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Synthesis and Cation-Binding Properties of Dihydroxycrownophanes and Their Derivatives

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Dihydroxycrownophanes (**2a**—**c**) were conveniently synthesized by intramolecular [2+2] photocycloaddition, and their derivatives with two cation-ligating side chains (**3a**—**6a**) were also readily prepared by the reaction of **2a**—**c** and the corresponding halides in the presence of NaH. All of the crown compounds obtained were used as ionophores in single extraction experiments of heavy metal cations including transition metal cations in a H_2O–CH_2Cl_2 system. Although **3a** did not extract any alkaline earth metal cation at pH 7.0, it showed high affinity toward Pb^{2+} even under acidic conditions (pH 4.7). Crownophanes (**4a**—**c**) having two 2-pyridylmethyl ligands efficiently extracted Ag^+ with excellent selectivity.

Cyclic and acyclic polyethers containing carboxyl group(s) in the side chain(s) have been extensively studied as the carriers in liquid membrane transport systems[1—16] and the extractants for alkali or alkaline earth metal cations in liquid–liquid systems.[17—23] The crown compounds bearing nitrogen atom(s) and/or sulfur atom(s) in the ring[24—31] or the side chains[32—35] usually show affinity toward Ag^+ ion.

There are several methodologies to modify crown ethers. Although a number of methods have been reported for the preparation of crown compounds during past two decades, convenient ones are limited. Okahara's cyclization can be mentioned as one of the excellent methods.[36] Recently, we have found another excellent synthetic method for a new kind of crown compounds having cyclophane skeletons by means of intramolecular [2+2] photocycloaddition of styrene derivatives, which have been named "crownophanes."[37] Combined with dodecanoic acid on the liquid–liquid extraction and liquid membrane transport experiments,[38] they showed Li^+-selectivity over the other alkali metal cations. In this paper, we would like to describe the convenient preparation and the metal-ligating properties of crownophanes with two hydroxyl groups on the polyether linkages and their derivatives.

Results and Discussion

Synthesis of Dihydroxycrownophanes and Their Derivatives. α-(*p*-Vinylphenyl)-ω-(*p*-vinylphenoxy)oligo(oxyethylene)s **1a**—**c** were easily prepared by the treatment of *p*-vinylphenol with corresponding oligoethylene glycol diglycidyl ethers in the presence of pulverized potassium hydroxide at 50 °C. Yields were 56—72%. Commercially available *p*-vinylphenol shortened this preparative sequence dramatically, compared with the previous one beginning from *p*-acetylphenol.[38] Photoreaction of **1a**—**c** was done in acetonitrile for 5 h (see Experimental section).[37] After evaporation, the crude products were purified through column chromatography to give dihydroxycrownophanes **2a**—**c** in the yields of 61—68%. Crownophane derivatives bearing cation-ligating side chains **3a**—**6a** were easily obtained from the reaction of **2** and corresponding halides in the presence of NaH.

Extraction of Metal Cations by Crownophanes with Two Cation-Ligating Side Chains. Crown ethers[18,23] and acyclic polyethers[12,13,19] with carboxylic acid moieties have efficiently transported or extracted alkaline earth metal cations. However, transport and extraction of heavy metal cations including transition metal cations by these kinds of ligand have not been well exploited.

Silver is the most important metal in the photographic industries and its complete recovery from the photographic waste stream is much required for resource saving and environmental preservation points of view.[29] Selective transport or extraction of lead cation is also of interest in relation to environmental and human toxicity.[39] So we have been stimulated to synthesize some crownophanes with alkylthio, 2-pyridylmethyl or carboxyl groups in the side chains, expecting them to have such silver and lead extraction abilities.

All compounds obtained were used in solvent extraction experiments of metal nitrates from aqueous solution into CH_2Cl_2 solution. Results are summarized in Table 1.

Although dihydroxycrownophane **2a** did not extract any cations significantly, crownophane dicarboxylic acid **3a** efficiently extracted almost all cations examined in this work. Especially Pb^{2+} was extracted most efficiently among the divalent cations, and the extraction percentage was higher than that of Ag^+ in spite of the similar ionic diameter (Pb^{2+}, 2.38 Å; Ag^+, 2.32 Å). The binding behavior of **3a** to Pb^{2+} and Ag^+ was studied by a continuous variation method on the extraction experiments (see Figs. 1a and 1b). Percent extractions of both cases reached a maximum at the 0.5 molar fraction. This fact clearly indicates that both Ag^+ and Pb^{2+} form 1:1 complexes with **3a**, and also suggests that the cavity of **3a** fits Pb^{2+} and Ag^+. The neutralization of the charges between the host and metal cation must occur more favorably with Pb^{2+} than with Ag^+, because 1:1 complexes must exist in the organic phase. As a result, it is considered that the **3a**–Pb^{2+} complex

Table 1. Extraction of Metal Nitrates with Crownophanes Bearing Two Ligands on the Polyether Moieties[a)]

Ligands	Percent extraction							
	Ag^+	Cu^{2+}	Pb^{2+}	Ni^{2+}	Zn^{2+}	Co^{2+}	Mn^{2+}	Fe^{3+}
3a	43(4.0)	54(4.1)	82(4.7)	18(6.7)	35(5.4)	6(6.2)	18(6.2)	12(2.0)
4a	87(4.3)	0(4.2)	2(4.8)	3(6.8)	2(5.9)	0(6.7)	0(6.7)	14(2.0)
4b	84(4.2)	0(4.2)	4(4.7)	0(6.7)	0(5.2)	0(5.9)	0(5.8)	0(2.0)
4c	77(4.4)	0(4.2)	1(4.7)	3(6.9)	0(5.5)	0(6.2)	0(6.2)	0(1.8)
5a	0(4.3)	0(4.2)	2(4.8)	3(6.8)	1(5.9)	0(6.6)	0(6.6)	7(2.0)
6a	3(4.3)	0(4.3)	0(4.5)	0(6.9)	3(6.0)	0(5.2)	0(5.2)	0(2.0)
2a	5(4.2)	3(4.2)	4(4.8)	11(6.6)	11(6.6)	0(5.8)	0(5.8)	7(2.0)

a) Extraction conditions: Aq phase, [metal nitrate] $= 1\times10^{-1}$ mol dm^{-3}, 5 cm^3; org. phase, CH_2Cl_2, [ligand] $= 1\times10^{-4}$ mol dm^{-3}, 5 cm^3. Values in parentheses are equilibrium pH of the aqueous phase.

becomes more lipophilic than the **3a**–Ag^+ complex, so that the former is more easily extracted into CH_2Cl_2 phase than the latter. In fact, Pb^{2+} was extracted with **3a** more than Ag^+.

It is clear that **3a** is an useful ligand for recovering heavy metal cations including transition metal cations, especially Ag^+ and Pb^{2+}, from neutral water or sea water, which contains plenty of alkali and alkaline metal cations, because **3a** did not extract any alkali or alkaline earth metal cation even at pH 7 (see Experimental section).

Cyclic and acyclic sulfide moieties in the side chains are considered to act as covers on the crownophane cavities rather than cation-ligating groups since both crownophane derivatives **5a** and **6a** could not extract any cations examined, like that described previously (Scheme 1).[35)]

Crownophanes with two pyridine moieties in the side chains showed excellent selectivities and high efficiencies toward Ag^+. These results can be explained from the specific affinity[29,34)] between nitrogen atoms of pyridine rings and Ag^+ cation, and also the high lipophilicity of the complexes composed of single charged Ag^+ ion and the host molecules, compared with the other complexes formed from the crownophanes and multivalent cations which require two or three species of hydrophilic nitrate anions. It is suggested that the 2-pyridylmethyl groups on the side chains also play a predominant role to bind Ag^+ ion in intramolecular cooperation between the 2-pyridylmethyl groups and the polyether moiety on the extraction. This trend can be seen from the results of similar extraction by **4a**, **4b**, and **4c** of Ag^+ ion.

The binding behavior of Ag^+ ion to **4a** and **4b** was measured by the continuous variation method (Figs. 1c and 1d). The maxima are seen above the 0.5 molar fraction. Moreover, these figures are much different from those of Figs. 1a and 1b in shape. Although they really show that several kinds of complexes such as 1 : 1 and 1 : 2 (host/guest) complexes are formed, the ratios have not been measured.

Consequently, dihydroxycrownophanes were conveniently prepared in good yields. The side chains, introduced on the polyether linkages of the crownophanes, acted as efficient cation-ligating parts for Pb^{2+} or Ag^+, cooperatively with the polyether rings on the liquid–liquid extraction.

Experimental

Apparatus. ^{1}H NMR spectra were recorded on a Varian Gemini-200 FT NMR spectrometer. HPLC analysis was done with a Shimadzu LC-6A pump, an LC-6A UV detector, and an RC-4A data processor. Metal cations were analyzed by a Hitachi 170-50 atomic absorption spectrophotometer.

Reagents. Benzene, dioxane, and THF were purified by distillation over Na after prolonged reflux under a nitrogen atmosphere. Guaranteed reagent grade CH_2Cl_2 was distilled before use.

Commercially available highest grade of $MgCl_2$, $CaCl_2$, $BaCl_2$, LiCl, NaCl, KCl, tris(hydroxymethyl)aminomethane, $AgNO_3$, $Cu(NO_3)_2$, $Pb(NO_3)_2$, $Ni(NO_3)_2$, $Zn(NO_3)_2$, $Co(NO_3)_2$, $Mn(NO_3)_2$, and $Fe(NO_3)_3$ were used. All aqueous solutions were prepared with distilled, deionized water.

Preparation of α-(*p*-vinylphenyl)-ω-(*p*-vinylphenoxy)oligo(oxyethylene)s 1a—c. A mixture of pulverized KOH (0.80 g, 3.80 mmol), *p*-vinylphenol (2.10 g, 17.5 mmol), and dioxane (20 cm^3) were stirred under a nitrogen atmosphere at 50 °C for 1 h. From the additional funnel, 6.87 mmol of a corresponding oligoethylene glycol diglycidyl ethers dissolved in dioxane (30 cm^3) was added dropwise to the mixture with stirring over a period of 30 min. After it was stirred at 80 °C for 1 h, the reaction mixture was cooled to room temperature, and the solid material was filtered off. The filtrate was condensed by evaporation and the residue was purified by column chromatography (SiO_2, benzene-acetone) to afford **1a**—**1c** (**1a**, 72%; **1b**, 62%; **1c**, 56%) as yellowish viscous oil.

1a: ^{1}H NMR ($CDCl_3$) $\delta=7.32$ (4H, ABq, $J=8.7$ Hz), 6.86 (4H, ABq, $J=8.7$ Hz), 6.66 (2H, dd, $J=16.8$ & 11.6 Hz), 5.60 (2H, dd, $J=16.8$ & 0.94 Hz), 5.12 (2H, dd, $J=11.6$ & 0.94 Hz), 4.17 (2H, m), 4.01 (4H, m), 3.70 (14H, m). Anal. Calcd for $C_{26}H_{34}O_7$: C, 68.10; H, 7.47%. Found: C, 68.22; H, 7.50%.

1b: ^{1}H NMR ($CDCl_3$) $\delta=7.30$ (4H, ABq, $J=6.8$ Hz), 6.87 (4H, ABq, $J=6.8$ Hz), 6.65 (2H, dd, $J=17.6$ & 11.0 Hz), 5.60 (2H, dd, $J=17.6$ & 0.94 Hz), 5.12 (2H, dd, $J=11.0$ & 0.94 Hz), 4.17 (2H, m), 4.02 (4H, m), 3.66 (18H, m). Anal. Calcd for $C_{28}H_{38}O_8$: C, 66.91; H, 7.62%. Found: C, 66.88; H, 7.61%.

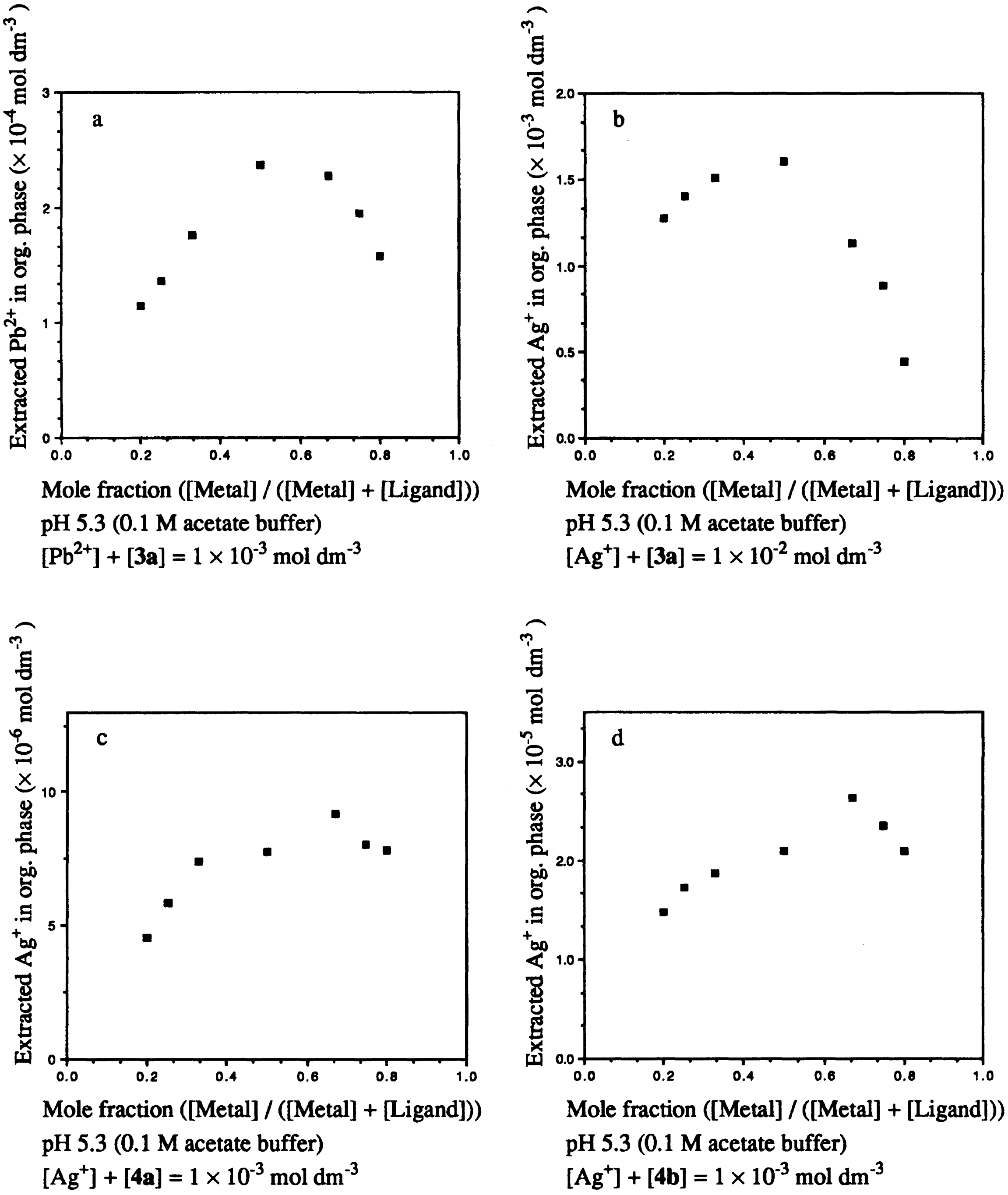


Fig. 1. Job plots of the extraction of cations by crownophanes.

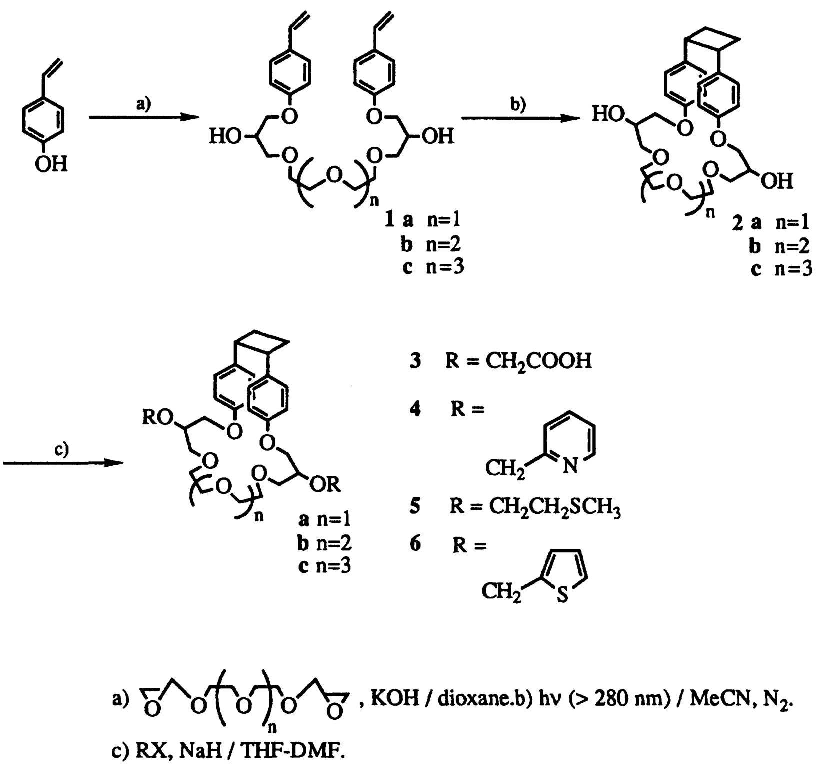
1c: ^{1}H NMR (CDCl$_3$) δ=7.30 (4H, ABq, J=6.8 Hz), 6.87 (4H, ABq, J=6.8 Hz), 6.65 (2H, dd, J=17.6 & 11.0 Hz), 5.60 (2H, dd, J=17.6 & 0.94 Hz), 5.12 (2H, dd, J=11.0 & 0.94 Hz), 4.17 (2H, m), 4.02 (4H, d, J=6.0 Hz), 3.91 (2H, d, J=4.8 Hz), 3.66 (18H, m), 2.54 (2H, m). Anal. Calcd for $C_{30}H_{42}O_9$: C, 65.92; H, 7.74%. Found: C, 65.89; H, 7.71%.

Preparation of Dihydroxycrownophanes 2a—c. Into a 1000-cm^3 Pyrex flask with a magnetic stirrer and N$_2$ inlet was placed 2.0 mmol of α-(p-vinylphenyl)-ω-(p-vinylphenoxy)oligo(oxyethylene)s **1a**—**c** dissolved in acetonitrile (800 cm^3), and nitrogen was bubbled for 15 min. The solution was irradiated by a 400-W high-pressure mercury lamp. The progress of the reaction was followed by HPLC. After irradiation for 5 h, the reaction mixture was evaporated. The crude reaction product was purified by column chromatography (SiO$_2$, benzene-acetone) to afford **2a**—**c** (**2a**, 61%; **2b**, 68%; **2c**, 62%) as a yellowish clear viscous oil.

2a: ^{1}H NMR (CDCl$_3$) δ=6.73 (4H, ABq, J=8.8 Hz), 6.63 (4H, ABq, J=8.8 Hz), 3.93 (7H, m), 3.66 (12H, m), 2.40 (7H, m). Anal. Calcd for $C_{26}H_{34}O_7$: C, 68.10; H, 7.47%. Found: C, 68.21; H, 7.50%.

2b: ^{1}H NMR (CDCl$_3$) δ=6.75 (4H, ABq, J=8.8 Hz), 6.65 (4H, ABq, J=8.8 Hz), 3.94 (8H, m), 3.65 (16H, m), 3.38 (2H, m), 2.39 (4H, m). Anal. Calcd for $C_{28}H_{38}O_8$: C, 66.91; H, 7.62%. Found: C, 66.93; H, 7.74%.

2c: ^{1}H NMR (CDCl$_3$) δ=6.75 (4H, ABq, J=7.7 Hz),



Scheme 1. Synthetic routes to dihydroxycrownophanes and their derivatives.

6.63 (4H, ABq, J=7.7 Hz), 3.94 (8H, m), 3.64 (22H, m), 2.38 (4H, m). Anal. Calcd for $C_{30}H_{42}O_9$: C, 65.92; H, 7.74%. Found: C, 66.00; H, 7.81%.

Preparation of Crownophane Having Two Carboxylic Acid Ligands 3a. A THF solution of dihydroxycrownophane **2a** (1.64 g, 3.58 mmol) was added dropwise to a suspension of NaH (60% in mineral oil, 1.71 g, 43.0 mmol, washed with hexane and then THF) in THF (50 cm^3). Then the mixture was stirred at room temperature for 20 min. From the additional funnel, bromoacetic acid (1.99 g, 14.3 mmol) dissolved in THF (50 cm^3) was added dropwise to the mixture with stirring over a period of 1 h. Then the mixture was refluxed for 16 h. The reaction mixture was cooled to room temperature, neutralized with hydrochloric acid (water : ethanol=1 : 9) and condensed by evaporation. The residue was acidified (pH=4) with 6 mol dm^{-3} -HCl and extracted with CH_2Cl_2 (150 cm^3×3). The combined CH_2Cl_2 solution was dried over $MgSO_4$ and condensed by evaporation. The residue was purified by column chromatography (SiO_2, benzene-acetone) to afford **3a** (77%) as a brownish viscous oil. ^{1}H NMR ($CDCl_3$) δ=6.78 (4H, ABq, J=8.6 Hz), 6.65 (4H, ABq, J=8.6 Hz), 4.33 (4H, s), 4.06 (4H, d, J=4.8 Hz), 3.91 (4H, m), 3.72 (10H, m), 3.62 (8H, m), 2.40 (4H, m). Anal. Calcd for $C_{30}H_{38}O_{11}$: C, 62.71; H, 6.67%. Found: C, 62.73; H, 6.65%.

Preparation of Crownophanes Having Two Pyridine Ligands 4a—c. A mixture of NaH (0.70 g, 17.44 mmol), a corresponding dihydroxycrownophane (2.18 mmol), and THF–DMF (5 : 1 mixed solvent, 10 cm^3) was stirred at room temperature for 30 min. From the additional funnel, 2-pyridylmethyl chloride hydrochloride (1.43 g, 8.72 mmol) dissolved in THF–DMF (5 : 1 mixed solvent, 10 cm^3) was added dropwise to the mixture with stirring over a period of 1 h. After it was stirred at 70 °C for 1 h, the reaction mixture was cooled to room temperature, and the solid material was filtered off. The filtrate was condensed by vacuum distillation and the residue was purified by column chromatography (SiO_2, benzene–acetone) to afford **4a**—**c** (**4a**, 80%; **4b**, 71%, **4c**, 56%) as a yellowish viscous oil.

4a: ^{1}H NMR ($CDCl_3$) δ=8.54 (2H, m), 7.68 (2H, t), 7.52 (2H, d, J=7.7 Hz), 7.18 (2H, t), 6.78 (4H, ABq, J=8.7 Hz), 6.65 (4H, ABq, J=8.7 Hz), 4.80 (4H, d, J=3.6 Hz), 4.06 (4H, d, J=4.8 Hz), 3.91 (4H, m), 3.72 (10H, m), 3.62 (8H, m), 2.40 (4H, m). Anal. Calcd for $C_{38}H_{44}O_7N_2$: C, 71.23; H, 6.92; N, 4.30%. Found: C, 71.26; H, 7.01; N, 4.22%.

4b: ^{1}H NMR ($CDCl_3$) δ=8.53 (2H, m), 7.67 (2H, m), 7.53 (2H, d, J=8.1 Hz), 7.18 (2H, m), 6.83 (4H, ABq, J=8.8 Hz), 6.67 (4H, ABq, J=8.8 Hz), 4.82 (4H, d, J=5.3 Hz), 4.00 (8H, m), 3.72 (4H, d, J=5.1 Hz), 3.61 (12H, m), 2.39 (4H, m). Anal. Calcd for $C_{40}H_{48}O_8N_2$: C, 70.15; H, 7.06; N, 4.12%. Found: C, 70.22; H, 7.03. N, 4.04%.

4c: ^{1}H NMR ($CDCl_3$) δ=8.54 (2H, m), 7.69 (2H, m), 7.56 (2H, d, J=7.6 Hz), 7.19 (2H, m), 6.87 (4H, ABq, J=8.8 Hz), 6.70 (4H, ABq, J=8.8 Hz), 4.85 (4H, s), 4.04 (8H, m), 3.74 (6H, d, J=5.0 Hz), 3.65 (14H, m), 2.42 (4H, m). Anal. Calcd for $C_{42}H_{52}O_9N_2$: C, 69.21; H, 7.19; N, 3.84% Found: C, 69.36; H, 7.08; N, 3.84%.

Preparation of Crownophanes Having Two Alkyl Sulfide Ligands 5a. A mixture of NaH (0.34 g, 8.72 mmol), **2a** (1.00 g, 2.18 mmol), and THF–DMF (5 : 1 mixed solvent, 10 cm^3) was stirred at room temperature for 30 min. From the additional funnel, 2-chloroethyl methyl sulfide (0.96 g, 8.72 mmol) dissolved in THF–DMF (5 : 1 mixed solvent, 10 cm^3) was added dropwise to the mixture with stirring over a period of 1 h. After it was stirred at 70 °C for 90 min, the reaction mixture was cooled to room temperature, and the solid material was filtered off. The filtrate was condensed by vacuum distillation and the residue was purified by column chromatrography (SiO_2, benzene–acetone) to afford **5a** (49%) as a brownish viscous oil. ^1H NMR ($CDCl_3$) $\delta=6.76$ (4H, ABq, $J=8.9$ Hz), 6.67 (4H, ABq, $J=8.9$ Hz), 3.94 (8H, m), 3.66 (12H, m), 2.40 (4H, m), 1.64 (14H, m). Anal. Calcd for $C_{32}H_{46}O_7S_2$: C, 63.34; H, 7.64; S, 10.57%. Found: C, 63.40; H, 7.81; S, 10.42%.

Preparation of Crownophanes Having Two Thiophene Ligands 6a. A mixture of NaH (0.17 g, 4.36 mmol), **2a** (0.50 g, 1.09 mmol), and THF–DMF (5 : 1 mixed solvent, 10 cm^3) were stirred at room temperature for 30 min. From the additional funnel, 2-(bromomethyl)thiophene (0.77 g, 4.36 mmol) dissolved in THF–DMF (5 : 1 mixed solvent, 10 cm^3) was added dropwise to the mixture with stirring over a period of 1 h. After it was further stirred at 40 °C for 2 h, the reaction mixture was cooled to room temperature, and the solid material was filtered off. The filtrate was condensed by vacuum distillation and the residue was purified by column chromatography (SiO_2, benzene–acetone) to afford **6a** (85%) as a brownish viscous oil. ^1H NMR ($CDCl_3$) $\delta=6.98$ (6H, m), 6.77 (4H, ABq, $J=8.8$ Hz), 6.63 (4H, ABq, $J=8.8$ Hz), 4.84 (4H, d, $J=2.1$ Hz), 3.92 (8H, m), 3.58 (12H, m), 2.39 (4H, m). Anal. Calcd for $C_{36}H_{42}O_7S_2$: C, 66.44; H, 6.50; S, 9.85%. Found: C, 66.68; H, 6.54; S, 9.60%.

Solvent Extraction of Alkaline Earth Metal Cations by Crownophane 3a. A CH_2Cl_2 solution of **3a** (0.05 mol dm^{-3}, 2 cm^3) and an aqueous solution of three alkaline earth metal chlorides ($[MgCl_2]=[CaCl_2]=[BaCl_2]=0.05$ mol dm^{-3}, 2 cm^3) or three alkali metal chlorides ($[LiCl]=[NaCl]=[KCl]=0.10$ mol dm^{-3}, 2 cm^3), the pH of which was adjusted to 7.0 or 4.0 with Tris buffer, were stirred vigorously for 10 h. A sample (0.10 cm^3) of the aqueous phase was diluted to the prescribed volume with deionized, distilled water and the amount of each cation was measured by atomic absorption analysis and/or flame analysis, but there was no detectable amount of any cation in the solution.

Solvent Extraction of Heavy Metal Cations Including Transition Metal Cations. A CH_2Cl_2 solution of crownophane (1×10^{-4} mol dm^{-3}, 5.0 cm^3) and an aqueous metal nitrate solution (0.1 mol dm^{-3}, 5.0 cm^3), the pH of which was adjusted as high as possible without precipitating the hydroxides, were shaken in a 20 cm^3 test tube with a ground-glass stopper at ambient temperature (18—20 °C) for 2 h. Two liquid phases were separated, and the equilibrium pH of the aqueous phase was measured. A sample (2 cm^3) of the organic phase was evaporated under reduced pressure, and then dilute HNO_3 aqueous solution (2 cm^3) was added to the residue, and finally the extracted cation was analyzed by atomic absorption analysis.

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