Silver Ion Selective Extraction with Dithiaza-, Tetrathiaza-, and Tetrathiadiazacrown Ether Derivatives

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Dithiazacrown, tetrathiazacrown, and two tetrathiadiazacrown ether derivatives, bearing a phenyl group on each nitrogen atom at the periphery, were synthesized, and the solvent extractions of some transition metal ions with these compounds were carried out using an H_2O–1,2-dichloroethane system. All of the thiazacrown compounds employed exhibited Ag^+ selectivity, and formed 1 : 1 : 1 complexes of Ag^+ : ligand : laurate ion as a counter anion to be extracted into a 1,2-dichloroethane solution. The extractabilities (extraction constants, K_{ex}) for Ag^+ decreased in the order: 7,16-diphenyltetrathia-7,16-diaza-18-crown-6 (**3**) ($\log K_{ex}=1.18\pm0.13$)> 13-phenyltetrathia-13-aza-15-crown-5 (**2**) (0.75 ± 0.09)>7-phenyldithia-7-aza-9-crown-3 (**1**) (-0.47 ± 0.06)>13,16-diphenyltetrathia-13,16-diaza-18-crown-6 (**4**) (-0.62 ± 0.16).

It is known that cyclic or acyclic polythioethers incorporating some sulfur atoms as donor atoms have high complexabilities for some transition metal ions, and possible structures of some metal complexes of the compounds have been proposed so far.[1—3] The extraction behavior of the polythioethers for metal ions has also been examined. The extraction of Ag^+ from an aqueous solution into an organic solution was also observed using the polythioethers. The ion selectivities of most of the polythioethers for Ag^+ were, however, poor and the extractabilities for Ag^+ were close to or less than those of Cu^+ and Hg^{2+}.[4,5] Some attempts have been made to develop new polythioethers, especially thiacrown ethers, which have high Ag^+-selective complexability in order to use them in the field of analytical chemistry, e.g., solvent extraction,[6—8] ion-selective electrodes (ISE),[9,10] ion-selective field-effect transistors (ISFET),[11] and liquid chromatography.[12]

There have only been a few reports concerning the Ag^+ complexabilities and selectivities of thiazacrown ether derivatives containing sulfur and nitrogen atoms on the crown rings.[13,14] We previously reported on polythiapolyazacrown ether dyes which exhibit high Ag^+-selectivities in solvent extraction.[15] In the present paper we describe the syntheses of 7-phenyldithia-7-aza-9-crown-3 (**1**), 13-phenyltetrathia-13-aza-15-crown-5 (**2**), 7,16-diphenyltetrathia-7,16-diaza-18-crown-6 (**3**), and 13,16-diphenyltetrathia-13,16-diaza-18-crown-6 (**4**) (Fig. 1), as well as their solvent extraction behavior for some transition metal ions, and the Ag^+ extractabilities of these thiazacrown ethers together with analogous compounds, 13-phenyl-13-aza-15-crown-5 (**5**) and 7,16-diphenyl-7,16-diaza-18-crown-6 (**6**).

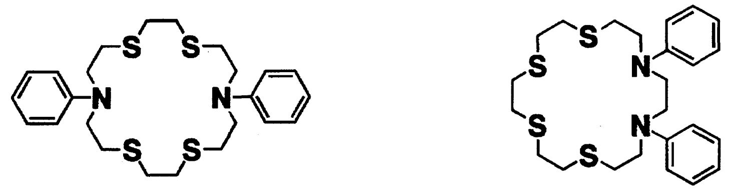
Experimental

Chemicals. Unless otherwise specified, the reagents employed for the solvent extraction were of analytical grade, and the others were of guaranteed-reagent grade. 13-Phenyl-1,4,7,10-tetraoxa-13-azacyclopentadecane (or 13-phenyl-13-aza-15-crown-5) (**5**) was purchased from Merck & Co., Inc., and was used without further purification. All of the organic solvents were purified in the usual way. Water was doubly distilled.

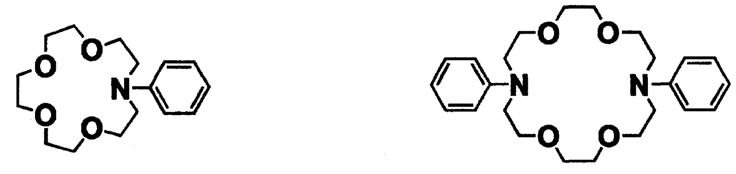
Spectroscopic and Physical Methods. Mass spectra were measured with a JEOL JMS-DX303 instrument. Melting points were determined with a Yanaco melting point apparatus and were uncorrected. ^{1}H NMR spectra were recorded on a Hitachi R-90 spectrometer with $CDCl_3$ solutions containing tetramethylsilane as an internal standard. The pH measurements were made using a TOA pH Meter HM-30S equipped with a TOA GST-5311C glass electrode. The concentrations of metal ions in aqueous solutions were determined by atomic absorption spectrophotometry (Seiko SAS/727) or by ICP-AES (Seiko SPS/7000A).

Syntheses. 7-Phenyldithiaza-9-crown-3 (or 7-Phenyl-1,4-dithia-7-azacyclononane) (1), and 7,16-Diphenyltetrathia-7,16-diaza-18-crown-6 (or 7,16-Diphenyl-1,4,10,13-tetrathia-7,16-diazacyclooctadecane) (3): The reaction of 3-phenyl-1,5-bis(*p*-tolylsulfonyloxy)-3-azapentane (**7**), which was given by the tosylation of 3-phenyl-3-azapentane-1,5-diol,[16] with NaI in acetone yielded 1,5-diiodo-3-phenyl-3-azapentane (**8**) (87%).[17] In dry DMF (500 cm^3) Cs_2CO_3 (4.24 g, 0.011 mol) was suspended, and the solution was stirred at 60 °C under a nitrogen atmosphere. To the suspension was added dropwise a dry DMF solution (100 cm^3) containing ethane-1,2-dithiol (1.00 g, 0.011 mol) and **8** (4.41 g, 0.011 mol) for 12 h. After the addition was completed, the mixture was stirred at 60 °C for 24 h. After the reaction, the mixture was first concentrated, and then 200 cm^3 of water was added. The solution was extracted with $CHCl_3$ ($100\ cm^3\times4$). The combined ex-

7-Dhenyldithia-7-aza-9-crown-3 (**1**) 13-Phenyltetrathia-13-aza-15-crown-5 (**2**)



7,16-Diphenyltetrathia-7,16-diaza-18-crown-6 (**3**) 13,16-Diphenyltetrathia-13,16-diaza-18-crown-6 (**4**)



13-Phenyl-13-aza-15-crown-5 (**5**) 7,16-Diphenyl-7,16-diaza-18-crown-6 (**6**)

Fig. 1. Structural formulas of polythiamonoaza- and polythiadiazacrown ethers and their analogs employed here.

tract was dried over Na_2SO_4. The solvent was then removed by rotary evaporation. The residue was subjected to column chromatography (silica gel; eluent, benzene). **1**: White solid (35%); mp 49—50 °C; ^{1}H NMR ($CDCl_3$) $\delta=2.71$—2.95 (m, 8H, SCH_2), 3.48—3.71 (m, 4H, NCH_2), 6.64—7.40 (m, 5H, ArH); MS (EI), m/z 239 (M^+). **3**: White solid (2%); mp 145—146 °C; ^{1}H NMR ($CDCl_3$) $\delta=2.71$—2.95 (m, 16H, SCH_2), 3.48—3.71 (m, 8H, NCH_2), 6.64—7.40 (m, 10H, ArH); MS (EI) m/z 478 (M^+).

13-Phenyltetrathia-13-aza-15-crown-5 (or 13-Phenyl-1,4,7,10-tetrathia-13-azacyclopentadecane) (2): The reaction of 3,6-dithiaoctane-1,8-dithiol (1.07 g, 0.005 mol) with **8** (2.00 g, 0.005 mol) yielded **2** in a similar way to **1** and **3**, except for purification by recrystallization from a mixed solvent of ethanol and benzene. **2**: White solid (61%); mp 130—131 °C; ^{1}H NMR ($CDCl_3$) $\delta=2.64$—2.90 (m, 16H, SCH_2), 3.46—3.68 (m, 4H, NCH_2), 6.60—7.38 (m, 5H, ArH); MS (EI) m/z 359 (M^+).

13,16-Diphenyltetrathia-13,16-diaza-18-crown-6 (or 13,16-Diphenyl-1,4,7,10-tetrathia-13,16-diazacyclooctadecane) (4): A suspended aqueous solution (300 cm^3) of *N*-(2-hydroxyethyl)aniline (80.2 g, 0.585 mol), 1,2-dichloroethane (26.3 g, 0.266 mol), and $CaCO_3$ (39.9 g, 0.399 mol) was refluxed with stirring for 2 d in a nitrogen atmosphere. After the mixed solution was extracted with benzene (100 cm^3×3), the extract was dried over Na_2SO_4. The solvent was then removed by rotary evaporation. The residue was recrystallized from hexane/ethanol to give **9** as a white solid. **9** (31%): Mp 85.0—85.5 °C; ^{1}H NMR ($CDCl_3$) $\delta=2.54$ (s, 2H, OH), 3.34—3.78 (m, 12H, CH_2), 6.65—7.34 (m, 10H, ArH). The cyclization reaction of **10** (2.13 g, 0.005 mol), which was yielded by the bromination of **9** with phosphorus tribromide, and 3,6-dithiaoctane-1,8-dithiol (1.07 g, 0.005 mol) gave **4** as a white solid in a manner similar to that for **1** and **3**. **4** (11%): Mp 150—151 °C; ^{1}H NMR $\delta=2.70$—2.91 (m, 16H, SCH_2), 3.48—3.71 (m, 8H, NCH_2), 6.62—7.40 (m, 5H, ArH); MS (EI) m/z 477 (M^+).

7,16-Diphenyl-7,16-diaza-18-crown-6 (or 7,16-Diphenyl-1,4,10,13-tetraoxa-7,16-diazacyclooctadecane) (6): The suspended aqueous solution (200 cm^3) containing aniline (46.5 g, 0.5 mol), 2-(2-chloroethoxy)ethanol (155.6 g, 1.25 mol), and $CaCO_3$ (70.0 g, 0.7 mol) was refluxed with stirring under a nitrogen atmosphere for 12 h. After the reaction, the mixture was extracted with $CHCl_3$ (100 cm^3×3). The combined extract was dried over Na_2SO_4 and concentrated by rotary evaporation. After the residue was dissolved in diethyl ether, HCl gas was bubbled into the solution to precipitate 6-phenyl-3,9-dioxa-6-azaundecane-1,11-diol monohydrochloride, which was recrystallized from ethanol/THF for purification. The reaction of the diol monohydrochloride with *p*-toluenesulfonyl chloride afforded 6-phenyl-1,11-bis(*p*-tolylsulfonyloxy)-3,9-dioxa-6-azaundecane in a matter similar to that for **7**. Potassium *t*-butoxide (4.94 g, 0.044 mol) was suspended in a dry THF solution (200 cm^3) at 60 °C under nitrogen. To the suspension was dropwise added a mixed THF solution (200 cm^3) of 3-phenyl-3-azapentane-1,5-diol (3.62 g, 0.02 mol) and the ditosylate obtained as mentioned above (11.55 g, 0.02 mol) for 6 h. After the addition was completed, the reaction mixture was refluxed with stirring for 40 h, and then concentrated in vacuo. Water (100 cm^3) was added to the residue, and the solution was extracted with $CHCl_3$ (100

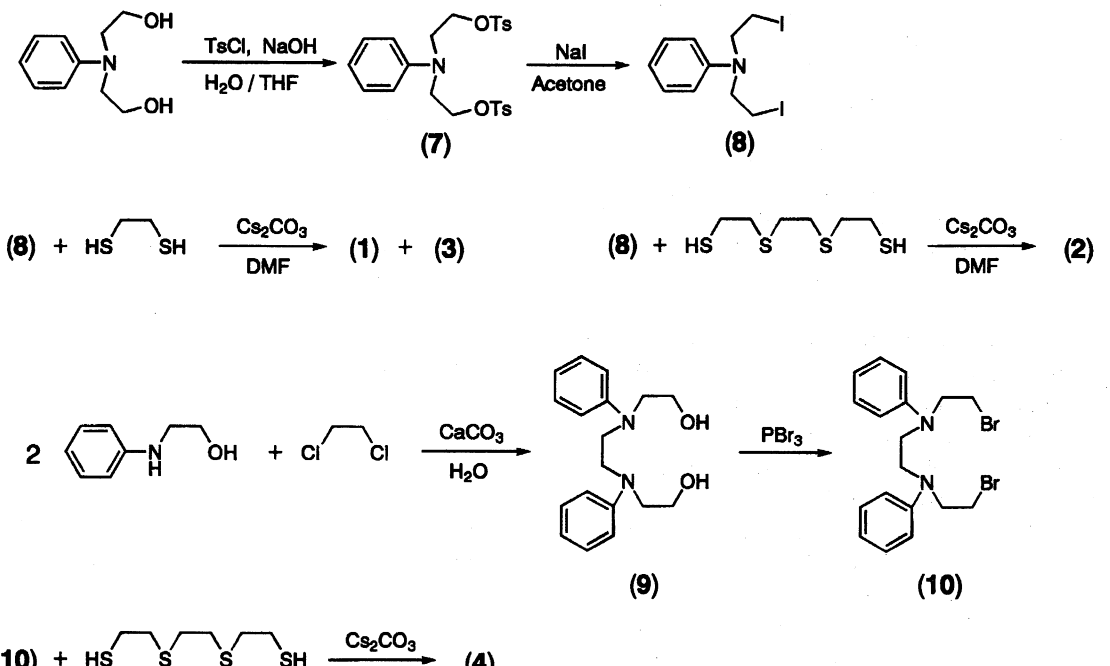
$cm^3 \times 3$). The combined extract was dried over Na_2SO_4 and evaporated to afford the crude **6**, which was recrystallized from hexane/ethanol for purification. **6**: White solid (18%); mp 93—94 °C; ^{1}H NMR ($CDCl_3$) δ=3.51—3.80 (m, 24H, CH_2NCH_2 and CH_2OCH_2), 6.51—7.31 (m, 10H, ArH); MS (EI) m/z 412 (M^+).

Solvent Extraction of Metal Ions. In the solvent extraction of metal ions, laurate ion given by deprotonation of lauric acid was chosen as a counter anion for the metal ion–ligand complex. Extraction experiments for a qualitative comparison of the metal ion extractabilities were carried out as follows. In a 50 cm^3 stoppered centrifuge tube were placed an aqueous solution (5 cm^3), which was adjusted to pH 6.0 with a buffer of 0.01 mol dm^{-3} 2-(N-morpholino)ethanesulfonic acid (MES) and KOH and contained 2.0×10^{-5} mol dm^{-3} metal ion as sulfate and 0.2 mol dm^{-3} potassium sulfate for adjusting the ionic strength, and a 1,2-dichloroethane solution (5 cm^3) of 1.0×10^{-4} mol dm^{-3} ligand and 1.0×10^{-3} mol dm^{-3} lauric acid. The mixture was shaken for 1 h at 25.0±0.2 °C. After standing for 2 h, an aliquot (0.1 cm^3) of the aqueous solution was subjected to atomic absorption spectrometry, except for those cases using Hg^{2+} and Tl^+ solutions, which were determined with ICP-AES. For estimating the Ag^+ extraction behavior of the ligand, extraction was carried out by fixing the initial Ag^+ concentration constant at 1.0×10^{-5} mol dm^{-3} and varying the ligand, lauric acid or proton concentrations. The ligand and lauric acid concentrations and pH were changed over the ranges of 1.0×10^{-5}—6.0×10^{-4} mol dm^{-3} and 2.0×10^{-4}—3.0×10^{-3} mol dm^{-3} and 5.5—7.1, respectively. When one concentration factor was changed, the values of the other concentrations, i.e., those of ligand and lauric acid, and pH were kept at 2.0×10^{-4} and 1.0×10^{-3} mol dm^{-3} and 6.4, respectively.

Results and Discussion

Syntheses. Polythiamonoaza- and polythiadiazacrown ether derivatives were synthesized by the cyclization reaction of ethane-1,2-dithiol or 3,6-dithiaoctane-1,8-dithiol with appropriate halides in the presence of Cs_2CO_3 as a base in DMF, as shown in Scheme 1.[9,18—20] A cyclization reaction using Cs_2CO_3 is known to be superior in terms of the yield of macrocyclic compounds to that using sodium ethoxide as a base,[18] although sodium ethoxide has been used for the synthesis of alkyl sulfides by the reaction of thiol with halides.[19,21,22] The synthesis of 7-phenyldithia-7-aza-9-crown-3 (**1**) was performed by the reaction of ethane-1,2-dithiol with 1,5-diiodo-3-phenyl-3-azapentane (**8**), not with ditosylate (**7**), because iodide reacts with thiolate more easily than does tosylate.[9] This cyclization reaction also afforded a slight amount of 7,16-diphenyltetrathia-7,16-diaza-18-crown-6 (**3**) as one of the products of the 2:2 reaction of both of the reactants, although a high dilution condition of the reaction mixture was used in order to prevent polymerization. The reaction of **8** with 3,6-dithiaoctane-1,8-dithiol gave 13-phenyltetrathia-13-aza-15-crown-5 (**2**) in high yield; no compound formed by the 2:2 cyclization reaction of the reactants could be isolated. Such a difference in the cyclization yields between dithiaza-9-crown-3 (**1**) and tetrathiaza-15-crown-5 (**2**) is related to the much higher conformational constraint of **1** than that of **2**.[23)]

13,16-Diphenyltetrathia-13,16-diaza-18-crown-6 (**4**), which has a low symmetrical structure bearing two nitrogen atoms at neighboring heteroatomic places on the



Scheme 1. Syntheses of polythiamonoaza- and polythiadiazacrown ethers.

Table 1. Extraction (%) of Some Metal Ions[a)]

	Extraction/%								
Compound	Mn^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}	Ag^+	Cd^{2+}	Hg^{2+}	Tl^+
1	0	0	0	1	0	21	0	<5	1
2	0	0	0	0	0	62	0	<5	0
3	0	1	0	2	2	71	0	7	0
4	0	0	2	1	0	21	0	<5	1
5	0	0	0	0	0	0	0	<5	0
6	0	0	0	0	0	0	0	<5	0

a) The errors were within ±3% (95% confidence) except for the case of Hg^{2+}, of which detection error was within ±5% (90% confidence).

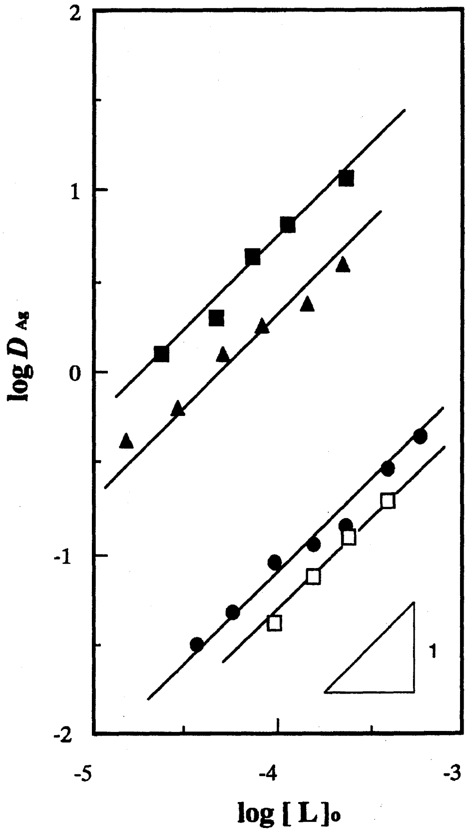


Fig. 2. Plots of log D_{Ag} vs. log [L] in solvent extraction of Ag^+–ligand–laurate ion using H_2O–1,2-dichloroethane system. Ligand: **1** (●), **2** (▲), **3** (■), **4** (□).

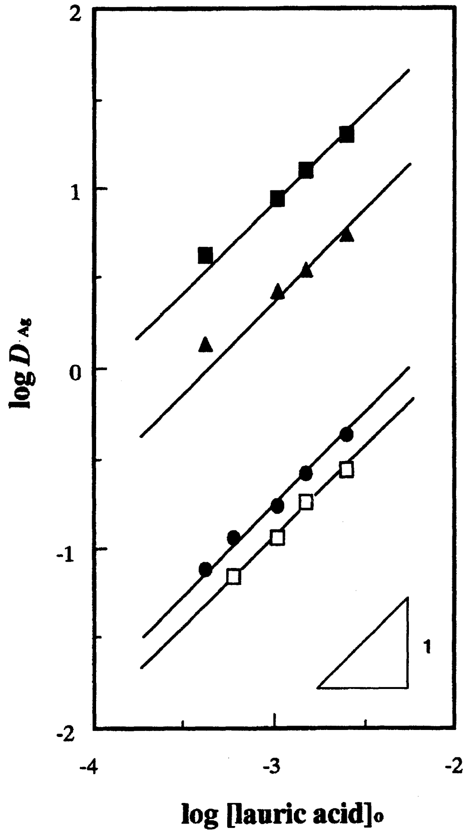


Fig. 3. Plots of log D_{Ag} vs. log [lauric acid] in solvent extraction of Ag^+–ligand–laurate ion using H_2O–1,2-dichloroethane system. Ligand: **1** (●), **2** (▲), **3** (■), **4** (□).

periphery, was synthesized by the cyclization reaction of 1,8-dibromo-3,6-diphenyl-3,6-diazaoctane (**10**) with 3,6-dithiaoctane-1,8-dithiol with a much lower yield than that of **2** obtained by a similar reaction. Such a low yield of **4** should be attributed to an inhibition of the proximity of two bromine atoms on both ends of **10** due to the steric hindrance of two phenyl groups, rather than the lower reactivity of bromide.

Cation Extraction. In the solvent extraction of metal ions with an electrically neutral ligand, metal ion-ligand complexes are extracted as ion-pair complexes with a counter anion from an aqueous solution into an organic solution. Therefore, picrate ion has been frequently used as a lipophilic counter anion.[24)] Laurate ion was used here instead of picrate ion in order to estimate the metal ion extraction selectivity, and, especially, the extraction equilibria, because the deprotonation of lauric acid, the pK_a of which is 5.3, is more sensitive to a pH change in the neutral region than that of picric acid. No extraction of any metal ion was observed in the absence of the ligand and/or lauric acid under the conditions employed in this study. The results of the solvent extractions of some transition metal ions with polythiamonoaza- and polythiadiazacrown ether derivatives **1**—**4** and monoaza- and diazacrown ethers,

Table 2. Extraction Constants (K_{ex})[a] for Ag^+–Thiazacrown Ether–Lauric Acid (1 : 1 : 1) Complexes

Compound	**1**	**2**	**3**	**4**
log K_{ex}	−0.47± 0.06	0.75± 0.09	1.18± 0.13	−0.62± 0.16

a) In 1,2-dichloroethane–H_2O system at 25±0.2 °C.

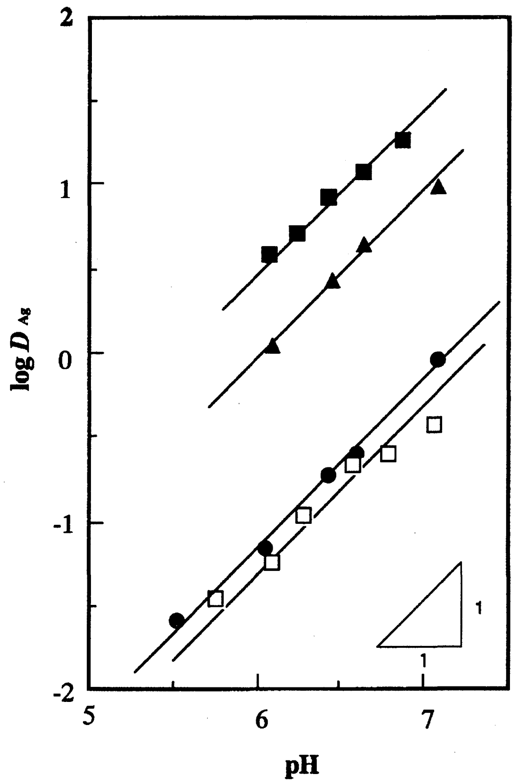


Fig. 4. Plots of log D_{Ag} vs. pH in solvent extraction of Ag^+–ligand–laurate ion using H_2O–1,2-dichloroethane system. Ligand: **1** (●), **2** (▲), **3** (■), **4** (□).

5 and **6**, are shown in Table 1. It should be noted that **1**—**4** extracted Ag^+ selectively, while the other metal ions, even Hg^{2+} which is well-known to have affinity for thioethers,[4,12,25] were hardly extracted. Especially, **2** and **3** have high Ag^+ extractabilities compared with those of **1** and **4** and high Ag^+ selectivities against Hg^{2+}. Such Ag^+ selectivities are comparable with that of 2,3-(4′-acryloylamidobenzo)-7,10,13-trithia-15-crown-5 which is one of the most Ag^+-selective extractants as far as we know, although the extraction conditions were different.[6]

Alkali and alkaline earth metal ions were scarcely extracted with **1**—**4**. On the other hand, the extraction of any transition metal ion was hardly observed in the case of using monoaza- and diaza-crown ethers, **5** and **6**, being analogs of **2** and **3**, respectively.

Silver(I) Ion Extraction. The extraction behavior of **1**—**4** for Ag^+ was examined by changing the concentrations of lauric acid and the ligand as well as the pH. Assuming the composition of the extracted species to be a 1 : m : n+1 complex of Ag^+ : ligand : lauric acid, the composition and the extraction constant are defined by the following equations:

$$Ag^+ + m(L)_o + (n+1)(HA)_o \overset{K_{ex}}{\rightleftharpoons} (AgL_mA(HA)_n)_o + H^+ \quad (1)$$

$$K_{ex} = \frac{[AgL_mA(HA)_n]_o[H^+]}{[Ag^+][L]_o^m[HA]_o^{n+1}} \quad (2)$$

$$D_{Ag} = \frac{[AgL_mA(HA)_n]_o}{[Ag^+] + [AgL_mA(HA)_n]} \quad (3)$$

where L, HA, A^-, and $AgL_mA(HA)_n$ are the ligand, lauric acid, laurate ion, and extracted complex, respectively, and the subscript "o" and without the subscript respectively denote the organic and the aqueous solutions. Here, K_{ex} and D_{Ag} mean the extraction constant of the silver ion–ligand–laurate ion complex and the distribution constant of Ag^+, respectively. If $[Ag^+] \gg [AgL_mA(HA)_n]$, the logarithmic form of Eq. 2 can be rewritten by the substitution of Eq. 3 as follows:

$$\log D_{Ag} = \log K_{ex} + m \log [L]_o + (n+1) \log [HA]_o + pH. \quad (4)$$

The slopes, m and (n+1), of the straight lines for plots of log D_{Ag} vs. log $[L]_o$ and log D_{Ag} vs. log $[HA]_o$ afford the ratios of the ligand and lauric acid to Ag^+, respectively, and the value of K_{ex} can be given by the intercept of the line. The slope of the straight line for the plot of log D_{Ag} vs. pH shows the ratio of laurate ion, which is formed by the deprotonation of lauric acid, to the Ag^+-ligand complex of the extracted complex. Plots of log D_{Ag} vs. log $[L]_o$, log $[HA]_o$, and pH in the extraction of Ag^+ with **1**—**4** are shown in Figs. 2, 3, and 4, respectively. These plots show linear relationships with a slope of unity in every case, indicating that 1 : 1 : 1 complexes of Ag^+ : ligand : laurate ion, that is AgLA, were extracted.

Thus, the obtained K_{ex} values are listed in Table 2. It is realized from this table that the extractabilities of the ligands for Ag^+ decreased in the order **3**>**2**>**1**>**4**. Compounds **2** and **3** should be efficiently used as extractants for Ag^+. If picrate ion is used instead of laurate ion as a counter anion, the extractability for Ag^+ would be remarkably enhanced; especially, Ag^+ might be quantitatively extracted by using **2** and **3** under the conditions employed here.

7,16-Diphenyltetrathia-7,16-diaza-18-crown-6 (**3**) with possible C_2-symmetry, assigned from space-filling models, extracted Ag^+ most effectively, while the structural isomer **4** exhibited the lowest extractability, being lowered by a log K_{ex} value of 1.8 compared to that of **3**. Some studies on structures of complexes of tetrathia-

7,16-diaza-18-crown-6 and its 7,16-dimethylated derivative with transition metal ions have been reported.[26,27] Tetrathia-7,16-diaza-18-crown-6 forms a stable inclusion complex with Ag^+,[25] although the complex is known to have a distorted octahedral arrangement using the six donor atoms by an X-ray study of these complexes.[27] On the other hand, the Ag^+ complexes of 7,16-dimethyltetrathia-7,16-diaza-18-crown-6 have two different distorted configurations of the coordinated macrocycle, while in both of the complexes the crown rings surround Ag^+. Especially, in the major component of these complexes of 7,16-dimethyltetrathia-7,16-diaza-18-crown-6, the macrocycle behaves as a pentadentate ligand with one nitrogen and four sulfur donor atoms; the second nitrogen atom of the macrocycle does not interact with Ag^+. It is postulated that compound **3** forms a complex with Ag^+ similar to that of 7,16-dimethyltetrathia-7,16-diaza-18-crown-6. Furthermore, an asymmetrical structural analog **4** should have a much higher distorted conformation upon complexation with Ag^+ according to the adjacent phenyl groups,[14] and, therefore, hardly forms any complex with Ag^+.

Dithia-7-aza-9-crown-3 has been reported to form a stable 1 : 2 (Ag^+ : crown unit) complex with Ag^+ in an aqueous solution.[28] It was, however, observed here that 7-phenyldithia-7-aza-9-crown-3 (**1**) formed only a much lower stable 1 : 1 complex to extract Ag^+ from an aqueous solution into an organic solution, because a bulky phenyl group on the nitrogen atom prevented the formation of the 1 : 2 complex. As far as we know, the complexation of tetrathiaza-15-crown-5 with Ag^+ has never been reported. An examination of space-filling models for 13-phenyltetrathia-13-aza-15-crown-5, though the conformation may be changed with complexation with Ag^+ and/or the kind of counter anion for the complex cation, reveals that Ag^+ cannot be fully accomodated in the cavity of the crown ether because lone pairs of the sulfur atoms point out of the ring.[29] It, however, appears that Ag^+ can lie above the plane comprising the five hetero atoms of the crown ring.

References

1) R. M. Izatt, K. Pawlak, J. S. Bradshaw, and R. L. Bruening, *Chem. Rev.*, **91**, 1721 (1991).

2) S. R. Cooper and S. C. Rawle, *Struct. Bonding (Berlin)*, **72**, 1 (1990).

3) A. J. Blake and M. Schröder, *Adv. Inorg. Chem.*, **35**, 1 (1990).

4) K. Chayama and E. Sekido, *Anal. Sci.*, **3**, 535 (1987).

5) S. S. Lee, J. H. Jung, S. B. Cho, J. S. Kim, J. Kim, and S. Kim, *Bull. Korean Chem. Soc.*, **13**, 704 (1992).

6) M. Oue, K. Kimura, and T. Shono, *Anal. Chim. Acta*, **194**, 293 (1987).

7) F. Dietze, K. Gloe, R. Jacobi, P. Mühl, J. Beger, M. Petrich, L. Beyer, and E. Hoyer, *Solvent Extr. Ion Exch.*, **7**, 223 (1989).

8) K. Saito, S. Murakami, A. Muromatsu, and E. Sekido, *Polyhedron*, **12**, 1587 (1993).

9) M. Oue, K. Akama, K. Kimura, M. Tanaka, and T. Shono, *J. Chem. Soc., Perkin Trans. 1*, **1989**, 1675.

10) J. Casabó, L. Mestres, L. Escriche, F. Teixidor, and C. Pérez-Jiménez, *J. Chem. Soc., Dalton Trans.*, **1991**, 1969.

11) Z. Brzozka, P. L. H. M. Cobben, D. N. Reinhoudt, J. J. H. Edema, J. Buter, and R. M. Kellogg, *Anal. Chim. Acta*, **273**, 139 (1993).

12) R. L. Bruening, B. J. Tarbet, K. E. Krakowiak, M. L. Bruening, R. M. Izatt, and J. S. Bradshaw, *Anal. Chem.*, **63**, 1014 (1991).

13) K. R. Adam, D. S. Baldwin, A. Bashall, L. F. Lindoy, M. McPartlin, and H. R. Powell, *J. Chem. Soc., Dalton Trans.*, **1994**, 237.

14) A. S. Craig, R. Kataky, D. Parker, H. Adams, N. Bailey, and H. Schneider, *J. Chem. Soc., Chem. Commun.*, **1989**, 1870.

15) H. Sakamoto, J. Ishikawa, T. Mizuno, K. Doi, and M. Otomo, *Chem. Lett.*, **1993**, 609.

16) Y. Liu, Y. Inoue, and T. Hakushi, *Bull. Chem. Soc. Jpn.*, **63**, 3044 (1990).

17) M. J. Calverley and J. Dale, *Acta Chem. Scand., Ser. B*, **36**, 241 (1982).

18) J. Buter and R. M. Kellogg, *J. Org. Chem.*, **46**, 4481 (1981).

19) R. E. Wolf, Jr., J. R. Hartman, J. M. E. Storey, B. M. Foxman, and S. R. Cooper, *J. Am. Chem. Soc.*, **109**, 4328 (1987).

20) J. S. Bradshaw, K. E. Krakowiak, R. M. Izatt, R. L. Bruening, and B. J. Tarbet, *J. Heterocycl. Chem.*, **27**, 347 (1990).

21) W. Rosen and D. H. Busch, *J. Am. Chem. Soc.*, **91**, 4694 (1969).

22) L. A. Ochrymowycz, C. Mak, and J. D. Michna, *J. Org. Chem.*, **39**, 2079 (1974).

23) S. R. Cooper, S. C. Rawle, R. Yagbasan, and D. J. Watkin, *J. Am. Chem. Soc.*, **113**, 1600 (1991).

24) Y. Takeda, *Top. Curr. Chem.*, **121**, 1 (1984).

25) K. Chayama, N. Awano, Y. Tamari, H. Tsuji, and E. Sekido, *Bunseki Kagaku*, **42**, 687 (1993).

26) G. Reid and M. Schröder, *Chem. Soc. Rev.*, **19**, 239 (1990).

27) A. J. Blake, G. Reid, and M, Scröder, *J. Chem. Soc., Dalton Trans.*, **1991**, 615.

28) A. S. Craig, R. Kataky, R. C. Matthews, D. Parker, G. Ferguson, A. Lough, H. Adams, N. Bailey, and H. Schneider, *J. Chem. Soc., Perkin Trans. 2*, **1990**, 1523.

29) A. J. Blake, D. Collison, R. O. Gould, G. Reid, and M. Schröder, *J. Chem. Soc., Dalton Trans.*, **1993**, 521.