Journal of Inclusion Phenomena and Macrocyclic Chemistry **39:** 35–40, 2001.

Synthesis and Complexing Ability of Azacrownophanes: The Cyclodextrin Catalysis of the Photochemical Cyclization Reaction

SEIICHI INOKUMA, KOICHI KIMURA, TAKASHI FUNAKI and JUN NISHIMURA*
Department of Chemistry, Gunma University, 1-5-1 Tenjin-cho, Kiryu 376-8515, Japan

(Received: 8 September 1999; in final form: 21 December 1999)

Key words: azacrown ether, cation complexation, crownophane, [2 + 2] cycloaddition, cyclodextrin catalysis

Abstract

Azacrownophanes were efficiently prepared by the irradiation of precursor ammonium chlorides in the presence of γ-CD (γ-cyclodextrin) in aqueous solution, by repressing the amino group-quenching effect by inclusion of the styrene moieties in γ-CD. In liquid–liquid extraction, azacrownophanes **(6** and **7**) showed affinity toward both Ag^+ and Pb^{2+} cations in a series of heavy metal nitrates. Both **6** and **7** formed 1:1 complexes with the above two cations, according to ^{13}C NMR titration and ESI-MS analysis.

Introduction

Both stability constant and substrate selectivity should be taken into consideration when constructing host molecules. Some simple and appropriate modifications of crown compounds including the above two factors have been performed to improve the complexing ability. Adding a side arm(s) to crown compounds is the simplest method to increase the stability constants toward alkali metal cations. A remarkable improvement of the stability constants was achieved by azacrown ether derivatives [1] and Okahara's *C*-pivot lariat ethers [2]. BiBLEs [3] or double armed crown compounds [4] derived from diazacrown ethers also show unique complexing abilities by intramolecular cooperation of the ligating side chains in equilibrium, extraction, and/or transport systems. Cryptands also derived from diazacrown ethers, three dimensional diazacrown ethers first prepared by Lehn, show extraordinarily high stability constants for various kinds of cations in the crown ether family [5]. Since the synthetic route requires many steps including the high dilution method with the simultaneous addition of the coupling reagents, those compounds, however, are not so easily prepared [6].

We have succeeded in preparing prototypical crownophanes conveniently and efficiently by means of the intramolecular [2 + 2] photocycloaddition of styrene derivatives having oligo(oxyethylene) linkages [7]. Their sulfur analogs (thiacrownophanes) have also been prepared by the method and found to exhibit a high affinity to Ag^+ cation [8].

Although the irradiation of *N*,*N*-dimethylaminostyrene afforded cyclodimerized products [9], crownophanes possessing amino groups in polyether linkages were not thought to be prepared by simply applying this method, since aliphatic tertiary amines are known to act as a quencher for the singlet excited state of styrene due to the formation of an exciplex [10]. The corresponding monoazacrown compounds, however, are able to form a great variety of compounds having potential usefulness such as lariat ethers and biscrown ethers [11], and three dimensional diazacrown compounds are expected to show some interesting complexing ability due to the unique crownophane skeleton [7].

In this paper, we would like to describe the synthesis of crownophanes possessing a secondary amine residue or two tertiary amine residues in their polyether linkage under some modified conditions, and their complexing ability toward heavy metal cations.

Experimental

Apparatus

^1H NMR spectra were recorded on a JEOL α-500 FT NMR spectrometer (500 MHz) using tetramethysilane as an internal standard. Elemental analysis was carried out in the Technical Research Center for Instrumental Analysis, Gunma University. Electrospray ionization mass spectra (ESI-MS) were obtained on a Perkin-Elmer API-100 electrospray ionization mass spectromer under the following conditions: A sample solution was sprayed at a flow rate of 2 μL min^{-1} at the tip of a needle biased by a voltage of 4.5 kV higher than that of a counter electrode.

Reagents

Dioxane and toluene were purified by distillation over Na after prolonged reflux under a nitrogen atmosphere. Guaranteed reagent grade MeCN and CH_2Cl_2 were distilled before

* Address for correspondence.

use. Reagent grade monoaza-15-crown-5 (**8**), diaza-18-crown-6 (**9**), and cryptand[2.2.2] (**10**) were used without further purification. The commercially available highest grade of $AgNO_3$, $Pb(NO_3)_2$, $Cu(NO_3)_2$, $Mn(NO_3)_2$, $Zn(NO_3)_2$, $Ni(NO_3)_2$, $Co(NO_3)_2$, and $Fe(NO_3)_3$ were used after vacuum drying. All aqueous solutions were prepared with distilled, deionized water.

Synthesis

Preparation of 2(p-bromophenyl)oxyethanol, (**1**)
A mixture of *p*-bromophenol (25.0 g, 0.145 mol) and 2-chloroethanol (116.3 g, 1.45 mol) in 10% aqueous NaOH solution (600 mL) was stirred under a nitrogen atmosphere at room temperature for 24 h. The mixture was extracted with CH_2Cl_2 (3×300 mL). The CH_2Cl_2 extracts were combined, washed with 10% aqueous NaOH solution (2×500 mL) and with water (3×500 mL), and dried over anhydrous $MgSO_4$. After the solvent was evaporated, the residue was recrystallized from hexane-ethanol to give **1** as white crystals (30.1 g, 96% yield). Mp 52.0–53.0 °C. ^{1}H NMR ($CDCl_3$) δ = 7.39 (2H, ABq, *J* = 7.0 Hz), 6.82 (2H, ABq, *J* = 7.0 Hz), 4.06 (2H, m), 3.96 (2H, m).

Preparation of 2-(p-bromophenoxy)ethyl p-toluenesulfonate, (**2**)
p-Toluenesulfonyl chloride (26.3 g, 0.138 mol) was added portionwise to a pyridine (200 mL) solution of **1** (20.0 g, 9.21×10^{-2} mol) at 0–5 °C in 15 min with stirring. The mixture was stirred for an additional 12 h at the same temperature. After the mixture was poured into water (500 mL), it was extracted with CH_2Cl_2 (3×300 mL), washed with water (3×500 mL) and 3% HCl (3×500 mL), and again with water (3×500 mL). The organic layer dried over $MgSO_4$ was evaporated *in vacuo* and the residue was purified by recrystallization from a mixed solvent of acetone and hexane to afford **2** as colorless crystals (25.9 g, 76% yield). Mp 75.5–76.3 °C. ^{1}H NMR ($CDCl_3$) δ = 7.80 (2H, A<u>B</u>q, *J* = 8.0 Hz), 7.35 (2H, A<u>B</u>q, *J* = 8.0 Hz), 7.34 (2H, A<u>B</u>q, *J* = 9.1 Hz), 6.66 (2H, A<u>B</u>q, *J* = 9.l Hz), 4.36 (2H, m), 4.12 (2H, m), 2.45 (3H, s).

Preparation of 2-(p-vinyphenyl)oxyethyl p-toluenesulfonate, (**3**)
A solution of **2** (20.0 g, 5.39×10^{-2} mol), tri-*n*-butylvinylstannane (23.3 g, 7.33×10^{-2} mol), $Pd(PPh_3)_4$ (4.17 g, 4.08×10^{-3} mmol), and 2,6-di-*tert*-butyl-4-methylphenol (15 mg) in toluene (250 mL) was heated to reflux for 20 h. After the mixture was cooled to ambient temperature, a large excess of 2 M aqueous KF solution was added, and the resulting mixture was stirred overnight at the same temperature. The organic layer was separated from the sludge and aqueous layers, and then dried over $MgSO_4$. The concentrated crude material was purified by column chromatography (SiO_2, a gradient mixture of toluene and ethyl acetate) to afford vinyl compound (**3**) (6.19 g, 36% yield). White solid (mp 76.4–77.5 °C). ^{1}H NMR ($CDCl_3$) δ=7.79 (2H, A<u>B</u>q, *J* =8.0 Hz), 7.30 (2H, A<u>B</u>q, *J* = 8.0 Hz), 7.28 (2H, A<u>B</u>q, *J* =8.8 Hz), 6.74 (2H, A<u>B</u>q, *J* = 8.8 Hz), 6.64 (1H, dd, *J* = 17.7), and 11.0), 5.61 (1H, d, *J* = 17.7), 5.14 (1H, d, *J* =11.0), 4.37 (2H, m), 4.15 (2H, m), 2.45 (3H, s). The spectral data agreed with those mentioned previously [8].

Preparation of N,N′-bis[5-(p-vinyphenyloxy)-3-oxa-pentyl]amine, (**4**)
A dioxane solution (150 mL) of **3** (5.91 g, 1.86×10^{-2} mol) was added to a mixture of potassium *tert*-butoxide (1.60 g, 1.43×10^{-2} mol), diethanol amine (0.50 g, 4.75×10^{-3} mol), and *tert*-butyl alcohol (60 mL) at room temperature for 1 h. After the mixture was stirred at 40 °C for 24 h, it was cooled to room temperature and filtered. The filtrate was evaporated *in vacuo* and the residue was purified by column chromatography (SiO_2, a gradient mixture of toluene and ethyl acetate) to afford **4** (0.53 g, 28% yield) as a transparent viscous liquid. TLC (silica gel) R*f* = 0. 15 (EtOH/conc. NH_3 aqueous solution, 100:5). ^{1}H NMR ($CDCl_3$) δ = 7.32 (4H, ABq, *J* = 8.7 Hz), 6.86(4H, ABq, *J* = 8.7 Hz), 6.65 (2H, dd, *J* = 16.2 and 10.8), 5.60 (2H, d, *J* = 16.2), 5.12 (1H, d, *J* = 10.8), 4.10 (4H, t, *J* = 4.7), 4.07 (4H, t, *J* = 4,7), 3.66 (4H, t, *J* = 5.2), 2.84 (4H, t, *J* = 5.1).

Preparation of N,N′-bis[2-(p-vinylphenoxy)ethyl]diaza-18-crown-6, (**5**)
A mixture of potassium carbonate (0.41 g, 2.98×10^{-3} mol), diaza-18-crown-6 (0.26 g, 9.91×10^{-4} mol), **3** (0.95 g, 2.98×10^{3} mol), and acetonitrile (50 mL) was stirred with refluxing for 24 h. The mixture was cooled to room temperature and filtered. The filtrate was evaporated *in vacuo* and the residue was purified by column chromatography (SiO_2, a gradient mixture of ethyl alcohol and 20% aqueous ammonium hydroxide) to afford **5** (0.19 g, 36% yield) as a pale yellow viscous liquid. TLC (silica gel) R*f* = 0. 10 (EtOH/conc. NH_3 aqueous solution, 100:5). ^{1}H NMR ($CDCl_3$) δ = 7.33 (4H, A<u>B</u>q, *J* = 8.9 Hz), 6.86 (4H, A<u>B</u>q, *J* = 8.9 Hz), 6.65 (2H, dd, *J* =17.0 and 12.0), 5.62 (2H, d, *J* = 17.0), 5.15 (2H, d, *J* = 12.0), 4.69 (4H, m), 3.62 (20H, m), 2.94 (8H, m).

Preparation of monoazacrownophane, (**6**)
This compound was prepared under the three different conditions shown in Scheme 2. First, the photocycloaddition was carried out by a conventional method developed by us [7]. Into a 300-mL flask with a magnetic stirring and N_2 inlet was placed 2.00×10^{-4} mol of olefin (**4**) dissolved in acetonitrile (200 mL), and nitrogen gas was bubbled in for 20 min. The solution was irradiated by a 400-W high-pressure mercury lamp through a Pyrex filter. The progress of the reaction was followed by HPLC. After the disappearance of the olefin (*ca.* 1 h), the reaction mixture was evaporated. The yield (9%) of azacrownophane (**6**) was measured by ^{1}H NMR spectroscopy, and then the crude reaction product was purified by column chromatography (SiO_2, ethanol) to afford **6** as a transparent viscous liquid. ^{1}H NMR ($CDCl_3$) δ = 6.74 (4H, A<u>B</u>q, *J* = 8.5), 6.59 (4H, A<u>B</u>q, *J* = 8.5 Hz), 3.98 (4H, t, *J* = 4.5), 3.93 (2H, m), 3.72 (4H, m), 3.60 (4H, t, *J* = 5.0), 2.77 (4H, t, *J* = 5.2), 2.41 (4H, m). Anal. Calcd for

$C_{24}H_{31}NO_4$: C, 72.52; H, 7.86; N, 3.52, Found: C, 72.38; H, 7.23; N, 3.46. In the second method, **4** was acidified (pH 3) with aqueous HCl and then the salt was irradiated in an aqueous solution in the same manner as described above. The reaction mixture was neutralized by aqueous NaOH, and extracted with $CHCl_3$. The organic layer was evaporated in vacuo. The yield of **6** was found to be slightly better (10%) by ^{1}H NMR measurement than above. In the third method, γ-cyclodextrin (10 eq.) was added to olefin (**4**) acidified in aqueous solution. Employing the same irradiation, working-up procedure, and the analysis as mentioned above, target crownophane **6** was obtained in the highest yield, 39%.

Preparation of diazacryptocrownophane, (**7**)

Attempts were made to prepare this compound using three different conditions, which are the same as mentioned in the preparation of **6**, shown in Scheme 3. Although the first and second methods did not afford the target compound, only the third method including an addition of γ-cycodextrin (10 eq.) did in 23% yield after purification as a pale yellow transparent viscous liquid. ^{1}H NMR ($CDCl_3$) δ = 6.74 (4H, ABq, J = 9. 1), 6.61 (4H, ABq, J = 9.1 Hz), 4.9 (4H, m), 3.90 (2H, m), 3.67 (8H, m), 3.62 (8H, m), 3.60 (4H, m), 3.48 (4H, m), 3.0 (4H, m), 2.39 (4H, m). Anal. Calcd for $C_{32}H_{46}N_2O_6$: C, 69.29; H, 8.36; N, 5.05, Found: C, 69.43; H, 8.33; N, 5.02.

Solvent extraction of heavy metal nitrates

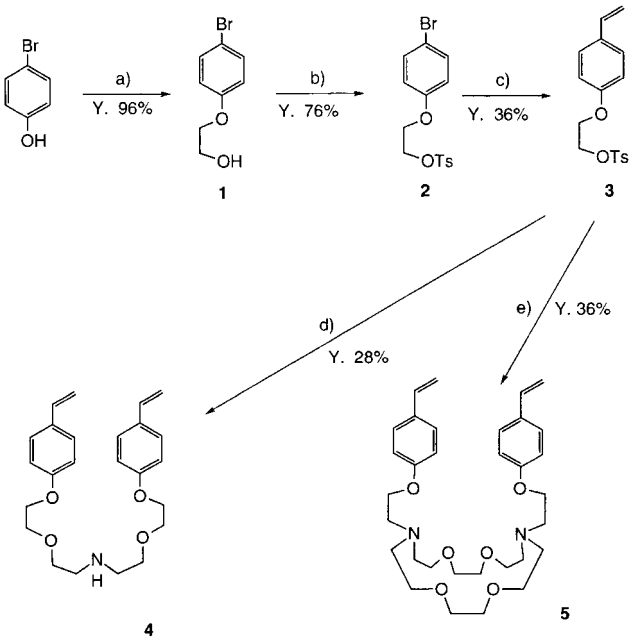
A CH_2Cl_2 solution of azacrownophane (1×10^{-4} M, 5.0 mL) and an aqueous metal nitrate solution (0.1 M, 5.0 mL), whose pH value was adjusted as high as possible without precipitation of the hydroxides, were shaken in a 20-mL test tube with a ground-glass stopper at ambient temperature (18–20 °C) for 2 h. Two liquid phases were separated. Then the cation extracted into the organic phase was measured by the same manner as previously described [8].

*^{13}C NMR titration of azacrownophanes (**6** and **7**) with silver or lead perchlorate*

A MeCN solution of **6** or a DMF-d_7-D_2O [4:1 (v/v)] solution of **7** (2.5×10^{-2} mM) was prepared. 500 μL of this solution was placed in an NMR tube. A second solution was made in the same mixed solvent with $AgClO_4$ or $Pb(ClO_4)_2$ (2.5 mM). An initial spectrum was recorded, then an appropriate volume of the salt solution was added to the NMR tube. The spectrum was then recorded again. This procedure was repeated until the salt concentration reached three equivalents of that of the crownophane.

*ESI-MS measurement of azacrownophanes (**6** and **7**) in the presence of metal perchlorate*

The sample solution (MeCN-H_2O [4:1 (v/v)]) contained a crownophane (**6** and **7**, 0.1 mM) and metal perchlorate ($AgClO_4$ or $Pb(ClO_4)_2$, 0.1 mM).



Scheme 1. Synthesis of precursor olefins.

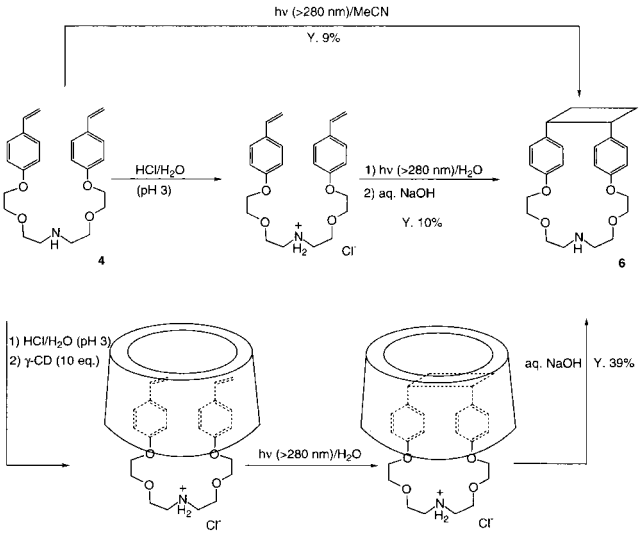
Results and discussion

Synthesis of azacrownophanes

The precursor olefins were prepared from the reaction of the corresponding amines with **3**, which was derived from **2** by the Stille reaction [12], shown in Scheme 1.

Photocycloaddition of **4** was carried out by using a 400-W high-pressure mercury lamp through a Pyrex filter in MeCN and aqueous phases in the absence or presence of γ-cyclodextrin (γ-CD) as shown in Scheme 2. As mentioned in the introduction aliphatic tertiary amines act as a quencher for the S_1 state of styrene [10], though the secondary amine has never been disclosed to be a quencher. Thus, we tried to prepare monoazacrownophane (**6**) possessing a secondary amine residue in the polyether linkage by using our efficient photocycloaddition. Irradiation of the precursor olefin (**4**) in MeCN solution afforded the target product (**6**) in low yield (9%). To increase the yield of **6**, the hydrochloric acid salt of **4** was employed because the intramolecular quenching ability of free amine moieties for naphthalene and anthracene was decreased in acidic solution [13, 14]. The yield of **6**, however, was hardly enhanced in the acidic solution of **4** compared with the former yield in MeCN without any additive. Among CDs, γ-CD is able to accommodate the two vinyl phenyl moieties since it was found to incorporate two naphthalene moieties in an aqueous solution [15]. This γ-CD cavity is thought to effectively accept the two reaction sites. The hydrochloric acid salt of **4** was dissolved in water with γ-CD and irradiated, and then neutralized with aqueous NaOH solution to afford **6** in the yield of 39%.

Photocycloaddition of **5** was carried out in a similar manner to that of **4** as shown in Scheme 3. Thus, compound **5** was irradiated in MeCN and the hydrochloric acid salt of **5** in an aqueous system by a 400-W high-pressure mercury lamp through a Pyrex filter for 1.5 h, but the desired



Scheme 2. Synthesis of monoazacrownophane (**6**).

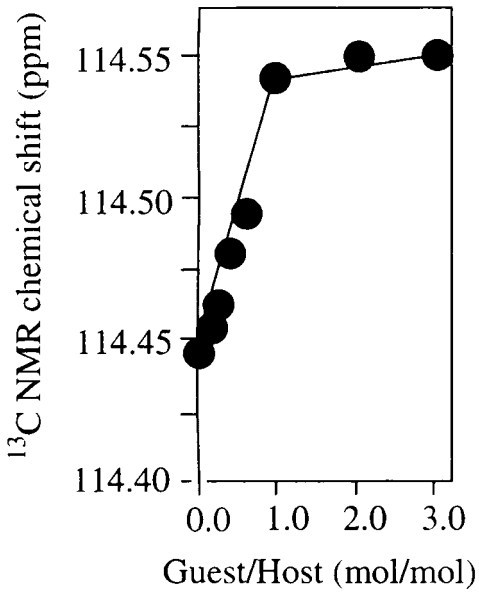


Figure 1. Ag^{+}-induced changes in the ^{13}C NMR chemical shifts of the monoazacrownophane (**6**) in MeCN-d_3. The shift was observed at the *o*-position of the phenoxy oxygen.

product was not obtained. This was because **5** acted as a quencher as mentioned above. Therefore, we tried to separate the quencher moiety from the styrene moieties by using γ-CD for the same reason as mentioned in the preparation of **6**. In fact, the aqueous olefin solution was acidified to pH 3 by the addition of conc. HCl, and then irradiated in the presence of γ-CD (10 equiv.) in the same manner as mentioned above. Diazacryptocrownophane (**7**) was obtained in 23% yield after neutralization, extraction with CH_2Cl_2, and then chromatographic separation, whereas neither a control experiment without γ-CD nor that with β-CD afforded diazacryptocrownophane (**7**).

The successful photoreaction can be explained as follows: As a result of incorporation of the vinylphenyl moieties into the γ-CD cavity due to their lipophilicity, the reaction sites are well separated from the quenching parts which are forced to be out of the CD cavity, and become closely adjacent at the same time. The explanation is also consistent with a recent report by Wenz, who showed that γ-CD efficiently worked as a reaction vessel for a stilbene derivative to afford its dimers in an aqueous solution [16]. Both the monoazacrownophane and diazacryptocrownophane were of cis-configuration which was proved by the specific methine proton signals at δ 3.90–3.93.

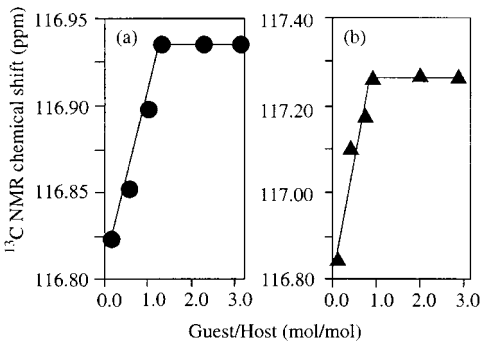


Figure 2. Metal cation-induced changes in the ^{13}C NMR chemical shifts of the diazacryptocrownophane (**7**) in DMF-d_7-D_2O (4:1); (a) Metal cation = Ag^{+}; (b) Metal cation = Pb^{2+}. The shift was observed at the *o*-position of the phenoxy oxygen.

Complexing behaviour of azacrownophanes

Azacrownophanes were used as extractants for heavy metal nitrates in a liquid–liquid system together with reference compounds (**8**)–(**10**). The results are summarized in Table 1.

As is well known, crown ethers having amino moieties in the ring show a high affinity to Ag^{+} and Pb^{2+} cations [17, 18].

Although monoazacrownophane (**6**) efficiently extracted Ag^{+} and moderately extracted Pb^{2+}, monoaza-15-crown-5 (**8**) did not exhibit any affinity toward the cations examined. This is explained mainly by the difference in their cavity size since they have the same arrangement of atoms in the polyether moiety. The cavity of **8** (ca. 2.0 Å estimated from

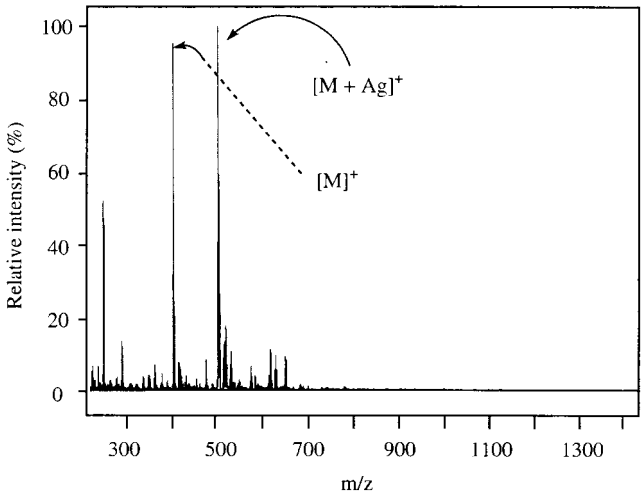
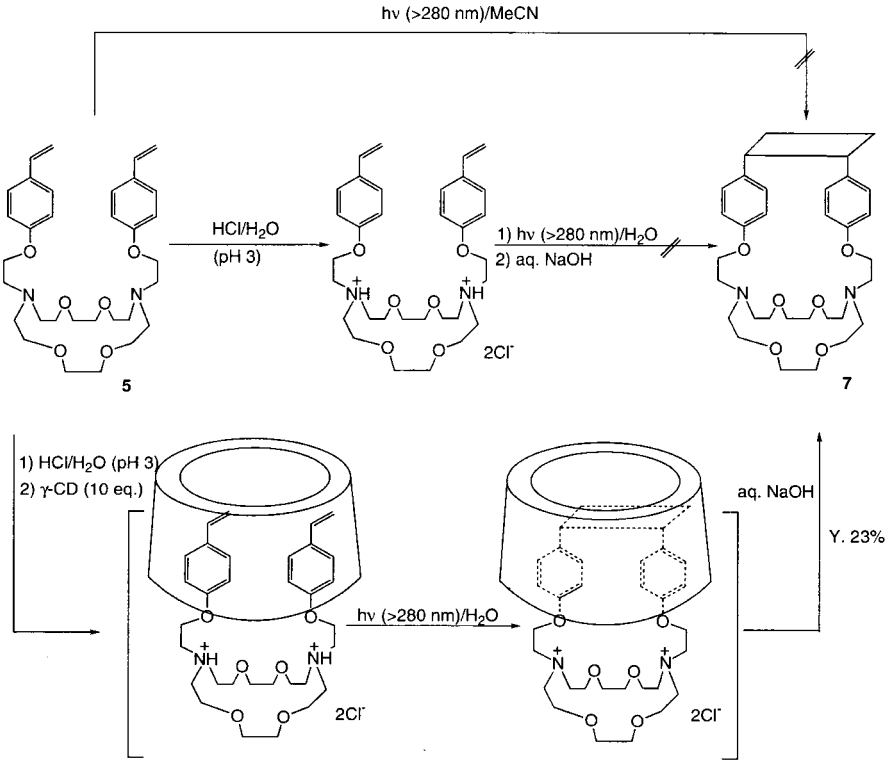


Figure 3. ESI-MS spectrum of monoazacrownophane (**6**) in 4:1 (v/v) CH_3CN-H_2O containing $AgClO_4$.



Scheme 3. Synthesis of diazacryptocrownophane (**7**).

Table 1. Extraction of heavy metal cations with ligands

Ligand	Extractability (%)[a]							
	Ag^{+}	Pb^{2+}	Cu^{2+}	Mn^{2+}	Zn^{2+}	Ni^{2+}	Co^{2+}	Fe^{3+}
6	40(6.0)	15(4.7)	0(4.4)	0(4.8)	0(5.7)	0(6.6)	0(6.2)	0(1.5)
7	42(6.3)	45(4.6)	0(4.2)	0(6.0)	0(6.1)	0(4.2)	0(6.2)	0(1.6)
8	0(6.0)	0(5.2)	0(4.6)	0(4.5)	0(6.3)	0(4.8)	0(5.8)	0(1.9)
9	3(4.9)	0(4.5)	0(4.1)	0(6.4)	0(5.6)	0(4.5)	0(6.1)	0(1.6)
10	47(6.0)	13(4.8)	0(4.4)	0(6.8)	2(6.1)	0(6.2)	0(6.7)	0(1.6)

[a] Extraction conditions: Aq. phase (5 mL), [metal nitrate] = 1.0×10^{-1} mol dm^{-3}; org. phase, CH_2Cl_2 5 mL, [ligand] = 1.0×10^{-4} mol dm^{-3}; ca. 20 °C, shaken for 1 h. The values were based on the concentration of crown compounds. Reference compounds **8**, **9**, **10** are monoaza-15-crown-5, 3,13-diaza-18-crown-6, and cryptand[2.2.2], respectively. Values in parentheses are the equilibrium pH of aqueous phase.

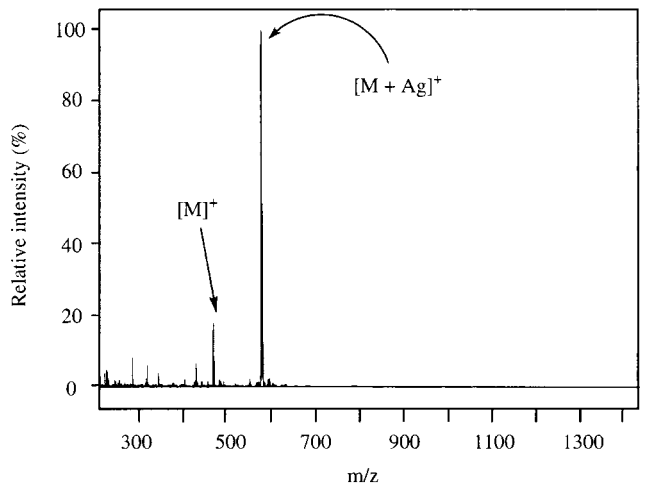


Figure 4a. ESI-MS spectrum of diazacryptocrownophane (**7**) in 4:1 (v/v) CH_3CN-H_2O containing $AgClO_4$.

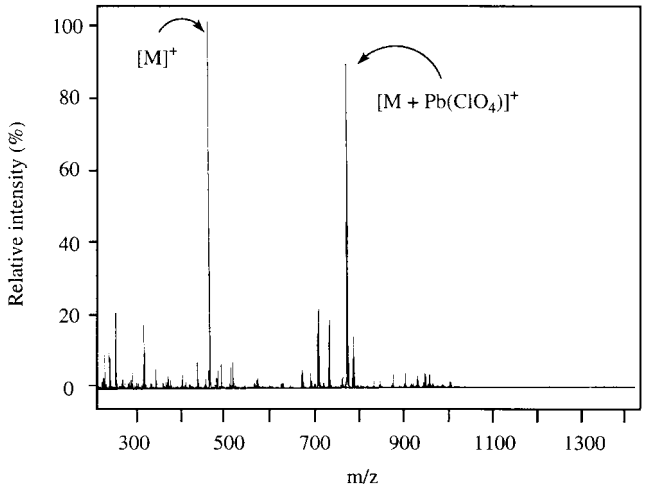


Figure 4b. ESI-MS spectrum of diazacryptocrownophane (**7**) in 4:1 (v/v) CH_3CN-H_2O containing $Pb(ClO_4)_2$.

space-filling model) is too small to accommodate Ag^+ (diameter, 2.32 Å) [17], while that of monoazacrownophane (**6**), whose ring is enlarged by the repulsion of the two aromatic nuclei linked with a cyclobutane ring, is large (maximal diameter is ca. 4.0 Å estimated from space-filling model) enough to incorporate Ag^+.

Diaza-18-crown-6 (**9**) hardly extracted these cations, while cryptand[2.2.2] (**10**) showed a higher affinity for Ag^+ than Pb^{2+}. This is due to a great difference of complexing ability between monocyclic **9** and bicyclic **10**. Bicyclic diazacryptocrownophane (**7**) efficiently extracted both Ag^+ and Pb^{2+}. Since the ionic diameters of both cations are similar, the phenomenon cannot be explained by only the size-fit argument between the cation and host. Other stereochemical factors besides the size can be responsible for the strength of the complexing ability [17]. A macrocyclic compound-Ag^+ complex, however, is generally more lipophilic than a corresponding Pb^{2+}-complex, because the former complex is accompanied by only one hydrophilic counter anion, in contrast to two for the latter. Consequently, the distribution coefficient of the former to the organic phase should be larger than that of the latter. On the other hand, it is considered that there is no great difference of the distribution coefficient between the two complexes when the complexing ability of the host compound toward both cations compared is high enough in addition of the high lipophilicity of the host, resulting in similar percent extractions. In fact, the lipophilicity of **7** is considerably high in comparison with that of **10** from the hydrophilic–lipophilic balance (HLB) [19].

To study the complex structures more clearly, we examined the interaction between **6** and Ag^+ in CD_3CN (Figure 1), and between **7** and Ag^+ and Pb^{2+} in DMF-d_7 (Figure 2) by the ^{13}C NMR titration method. The chemical shifts of their aromatic carbons significantly changed on increasing the amount of $AgClO_4$ or $Pb(ClO_4)_2$ added to the host solution, until the host/guest molar ratio became unity. It strongly suggested 1:1 complexation.

Furthermore, to disclose the complexing behavior of **6** and **7** with Ag^+ and Pb^{2+} in a more polar system, we investigated the interaction in CH_3CN-H_2O by using electrospray ionization mass spectroscopy (ESI-MS). As shown in Figure 3, only the 1:1 complex (**6**/Ag^+) other than the free host molecule was observed, which is in good agreement with the stoichiometry of the complex obtained from the ^{13}C NMR titration measured in the MeCN-d_3 system. Both the complex and the free host peaks were almost the same with regard to relative intensity, which is in good agreement with the extent determined by the extraction experiment in the CH_2Cl_2-H_2O system. Thus, it was found that the complexing behavior of **6** with Ag^+ is not affected by the polarity of the solvent used.

In agreement with the results of ^{13}C NMR titration, host (**7**) formed only 1:1 complexes with Ag^+ and Pb^{2+} in the polar solvent, respectively. The relative intensity of these peaks, however, did not entirely agree with the extent of percent extraction. In contrast to almost the same percent extraction of **7** for both cations, the relative intensity of [**7**-Ag]$^+$ is extraordinarily larger than that of [**7** + $Pb(ClO)_4$]$^+$. That is, it was found that **7** showed very high complexing ability to Ag^+ in the CH_3CN-H_2O homogeneous system different from the CH_2Cl_2-H_2O two phase system.

In conclusion, the [2 + 2] photocycloaddition was extended to the preparation of a crownophane possessing aliphatic amino groups by using γ-CD in aqueous solution.

Acknowledgement

This work was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science, Sport, and Culture of Japan.

References

1. G.W. Gokel, D.M. Dishong, and C.J. Diamond: *J. Chem. Soc. Chem. Commun.* 1053 (1980).
2. Y. Nakatsuji, T. Nakamura, M. Okahara, D.M. Dishong, and G.W. Gokel: *J Org. Chem.* **48**, 123 (1983).
3. V.J Gatto and G.W. Gokel: *J. Am. Chem. Soc.* **106**, 8240 (1984).
4. H. Tsukube: *J. Chem. Soc. Chem. Commun.* 315 (1984).
5. J.M. Lehn, *Structure and Bonding*, Vol. 16, Springer-Verlag (1973), p. 1.
6. B. Dietrich, J.M. Lehn, and J.P. Sauvage: *Tetrahedron Lett.* 2885 (1969).
7. S. Inokuma, S. Sakai and J. Nishimura: *Top. Curr. Chem.* **127**, 88 (1994).
8. S. Inokuma, A. Kobayashi, R. Katoh, T. Yasuda, and J. Nishimura: *Heterocycles* **40**, 401 (1994).
9. T. Asanuma, M. Yamamoto, and Y. Nishijima: *J. Chem. Soc., Chem. Commun.* 56 (1975).
10. R.L. Brentnall, P.M. Crosby, and K. Salisbury: *J. Chem. Soc., Perkin Trans. 2*, 2002 (1977).
11. M.R. Johnson, I.O. Sutherland, and R.F. Newton: *J. Chem. Soc., Perkin Trans. 1*, 586 (1980).
12. D.R. McKean, G. Parrinello, A.F. Renaldo, and J.K. Stille: *J. Org. Chem.* **52**, 422 (1987).
13. G.S. Cox and N.J. Turro: *J. Am. Chem. Soc.* **106**, 422 (1984).
14. E.U. Akkaya, M.E. Huston, and A.W. Czarnik: *J. Am. Chem. Soc.* **112**, 359 (1990).
15. A. Ueno, K. Takahashi, and T. Osa: *J. Chem. Soc., Chem. Commun.* 921 (1980).
16. W. Herimenn, S. Wehrle, and G. Wenz: *J. Chem. Soc., Chem. Commun.* 1709 (1997).
17. R.M. Izatt, G. C. Lind, R.L. Bruening, P. Hunszthy, C.W. McDaniel, J.S. Bradshaw and J.J. Christensen: *Anal. Chem.* **60**, 1694 (1988).
18. H. Tsukube, H. Minatogawa, M. Munakata, M. Toda, and K. Matsumoto: *J. Org. Chem.* **57**, 542 (1992).
19. I.J. Lin, J.P. Friend, and Zimmels: *J. Colloid Interface Sci.* **45**, 378 (1973).