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Synthesis and Specific Binding Property of A New Doubly Armed Crownophane

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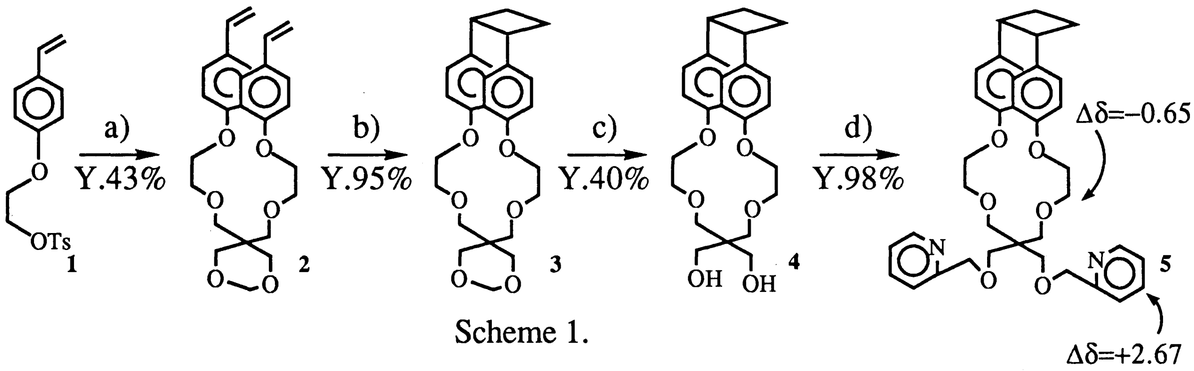
A new doubly armed crown compound fused in a cyclophane skeleton was prepared by intramolecular [2 + 2] photocycloaddition. The compound efficiently extracted Ag^+ with excellent selectivity in a liquid-liquid system, and the high Ag^+-affinity was not reduced even at low pH region.

A variety of crown compounds possessing cation-ligating side chain(s) have been synthesized while searching more specific and/or more efficient complexing ability. These functional crown compounds were named "lariat ethers"1) and "BiBLEs"2) by Gokel and co-workers. Okahara and co-workers3) and Inokuma4) reported the relationships between the structures and complexing abilities with alkali metal cations for some lariat ethers and BiBLEs. Tsukube and co-workers disclosed specific cation-binding properties of "double-armed crown ethers".5)



Scheme 1.

a) 1,3-dioxane-5,5-dimethanol, NaH / THF. b) hν(>280nm) / MeCN, N_2.
c) conc. HCl / dioxane. d) 2-(chloromethyl)-pyridine, NaH / THF.

Recently, we have successfully synthesized a new kind of crown compounds fused in cyclophane skeletons using intramolecular [2 + 2] photocycloaddition of styrene derivatives, and named them "crownophanes".6) In this communication, we report the synthesis of a new type of crownophane, which is similar to the prototypical one showing high affinity toward Li^+7), and at the same time has two cation-ligating side chains.

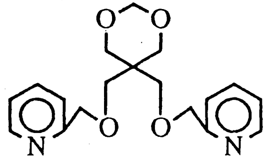
The synthetic route is shown in Scheme 1. Styrene derivative **2** was prepared by etherification of 5,5-bis(hydroxymethyl)-1,3-dioxane with tosylate **1** in moderate yield. Spiro-bounded crownophane **3** was readily obtained by the photoreaction.[6] Crownophane **4** possessing two hydroxyl groups was obtained by the conventional reaction with picolyl chloride in the presence of NaH to afford the target ionophore **5** in a good yield. Analytical data of new materials prepared are given.[9]

Cation binding properties of **5** were examined by the liquid-liquid extraction method. Results are summarized in Table 1 with some reference compounds.

Table 1. Extraction of Metal Nitrates with Ligands

	Extractability / %[a]						
Ligand	Ag^+	Cu^{2+}	Pb^{2+}	Ni^{2+}	Zn^{2+}	Co^{2+}	Mn^{2+}
4	2(3.4)	0(4.7)	0(3.9)	0(6.9)	0(6.0)	0(7.1)	0(6.0)
5	78(3.0)	4(4.4)	0(4.9)	0(6.9)	0(5.7)	0(6.9)	0(5.7)
6	3(3.4)	0(4.5)	0(4.9)	0(6.9)	0(6.1)	0(7.1)	0(6.7)
7	3(3.4)	0(4.5)	0(4.9)	0(6.9)	0(6.2)	0(7.2)	0(6.8)
8	65(3.4)	2(4.5)	3(4.9)	0(6.9)	2(6.2)	0(7.2)	0(6.8)

a) Extraction conditions: Aq. phase, [metal nitrate]=1×10^{-1} mol dm^{-3}, 5 ml; Org. phase, CH_2Cl_2, [ligand]=1×10^{-4} mol dm^{-3}, 5 ml. Values in parentheses are equilibrium pH of aquious phase.



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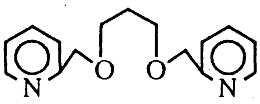

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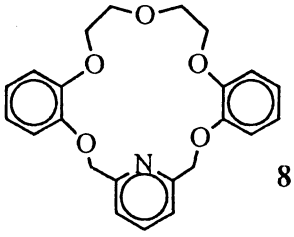

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Crownophanes **4** and **5** hardly extracted any alkali metal cation in this experimental system which did not contain any lipophilic counter anion like a picrate. Although parent compound **4** and linear reference compounds **6** and **7** showed low extractabilities toward Ag^+, doubly armed crownophane **5** efficiently extracted Ag^+ with excellent selectivity which are superior than that of commercially available dibenzopyridino-18-crown-6 **8**. Ouchi and co-workers reported that a pair of polyether side chains attached at the same carbon atom of a crown ether can interact with various kinds of cations, but both side chains cannot work simultaneously with the crown ether ring, according to the consideration of bond-angles.[8] Therefore, our results mentioned above is considered due to that the synergism of crownophane moieties and one side chain play an significant role on the complexation of **5** and Ag^+. In order to prove the synergism, we examined the ^{13}C NMR chemical shift differences between those before and after the addition of equimolar $AgClO_4$, and the composition of the ion-ionophore complex. As indicated in Scheme 1, both pyridine and polyether moieties show considerable shifts just as same as the reported one composed by two pyridine-arms, one crown ether ring, and one Ag ion.5g) Moreover, as shown in Fig. 1, the percent extractions reach maximum at 0.5 mole fraction for this cation. The fact clearly indicates that Ag$^+$ forms 1:1 complex with **5**. Thus we could prove the synergism of the crown ether moiety and one pyridine-arm at the complexation.

To know the pH limitation for the extractions is meaningful from a practical point of view. As shown in Fig. 2, high extractability of **5** was retained even in low pH region (pH~1) of contacting aqueous phase (equilibrium pH). The reference compounds **6** and **7**, however, always exhibited very low extractability. The results clearly suggest that new crownophane **5** can be a useful ionophore for recovery of Ag$^+$ not only from natural or sea water but also from waste stream10) generally showing low pH values.

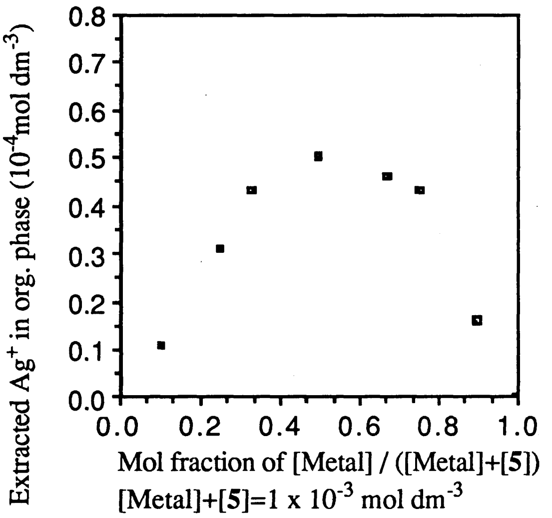

Fig. 1 Continuous variation plot of the extraction of Ag$^+$ with host **5**.

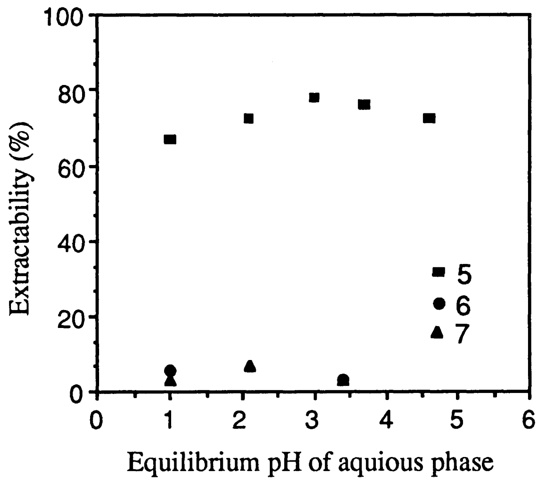

Fig. 2 pH Effect on the extraction of Ag$^+$.

Further investigation is in progress on the extraction property of **5** and its analogs and on the specific Ag$^+$ affinity of **5**, which was kept in low pH media despite of the existence of basic pyridine moieties.

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9) Melting points and ^{1}H NMR spectroscopic data ($CDCl_3$, 200 MHz): **2**; δ 3.54 (4H, s), 3.78 (8H, m), 4.08 (4H, m), 4.79 (2H, s), 5.13 (2H, d, *J*=11.8), 5.61 (2H, d, *J*=18.6), 6.65 (2H, dd, *J*=11.8 & 18.6), 6.88 (4H, $\underline{A}$Bq, *J*=8.7), 7.35 (4H, A$\underline{B}$q, *J*=8.7). **3**; m p 97.5–98.3 °C; δ 2.40 (4H, m), 3.44 (4H, s), 3.61 (4H, t, *J*=4.6), 3.77 (4H, d, *J*=2.6), 3.93 (2H, m), 4.11 (4H, t, *J*=4.6), 4.83 (2H, s), 6.63 (4H, $\underline{A}$Bq, *J*=8.8), 6.78 (4H, A$\underline{B}$q, *J*=8.8). **4**; m p 109.5–110.5 °C; δ 1.58 (2H, s), 2.42 (4H, m), 3.47 (4H, s), 3.64 (10H, m), 3.93 (2H, m), 4.11 (4H, m), 6.63 (4H, $\underline{A}$Bq, *J*=8.7), 6.80 (4H, A$\underline{B}$q, *J*=8.7). **5**; oil; δ 2.40 (4H, m), 3.53 (4H, s), 3.61 (8H, m), 3.93 (2H, m), 4.10 (4H, m), 4.64 (4H, d, *J*=5.6), 6.61 (4H, $\underline{A}$Bq, *J*=8.7), 6.75 (4H, A$\underline{B}$q, *J*=8.7), 7.25 (2H, t, *J*=7.5), 7.46 (2H, dd, *J*=7.5 & 4.0), 7.74 (2H, tt, 7.5 & 2.4), 8.53 (2H, d, *J*=4.8).

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