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Synthesis and Mercurophilic Properties of 2,2′-Oxybis(ethylenethio)ditropone and α-[2-(2-Troponylthio)ethyl]-ω-(2-troponylthio)oligo(oxyethylene)

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The condensation reactions of 2-(*p*-tolylsulfonyloxy)tropone with 2,2′-oxydiethanethiol and its α-(2-sulfanylethyl)-ω-sulfanyloligo(oxyethylene) derivatives afforded 2,2′-oxybis(ethylenethio)ditropone and α-[2-(2-troponylthio)ethyl]-ω-(2-troponylthio)oligo(oxyethylene). Reflecting the acyclic nature of the polyethylene glycol moiety, they formed the complexes with various metal ions. Among them, mercury(II) salts were exclusively transported through a liquid membrane at least under the conditions used.

We are currently interested in synthesizing metal ion-capturing dithio crown ethers having troponoid pendants (**1** and **2**).[1,2] Particularly noteworthy are their reversible complexation behaviors with mercury(II) salts to enable the transport of mercury(II) ions through a liquid membrane. In addition, the NMR spectroscopic behaviors of these complexes revealed an irregular change in the chemical shifts, i.e., a group of signals of a complex shifted down-field, while another group of signals shifted up-field, suggesting existence of dual coordination sites for complexation. This was parallel to the results of X-ray diffraction studies;[3—5] there are two kinds of coordination modes, one of which is the side-on type and the other the normal penetrated type. The shortest 5-oxa-2,8-dithiabicyclo[7.4.1]tetradeca-1(13),9,11-trien-14-one (**1a**) (Chart 1), whose crown ring is not large enough to provide a cavity to include mercury(II) ion, was also a reversible mercurophile, and its X-ray structural analysis showed that mercury(II) ion is coordinated with the tropone carbonyl group and the thioether sulfur atoms (side-on complex).[3] However, the most effective mercurophile, 23-dicyanomethylene-5,8,11,14,17-pentaoxa-2,20-dithiabicyclo[19.4.1]hexacosa-1(26),21,24-triene (**2e**), has five ethereal oxygen atoms with the suitable cavity size,[6] and, the X-ray diffraction study of its mercury(II) chloride complex showed that the mercury ion is at the center of the dithiocrown ring (normal penetrated complex).[5]

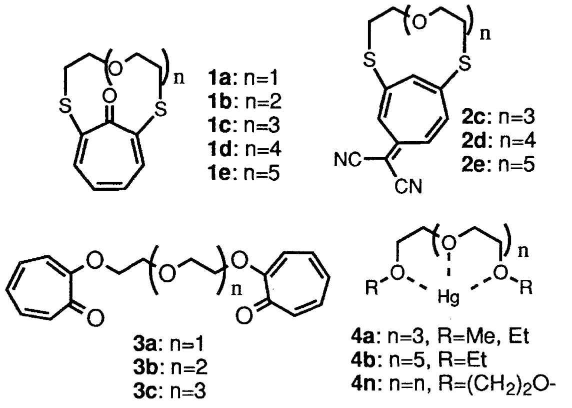


Chart 1.

Thus, although the selectivity in the podand series towards metal salts should be lower than that in the cyclic counterparts, it is interesting to investigate the selectivity on the mercurophilicity of acyclic analogs as well as the generality for various metal ions. In this respect, some studies have already been reported. Vögtle et al. synthesized oligoethylene glycol bis(2-troponyl) ethers (**3**) together with several other tropone-containing podands,[7] and, indeed, the analyzed metallophilic properties called for further works; compositions of metal complexes, deduced from combustion analyses, suggested a positive role of the tropone carbonyl groups in the podand molecules. Iwamoto observed also the complex formation of mercury(II) salts with poly(oxyethylene) dialkyl ethers (**4**)[8] as well as poly(oxyethylene) (**4n**);[9] the simplicity of these structures may have a potential in practical use.

It should be pointed out that the low reactivity of oxygen nucleophiles makes it difficult to synthesize a series of troponoid crown and podand derivatives. In view of an easy access to various dithiocrown derivatives of tropones and heptafulvenes, dithio analogs of troponoid podands should be promising in this respect. Herein described are the results on these points.

Results and Discussion

Spectral Analyses of Complexes. In tropone or 8,8-dicyanoheptafulvene-attached cyclic dithiocrown derivatives, a number of cases showed no UV spectral change upon complexation. This is true since the complexations did not always result in a change of electronic states of the seven-membered conjugated systems. The X-ray diffraction analysis of the 1 : 1-complex of mercury(II) chloride and **2e**, the most efficient mercury(II) ion carrier, showed that the primarily coordinated hetero atoms to the mercury(II) ion were five ethereal oxygen atoms,[5)] but two thioether sulfur atoms and the tropone carbonyl group were far distant from the center of complexation. This inverted order of mercurophilicity, oxygen > sulfur, is rather unexpected. However, although conformationally mobile podand derivatives might be less selective for the complexations with metal ions, the analysis of mercurophilicity will be worthy of investigations.

Should the thioether sulfur atoms play a role in complexation, it should cause a change of electronic structures of the tropone system. Therefore, the UV spectra of **7a** to **7e** with various metal salts were measured with the concentration range of 0.02 mmol of **7** in 1 dm^3 of acetonitrile (MeCN) and 0.01, 0.1, 2, and 20 mmol of metal salts in 1 dm^3 of MeCN; with **7c**, **7d**, and **7e**, the most pronounced change in the absorption spectra was observed with barium(II) ion, which was followed by calcium(II) and cadmium(II) ions (Scheme 1).

A typical example of the outstanding UV-spectral changes of **7e** caused upon additions of various amounts of metal ions is shown in Fig. 1. Similar spectral changes were observed for **7a**—**d**. Using such spectral changes, the molar compositions of complexes were determined to be always 1 : 1 from the Benesi–Hildebrand analysis[10)] and curve-fitting analysis.[11)] As the representative examples, results of **7e** with $Ba(SCN)_2$ and $Ca(SCN)_2$ are shown in Fig. 2. The association constants could be determined (Fig. 3); the calculated figures are summarized in Table 1. In the same time, the UV spectral changes which provided the large association constants for the alkali earth metal salts, in particular for barium salt, are noteworthy. The most outstanding feature is that the association constants with the higher derivatives are larger than those of the cyclic dithiocrown derivatives.

In general, association constants of podands are smaller than those of crown ethers; e.g., $\log K$(hexaglyme) = 1.60 for Na^+ and 2.55 for K^+; $\log K$(18-crown-6) = 4.32 for Na^+; and 6.10 for K^+.[12)] However, the present results obtained from the experiments of alkali earth and cadmium salts were just the opposite. In our case, freedom in the conformational change of the ethers played an important role to stabilize the complexes. This means that the terminal tropone ring on the ethereal chain behaved as a sterically hindered group.

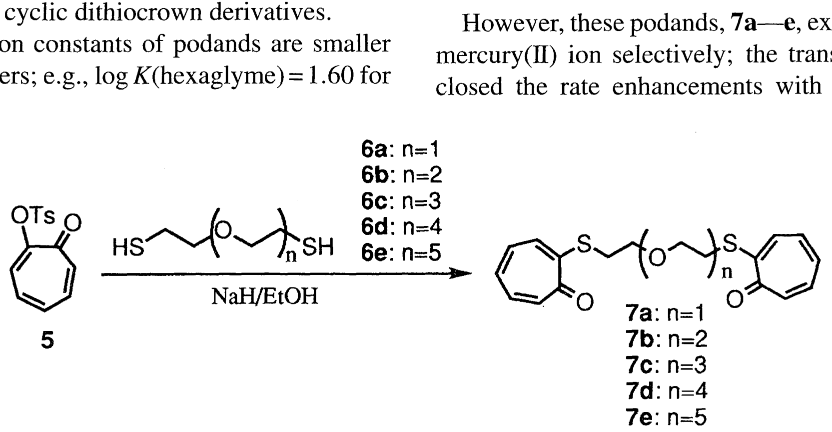
Table 1. Association Constants ($\log K_s$) for 1 : 1 Complexes of a Series of **7** and **1d** with Several Metal Salts, $M(SCN)_2$, in Acetonitrile at 25 °C

	Ca^{2+}	Ba^{2+}	Cd^{2+}	Mg^{2+}
7a	2.96			
7b	3.18			
7c	2.44	2.84	2.02	
7d	3.57	4.38	2.93	
7e	5.22	5.31	2.98	2.06
1d	3.86	3.73	1.86	1.30

Although no appreciable change of the electronic spectra was observed for mercury(II) salt, the ^{1}H NMR spectral changes of **7e** were clearly discernible in the complexes of mercury(II) and silver(I) salts, as shown in Fig. 4. Similar spectral changes for **7c** and **7d** were observed. This suggests that the sulfur atoms of **7** might not play a significant role for the complexation with mercury(II) and silver(I) ions. This behavior might be characteristic for troponyl thioether groups, as can be seen from the X-ray structure evidence on **2e**;[5)] the 6π-electron stabilization of the tropone system decreases the electron density of thioether sulfur atoms to disfavor the complexation. No other metals such as zinc(II), cadmium(II), calcium(II), barium(II), and copper(II) revealed any indication of complexations in the ^{1}H NMR chemical shifts criteria.

While UV-spectroscopy indicated the complexation of **7** with cadmium(II) ion, it could not be transported by **7** with a U-type cell (the same apparatus used in the previous study),[2)] which was set to contain the source phase (Aq. I) (0.05 mmol of the metal salt in 10 cm^3 of water), chloroform (0.05 mmol of **7** or **1d** in 20 cm^3), and the receiving phase (Aq. II) (10 cm^3 of 5 M HCl) (1 M = 1 mol dm^{-3}); after continuous stirring for 24 h, no metal salt was transported in Aq. II. Similarly, calcium and barium ions were not transported.

However, these podands, **7a**—**e**, extracted and transported mercury(II) ion selectively; the transport experiments disclosed the rate enhancements with increased numbers of



Scheme 1.

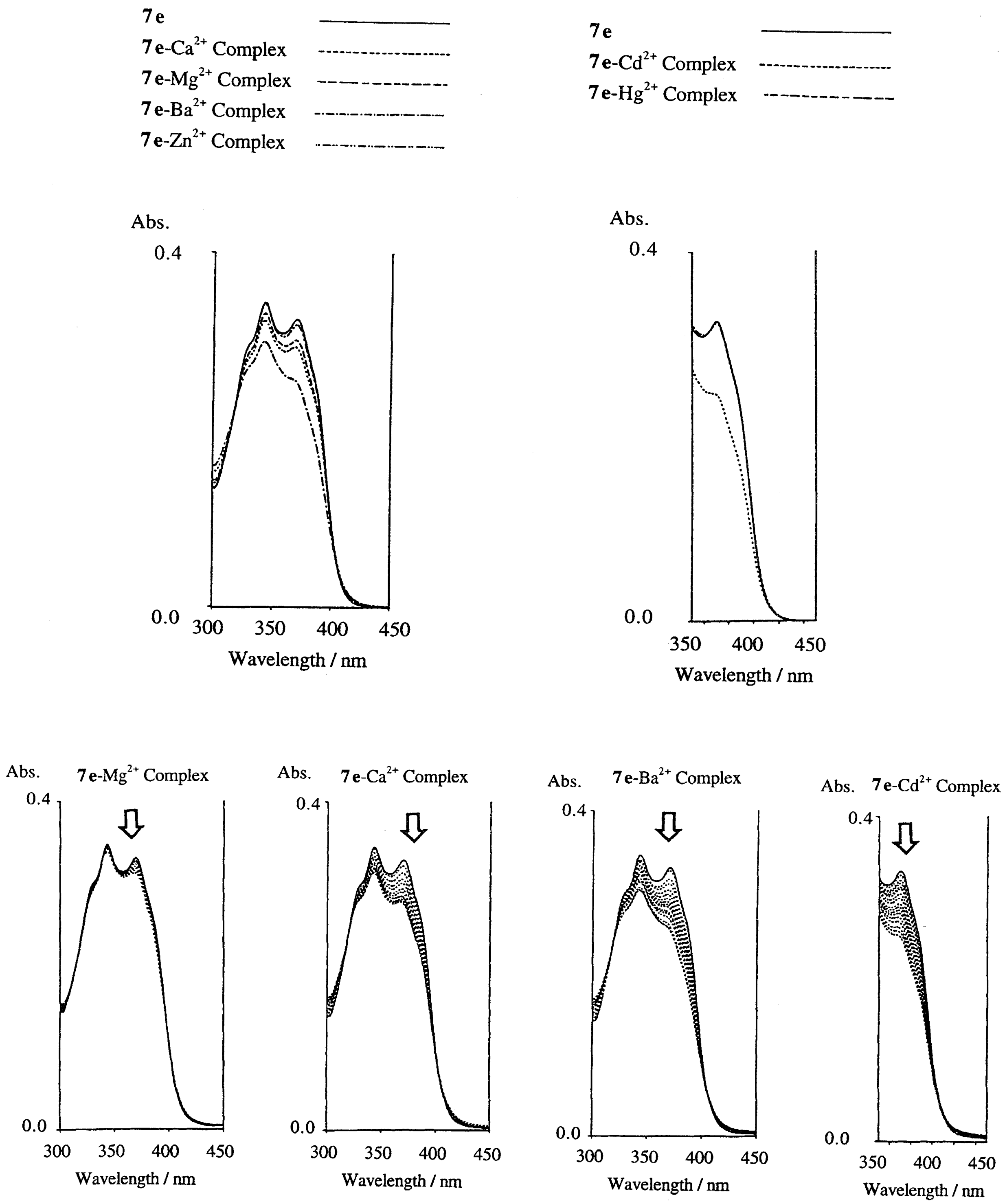


Fig. 1. UV-spectral change of **7a**—**e** (2.0×10^{-3} M) by added various metal salts (0—2.0×10^{-3} M) in acetonitrile at 25 °C.

ethereal hetero atoms. In the case of **7e**, five ethereal oxygens took the principal role, and the rest of the thioether parts might decrease repulsive steric interactions between two tropone rings.[13] Representative results are shown in Figs. 5 and 6.

It is noteworthy that mercury(II) ion was transported with all **7a**—**e**, but the longer the chain length, the faster the rate of transport. In cases of **1a**—**e**, **1d**, which has the preferred ring size, was the fastest. As **7a**—**e** possess conformational mobility, the selectivity towards metal ions could be diminished as compared with the cyclic crown derivatives. The experimental results show that still the difference is significant; zinc(II), cadmium(II), and copper(II) ions all remained in the Aq. I.

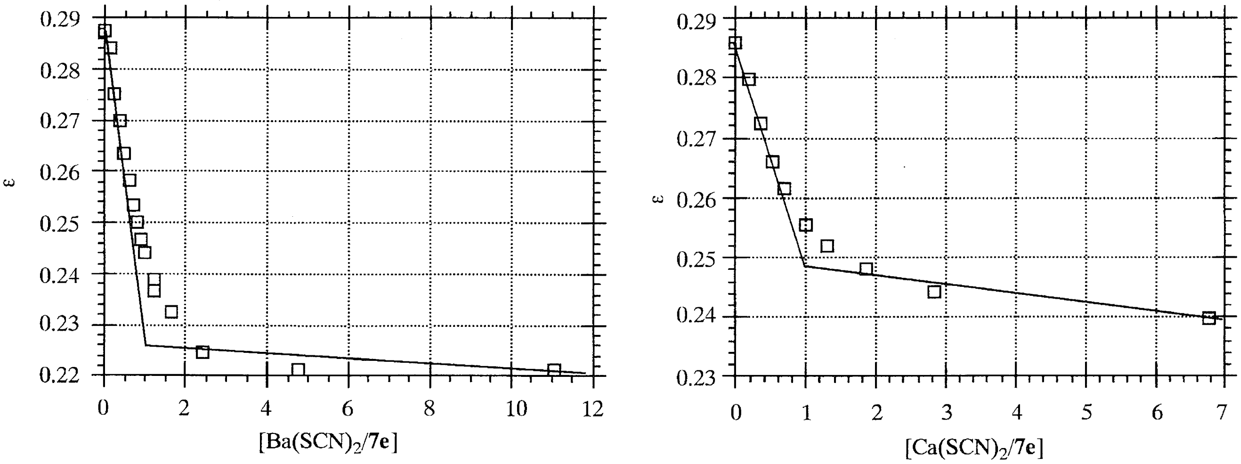


Fig. 2. Determination of molar compositions of **7e**-Ba(SCN)$_2$ and **7e**-Ca(SCN)$_2$ [concentration of **7e**; 2.0×10^{-3} M, concentration of metal salts; 0—2.0×10^{-3} M].

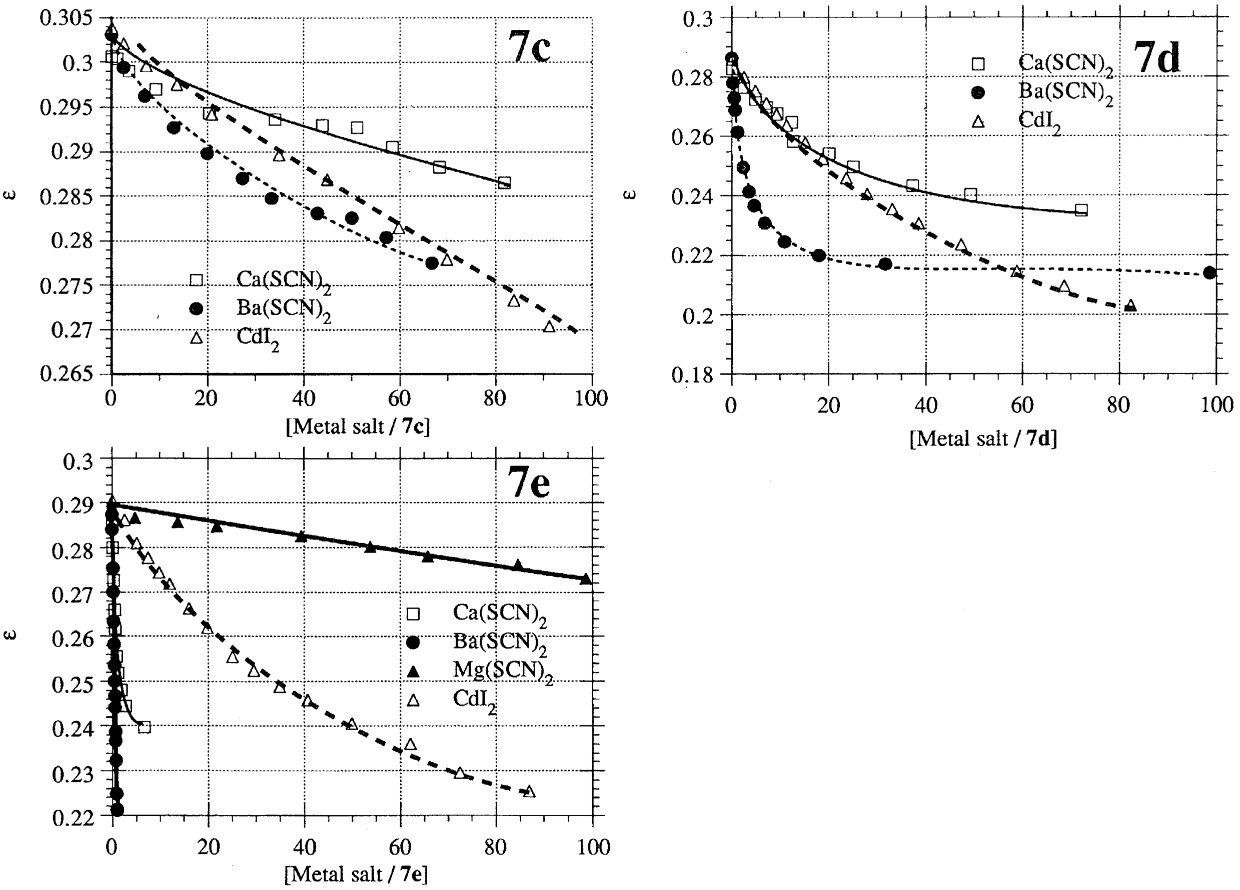


Fig. 3. Dependence of absorptions of **7c**—**e** (2.0×10^{-3} M) at 370 nm on the concentration (0—2.0×10^{-3} M) of metal salts in acetonitrile at 25 °C.

Conclusion

It was outstanding that the podand type dithioether derivatives showed the larger affinity towards alkali earth metals than the dithiocrown derivatives. These podand dithioether derivatives also showed pronounced mercurophilic properties according to the transport experiments. And again, although the complexation constants of zinc(II), cadmium(II), and copper(II) salts are larger than that of mercury(II) salt, only mercury(II) ion was transported through the chloroform layer.

Experimental

The elemental analyses were performed at the elemental analysis laboratory, in the Institute of Advanced Material Study, Kyushu University. The melting points were obtained on a Yanagimoto

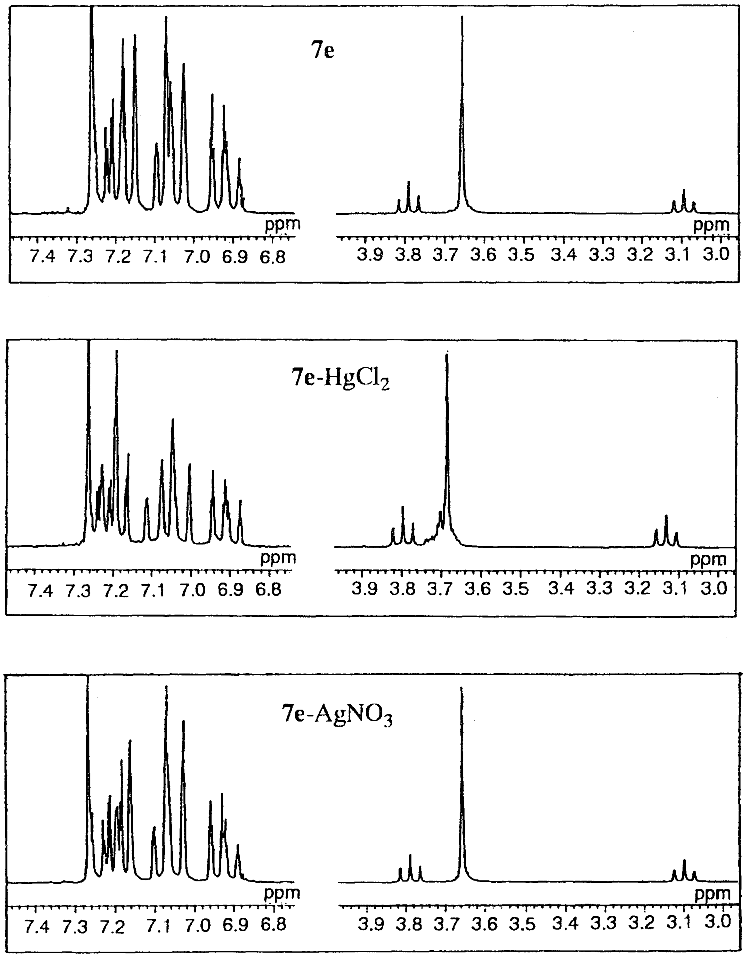


Fig. 4. ^{1}H NMR Spectral changes of **7c**—**e** by addition of 10 equivalents of $HgCl_2$ or $AgNO_3$ in $CDCl_3$ at 27 °C.

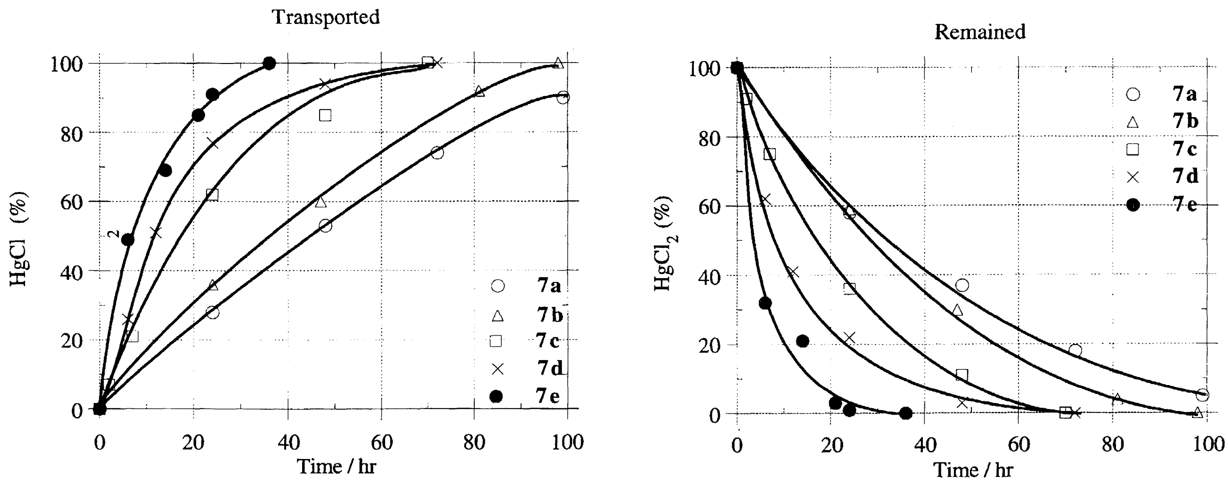


Fig. 5. Transport experiments of $HgCl_2$ with **7a**—**e**. Conditions: source phase; 10 cm^3 of MCl_2 (0.05 mmol), receiving phase; 10 cm^3 of 5 M-HCl, carrier; **7a**—**e**; 0.05 mmol in 20 cm^3 of $CHCl_3$.

Micro Melting Point Apparatus and are uncorrected. The NMR spectra were measured on a JEOL FX 100 Model or a GSX 270H Model spectrometer in $CDCl_3$; the chemical shifts are expressed in δ units. The mass spectra were measured with a JEOL 01SG-2 spectrometer. The IR spectra were recorded on a JASCO IR-A102 spectrometer with KBr disks for crystalline compounds or with liquid films inserted between NaCl plates for oily compounds. The UV spectra were measured using a Hitachi U-3200 spectrophotometer. The stationary phase for the column chromatography was Wakogel C-300 and the eluant was a mixture of ethyl acetate, chloroform, and hexane.

Synthesis of α-[2-(2-Troponylthio)ethyl]-ω-(2-troponylthio)-

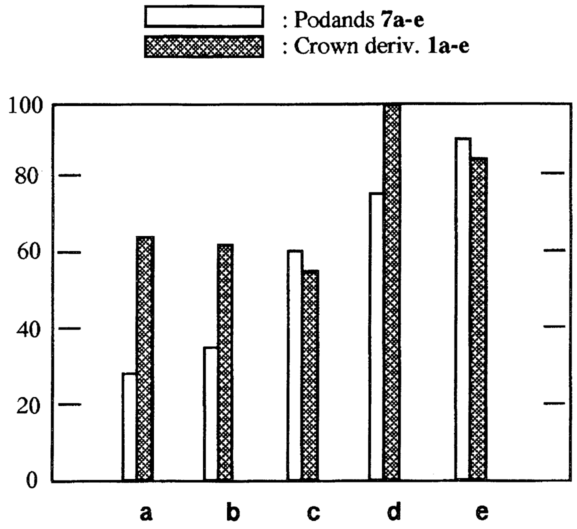


Fig. 6. Comparison of rates of transport of $HgCl_2$ with **7a**—**e** and **1a**—**e**.

oligo(oxyethylene). (General Method). To 2-(*p*-tolylsulfonyloxy)tropone (**5**) (1.1 mmol) in a refluxing mixture of EtOH (50 cm^3) and toluene (50 cm^3) was added *α*-(2-mercaptoethyl)-*ω*-(mercapto)oligo(oxyethylene) (**6**) (0.5 mmol) and NaH (1.1 mol) in EtOH (25 cm^3) for 3-h period by an aid of a microfeeder under an N_2 atmosphere. Refluxing of the solution was continued for another 3 h. The mixture was then cooled off, and the solvents were removed in vacuo. The residue thus obtained was extracted with $CHCl_3$, and chromatographed on a silica-gel column to give the desired condensates.

2,2′-Oxybis(ethylenethio)ditropone (7a): Yellow crystals, mp 121—122 °C; 90%. Found: C, 62.28; H, 5.10%. Calcd for $C_{18}H_{18}O_3S_2$: C, 62.40; H, 5.24%. ^{1}H NMR $\delta = 3.09$ (t, $J = 6.5$ Hz, 4H), 3.82 (t, $J = 6.5$ Hz, 4H), 6.93 (ddt, $J = 10.3$, 8.1, 1.1 Hz, 2H), 7.06 (d, $J = 11.0$ Hz, 2H), 7.08 (dd, $J = 10.3$, 8.1 Hz, 2H), 7.18 (d, $J = 8.1$ Hz, 2H), and 7.23 (ddd, $J = 11.0$, 8.1, 1.1 Hz, 2H); ^{13}C NMR $\delta = 31.5$ (2C), 68.6 (2C), 127.5 (2C), 130.1 (2C), 132.6 (2C), 134.8 (2C), 136.2 (2C), 158.6 (2C), and 183.4 (2C); IR ν 2960, 2920, 2890, 1615, 1546, 1479, 1461, 1419, 1385, 1370, 1299, 1272, 1249, 1219, 1194, 1086, 1056, 1036, 983, 963, 951, 915, 871, 846, 796, 773, 686, 676, and 574 cm^{-1}; UV $\lambda_{\max}^{CHCl_3}$ 251 nm (ε 26000), 281 (13900), 292 (10500, sh), 328 (15900, sh), 345 (19600), 372 (18100), and 389 (14100, sh); UV $\lambda_{\max}^{CH_3CN}$ 227 nm (ε 20900), 249 (24000), 279 (12200), 328 (15000, sh), 343 (17600), 370 (16700), and 387 (12600, sh).

2,2′-Ethylenebis(oxyethylenethio)ditropone (7b): Yellow crystals, mp 89.5—90 °C; 92%. Found: C, 61.51; H, 5.68%. Calcd for $C_{20}H_{22}O_4S_2$: C, 61.29; H, 5.68%. ^{1}H NMR $\delta = 3.10$ (t, $J = 6.6$ Hz, 4H), 3.67 (br s, 4H), 3.81 (t, $J = 6.6$ Hz, 4H), 6.92 (ddt, $J = 10.4$, 8.4, 1.1 Hz, 2H), 7.05 (d, $J = 11.9$ Hz, 2H), 7.07 (dd, $J = 10.4$, 8.4 Hz, 2H), 7.17 (d, $J = 8.4$ Hz, 2H), 7.20 (ddd, $J = 11.9$, 8.4, 1.1 Hz, 2H); ^{13}C NMR $\delta = 31.4$ (2C), 68.6 (2C), 70.6 (2C), 127.3 (2C), 129.9 (2C), 132.5 (2C), 134.7 (2C), 136.1 (2C), 158.8 (2C), and 183.4 (2C); IR (KBr) ν 2912, 2880, 2856, 1620, 1575, 1557, 1479, 1466, 1422, 1406, 1387, 1374, 1355, 1268, 1247, 1214, 1127, 1099, 1076, 1052, 1015, 987, 918, 774, and 680 cm^{-1}; UV $\lambda_{\max}^{CH_3CN}$ 228 nm (ε 21900), 248 (24100), 279 (12200), 292 (9100, sh), 327 (14700, sh), 343 (17500), 371 (16500), and 387 (12600, sh).

***α*-[2-(2-Troponylthio)ethyl]-*ω*-(2-troponylthio)tri(oxyethylene) (7c):** Yellow crystals, mp 113.5—115.5 °C; 95%. Found: C, 60.80; H, 5.92%. Calcd for $C_{22}H_{26}O_5S_2$: C, 60.80; H, 6.03%. ^{1}H NMR $\delta = 3.10$ (t, $J = 6.8$ Hz, 4H), 3.61—3.74 (m, 8H), 3.80 (t, $J = 6.8$ Hz, 4H), 6.92 (ddt, $J = 10.4$, 8.1, 1.1 Hz, 2H), 7.04 (d, $J = 12.1$ Hz, 2H), 7.06 (dd, $J = 10.4$, 8.1 Hz, 2H), 7.16 (d, $J = 8.1$ Hz, 2H), and 7.21 (ddd, $J = 12.1$, 8.1, 1.1 Hz, 2H); ^{13}C NMR $\delta = 31.4$ (2C), 68.6 (2C), 70.6 (2C), 70.7 (2C), 127.3 (2C), 129.9 (2C), 132.5 (2C), 134.7 (2C), 136.1 (2C), 158.8 (2C), and 183.4 (2C); IR ν 2890, 1621, 1571, 1469, 1419, 1385, 1353, 1297, 1272, 1247, 1215, 1132, 1107, 1078, 1055, 1039, 1011, 985, 926, 883, 873, 844, 835, 781, 679, and 561 cm^{-1}; UV $\lambda_{\max}^{CH_3CN}$ 227 (ε 20900), 249 (24000), 279 (12200), 328 (15000, sh), 343 (17600), 370 (16900), and 387 (12600, sh).

***α*-[2-(2-Troponylthio)ethyl]-*ω*-(2-troponylthio)tetra(oxyethylene) (7d):** A yellow oil; 90%. Found: *m*/*z* 479.1566 [(M+1)$^+$]. Calcd for $C_{24}H_{31}O_6S_2$: M+H, 479.1562. ^{1}H NMR $\delta = 3.09$ (t, $J = 6.8$ Hz, 4H), 3.64—3.67 (m, 12H), 3.79 (t, $J = 6.8$ Hz, 4H), 6.91 (ddt, $J = 10.5$, 8.4, 1.1 Hz, 2H), 7.05 (dd, $J = 12.2$, 1.1 Hz, 2H), 7.07 (ddd, $J = 10.5$, 8.4, 1.1 Hz, 2H), 7.16 (dd, $J = 8.4$, 1.1 Hz, 2H), and 7.21 (ddd, $J = 12.2$, 8.4, 1.1 Hz, 2H); ^{13}C NMR $\delta = 31.3$ (2C), 68.5 (2C), 70.48 (2C), 70.54 (4C), 127.3 (2C), 129.9 (2C), 132.5 (2C), 134.6 (2C), 136.0 (2C), 158.7 (2C), and 183.3 (2C); IR ν 2866, 1617, 1554, 1462, 1385, 1352, 1268, 1219, 1107, 986, 915, and 771 cm^{-1}; UV $\lambda_{\max}^{CH_3CN}$ 227 nm (ε 18200), 249 (20400), 279 (10400), 328 (13000, sh), 343 (15400), 370 (14500), and 387 (11100, sh); MS *m*/*z* 478 (M$^+$; 1), 166 (16), 165 (86), 164 (92), 131 (20), 110 (34), 109 (100), and 77 (20).

***α*-[2-(2-Troponylthio)ethyl]-*ω*-(2-troponylthio)penta(oxyethylene) (7e):** A yellow oil; 95%. Found: C, 57.72; H, 6.57%. Calcd for $C_{26}H_{34}O_7S_2 \cdot H_2O$: C, 57.77; H, 6.71%. ^{1}H NMR $\delta = 3.09$ (t, $J = 6.8$ Hz, 4H), 3.64—3.67 (m, 16H), 3.79 (t, $J = 6.8$ Hz, 4H), 6.92 (ddt, $J = 10.6$, 8.4, 1.1 Hz, 2H), 7.04 (d, $J = 12.3$ Hz, 2H), 7.07 (ddd, $J = 10.6$, 8.4, 1.1 Hz, 2H), 7.17 (d, $J = 8.4$ Hz, 2H), and 7.22 (ddd, $J = 12.3$, 8.4, 1.1 Hz, 2H); ^{13}C NMR $\delta = 31.3$ (2C), 68.5 (2C), 70.46 (4C), 70.54 (4C), 127.3 (2C), 129.9 (2C), 132.4 (2C), 134.6 (2C), 136.0 (2C), 158.7 (2C), and 183.3 (2C); IR ν 2886, 1618, 1567, 1556, 1470, 1385, 1351, 1297, 1269, 1105, 1037, 987, 917, 775, and 681 cm^{-1}; UV $\lambda_{\max}^{CH_3CN}$ 227 nm (ε 20600), 249 (23300), 280 (12000), 327 (14300, sh), 343 (17000), 370 (16200), and 387 (12200, sh).

Transport Experiments of Metal Ions by Means of a U-Type Cell. The apparatus is the same as the one used in the previous study.[2] The metal ions were dissolved in water (10 cm^3, Aq I) and 5 M-HCl (10 cm^3, Aq. II) connected with $CHCl_3$ layer (10 cm^3) and mixtures were stirred with a magnetic bar. Occasionally, aliquots of Aq. I and Aq. II were taken for the UV spectrophotometry.

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