). A pyridine solution (10 cm^3) of 7-bromohinokitiol (1.65 g) was treated with TsCl (1.91 g; 11 mmol) at room temperature and mechanically stirred for 24 h. The mixture was then diluted with water, extracted with EtOAc, and chromatographed on a silica-gel column to give **5** [colorless prisms, mp 109—110 °C. 2.69 g; 100%. Found: C, 51.44; H, 4.55%. Calcd for $C_{17}H_{17}O_4SBr$: C, 51.39; H, 4.31%. ^{1}H NMR δ=1.25 (6H, d, J=7.0 Hz), 2.45 (3H, s), 2.84 (1H, sept, J=7.0 Hz), 6.79 (1H, dd, J=9.9, 1.5 Hz), 7.36 (2H, d, J=8.4 Hz), 7.47 (1H, d, J=1.5 Hz), 7.94 (2H, d, J=8.4 Hz), and 8.09 (1H, d, J=9.9 Hz). ^{13}C NMR δ=21.8, 22.7 (2C), 37.9, 128.2 (2C), 129.7 (2C), 131.4, 133.0, 140.0, 140.1, 145.7, 151.2, 153.0, and 172.8. MS m/z 398 and 396 (M^+, 6 and 6), 332 (81), 155 (100), and 91 (39). IR ν 2962, 1626, 1605, 1379, 1188, 1086, 1067, 1046, 847, 812, 756, 720, and 655 cm^{-1}. UV $\lambda_{\max}^{\mathrm{CHCl_3}}$=224 nm ($\varepsilon$=24300), 250 (20200), 256 (19100, sh), and 333 (9900)].

Condensations of 1 or 5 with 2 (General Method). Formation of 3, 4, 6, and 7. To a refluxing EtOH solution (25 cm^3) of NaOEt (143 mg; 2.3 mmol) and **2** (1.15 mmol) was added dropwise **1** (303 mg; 1.15 mmol) or **5** (457 mg; 1.15 mmol) dissolved in EtOH (15 cm^3) and benzene (10 cm^3) for 3 h. After additional refluxing for 2 h, the mixture was distilled in vacuo and the residue thus obtained was chromatographed on a silica-gel column to give the products.

3a: Yellow plates, mp 126—127 °C. ^{1}H MNR δ=2.65 (2H, ddd, J=14.8, 5.9, 1.8 Hz), 3.45 (2H, ddd, J=14.8, 8.8, 2.2 Hz), 3.75 (2H, ddd, J=11.0, 5.9, 2.2 Hz), 3.93 (2H, ddd, J=11.0, 8.8, 1.8 Hz), 6.5—6.6 (2H, m), and 7.3—7.4 (2H, m). ^{13}C NMR δ=33.2 (2C), 75.5 (2C), 76.6 (2C), 129.7 (2C), 133.5 (2C), 143.7 (2C), and 185.9. MS m/z 240 (M^+, 100), 197 (28), 196 (48), 169 (19), 153 (30), 141 (20), 140 (30), and 96 (22). IR ν 2956, 2918, 2850, 1626, 1593, 1439, 1401, 1330, 1283, 1098, 773, 729, and 669 cm^{-1}. UV $\lambda_{\max}^{\mathrm{CHCl_3}}$=286 nm ($\varepsilon$=4500), 316 (6100), and 371 (5000). Found: C, 54.75; H, 4.98%. Calcd for $C_{11}H_{12}O_2S_2$: C, 54.97; H, 5.03%.

3b: A yellow oil. ^{1}H NMR δ=3.19 (4H, t, J=5.5 Hz), 3.34 (4H, s), 3.60 (4H, t, J=5.5 Hz), 6.77—6.86 (2H, m), and 7.38—7.47 (2H, m). ^{13}C NMR δ=32.4 (2C), 69.7 (2C), 70.7 (2C), 129.2 (2C), 132.9 (2C), 145.6 (2C), and 181.8. MS m/z 284 (M^+, 100), 196 (63), 170 (28), 163 (30), 162 (30), 153 (29), 140 (42), and 96 (32). IR ν 2890, 2860, 1606, 1581, 1450, 1405, 1366, 1337, 1286, 1243, 1134, 1118, 1028, 1005, 972, 907, 766, 697, and 656 cm^{-1}. UV $\lambda_{\max}^{\mathrm{CHCl_3}}$=318 ($\varepsilon$=8900) and 386 (7200). Found: m/z 284.0542 (M^+). Calcd for $C_{13}H_{16}O_3S_2$: M, 284.0540.

3c: Yellow crystals, mp 138—139 °C. ^{1}H NMR δ=3.21 (4H, t, J=5.5 Hz), 3.29—3.32 (4H, m), 3.43—3.46 (4H, m), 3.67 (4H, t, J=5.5 Hz), 6.83—6.92 (2H, m), and 7.50—7.59 (2H, m). ^{13}C NMR δ=31.2 (2C), 70.4 (2C), 70.8 (2C), 70.9 (2C), 129.0 (2C), 132.1 (2C), 148.4 (2C), and 180.5. MS m/z 328 (M^+, 100), 222 (43), 196 (75), 195 (33), 140 (39), 96 (33), 70 (39), and 45 (41). IR ν 2866, 1555, 1392, 1357, 1341, 1289, 1123, 1107, 1090, 1034, 1020, 974, 801, 764, and 696 cm^{-1}. UV $\lambda_{\max}^{\mathrm{CHCl_3}}$=315 nm ($\varepsilon$=11000), 374 (8000, sh), and 396 (9500). Found: C, 55.06; H, 6.15%. Calcd for $C_{15}H_{20}O_4S_2$: C, 54.85; H, 6.14%.

3d: A yellow oil. ^{1}H NMR δ=3.18 (4H, t, J=5.5 Hz), 3.29 (4H, s), 3.42—3.55 (8H, m), 3.75 (4H, t, J=5.5 Hz), 6.92—7.01 (2H, m), and 7.48—7.57 (2H, m). ^{13}C NMR δ=31.2 (2C), 70.6 (2C), 70.7 (2C), 71.5 (2C), 128.6 (2C), 130.4 (2C), 149.5 (2C), and 179.5. MS m/z 372 (M^+, 73), 222 (66), 196 (100), 163 (46), 162 (48), 140 (44), 70 (45), and 45 (58). IR ν 2860, 1563, 1534, 1342, 1116, 1032, 974, 769, and 669 cm^{-1}. UV $\lambda_{\max}^{\mathrm{CHCl_3}}$=310 nm ($\varepsilon$=12800), 382 (10900), and 403 (11800). Found: m/z (FAB-MS), 373.1141 (M+H)$^+$. Calcd for $\mathrm{C_{17}H_{24}O_5S_2}$: M+H, 373.1143.

3e: A yellow oil. ^{1}H NMR δ=3.16 (4H, t, J=5.9 Hz), 3.45 (8H, s), 3.51—3.61 (8H, m), 3.79 (4H, t, J=5.9 Hz), 6.93—7.02 (2H, m), and 7.42—7.51 (2H, m). ^{13}C NMR δ= 31.6 (2C), 69.9 (2C), 70.6 (2C), 70.7 (2C), 70.9 (2C), 71.0 (2C), 128.5 (2C), 129.6 (2C), 149.9 (2C), and 179.2. MS m/z 416 (M$^+$, 47), 222 (68), 196 (100), 195 (40), 194 (40), 163 (42), 162 (48), and 45 (61). IR ν 2860, 1597, 1555, 1537, 1458, 1415, 1399, 1343, 1294, 1252, 1195, 1115, 1032, 1003, 975, 944, 909, 771, 743, 701, and 650 cm^{-1}. UV $\lambda_{\max}^{\mathrm{CHCl_3}}$= 310 nm ($\varepsilon$=11200), 379 (8900), and 403 (10100). Found: m/z (FAB-MS) 417.1392 (M+H)$^+$. Calcd for $\mathrm{C_{19}H_{28}O_6S_2}$: M+H, 417.1406.

4a: Yellow crystals, mp 256—258 °C. ^{1}H NMR δ=3.06 (8H, t, J=5.5 Hz), 3.79 (8H, t, J=5.5 Hz), 6.91—7.00 (4H, m), and 7.30—7.39 (4H, m). ^{13}C NMR δ=31.7 (4C), 70.0 (4C), 129.0 (4C), 129.4 (4C), 149.6 (4C), and 178.6 (2C). MS m/z 480 (M$^+$, 2), 196 (30), 195 (40), 170 (34), 138 (36), 136 (33), 61 (100), 60 (47), 45 (35), and 26 (37). IR ν 2914, 2854, 1571, 1538, 1524, 1469, 1454, 1402, 1362, 1346, 1252, 1234, 1105, 1058, 1037, 1000, 973, 950, 765, 729, 702, and 644 cm^{-1}. UV $\lambda_{\max}^{\mathrm{CHCl_3}}$=305 nm ($\varepsilon$=17800), 359 (11300), 378 (14800), and 402 (13100). Found: C, 54.86; H, 5.01%. Calcd for $\mathrm{C_{22}H_{24}O_4S_4}$: C, 54.97; H, 5.03%.

4b: Yellow crystals, mp 195—197 °C. ^{1}H NMR δ=3.02 (8H, t, J=6.2 Hz), 3.61—3.65 (8H, m), 3.73 (8H, t, J=6.2 Hz), 6.92—7.00 (4H, m), and 7.25—7.33 (4H, m). ^{13}C NMR δ=31.2 (4C), 69.6 (4C), 71.0 (4C), 128.6 (4C), 128.7 (4C), 150.4 (4C), and 178.7 (2C). IR ν 2908, 2866, 1548, 1532, 1457, 1334, 1134, 1108, 977, 910, 770, 710, and 664 cm^{-1}. MS m/z 568 (M$^+$, 9), 196 (55), 195 (41), 163 (32), 140 (48), 96 (37), 61 (100), 60 (56), and 59 (44). UV $\lambda_{\max}^{\mathrm{CHCl_3}}$=307 nm ($\varepsilon$=31800), 360 (18400, sh), 380 (25600), and 403 (25800). Found: C, 54.53; H, 6.05%. Calcd for $\mathrm{C_{26}H_{32}O_6S_4}$: C, 54.91; H, 5.67%.

4c: Yellow crystals, mp 141—142 °C. ^{1}H NMR δ=3.07 (8H, t, J=6.6 Hz), 3.65 (16H, s), 3.78 (8H, t, J=6.6 Hz), 6.94—7.02 (4H, m), and 7.20—7.27 (4H, m). ^{13}C NMR δ= 30.7 (4C), 68.0 (4C), 69.7 (4C), 69.8 (4C), 127.3 (4C), 127.5 (4C), 149.5 (4C), and 177.6 (2C). IR ν 2942, 2856, 1567, 1546, 1532, 1396, 1368, 1343, 1255, 1132, 1115, 1012, 977, 768, and 740 cm^{-1}. MS m/z 656 (M$^+$, 16), 328 (58), 222 (66), 208 (54), 196 (100), 195 (66), 163 (48), 61 (48), and 45 (79). UV $\lambda_{\max}^{\mathrm{CHCl_3}}$=308 nm ($\varepsilon$=29500), 359 (16500, sh), 380 (23900), and 403 (24900). Found: C, 54.96, H, 6.16%. Calcd for $\mathrm{C_{30}H_{40}O_8S_4}$: C, 54.85; H, 6.14%.

6a: Yellow plates, mp 93—95 °C. ^{1}H NMR δ=1.15 (3H, d, J=7.0 Hz), 1.17 (3H, d, J=7.0 Hz), 2.6—2.7 (3H, m), 3.33 (1H, ddd, J=15.0, 8.1, 2.2 Hz), 3.49 (1H, ddd, J=15.0 8.8, 2.2 Hz), 3.7—3.8 (2H, m), 3.85—3.95 (2H, m), 6.45 (1H, J=8.8, 1.5 Hz), 7.35 (1H, d, J=1.5 Hz), and 7.36 (1H, d, J=8.8 Hz). ^{13}C NMR δ=22.7, 23.1, 23.7, 33.6, 37.0, 75.2 (2C), 125.3, 134.6, 135.1, 140.8, 143.5, 150.7, and 185.7. MS m/z 282 (M$^+$, 100), 239 (41), 167 (36), 134 (22), and 91 (22). IR ν 2962, 2922, 2856, 1624, 1595, 1463, 1406, 1347, 1297, 1205, 1098, 1038, 840, and 753 cm^{-1}. UV $\lambda_{\max}^{\mathrm{CHCl_3}}$=244 nm ($\varepsilon$=5700), 288 (4400), 314 (5200), and 364 (4500). Found: C, 59.83; H, 6.37%. Calcd for $\mathrm{C_{14}H_{18}O_2S_2}$: C, 59.83; H, 6.37%.

6b: A yellow oil. ^{1}H NMR δ=1.22 (6H, d, J=7.0 Hz), 2.77 (1H, sept, J=7.0 Hz), 3.18 (2H, t, J=6.0 Hz), 3.19 (2H, t, J=6.0 Hz), 3.36 (4H, s), 3.59 (4H, t, J=6.0 Hz), 6.67 (1H, dd, J=9.2, 1.5 Hz), 7.39 (1H, d, J=1.5 Hz), and 7.40 (1H, d, J=9.2 Hz). ^{13}C NMR δ=23.2 (2C), 32.2 (2C), 37.4, 69.4, 69.7, 70.6 (2C), 125.3, 134.6, 135.1, 140.8, 143.5, 150.7, and 185.7. MS m/z 226 (M$^+$, 100), 238 (61), 212 (33), 167 (33), and 134 (29). IR ν 2960, 2866, 1608, 1584, 1465, 1407, 1351, 1298, 1136, 1027, 1002, and 753 cm^{-1}. UV $\lambda_{\max}^{\mathrm{CHCl_3}}$=204 nm ($\varepsilon$=10500), 244 (7400), 317 (8700), and 374 (6200). Found: m/z 326.1007 (M$^+$). Calcd for $\mathrm{C_{16}H_{22}O_3S_2}$: M, 326.1009.

6c: A yellow oil. ^{1}H NMR δ=1.25 (6H, d, J=7.0 Hz), 2.83 (1H, sept, J=7.0 Hz), 3.19 (2H, t, J=5.1 Hz), 3.21 (2H, t, J=5.1 Hz), 3.26— 3.47 (4H, m), 3.55 (2H, t, J=5.5 Hz), 3.67 (2H, t, J=5.5 Hz), 6.77 (1H, dd, J=9.5, 1.4 Hz), 7.51 (1H, d, J=1.4 Hz), and 7.54 (1H, d, J=9.5 Hz). ^{13}C NMR δ=23.5 (2C), 31.1, 38.0, 70.3, 70.4, 70.5, 70.7, 70.8, 70.9, 126.0, 132.9, 133.5, 144.8, 150.5, and 179.9. MS m/z 226 (M$^+$, 100), 238 (61), 212 (33), 167 (33), and 134 (29). IR ν 2960, 2866, 1608, 1584, 1465. 1407, 1351, 1298, 1136, 1027, 1002, and 753 cm^{-1}. UV $\lambda_{\max}^{\mathrm{CHCl_3}}$=205 nm ($\varepsilon$=14100), 242 (10700), 314 (12100), 373 (8700, sh), and 393 (9200). Found: m/z 370.1276 (M$^+$). Calcd for $\mathrm{C_{16}H_{22}O_3S_2}$: M, 370.1271.

6d: A yellow oil. ^{1}H NMR δ=1.28 (6H, d, J=7.0 Hz), 2.87 (1H, sept, J=7.0 Hz), 3.17 (2H, t, J=5.1 Hz), 3.19 (2H, t, J=5.1 Hz), 3.29 (4H, s), 3.45—3.48 (4H, m), 3.50—3.56 (4H, m), 3.72 (2H, t, J=5.5 Hz), 3.75 (2H, t, J=5.5 Hz), 6.86 (1H, dd, J=9.9, 1.1 Hz), 7.48 (1H, d, J=9.9 Hz), and 7.49 (1H, d, J=1.1 Hz). ^{13}C NMR δ=23.7 (2C), 31.0, 31.3, 38.3, 70.2, 70.6, 70.7 (4C), 71.4, 71.5, 126.0, 131.4, 131.5, 146.1, 149.0, 150.1, and 179.0. MS m/z 414 (M$^+$, 77), 264 (50), 238 (100), 221 (37), 204 (35), and 45 (49). IR ν 2956, 2862, 1551, 1463, 1355, 1297, 1248, 1118, 998, 936, 906, and 763 cm^{-1}. UV $\lambda_{\max}^{\mathrm{CHCl_3}}$=241 nm ($\varepsilon$=11300), 311 (14800), 375 (10400, sh), and 400 (11400). Found: m/z 414.1534 (M$^+$). Calcd for $\mathrm{C_{20}H_{22}O_3S_2}$: M, 414.1533.

6e: A yellow oil. ^{1}H NMR δ=1.28 (6H, d, J=7.0 Hz), 2.87 (1H, sept, J=7.0 Hz), 3.14 (2H, t, J=5.1 Hz), 3.16 (2H, t, J=5.1 Hz), 3.45 (4H, s), 3.46 (4H, s), 3.5—3.63 (8H, m), 3.76 (2H, t, J=6.2 Hz), 3.79 (2H, t, J=5.9 Hz), 6.85 (1H, dd, J=9.9, 1.5 Hz), 7.41 (1H, d, J=9.9 Hz), and 7.41 (1H, d, J=1.5 Hz). ^{13}C NMR δ=23.7 (2C), 31.3, 31.7, 38.4, 69.8, 69.9, 70.6, 70.7, 70.8 (4C), 70.9, 71.0 (2C), 126.0, 130.7, 130.8, 146.6, 149.3, 150.0, and 178.9. MS m/z 458 (M$^+$, 47), 264 (53), 238 (100), 221 (36), 204 (30), 167 (26), 134 (22), and 45 (55). IR ν 2186, 1553, 1463, 1354, 1297, 1251, 1115, 997, 937, 839, and 763 cm^{-1}. UV $\lambda_{\max}^{\mathrm{CHCl_3}}$=242 nm ($\varepsilon$=12900), 311 (17500), and 377 (12500). Found: m/z 458.1797 (M$^+$). Calcd for $\mathrm{C_{20}H_{22}O_3S_2}$: M, 458.1795.

7a: Yellow prisms, mp 150—151 °C. ^{1}H NMR δ=1.28 (12H, d, J=7.0 Hz), 2.87 (2H, sept, J=7.0 Hz), 2.99 (4H, t, J=5.9 Hz), 3.07 (4H, t, J=5.9 Hz), 3.71 (4H, t, J=5.9 Hz), 3.75 (4H, t, J=5.9 Hz), 6.84 (1H, dd, J=9.9, 1.4 Hz), 7.27 (1H, d, J=9.9 Hz), and 7.34 (1H, d, J=1.4 Hz). ^{13}C NMR[8] δ=23.7 (4C), 31.4 (2C), 31.7 (2C), 38.3 (2C), 69.9 (4C), 126.5 (2C), 130.6 (2C), 131.5 (2C), 146.5 (2C), 148.3 (2C), 149.9 (2C), and 178.5 (2C). MS m/z 564 (M$^+$, 100), 282 (82), 265 (61), 237 (81), 205 (37), 167 (36), 134 (37), and 43 (35). IR ν 2956, 2914, 2860, 1570, 1547, 1465, 1408, 1362, 1104, 991, 827, and 763 cm^{-1}. UV $\lambda_{\max}^{\mathrm{CHCl_3}}$=240 nm ($\varepsilon$=23000), 306 (30600), 374 (22500), and 397 (19900, sh). Found: C, 59.34; H, 6.26%. Calcd for $C_{28}H_{36}O_4S_4$: C, 59.54; H, 6.42%.

7b: Yellow prisms, mp 174—175 °C. ^{1}H NMR δ=1.27 (12H, d, J=7.0 Hz), 2.8—3.1 (10H, m), 3.5—3.7 (16H, m), 6.86 (2H, dd, J=10.3, 1.5 Hz), 7.20 (1H, d, J=10.2 Hz), 7.24 (1H, d, J=10.3 Hz), 7.24 (1H, d, J=1.5 Hz), and 7.28 (1H, d, J=1.5 Hz). ^{13}C NMR δ=23.8 (4C), 31.3 (2C×0.5), 31.4 (2C×0.5), 31.7 (2C×0.5), 31.8 (2C×0.5), 38.4 (4C), 69.2 (2C×0.5), 69.4 (2C), 69.6 (2C×0.5), 70.8 (2C), 71.0 (2C), 126.0 (2C), 129.6 (4C×0.5), 130.1 (4C×0.5), 147.2 (2C×0.5), 147.3 (2C×0.5), 149.5 (2C×0.5), 149.6 (2C×0.5), 149.7 (2C), and 178.3 (2C). MS m/z 652 (M^+, 7), 506 (5), 326 (32), 238 (41), 204 (60), and 61 (100). IR ν 2954, 2862, 1547, 1456, 1401, 1358, 1248, 1124, 1092, 1037, 994, 848, 746, and 633 cm^{-1}. UV $\lambda_{\rm max}^{\rm CHCl_3}$=241 nm ($\varepsilon$=23900), 307 (32300), 376 (23300), and 400 (23900). Found: C, 58.83; H, 6.74%. Calcd for $C_{32}H_{44}O_6S_4$: C, 58.86; H, 6.79%.

7c: A yellow oil. ^{1}H NMR δ=1.26 (12H, d, J=7.0 Hz), 2.87 (2H, sept, J=7.0 Hz), 3.0—3.1 (8H, m), 3.59 (8H, d, J=1.1 Hz), 3.63 (8H, s), 3.67—3.75 (8H, m), 6.67 (2H, dm, J=10.3 Hz), and 7.15—7.25 (4H, m). ^{13}C NMR δ= 23.8 (4C), 31.3 (2C), 31.7 (2C), 38.4 (2C), 69.0 (4C), 70.7 (4C), 70.8 (4C), 126.0 (2C), 129.1 (2C), 129.3 (2C), 147.3 (2C×0.5), 147.4 2C×0.5), 149.5 (2C), 149.8 (2C), and 178.2 (2C). MS m/z 740 (M^+, 2), 371 (14), 238 (35), 204 (18), and 61 (100). IR ν 2956, 2866, 1554, 1528, 1463, 1356, 1295, 1251, 1116, 1000, and 937 cm^{-1}. UV $\lambda_{\rm max}^{\rm CHCl_3}$=241 nm ($\varepsilon$=21500), 307 (29100), 376 (21400), and 401 (21900). Found: m/z 740.2540 (M^+). Calcd for $C_{36}H_{52}O_8S_4$: M, 740.2542.

Extraction Experiments of Hg^{2+} Ion by 3a—3e. A standard aqueous solution (10 cm^3) containing $HgCl_2$ (0.15 mM) was shaken with $CHCl_3$ solution (10 cm^3) of **3a**—**3e** (each 0.15 mmol) for 5 min (1 M=1 mol dm^{-3}). Aqueous layer was titrated photometrically (λ=490 nm or 610 nm) in the phosphate buffer (10 cm^3, pH=6.0) with added 1,5-diphenylthiocarbazone solution (5 cm^3, 0.0006%).

Selective Transportation of Hg^{2+} from an Equimolar Mixture of Hg^{2+} and Cu^{2+} Ion by 3d. To the above standard solution (10 cm^3) of $HgCl_2$ (0.05 mmol), an equimolar amount of Cu^{2+} was added, and placed as aq I. As described previously, transportation experiments with aq I were done using a U-type cell consisted of $CHCl_3$ (20 cm^3) containing **3d** (18.6 mg) and 5 M HCl (10 cm^3, aq II), at room temperature. Occasionally, 0.5 cm^3 of samples were taken from aq I and aq II and diluted with water to 50 cm^3, from which, 0.5 cm^3 was taken to titrate Hg^{2+};[9] i. e., the solution was acidified with 0.05 M H_2SO_4, and 50%-aqueous NH_2OH solution (4 cm^3) and 0.1 M ethylenediaminetetraacetic acid (EDTA) solution (2 cm^3) were added and shaken for 1 min. To the mixture, $CHCl_3$ solution (5 cm^3) containing 0.0006% 1,5-diphenylthiocarbazone was then added and extracted. The organic layer was dried on a filter paper and Hg^{2+} ion was measured photometrically (λ=490 nm or 610 nm).

To measure Cu^{2+},[10] 0.5 cm^3 were also taken from aq I and aq II and diluted with water to 5 cm^3, to 0.5 cm^3 of which, aqueous citric acid solution (2.00 g in 10 cm^3) was added to acidify the solution, and then aqueous EDTA solution (500 mg of EDTA dihydrate in 10 cm^3) was added. The mixture was brought to pH=9.0 by adding NH_3. After 20 min, the mixture was transferred into a separatory funnel, and diluted with water to 50 cm^3. The sodium diethyldithiocarbamate (DDTC) solution (5 cm^3) was added and shaken with $CHCl_3$ solution (10 cm^3). The organic layer was dried on a filter paper, and photometrically (λ=440 nm) measured.

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6) For the $\Delta\delta$ values ($=\delta_3-\delta_{3-{\rm Hg}^{2+}}$), the plus sign indicates a high field shift.

7) The X-ray study will be reported independently.

8) Assignment for these ^{13}C NMR spectra of 1 : 1-mixtures of isomers of **7a**, **7b**, and **7c** was elaborated from the comparisons with **4** as well as mutual comparisons. Concerning the numbers of carbons involved, nC means either nC or 2nC×0.5, unless otherwise stated.

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