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Remarkably Selective Ag$^+$ Extraction and Transport by Thiolariat Ethers

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Synthesis and metal binding properties of thiolariat ethers, where a sulfide side chain is introduced into a framework of a crown ether, have been performed. Remarkably high Ag$^+$ selectivity among heavy metal ions was observed in solvent extraction and transport across a liquid membrane using thiolariat ethers with a 15-crown-5 ring as carriers. Thiolariat ethers with a 12-crown-4 or a 18-crown-6 do not exhibit such a high Ag$^+$ selectivity. The former binds metal ions weakly, and the latter recognizes Pb^{2+} as well as Ag$^+$. The corresponding oxygen analogs, *i.e.* lariat ethers, do not show Ag$^+$ selectivity. The Ag$^+$ binding strength of the sulfoxide and sulfone analogs is much lower than that of thiolariat ethers. Thiolariat ethers with a benzocrown framework containing a sulfide chain at the 4 position of the benzene nucleus showed very low affinity to Ag$^+$. Extractability and transport ability using various thiolariat ether derivatives strongly suggested that this high Ag$^+$ selectivity is a result of the synergistic coordination of the ring oxygen and the sulfur atom of the thiolariat ether. NMR chemical shifts of protons and carbons in the proximity of the sulfur atom of the thiolariat ether were changed significantly in accordance with the synergistic coordination described above. 1:1 Complexation between a thiolariat ether and Ag$^+$ were supported by a Job plot using the chemical shift of the methylene protons adjacent to the sulfur atom.

The binding affinity of crown ethers is easily modulated by introducing a polyether side chain into the crown ring, because in the modified crown ethers, *i.e.*, lariat ethers, synergistic coordination of the ring oxygen and the additional oxygen atoms of the side chain to metal ions can take place.[1−4] Hence, this simple modification of the metal binding site results in effective changes of thermodynamic as well as kinetic binding behavior of crown ethers.[5,6] A side chain containing soft ligating atom(s) or a functional group can also be incorporated into the cyclic frameworks.[7−13] Preparation of crown ethers with several side chains can be performed, and drastic improvement of binding selectivity toward metal ions has been achieved.[7,14−17] Crown ethers with catalytic activity for amide bond formation were also synthesized by introducing side chains.[18−20] Consequently, various macrocyclic hosts with diverse affinity toward metal ions and other functions should be readily synthesized by changing the combination of the atoms forming the ring framework and the side chain.[21−24]

Strong Ag$^+$ recognition is important for ^{111}Ag-based radioimmunotherapy[25−27] and probably useful for photographic technology and recovery of Ag$^+$ from waste water. Several Ag$^+$ binders have been reported, *e.g.* crown ethers containing sulfur atom(s) in the cyclic structure,[28−32] double-armed[14,15] or multiarmed macrocycles,[25,26] and recently the calixspherands.[27] Regulation of Ag$^+$ binding

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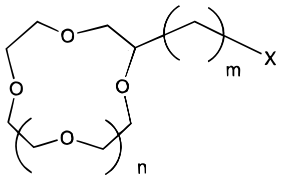
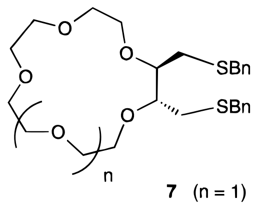
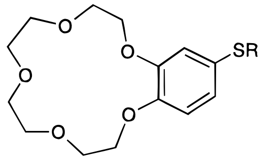
has also been achieved by redox reactions between thiol and disulfide of crown ethers containing sulfur atoms[33-35] and by metal coordination to change the conformation of the binding site using pseudocrown ethers.[36]



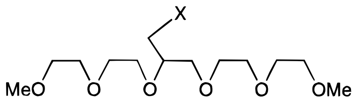
Host	n	m	X
1a	1	1	SBn
1b	1	1	S-n-Bu
2a	2	1	SBn
2b	2	1	S-n-Bu
2c	2	1	S-n-$C_{12}H_{25}$
3a	3	1	S-Bn
3c	3	1	S-n-$C_{12}H_{25}$
4	2	1	$SCH_2CH_2OCH_3$
5	2	1	SCH_2CH_2SBn
6	2	3	SBn
9	2	1	S(O)Bn
10	2	1	$S(O)_2Bn$
15	1	1	OBn
16	2	1	OBn
17	3	1	OBn



7 (n = 1)
8 (n = 2)



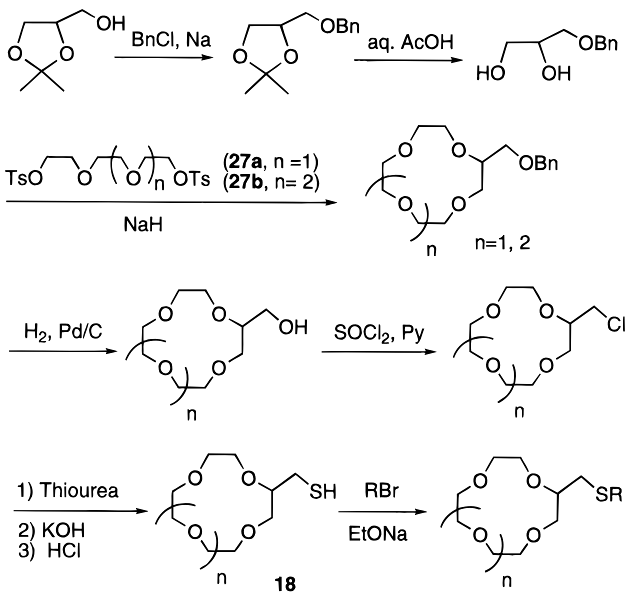
11 R = Bu
12 R = Bn



13 X = SBn
14 X = OBn

We have recently synthesized thiolariat ethers, which contain a sulfide group as a side chain, and found a remarkably high Ag^+ selectivity of thiolariat ethers during solvent extraction.[37,38] For metal binding, thiolariat ethers may possess an advantage over the crown ethers containing a sulfur atom in the cyclic framework, because the introduction of a sulfur atom into a crown ring gives rise to an unfavorable entropic change upon complexation with a metal ion.[25,39]

Scheme 1



Here we wish to report improved methods for the preparation of various thiolariat ethers **1**-**6** and their affinity toward metal ions. Thiolariat ethers with a 15-crown-5 ring exhibit very high Ag^+ selectivity compared to other heavy metal ions during solvent extraction and transport through a liquid membrane. The importance of the synergistic coordination of the crown ring and the sulfur atom outside the ring has also been proved by extraction, transport, and NMR complexation studies. This surprising effect, involving only one sulfide side arm, on the binding preference of macrocycles promises versatility of thiolariat ethers in the design of Ag^+ binders for various application, because of ease with which the host molecules can be chemically modified.

Results and Discussion

Synthesis of Thiolariat Ethers. We have previously described a synthetic route to thiolariat ethers from 2,2-dimethyl-1,3-dioxolane-4-methanol in seven steps (Scheme 1).[37] The pathway is laborious and the overall yields are low. Moreover, this route involves the preparation of mercaptomethyl crown ethers **18** as intermediates which are useful to functionalize the cyclic framework easily, but is sensitive to autoxidation. Modification of the synthetic method was undertaken to increase the reaction yields and to reduce the number of reaction steps, but not to decrease the usefulness for preparing various thiolariat ethers.[38] As shown in Scheme 2, sulfides **19** obtained by alkylation of thioglycerol by alkyl or benzyl halide were treated with oligoethylene glycol ditosylate (**27**) to give the corresponding thiolariat ethers **1**-**3**. Crown ethers (**4**, **5**) containing [(2-methoxyethyl)thio]methyl and [[2-(benzylthio)ethyl]thio]methyl groups were prepared from 2,2-dimethyl-1,3-dioxolane-4-methanol tosylate (**23**) (Scheme 3). Deprotection of ketals (**25**, **28**) under acidic conditions was carried out to give the corresponding diols (**26**, **29**). Cyclization reaction between the diols and ditosylate **27b** was performed under similar conditions to those for thiolariat ethers **2**.[38] Host **6**, where length of the methylene spacer between the

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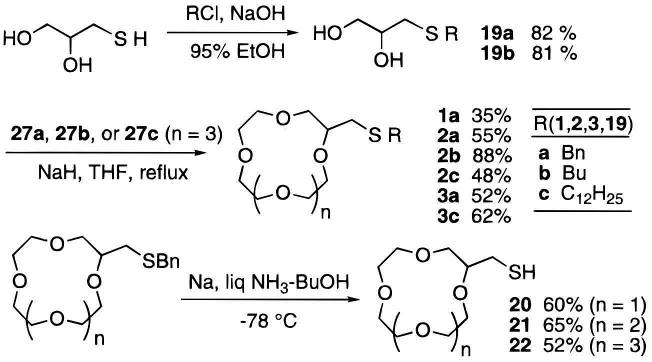
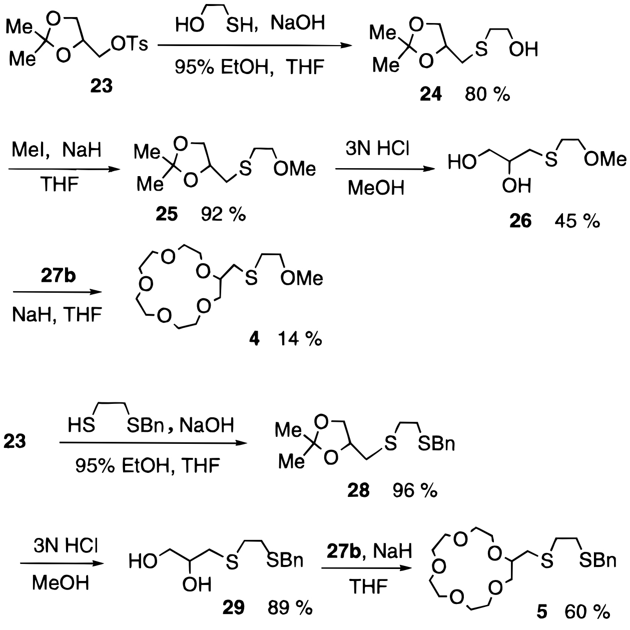
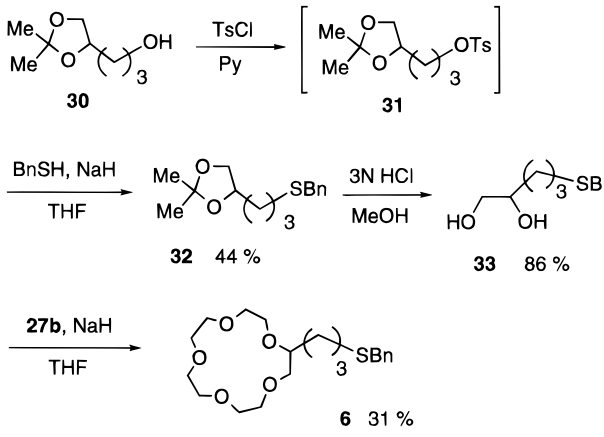
Scheme 2



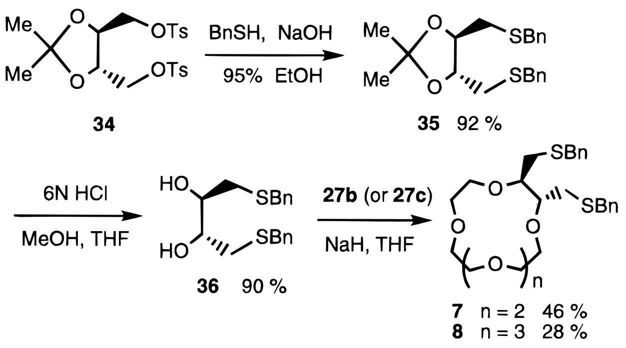
Scheme 3



Scheme 4



Scheme 5



Scheme 6

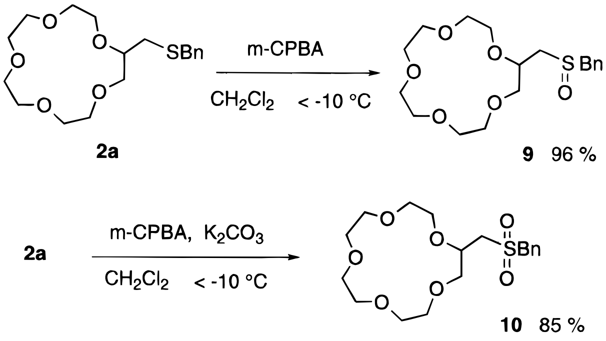


Table 1. Solvent Extraction of Alkali Metal Ions

host	extractability (%)[a]				
	Li^+	Na^+	K^+	Rb^+	Cs^+
1a	1	2	1	1	–
2a	3	16	19	15	9
2b	3	18	23	15	–
2c	3	21	22	17	–
3a	–	22	93	82	57
4	–	22	24	22	10
9	–	14	10	12	6
10	–	6	6	9	4
11	1	6	17	9	–
12	3	4	18	13	–
13	–	4	7	10	5
14	–	5	10	12	7
15	2	3	1	1	–
16	3	21	20	17	–
17	6	29	94	84	61
none	0	0	0	0	0

[a] Organic phase (CH_2ClCH_2Cl); [host] = 1.0×10^{-4} M. Aqueous phase; [metal picrate] = 3.0×10^{-5} M and [metal chloride] = 0.10 M.

crown ring and the sulfur atom is longer than **1**-**5**, was obtained in a similar way (Scheme 4). Tosylate **31** obtained from alcohol **30** was not purified and reacted directly with benzylmercaptan for preparation of sulfide **32**, because **31** is easily hydrolyzed. After deprotection the diol **33** was converted to the corresponding thiolariat ether **6**. The crown ethers (**7**, **8**), with two side chains, were also obtained via the cyclization of **27** and **36**, where the latter was prepared from diethyl (L)-tartarate in several steps (Scheme 5). The thiolariat ether **2a** was oxidized with *m*-chloroperbenzoic acid (*m*-CPBA) to afford the sulfoxide and sulfone analogs (**9**, **10**) in good yields (Scheme 6).

Solvent Extraction of Metal Ions. The affinities of thiolariat ethers and the analogs toward metal ions were examined by solvent extraction experiment using a 1,2-dichloroethane–water biphasic system. For alkali metal ions, an aqueous mixture of metal picrate (3.0×10^{-5} M) and metal chloride (0.10 M) was employed as an aqueous phase. A 1,2-dichloroethane solution of host (1.0×10^{-4} M) was used as an organic phase. The extractability of each metal ion was estimated from the decrease of the absorption (356 nm) of picrate anion in the aqueous phase. According to the definition (see Experimental Section), the value of the extractability is 100% when the absorbance of the picrate anion is null. The results are summarized in Table 1. The binding preference of thiolariat ethers toward alkali metal ions is almost the same as that of the corresponding lariat ethers. 12-

Table 2. Solvent Extraction of Transition and Heavy Metal Ions

	extractability (%)[a]							
host	Ag^+	Mn^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}	Cd^{2+}	Pb^{2+}
1a	25	1	5	2	1	1	2	1
2a	95	2	4	1	3	1	1	4
2b	95	2	2	2	3	3	3	5
2c	96	2	2	2	3	4	3	5
3a	97	8	6	6	13	5	7	73
3c	97	8	7	7	7	5	9	80
4	94	3	3	3	3	2	5	12
5	99	3	2	2	3	–	–	6
6	89	3	3	1	3	2	3	5
7	91	2	3	3	3	1	4	4
8	98	–	–	6	–	–	–	78
9	18	4	3	2	2	3	2	4
10	7	4	2	2	3	2	2	3
11	11	–	–	–	–	–	1	2
12	10	2	3	3	3	2	2	4
13	54	2	2	2	4	2	4	4
14	6	3	2	1	2	0	2	2
15	5	2	1	1	1	1	1	3
16	28	1	3	1	2	3	1	6
17	53	7	5	7	7	5	8	81
none	2	1	3	1	1	1	1	2

[a] Organic phase (CH_2ClCH_2Cl); [host] = 1.0×10^{-4} M. Aqueous phase; [picric acid] = 3.0×10^{-5} M and [metal nitrate] = 0.01 M.

Crown-4 derivatives (**1a**, **15**) showed very low extractability toward Li^+, Na^+, K^+, and Rb^+. However, 15-crown-5 (**2a**–**c**, **16**) and 18-crown-6 (**3a**, **17**) derivatives extracted alkali metal ions more efficiently. Good selectivity during solvent extraction between the Na^+, K^+, and Rb^+ ions was not observed with 15-crown-5 hosts. The hosts **3a** and **17**, which contain a 18-crown-6 ring, exhibited a characteristic preference order of extractability to alkali metal ions ($K^+ > Rb^+ > Cs^+ > Na^+$). As we expected, this preference reveals that the binding ability toward alkali metal ions can be ascribed to the affinity to the crown ring and that the side chains do not contribute to the binding properties significantly. The interaction between a sulfide group and an alkali metal ion should be very weak. The extractability of the 15-crown-5 derivatives, **9** and **10**, is lower than that of the corresponding thiolariat ethers. This decrease suggests that an oxygen atom of the sulfoxide or sulfone group prohibits coordination of a crown ring to alkali metal ions. However, the [[2-(benzylthio)ethyl]thio]methyl and the [(2-methoxyethyl)thio]methyl side chains do not affect the binding behavior, probably because the hetero atoms are located further from the binding cavity and thus can not influence the coordination of alkali metal ions. During the extraction of alkali metal ions, the usual ring size dependency of the crown ethers on the alkali-metal-binding selectivity was observed. Hence, the binding preference results mainly from the affinity of each crown ring. Moreover, the effect of the side chain containing a sulfur atom on the extractability is small, if any, under conditions employed here.

The extraction of heavy metal ions was carried out using a mixture of picric acid (3.0×10^{-5} M) and metal nitrate (0.01 M) as the aqueous phase and a 1,2-dichloroethane solution containing the host (1.0×10^{-4} M) as the organic phase. The extractability was evaluated according to a similar method using alkali metal ions (Table 2). In contrast to the cases using alkali metal ions, thiolariat ethers (**2a**–**c**) bearing a 15-crown-5 ring exhibited remarkably high Ag^+ selectivity. Some hosts (**2a**–**c**) extracted Ag^+ with high extractability (95, 95, and 96% for **2a**, **2b**, and **2c**, respectively) while, however, showing very low affinity toward the other metal ions. Compared to the thiolariat ethers, the corresponding lariat ether **16**, which has an ether chain instead of a sulfide group, has much less affinity toward Ag^+ (28%). It is noteworthy that the Ag^+ affinity is significantly perturbed by only one sulfur atom, which does not exist in the binding cavity but in the side chain.

An apparent ring-size effect of thiolariat ethers on the Ag^+ selectivity was observed. In 12-crown-4 derivative **1a**, extractability for Ag^+ drastically decreased (25%), although Ag^+ was extracted most preferentially among the heavy metal ions examined here. The host **1a** showed a low affinity to all the heavy metal ions employed here. In 18-crown-6 derivatives **3a** and **3c**, the Ag^+ selectivity also decreased considerably, because these hosts also extracted Pb^{2+} effectively. This good affinity to Pb^{2+} is to be expected from a 18-crown-6 framework, because a similar tendency is observed for the 18-crown-6 derivatives without a side chain.[40] As in the case of **16**, the lariat ethers (**15**, **17**) with a different cavity size exhibited much lower extractability toward Ag^+ than the corresponding thiolariat ethers. These results also show the importance of sulfur atom in the Ag^+ selectivity. The 18-crown-6 derivative **17** extracted both Ag^+ and Pb^{2+} with moderate extractability probably because of the 18-crown-6 structure as described above.

The neccessity of a cyclic structure for effective metal binding was obviously supported by the lower extractability (54%) of the linear polyether **13** compared to the thiolariat ethers. Hence, synergistic coordination of the ring oxygen and the sulfur atoms seems to be essential for the selectivity. The host **13** still maintains Ag^+ selectivity, while the extractability of the oxygen analog, **14**, is much less (6%). Thus, in the linear systems only one sulfur atom also affects Ag^+ affinity efficiently.

Coordination of sulfur atom in the side chain of thiolariat ethers was again proved to be very important for Ag^+ selectivity. In the sulfoxide and sulfone analogs, **9** and **10**, the Ag^+ extractability values are 18 and 7%, respectively. These results clearly indicate that the coordination of the lone pair(s) of the sulfur atom plays an important role in Ag^+ binding. Furthermore, the low extractabilities of the benzocrown derivatives (**11**, **12**) suggest the significance of the coordination of the sulfide group to Ag^+ (*vide infra*). The decrease in the affinity of the benzocrown hosts implies a 1:1 stoichiometry of the Ag^+ complexes of thiolariat ethers. It is not plausible that one Ag^+ is complexed with more than two hosts. If two hosts bind one Ag^+, a crown ring of one benzocrown host and a sulfur atom of the other host may coordinate Ag^+ synergistically in a tail-to-head fashion. In this case, the benzocrown derivatives (**11**, **12**) might exhibit much higher extractability. Upon 1:1 complexation, synergistic coordination of the sulfur atom and the oxygen atoms of the benzocrown ring cannot be performed. The CPK model inspection suggested that the sulfur atom is forced to be separate from the crown cavity. In compound **6** the extractability of the Ag^+ selectivity is slightly smaller than **2**. Probably the decrease is caused by the longer spacer of **6** which is unfavorable for an effective synergistic coordination involving both the oxygen and sulfur atoms. In the thiolariat ethers (**7**, **8**) bearing two sulfur atoms in the side arms, the Ag^+ affinity and selectivity

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Table 3. Transport of Heavy Metal Ions by Thiolariat Ethers

	concn of metal ion in the receiving phase (M) (after 30 h)[a]			
host	Ag^+	Cu^{2+}	Cd^{2+}	Pb^{2+}
2a	8.0×10^{-4}	0	0	0
2c	$8.5 \times \times 10^{-4}$	0	0	0
3a	1.2×10^{-3}	–	–	1.7×10^{-3}
3c	1.1×10^{-3}	0	–	1.2×10^{-3}
4	7.2×10^{-4}	0	0	0
5	1.3×10^{-3}	–	–	0
7	9.2×10^{-4}	0	0	0
9	4.7×10^{-5}	0	0	0
10	1.8×10^{-5}	0	0	0
16	1.2×10^{-4}	–	0	0
17	1.2×10^{-4}	–	–	1.6×10^{-3}

[a] Organic phase (CH_2ClCH_2Cl) 50 mL; [host] = 2.0×10^{-4} M. Source phase (distilled H_2O) 4 mL; [metal nitrate] = 0.10 M.

remain high. Existence of two side chains did not affect the binding behavior, probably because only one side chain can coordinate to the Ag^+ ion captured in the crown ring. The cationic radius of Ag^+ is between those of Na^+ and K^+.[5] Accordingly, upon complexation of Ag^+ with the thiolariat ethers bearing a 15-crown-5 ring, Ag^+ is considered to be slightly outside the cavity and, hence, to be coordinated by the sulfur atom in close proximity to the ring.

Transport of Metal Ions through a Liquid Membrane. The metal transport ability of thiolariat ethers was evaluated by a transport experiment across a 1,2-dichloroethane layer as a liquid membrane using a dual cylindrical cell.[41] Ag^+, Cu^{2+}, Cd^{2+}, and Pb^{2+} ions were used for the transport experiment. The source phase was a 0.10 M aqueous solution of metal nitrate, and the receiving phase consisted of deionized water. The organic layer was a 1,2-dichloroethane solution containing the host (2.0×10^{-4} M). The concentrations of metal ions transported into the receiving phase were determined by atomic absorption spectroscopy. The metal ion concentrations after 30 h are summarized in Table 3.

In the thiolariat ethers (**2a**, **2c**, **4**, **5**) a remarkably high Ag^+ selectivity was achieved in the metal ion transport as for the solvent extractions. The thiolariat ethers bearing a 15-crown-5 ring only carried Ag^+ effectively. No other metal ions were detected, within experimental errors, in the receiving phase after 30 h. In contrast, thiolariat ethers (**3a**, **3c**) with a 18-crown-6 ring transported both Pb^{2+} and Ag^+ efficiently. In the case of **3a** Pb^{2+} was carried more predominantly than Ag^+. This Pb^{2+} affinity probably results from the binding properties of a 18-crown-6 ring (*vide supra*). Much smaller amounts of Ag^+ were transported by the sulfoxide, sulfone analogs **9**, **10**, and lariat ether **16**. These results indicate the importance of the coordination of the side arm sulfur atom in Ag^+ selectivity, as seen with the solvent extraction. The coordination of one side chain is sufficient for high Ag^+ selectivity, because in host **7** an amount of Ag^+ comparable to that in **2a**, **2c**, **4**, and **5** was transported.

In competitive transport experiments using an aqueous mixture of Ag^+, Cu^{2+}, Cd^{2+}, and Pb^{2+} (0.01 M each) as a source phase, apparent enhancement of Ag^+ concentration and selectivity in the receiving phase was performed in 15-crown-5 derivative **2a**, compared to single ion transport (Table 4, a 0.01 M metal nitrate solution for the source phase). This change was probably caused by the increase in the total metal ion concentration of the source phase, because the concentration gradient between the receiving and source phases is a driving force of the transport. However, the Pb^{2+} selectivity of **3a** in the competitive transport is higher than that in the single ion transport. This can be attributed to the predominant occupation of the 18-crown-6 cavity with Pb^{2+}, so that the amounts of the cavity available for Ag^+ binding decreased.

Table 4. Transport of Transition and Heavy Metal Ions by 2a and 3a

		[metal ion] in the receiving phase ($\times 10^{-5}$ M) (after 24 h)			
conditions[a]	host	Ag^+	Cu^{2+}	Cd^{2+}	Pb^{2+}
noncompetitive transport[b]	**2a**	7.7	0	0	0
	3a	20	0	–	26
	none	0	0	0	0
competitive transport[c]	**2a**	19	0	0	0
	3a	25	0	0	58
	none	0	0	0	0

[a] Organic phase (CH_2ClCH_2Cl) 50 mL: [host] = 2×10^{-4} M. Source phase (distilled H_2O) 4 mL: [b] [metal nitrate] = 0.01 M. [c] $[AgNO_3] = [Cu(NO_3)_2] = [Cd(NO_3)_2] = [Pb(NO_3)_2] = 0.01$ M.

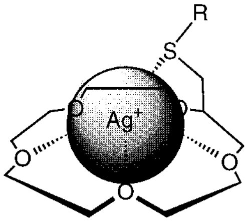

Figure 1. Schematic illustration of Ag^+ complex of thiolariat ether.

In both noncompetitive and competitive transport of metal ions, very high Ag^+ selectivity was achieved by thiolariat ethers (**2a**, **2c**, **4**, **5**) with a 15-crown-5 ring. The synergistic coordination of the sulfur and oxygen atoms of the carriers was strongly supported by the transport experiments as in the case of the solvent extraction studies.

Only one sulfur atom of each of the thiolariat ethers can coordinate to the Ag^+. Surprisingly, the sulfur atom affects both the extraction and transport selectivity enormously, although the atom is located outside the cyclic recognition site. However, the synergistic coordination is performed probably by the vicinity of the sulfur atom to the ring and due to ring size of a 15-crown-5 framework which is slightly smaller than the ionic diameter of Ag^+. The plausible structure of the Ag^+ complex is illustrated in Figure 1.

Spectral Changes of ^1H and ^{13}C NMR of Thiolariat Ether on the Addition of Ag^+. The synergistic coordination of the oxygen and sulfur atoms in thiolariat ether **2c** to Ag^+ is strongly supported by ^1H and ^{13}C NMR spectroscopy results. The ^1H NMR resonances of two sets of methylene protons ($H\alpha$, $H\beta$) adjacent to the sulfur atom were shifted noticeably to lower field (2.552 to 2.780 ppm and 2.637 to 2.999 ppm for $H\alpha$ and $H\beta$, respectively, in $CDCl_3-CD_3CN$ (9:1)), when 1 equiv of $AgNO_3$ was added. However, the chemical shift of the methyl protons of the dodecyl chain did not change significantly. Obvious but complicated changes were observed in methylene protons of the crown ring. These changes suggest that both the ring oxygen and the sulfur atoms in the side chain coordinate to the Ag^+ simultaneously. The Job plot using a resonance of $H\alpha$ for complexation between **2c** and Ag^+ has a maximum at a mole fraction of 0.5 indicative of formation of a 1:1 complex (Figure 2). A nonlinear-

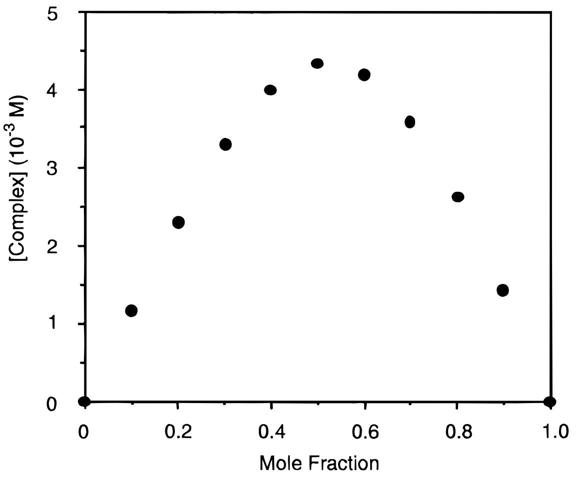

Figure 2. Plot (Job) of [**2c**$-Ag^+$ complex] versus the mole fraction [**2c**]/([**2c**] + [Ag^+]) at constant [**2c**] + [Ag^+].

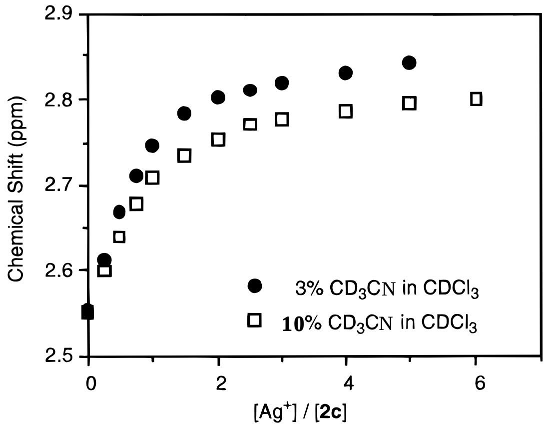

Figure 3. ^{1}H NMR titration for complexation between thiolariat ether **2c** and Ag^+ ([**2c**] = 3×10^{-3} M).

least-square analysis of a ^{1}H NMR titration curve using a resonance of Hα protons gave the stability constants between **2c** and Ag^+ of 1700 M^{-1} in 3% $CD_3CN-CDCl_3$ and of 1100 M^{-1} in 10% $CD_3CN-CDCl_3$ (Figure 3). The infinite δ values calculated are 2.88 ppm and 2.84 ppm, respectively.

In ^{13}C NMR definite changes of the resonances of **2c** were observed when mixed with 1 equiv of $AgNO_3$ (Table 5). The signals of carbons (C4, C5) adjacent to the sulfur atoms were apparently affected (downfield shifts, 2.354, 2.313 ppm, respectively). Changes in the chemical shifts of the ring carbons were also observed. The signal of C6 bearing a side chain was shifted most significantly to the higher field ($\Delta\delta = -2.822$ ppm) compared to the other ring carbons. In addition, C7 and C8 (assigned tentatively) carbons which exist near C6 were also affected ($\Delta\delta = -0.977, -0.886$ ppm). These changes are probably explained in terms of (1) metal$-$dipole interaction upon ligation of a crown ring to Ag^+ and (2) the conformational change of **2c** induced by the coordination of sulfur atom to Ag^+. Therefore, NMR spectroscopic examination performed here was in accordance with the synergistic coordination of a crown ring and a sulfur atom in the side arm to give a 1:1 complex between a thiolariat ether and Ag^+ in a fashion shown in Figure 1.

Elucidation of the crystal structure of the complex is important and useful to clarify reasons for the effective and selective coordination of a thiolariat ether to Ag^+. We are currently preparing suitable crystals of the complex for X-ray crystallography.

Conclusion

Thiolariat ethers bearing a 15-crown-5 ring exhibit remarkably high Ag^+ selectivity in solvent extraction and metal ion transport experiments. The results strongly suggested that the selectivity results from the synergistic coordination of the oxygen atoms of the appropriate crown ring size and sulfur atom to Ag^+. It is noteworthy that this tremendous perturbation of metal binding preference of crown ethers is caused by only one sulfur atom in the vicinity of the cavity, although the atom is located outside the cyclic framework.

Benzylsulfenyl derivatives (**1a**, **2a**, **3a**) are converted to the corresponding mercatomethyl crown ethers whose functionality is easily modified. Thus, the thiolariat ether frameworks can be combined with different functional moieties to prepare novel functional molecular systems. Preparation of various polymer-supporting materials which are useful to separate Ag^+ may be performed. Moreover diverse technological applications to utilize thiolariat ethers as functionalized materials for Ag^+ binder in the photographic technology and for the concentration and recovery of Ag^+ ions from industrial waste water are also promised.

Experimental Section

General methods were previously reported.[41]

4-[[(2-Hydroxyethyl)thio]methyl]-2,2-dimethyl-1,3-dioxolane (24). 2-Mercaptoethanol (5 mL, 71.3 mmol) and tosylate **23** (20.2 g, 70.5 mmol) were added successively to a solution of NaOH (3.41 g, 80.9 mmol) in 95% EtOH (100 mL) and THF (8 mL) under nitrogen. The reaction mixture was refluxed for 10 h. After cooling, the solvent was evaporated in vacuo. The residue thus obtained was mixed with 60 mL of water and then extracted with CH_2Cl_2 (60 mL × 3). The organic layer was washed with water, dried over anhydrous $MgSO_4$, and concentrated in vacuo. The crude product was purified by molecular distillation (150 °C, 2 mmHg) to give **24** as a colorless oil (10.8 g, 56.4 mol) in 80% yield: ^{1}H NMR (400 MHz, $CDCl_3$) 1.371 (s, 3H), 1.449 (s, 3H), 2.47 (t, $J = 5.8$ Hz, 1H), 2.69 (dd, $J = 6.2, 14$ Hz, 1H), 2.73$-$2.87 (m, 3H), 3.72 (dd, $J = 6.5, 8.4$ Hz, 1H), 3.69$-$3.82 (m, 2H), 4.11 (dd, $J = 6.1, 8.4$ Hz, 1H), 4.279 (quint, $J = 6.2$ Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) 25.61, 26.91, 35.03, 36.04, 61.14, 68.93, 75.86, 110.00; IR (neat) 3438 (br), 2985, 2932, 2876, 1455, 1407, 1380, 1371, 1254, 1215, 1153, 1060, 863, 843; MS (40 eV) *m/e* 192(M^+, 0.7%), 177(14.8), 174(19.1), 159(3.6), 134(9.1), 117(23.4), 101(100). HRMS (EI): calcd for $C_8H_{16}O_3S$ 192.0820, found 192.0863.

4-[[(2-Methoxyethyl)thio]methyl]-2,2-dimethyl-1,3-dioxolane (25). To a suspension of NaH (2.72 g, 62.4 mmol) in 30 mL of THF was added a solution of ketal **24** (10.8 g, 56.4 mmol) in 23 mL of THF under nitrogen. After stirring for several minutes at room temperature, methyl iodide (3.5 mL, 56 mmol) was added to the reaction mixture. The mixture was refluxed for 10 h and then concentrated in vacuo. The residue thus obtained was mixed with 80 mL of water and extracted with CH_2Cl_2 (80 mL × 3). The organic layer was washed twice with water and dried over anhydrous $MgSO_4$. The crude product obtained after evaporation of the solvent was purified by Kugelrohr distillation (110 °C, 3 mmHg) to give **25** (10.7 g, 51.5 mmol) in 92% yield: ^{1}H NMR (200 MHz, $CDCl_3$) 1.36 (s, 3H), 1.44 (s, 3H), 2.61$-$2.87 (m, 4H), 3.37 (s, 3H), 3.57 (t, $J = 6.5$ Hz, 2H), 3.73 (dd, $J = 6, 8$ Hz, 1H), 4.12 (dd, $J = 6, 8$ Hz, 1H), 4.20$-$4.34 (m, 1H); ^{13}C NMR

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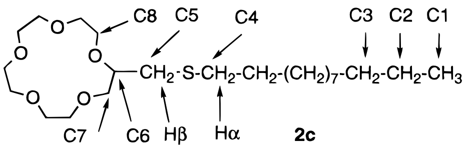
[41] Nabeshima, T.; Inaba, T.; Furukawa, N.; Hosoya, T.; Yano, Y. *Inorg. Chem.* **1993**, *32*, 1407$-$1416.

Table 5. Changes of ^{13}C NMR Chemical Shifts of Thiolariat Ether (2c) by the Addition of Ag$^+$ (1 equiv)

	Chemical Shft (ppm)			CDCl$_3$ - CD$_3$CN = 9 : 1 (v/v)				
	C1	C2	C3	C4^a	C5^a	C6	C7	C8^b
δ_1(**2c**)	14.182	22.787	32.212	33.212	34.176	79.779	72.917	70.444
δ_2(**2c** + Ag$^+$)	14.186	22.789	32.050	35.566	36.389	76.958	71.940	69.558
$\Delta\delta^c$	+0.004	+0.002	+0.002	+2.354	+2.313	-2.822	-0.977	-0.886

^{a} assigned by CHCOSY
^{b} assigned tentatively
^{c} $\Delta\delta = \delta_2 - \delta_1$



2c

(50 MHz, CDCl$_3$) 25.64, 27.02, 32.26, 35.72, 58.91, 69.07, 72.40, 75.87, 109.87; IR (neat) 2985, 2928, 2875, 1456, 1370, 1216, 1154, 1116, 1060, 960, 1060, 960, 915, 863. HRMS (EI): calcd for $C_9H_{18}O_3S$ 206.0977, found 206.0960.

1-[[(2-Methoxyethyl)thio]methyl]-2,3-propanediol (26). Ketal **25** (2.36 g, 11.4 mmol) was treated with 35 mL of methanol−3 N HCl (5:2, v/v) for 2 h at room temperature. The reaction mixture was concentrated in vacuo. The residue thus obtained was mixed with water and then extracted with CHCl$_3$. The organic layer was dried over anhydrous MgSO$_4$. After evaporation of the solvent, **26** was obtained as a pale yellow oil (1.00 g, 6.02 mmol) in 53% yield. The crude product was pure enough for the preparation of **4**. Very pure **4** was afforded by silica gel column chromatography (CHCl$_3$−MeOH, 20:1, v/v): ^{1}H NMR (200 MHz, CDCl$_3$) 2.58−2.83 (m, 6H), 3.39 (s, 3H), 3.51−3.64 (m, 3H), 3.68−3.89 (m, 2H); ^{13}C NMR (50 MHz, CDCl$_3$) 32.28, 36.25, 58.91, 65.50, 71.25, 72.44; IR 3400 (br), 2928, 2834, 1640, 1454, 1410, 1383, 1294, 1216, 1190, 1098, 1036, 957, 884. HRMS (EI): calcd for $C_6H_{14}O_3S$ 166.0664, found 166.0656.

[[(2-Methoxyethyl)thio]methyl]-15-crown-5 (4). According to a similar procedure for preparation of **2a**,[38] diol **26** (0.814 g, 4.90 mmol) was treated with tetraethylene glycol ditosylate (**27b**) (2.47 g, 4.92 mmol) and NaH (0.477 g, 10.9 mmol) in 25 mL of THF. The crude product was purified by flash column chromatography (SiO$_2$, CHCl$_3$) to give **4** (0.222 g, 0.684 mol) in 14% yield: ^{1}H NMR (200 MHz, CDCl$_3$) 2.71 (d, J = 5.3 Hz, 2H), 2.76 (t, J = 6.6 Hz, 2H), 3.37 (s, 3H), 3.56 (t, 6.6 Hz, 2H), 3.62−3.84 (m, 19H); ^{13}C NMR (125 MHz, CDCl$_3$) 32.38, 34.37, 58.71, 70.29, 70.47, 70.49, 70.56, 70.59, 70.80, 70.90, 71.08, 72.18, 72.61, 79.63; IR (neat) 2866, 1450, 1349, 1250, 1122, 985, 941, 869, 839. HRMS (EI): calcd for $C_{14}H_{28}O_6S$ 324.16066, found 324.15897.

4-[[[2-(Benzylthio)ethyl]thio]methyl]-2,2-dimethyl-1,3-dioxolane (28). To a solution of NaOH (1.34 g, 31.8 mmol) in 95% EtOH (42 mL)−THF (3 mL) were added 2-(benzylthio)ethylmercaptan (6.88 g, 28.0 mmol) and **23** (8.65 g, 30.2 mmol). The mixture was refluxed overnight and then concentrated in vacuo. The residue thus obtained was mixed with 60 mL of water, and the mixture was extracted with CH$_2$Cl$_2$ (60 mL × 3). The organic layer was washed with water and dried over anhydrous MgSO$_4$. The crude product obtained after evaporation of the solvent was purified by silica gel flash column chromatography (CHCl$_3$−*n*-hexane, 6:5, v/v) to give a pale yellow oil (8.63 g, 28.9 mmol) in 96% yield: ^{1}H NMR (200 MHz, CDCl$_3$) 1.35 (s, 3H), 1.41 (s, 3H), 2.5−2.8 (m, 6H), 3.67 (dd, J = 5, 7 Hz, 1H), 3.74 (s, 2H), 4.07 (dd, J = 5, 7 Hz, 1H), 4.10−4.25 (m, 1H), 7.21−7.32 (m, 5H); ^{13}C NMR (125 MHz, CDCl$_3$) 25.55, 26.93, 31.35, 32.46, 35.25, 36.41, 68.84, 75.57, 109.61, 127.17, 128.60, 128.85, 138.12; IR (neat) 2984, 2928, 2875, 1494, 1453, 1422, 1379, 1369, 1212, 1153, 1060, 862, 770, 700. MS *m/e* 298 (M$^+$). Anal. Calcd for $C_{15}H_{22}O_2S_2$: C, 60.37, H, 7.43. Found: C, 60.11, H, 7.42.

1-[[2-(Benzylthio)ethyl]thio]-2,3-propanediol (29). Ketal **28** (6.24 g, 20.9 mmol) was mixed overnight with 70 mL of methanol−3 N HCl (5:2, v/v) at room temperature. The resultant precipitates were collected by suction filtration, and dried in vacuo to give 4.77 g (18.5 mmol, 88%) of desired diol **29** as a pale yellow powder, which was used without further purification in the next step. An analytically pure sample was prepared by recrystallization from *n*-hexane: mp 52−54 °C. ^{1}H NMR (200 MHz, CDCl$_3$) 1.97 (t, J = 5.1 Hz, 1H), 2.50−2.78 (m, 7H), 3.45−3.60 (m, 1H), 3.65−3.75 (m, 2H), 3.76 (s, 2H), 7.2−7.4 (m, 5H); ^{13}C NMR (50 MHz, CDCl$_3$) 31.38, 32.28, 35.72, 35.84, 36.48, 65.46, 70.66, 127.56, 128.98, 129.25, 138.43; IR (KBr) 3312 (br), 2915, 1558, 1493, 1453, 1435, 1420, 1418, 1338, 1300, 1244, 1208, 1197, 1164, 1126, 1108, 1068, 1035, 1022, 1010, 955, 927, 896, 876, 806, 776, 744, 729, 697. MS *m/e* 258 (M$^+$). Anal. Calcd for $C_{12}H_{18}O_2S_2$: C, 55.78, H, 7.02. Found: C, 55.45, H, 6.87.

[[[2-(Benzylthio)ethyl]thio]methyl]-15-crown-5 (5). Diol **29** (2.00 g, 7.76 mmol) was added to a suspension of NaH (0.804 g, 18.4 mmol) in 20 mL of THF under nitrogen. To the mixture was added **27b** (4.05 g, 8.05 mmol) in 20 mL of THF by a syringe. The mixture was refluxed for 15 h and then concentrated in vacuo. The residue thus obtained was mixed with water and extracted with CH$_2$Cl$_2$. The organic layer was dried over MgSO$_4$. The crude product after evaporation of the solvent was purified by silica gel column chromatography (ethyl acetate) to give **5** (1.94 g, 4.65 mmol) as a yellow oil in 60% yield: ^{1}H NMR (200 MHz, CDCl$_3$) 2.5−2.8 (m, 6H), 3.5−3.9 (m, 19H), 3.74 (s, 2H), 7.2−7.4 (m, 5H); ^{13}C NMR (50 MHz, CDCl$_3$) 13.74, 22.04, 31.89, 32.87, 34.02, 70.43, 70.69, 70.75, 70.95, 71.10, 71.25, 72.93, 79.78; IR (neat) 3060, 3024, 2904, 2864, 1702, 1600, 1496, 1454, 1422, 1354, 1292, 1250, 1204, 1198, 1134, 1122, 986, 944, 938, 868, 840, 768, 700. HRMS (EI): calcd for $C_{20}H_{32}O_5S_2$ 416.1691, found 416.1715.

4-[3-(Benzylthio)propyl]-2,2-dimethyl-1,3-dioxolane (32). To a solution of DL-1,2-*O*-isopropylidenepentane-1,2,5-triol (**30**)[42] (2.50 g, 15.6 mmol) in 45 mL of pyridine was added 3.00 g (15.7 mmol) of tosyl chloride in 20 mL of pyridine so slowly (ca. 30 min) on an ice−salt bath that the temperature of the reaction mixture was kept below 0 °C. After stirring for additional 3 h at 0 °C, the mixture was concentrated very carefully at room temperature using a vacuum pump with a liquid N$_2$ trap to avoid decomposition of the tosylate. To the residue thus obtained were added NaH (0.757 g, 17.3 mmol), benzyl mercaptan (2.13 g, 17.2 mmol), and 50 mL of THF. The mixture was stirred for 18 h at room temperature and then concentrated in vacuo. The residue was mixed with 50 mL of water and extracted with CHCl$_3$ (50 mL × 4). The organic layers were combined and washed with water (150 mL × 3). The organic layer was dried over anhydrous MgSO$_4$ and concentrated in vacuo. The crude product was purified by silica gel column chromatography (CH$_2$Cl$_2$) to give **32** (1.81 g, 6.79 mmol) in 44% yield: ^{1}H NMR (200 MHz, CDCl$_3$) 1.34 (s, 3H), 1.40 (s, 3H), 1.50−1.75 (m, 4H), 2.45 (t, J = 7.0 Hz, 2H),

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[42] Hayashi, H.; Nakanishi, K.; Brandon, C.; Marmur, J. *J. Am. Chem. Soc.* **1973**, *95*, 8749−8757.

3.45-3.52 (m, 1H), 3.71 (s, 2H), 3.96−4.15 (m, 2H), 7.15−7.45 (m, 5H); ^{13}C NMR (50 MHz, $CDCl_3$) 25.45, 25.77, 27.01, 31.24, 32.72, 36.28, 69.51, 75.76, 109.03, 127.27, 128.81, 129.17, 138.89; IR (neat) 3411 (br), 3084, 3061, 1494, 1453, 1378, 1369, 1241, 1215, 1069, 858, 769, 702; MS (EI) *m/e* 266(M$^+$, 0.6%), 251(6.8), 208(25), 117(40.1), 91(100). HRMS (EI): calcd for $C_{15}H_{22}O_2S$ 266.1341, found 266.1390.

5-(Benzylthio)-1,2-pentanediol (33). According to a procedure similar to the preparation of **26**, a mixture of ketal **32** (0.889 g, 3.34 mmol) and 21 mL of methanol−3 N HCl (5:2, v/v) was stirred for 20 min at room temperature. The crude product obtained after evaporation was purified by silica gel chromatography using CH_2Cl_2 to afford **33** (0.651 g, 2.88 mmol) in 86% yield as a pale yellow oil: ^{1}H NMR (200 MHz, $CDCl_3$) 1.4−1.9 (m, 4H), 2.15 (br, 1H), 2.35 (br, 1H), 2.45 (t, *J* = 7.1 Hz, 2H), 3.3−3.5 (m, 1H), 3.5−3.7 (m, 2H), 3.71 (s, 2H), 7.2−7.4 (m, 5H); ^{13}C NMR (50 MHz, $CDCl_3$) 25.21, 31.37, 32.14, 36.35, 66.83, 72.01, 127.31, 128.84, 129.19, 138.85; IR (neat) 3372 (br), 3026, 2934, 1493, 1452, 1239, 1071, 869, 770, 701. HRMS (EI): calcd for $C_{12}H_{18}O_2S$ 226.1028, found 226.1024.

[3-(Benzylthio)propyl]-15-crown-5 (6). According to a procedure similar to that for **2a**, host **6** was prepared from NaH (0.278g, 6.37 mmol), diol **33** (0.638 g, 2.82 mmol), and **27b** (1.45 g, 2.89 mmol) in 40 mL of THF. The crude product was purified by silica gel column chromatography (ethyl acetate) to give **6** (0.333 g, 0.866 mmol) in 31% as a yellow oil: ^{1}H NMR (200 MHz, $CDCl_3$) 1.45−1.8 (m, 4H), 2.43 (t, *J* = 7.2 Hz, 2H), 3.4−3.8 (m, 19H), 3.70 (s, 2H), 7.2−7.35 (m, 5H); ^{13}C NMR (125 MHz, $CDCl_3$) 25.29, 31.25, 31.44, 36.26, 70.05, 70.50, 70.51, 70.60, 70.75, 71.02, 71.05, 74.14, 79.17, 126.89, 128.46, 128.82, 138.60; IR (neat) 3059, 3026, 2908, 2861, 1494, 1453, 1354, 1293, 1249, 1124, 984, 939, 855, 770, 703. HRMS (EI): calcd for $C_{19}H_{30}O_5S$ 370.1814, found 370.1809.

(−)-*trans*-4,5-Bis[(benzylthio)methyl]-2,2-dimethyl-1,3-dioxolane (35). A mixture of benzylmercaptan (2.39 mL, 20.4 mmol), ditosylate **34**[43] (4.56 g, 9.68 mmol), and NaOH (1.04 g, 24.7 mmol) in 30 mL of 95% ethanol and 4.5 mL of THF was refluxed overnight. After cooling, the mixture was concentrated in vacuo, suspended in water, and then extracted with CH_2Cl_2 three times. The combined organic layer was washed with water, dried over anhydrous $MgSO_4$, and concentrated in vacuo. The residue thus obtained was chromatographed on silica gel using CH_2Cl_2−*n*-hexane (7:3, v/v) as eluent to give **35** (3.32 g, 8.87 mmol) in 92% as a pale orange oil: ^{1}H NMR (400 MHz, $CDCl_3$) 1.408 (s, 6H), 2.54−2.67 (m, 4H), 3.71−3.82 (m, 4H), 3.85−3.92 (m, 2H), 7.2−7.3 (m, 10H); ^{13}C NMR (125 MHz, $CDCl_3$) 27.25, 33.38, 36.87, 79.81, 109.24, 127.10, 128.52, 129.05, 138.11; IR (neat) 3060, 3027, 2984, 2914, 2867, 1601, 1494, 1453, 1379, 1370, 1237, 1163, 1100, 1071, 1050, 1028, 901, 770, 747, 700. MS *m/e* 374 (M$^+$). Anal. Calcd for $C_{21}H_{26}O_2S_2$: C, 67.34, H, 7.00. Found: C, 67.17, H, 7.06.

1,4-Bis(benzylthio)-2,3-butanediol (36). A mixture of ketal **35** (3.44 g, 9.26 mmol), 42 mL of methanol−6 N HCl (5:2, v/v), and 8 mL of THF was stirred for 6 h at room temperature to give precipitates. The precipitates were collected by suction filtration, washed with water, and then recrystallized from *n*-hexane−$CHCl_3$−ethanol to afford **36** (2.79 g, 8.34 mmol) in 90% yield as pale yellow crystals: mp 105−106 °C. ^{1}H NMR (200 MHz, $CDCl_3$) 2.5−2.6 (m, 6H), 3.5−3.65 (m, 2H), 3.73 (s, 4H), 7.2−7.35 (m, 10H); ^{13}C NMR (125 MHz, $CDCl_3$) 35.30, 36.42, 70.58, 127.24, 128.63, 128.92, 137.98; IR (KBr) 3212(br), 2916, 1452, 1095, 1044, 1019, 931, 913, 894, 768, 706. MS *m/e* 334 (M$^+$). Anal. Calcd for $C_{18}H_{22}O_2S_2$: C, 64.64, H, 6.63. Found: C, 64.49, H, 6.65.

Bis[(benzylthio)methyl]-15-crown-5 (7). According to a procedure similar to that for **2a**, host **7** was prepared from diol **36** (1.03 g, 3.07 mmol), **27b** (1.62 g, 3.23 mmol), and NaH (0.285 g, 6.53 mmol) in 18 mL of THF. The crude product was purified by silica gel column chromatography using ethyl acetate−*n*-hexane (1:1, v/v) as eluent to give **7** (0.700 g, 1.42 mmol) as a colorless oil in 46% yield: ^{1}H NMR (200 MHz, $CDCl_3$) 2.39 (dd, *J* = 8, 13 Hz, 2H), 2.64 (dd, *J* = 3, 13 Hz, 2H), 3.5−3.9 (m, 18H), 3.74 (s, 4H), 7.15−7.4 (m, 10H); ^{13}C NMR (50 MHz, $CDCl_3$−CD_3CN = 9:1, v/v) 32.05, 36.98, 70.57, 70.77, 71.18, 71.77, 80.54, 127.35, 128.87, 129.44, 139.01; IR (neat) 3060, 3024, 2912, 2864, 1602, 1494, 1454, 1422, 1406, 1350, 1296, 1242, 1126, 1118, 1046, 1030, 990, 936, 834, 768, 702; HRMS (EI): calcd for $C_{26}H_{36}O_5S_2$ 492.2004, found 492.1982.

Bis[(benzylthio)methyl]-18-crown-8 (8). According to a procedure similar to that for **2c**,[38] host **8** was prepared from diol **36** (0.994 g, 2.97 mmol), pentaethylene glycol ditosylate (**27c**) (1.70 g, 3.12 mmol), and NaH (0.283 g, 6.49 mmol) in 14 mL of THF. The crude product was purified by silica gel column chromatography using ethyl acetate as eluent to give **8** (0.449 g, 0.837 mmol) as a pale yellow oil in 28% yield: ^{1}H NMR (200 MHz, $CDCl_3$) 2.51 (dd, *J* = 7, 14 Hz, 2H), 2.67 (dd, *J* = 5, 14 Hz, 2H), 3.5−3.8 (m, 22H), 3.74 (s, 4H), 7.2−7.35 (m, 10H); ^{13}C NMR (125 MHz, $CDCl_3$) 31.51, 36.85, 70.54, 70.64, 70.68, 70.76, 70.86, 79.85, 126.96, 128.46, 129.00, 138.48; IR (neat) 3060, 3028, 2908, 2872, 1700, 1600, 1494, 1454, 1420, 1352, 1292, 1250, 1128, 1114, 1030, 994, 948, 844, 766, 700; MS (FAB) 559 ([M + Na]$^+$), 537 ([M + H]$^+$). HRMS (EI): calcd for $C_{28}H_{40}O_6S_2$ 536.2266, found 536.2245.

[(Benzylsulfinyl)methyl]-15-crown-5 (9). To a methylene chloride (40 mL) solution of [(benzylthio)methyl]-15-crown-5 (**2a**) (1.50 g, 4.21 mmol) was added 1 equiv of *m*-CPBA (ca. 4.2 mmol) at −10 °C. The mixture was stirred for 5 h below −10 °C, and then NH_3 gas was bubbled into the mixture. After the precipitates thus obtained were filtered off, the filtrate was concentrated in vacuo. The residue was purified by silica gel column chromatography (CH_2Cl_2−methanol = 20:1, v/v) to give **9** (1.50 g, 4.03 mmol) as a pale yellow oil in 96% yield: ^{1}H NMR (200 MHz, $CDCl_3$) 2.67−3.06 (m, 2H), 3.5−3.9 (m, 18H), 3.95−4.2 (m, 3H), 7.2−7.4 (m, 5H); ^{13}C NMR (50 MHz, $CDCl_3$) 52.49, 55.47, 58.53, 59.14, 69.96, 70.57, 70.68, 70.73, 70.95, 71.12, 72.27, 72.68, 73.69, 73.82, 77.53, 128.63, 129.24, 130.40, 130.51, 130.67; IR (neat) 2904, 2864, 1496, 1456, 1408, 1356, 1296, 1250, 1128, 1118, 1040, 988, 942, 862, 840, 752, 700, 664. Anal. Calcd for $C_{18}H_{28}O_6S$: C, 58.04, H, 7.58. Found: C, 57.78, H, 7.77.

[(Benzylsulfonyl)methyl]-15-crown-5 (10). Compound **2a** (1.50 g, 4.21 mmol) was reacted with 2 equiv of *m*-CPBA (ca. 8.4 mmol) in the presence of K_2CO_3 (0.623 g, 4.51 mmol) in 80 mL of CH_2Cl_2 below −10 °C for 6 h. NH_3 gas was bubbled into the mixture, and then the resultant precipitates were filtered off. The filtrate was then concentrated in vacuo. The crude product was purified column chromatography (SiO_2, CH_2Cl_2−methanol = 20:1, v/v) to give **10** (1.39 g, 3.59 mmol) as a pale yellow oil in 85% yield: ^{1}H NMR (200 MHz, $CDCl_3$) 2.98 (d, *J* = 15 Hz, 1H), 3.28 (dd, *J* = 9.6, 15 Hz, 1H), 3.5−4.0 (m, 16H), 4.1-4.2 (m, 1H), 4.26 (d, *J* = 14 Hz, 1H), 4.40 (d, *J* = 14 Hz, 1H), 7.3−7.5 (m, 5H); ^{13}C NMR (50 MHz, $CDCl_3$) 53.85, 61.29, 70.46, 70.61, 70.71, 70.79, 70.95, 71.06, 71.32, 71.86, 75.12, 77.53, 128.60, 129.18, 131.55; IR (neat) 2904, 2868, 1496, 1456, 1396, 1356, 1300, 1256, 1200, 1132, 1118, 988, 938, 872, 830, 760, 700, 666. Anal. Calcd for $C_{18}H_{28}O_7S$: C, 55.65, H, 7.26. Found: C, 55.29, H, 7.24.

Solvent Extraction. The extraction of metal ions from the aqueous solution into 1,2-dichloroethane was performed in capped vials. After the biphasic mixture (the volumes of the aqueous and organic phases are 10 mL each) was stirred vigorously for 6 h at 25 ± 1 °C, the amounts of picrate anion in the aqueous phase were determined by UV−VIS spectroscopy monitoring at 356 nm. The extractability was calculated according to eq 1. All experiments were carried out in duplicate or triplicate and the respective results were averaged.

$$\text{extractability (\%)} = ([\text{Pic}^-]_{\text{aq},0} - [\text{Pic}^-])/[\text{Pic}^-]_{\text{aq},0} \times 100 \qquad (1)$$

where $[\text{Pic}^-]_{\text{aq},0}$ is the initial concentration of picrate in the aqueous phase (3×10^{-5} M), and $[\text{Pic}^-]$ is the concentration of picrate in the aqueous phase after extraction.

Transport through a Liquid Membrane. An apparatus (a dual cylindric cell) for the transport experiment across liquid membrane[41] was designed on the basis of that of Lamb et al.[44]

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[43] Rubin, L. J.; Lardy, H. A.; Fischer, H. O. L. *J. Am. Chem. Soc.* **1952**, *74*, 425−428.

The inner aqueous source phase contained metal nitrate (4 mL, see Table 3 and 4 for the concentrations), and the outer receiving phase consisted of deionized water (40 mL). 1,2-Dichloroethane (50 mL) containing ionophore (2.0×10^{-4} M) was used as a liquid membrane. The three phases in the transport cell were agitated carefully by a stirring bar (200 rpm) on the bottom of the cell at 25 ± 1 °C. The concentrations of the metal ion in the aqueous receiving phase were determined by atomic absorption spectroscopy at intervals during the transport run.

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Supporting Information Available: ^{13}C NMR for compounds **4**, **5**, **6**, **7**, **8**, **24**, **25**, **26**, **32**, and **33**, and COSY spectrum of **2c** (13 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of this journal, and may be ordered from the ACS; see any current masthead page for ordering information.

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(44) Lamb, J. D.; Christensen, J. J.; Oscarson, J. L.; Nielsen, B. L.; Asay, B. W.; Izatt, R. M. *J. Am. Chem. Soc.* **1980**, *102*, 6820−6824.