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Silver and Thallium(I) Complexation with Dibenzo-16-crown-4*,†

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Abstract—Dibenzo-16-crown-4 (**1**) indicates high silver and thallium(I) ion selectivity over sodium, potassium, and rubidium ion evaluated from the solvent extraction of metal picrates, while its cation-binding ability is lower than those of dibenzo-18-crown-6 (**2**) and dibenzo-22-crown-6 (**3**). Taking account of the highest thallium(I) ion selectivity for **1** obtained from extraction experiments, PVC membrane thallium(I)-selective electrodes based on **1** are prepared. The electrode shows the best potentiometric selectivity coefficients for thallium(I) over potassium and rubidium than those of **2** and **3**, and commercially available bis(crown ether)s (**4**). © 1999 Elsevier Science Ltd. All rights reserved.

Introduction

Studies on the control of cation-binding abilities of crown ethers has been devoted mainly to the complexation of alkali metal ions.[1] Monovalent heavy metal silver and thallium ions have a diameter of 2.30 Å,[2] and 3.00 Å,[2] respectively, which is quite similar size to those of sodium (2.04 Å)[2] against silver ion, potassium (2.76 Å)[2], and rubidium (2.98 Å)[2] against thallium ion. The separation of these metal ions using crown ethers has been considered a difficult problem due to the well-known hole-size concept.[3] Furthermore, in general, most crown ethers have higher cation-binding ability for Tl^+ than for K^+ and Rb^+. This is explained by the higher polarizability and the contribution of covalent bonding by Tl^+.[4] From the environmental and biological viewpoint, thallium poisoning is a critical point.[5] Moreover Tl^+ has been suggested as a probe for K^+ in biological systems.[6] Thus, direct determination of Tl^+ in biological materials using crown ethers is our special interest. Previously, we reported the complexation properties of ring-enlarged dibenzo-20- and 22-crown-6 ethers that showed a remarkably high selectivity for Tl^+ over K^+ and Rb^+.[7] Hence we got to know, rather unexpectedly, a new type of Tl^+ selective complexants in the area of crown ethers.

In the present study, we report the more pronounced Ag^+ and Tl^+ selectivity found for dibenzo-16-crown-4 (**1**) based on solvent extraction experiments and PVC membrane thallium (I) ion-selective electrode studies using the crown ether.

Results and Discussion

Synthesis

Dibenzo-16-crown-4 (**1**) is designed as the constituent of a triloop crown compound.[8] It was synthesized in 26% yield by a reaction of 1,2-bis(bromomethyl) benzene with ethylene glycol in the presence of NaH and LiOH (monohydrate) in THF.

Solvent extraction

The solvent extraction of metal picrates has been employed as a convenient method for evaluating cation-binding ability of crown ethers. The cation-binding ability of **1** was evaluated from the extraction of five metal picrates. The extraction equilibrium constants K_{ex} and the complex stoichiometries n for n:1 crown ether–cation complexes were determined.[9,10] Data are given in Table 1. In the present study, extraction of metal picrates (3 mM) were carried out at 25 °C with dichloromethane solutions of **1** (3–200 mM), and the results were compared with those for dibenzo-18-crown-6 (**2**) and dibenzo-22-crown-6 (**3**). Under the extraction conditions, **1** showed 1:1 complexes with alkali and heavy

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[*] Polytopic Cation Receptors, Part V. Part IV of this series, see ref 9.
[†] Preliminary results of this work have been presented: Ouchi, M.; Liu, Y.; Hakushi, T.; Shibutani, Y.; Yakabe, K.; Shono, T. 1995 International Chemical Congress of Pacific Basin Societies, Abstracts Part II. *Organic Chemistry*, No. 344 (1995).
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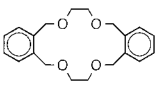
Table 1. Extraction equilibrium constants (K_{ex}) for 1:1 complexations of **1**, **2**, and **3** with alkali- and heavy metal picrates in a dichloromethane-water system at 25 °C

Compound	LogK_{ex}					Selectivity[a]					
	Na^+	K^+	Rb^+	Ag^+	Tl^+	Tl^+/Na^+	Tl^+/K^+	Tl^+/Rb^+	Ag^+/Na^+	Ag^+/K^+	Ag^+/Rb^+
1	1.97	1.86	1.93	3.44	3.75	60.0	77.6	66.0	29.5	38.0	32.3
2	2.81[b]	4.84[b]	4.43[b]	3.74[b]	5.02[b]	162.2	1.5	3.9	8.5	0.1	0.2
3	2.04[b]	2.82[b]	2.96[b]	3.19[b]	4.41[b]	234.4	38.9	28.2	14.1	2.3	1.7

[a] Relative cation selectivity determined by K_{ex}.
[b] ref 9.

metal cations employed. As already mentioned, high Tl^+ selectivity with reference to alkali metal cations, especially against Na^+, K^+, and Rb^+, has been observed for dibenzo-22-crown-6 (**3**)[6] (Table 1). It was surprising that the extraction data of **1** showed distinctly lower K_{ex} values for Na^+, K^+, and Rb^+ cations than **2** and **3**, while the small increase or decrease of the K_{ex} values for Ag^+ or Tl^+ was observed for **1**. Evidently **1** shows the higher Ag^+ and Tl^+ selectivities against Na^+, K^+, and Rb^+ ions among the dibenzo-crown ethers.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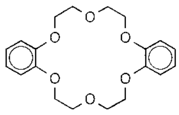
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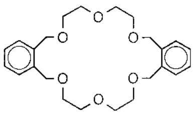
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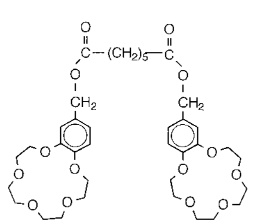
4

Nevertheless, from the present results, it is difficult to explain the high Ag^+ and Tl^+ selectivity of **1**, e.g. considering the hole-size/cation diameter relationship. From the cation selectivity values shown in Table 1, the authors paid special attention to the Tl^+ selectivity of **1** which is a promising candidate for the development of a Tl^+ sensing material.

Ion-selective electrode

Polymer membrane ion-selective electrodes are one of the most convenient and reliable analytical tools for estimating metal-ion concentrations.[11] There are a few reports on liquid-membrane thallium(I)-selective electrodes (Tl^+-ISEs) in the literature,[12] and recently, Tl^+-ISEs based on polythiamacrocycles have been reported.[13] However, Tl^+ selectivity over alkali metal ions has not been investigated. Moreover, PVC membrane Tl^+-ISEs based on bis(crown ether)s containing the benzo-15-crown-5 moiety (**4**) have been described previously.[14] This electrode exhibited a good electrode response, but the Tl^+ selectivity over K^+ was fairly poor. We have prepared Tl^+-ISEs based on dibenzo-22-crown-6 (**3**) and found that it showed higher Tl^+ selectivity over K^+ and Rb^+ compared with dibenzo-18-crown-6 (**2**).[15] Taking account of the highest Tl^+ selectivity for **1** obtained from extraction experiments, PVC membrane Tl^+-ISEs based on **1** were prepared according to the literature.[15] The potentiometric selectivity coefficients ($1/K_{TlM}$) for Tl^+ over Na^+, K^+, Rb^+ and Ag^+ were determined by the mixed solution method.[11] The results including comparable data for **3** and bis(crown ether)s **4**, are shown in Table 2.

As expected, the electrode based on **1** showed higher Tl^+/K^+ and Tl^+/Rb^+ selectivities than **3** and **4**, and these selectivities are improved by more than one order of magnitude compared to the electrode derived from commercially available bis(crown ether)s **4**, while **4** showed excellent Tl^+/Na^+ and Tl^+/Ag^+ selectivities. Some Tl^+-ISEs based on crown ethers have been developed by others.[16] However, the values of Tl^+/K^+, and Tl^+/Rb^+ selectivity for **1** from the present study are the best so far reported in this area.

Further investigations are now in progress toward elucidating the unusual Tl^+ selectivities of less-symmetrical benzo-crown ethers with different ring sizes by the method of solvent extraction.

Experimental

Spectroscopy. IR Spectra were recorded on a JASCO A-100 spectrometer. Melting points were measured with a Yanaco micro melting point apparatus and are uncorrected. Mass spectra were obtained at 70 eV on a Hitachi RMU-6E instrument. ^1H NMR spectra were recorded on a JEOL JNM-EX270 spectrometer. UV spectra were recorded on a JASCO 660 spectrophotometer.

Table 2. Potentiometric selectivity coefficients ($1/K_{TlM}$) with **1**, **3**, and **4**

Compound	$1/K_{TlM}$			
	Na^+	K^+	Rb^+	Ag^+
1	2690	132	129	7
3[a]	1120	54	40	23
4[b]	10 000	3	10	1660

[a] ref 17.
[b] ref 16.

Synthesis. Solvent tetrahydrofuran (THF) was distilled from sodium hydride. Sodium hydride (NaH) was obtained as a 60% dispersion in mineral oil; it was purified by adding hexane and stirring. The hexane was then removed. Other commercially available reagents were used in the synthesis without further purification.

Dibenzo-16-crown-4 (1). Sodium hydride (11.3 g, 0.47 mol), ethylene glycol (10.6 g, 0.17 mol) and THF (1000 mL) were introduced into a 2-L three necked flask equipped with a magnetic stirrer, reflux condenser, dropping funnel, and nitrogen inlet tube. To the stirred suspension at 66 °C was added lithium hydroxide monohydrate (7.1 g, 0.17 mol). Then 1,2-bis(bromomethyl)benzene (44.3 g, 0.17 mol) in THF (250 mL) was added dropwise. The stirring was continued for 60 h at 66 °C with continuous bubbling of nitrogen. Excess amount of NaH was decomposed by adding methanol. The solvent was evaporated and the residue was extracted with dichloromethane. The dichloromethane extract was dried over magnesium sulfate overnight and the solvent was evaporated. Distillation of the oily product under a reduced pressure gave 7.0 g (25%) of **1**. The obtained product **1** solidified in the receiver flask. The solid was then purified by recrystallization from acetone: bp 195 °C (0.2 Torr); mp 140–142 °C; MS (70 eV), *m/z* 328 (M^+); IR (KBr) 2860, 1605, 1485, 1360, 1095, 1030 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.19–7.29 (m, 8H), 4.63 (s, 8H), 3.72 (s, 8H); Anal. calcd for $C_{20}H_{24}O_4$: C, 73.15; H, 7.37. Found: C, 72.85; H, 7.46.

Metal picrates. Sodium, potassium, and rubidium picrates were prepared from picric acid and the corresponding metal hydroxide according to the reported method.[17] Silver and thallium picrates were prepared from picric acid and the corresponding metal oxide according to the reported method.[9]

Solvent extraction. The determination of the extraction equilibrium constants (K_{ex}) were carried out in the dichloromethane–water two-phase system according to the procedures reported previously.[18] Distilled dichloromethane and water were saturated with each other prior to use in order to prevent volume changes of the phases during extraction. Equal volumes (10 mL) of a CH_2Cl_2 solution of the crown ether **1** (3–200 mM) and an aqueous solution of the metal picrate (fixed at 3.0 mM) were introduced into a stoppered Erlenmeyer flask and shaken for 10 min at 25 °C in a Taiyo M100L incubator. The equilibrated mixture was then allowed to stand for 90 min at that temperature in order to complete phase separation. The organic phase was separated by filtration (Whatman filter paper no. 1PS). The concentration of metal picrates in the organic phase was determined from absorbance at 375–376 nm in a 1:1 mixture of CH_2Cl_2 and acetonitrile. In control runs, no detectable amounts of any picrates were extracted into the organic phase in the absence of **1**. The distribution coefficient (K_d) of **1** between aqueous and organic phase was determined at 25 °C by spectrophotometric analysis. The K_d value was shown to be $\ll 0.0$ and was therefore taken as zero in the calculation.

PVC membrane thallium(I)-selective electrode based on 1. The poly(vinyl chloride) (PVC) membrane containing dibenzo-16-crown-4 (**1**) was prepared according to the procedure reported previously.[19] PVC (average polymerization degree 1100) was purified by reprecipitation from tetrahydrofuran in methanol. *o*-Nitrophenyl octyl ether (NPOE) was used as the plasticizer. Potassium tetrakis-(*p*-chlorophenyl)borate (KTpClPB) was used as the additional salt. The membrane consisted of PVC (50 mg), **1** (5 mg), NPOE (125 mg), and KTpClPB (1 mg). A disc of 5 mm diameter was cut from the membrane and incorporated into the electrode body. The electrochemical cell for the e.m.f measurement was Ag-AgCl/1×10^{-3} M-$TlNO_3$/PVC membrane/sample solution/0.1 M-NH_4NO_3/4M-KCl/AgCl-Ag. The measurement was conducted at 25 °C. The selectivity coefficient, as defined in the Nicolsky–Eisenman equation,[20] was determined by the fixed interference method according to the IUPAC recommendation.[21]

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