Selective Transport of Hg²⁺ Ions by Kemp's Triacid-based Cleft Type Ionophores

**Hee-Kwang Park and Suk-Kyu Chang***

Department of Chemistry, Chung-Ang University, Seoul 156-756, Korea
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Membrane separation systems are one of the most thoroughly established methods for the efficient removal of heavy metal ions from waste streams.[1] In order to develop a selective and efficient membrane system, design of new carrier molecules is critical and numerous ionophores for the recognition of heavy metal ions have been devised.[2] The selective carriers thus developed for the Hg²⁺ ions are in general having various structures of polyazamacrocycles,[3] sulfides,[4,5] sulfonylcarboxamides,[6] thioamides,[7] and carboxylic acid derivatives.[8] Kemp's triacid motif is a versatile functional group for the design of novel supramolecular systems.[9] Rebek *et al.* reported that the basic skeleton of their cleft-type ionophores having two convergent carboxylic acid functions is well suited for an efficient carrier for doubly charged metal ions.[10] Starting from this work, selective ionophores of various derivatives having Kemp's triacid moiety toward alkali,[11] alkaline earth,[12,13] transition metal,[14] and some heavy metal cations have been reported.[15,16] However, in spite of the possible structural characteristic of **1-3** and related derivatives for the recognition of heavy metal ions, relatively few reports have been addressed on the binding of these target ions.[17] In this paper, we would like to report the selective and efficient transport of Hg²⁺ ion through chloroform liquid membrane by a series of simple cleft type ionophores having two convergent Kemp's triacid moieties in their molecular frameworks.

Kemp's triacid derivatives were prepared by the condensation of 2,6-diaminopyridine or *m*-phenylenediamine with two equivalents of Kemp's triacid following the reported procedure (Scheme 1).[11] To increase the lipophilicity and the solubility of the ionophore in common organic solvents, propyl analog of Kemp's triacid derivative was also prepared. Hexyloxyaniline derivative having only one Kemp's triacid moiety was employed for the purpose of comparison. As has been already reported,[11] the compounds investigated in the present study have a higher molecular flexibility than Rebek's original molecules due to the absence of the vicinal methyl groups for the amino groups in aromatic moiety. The enhanced molecular flexibility might exert beneficial effects on the ionophore by facilitating the release of the complexed metal ions into the receiving phase.[18]

The carrier properties of the ligands **1-4** were investigated by the competitive transport experiments. Transport experiments of heavy metal ions in the presence of some representative transition metal ions and/or alkaline earth metal ions through chloroform liquid membrane using U-tube (i.d. = 1.5 cm) were performed at 25 °C. The source phase was a mixture of metal acetates in acetate buffer (1.0 mM each in 5 mL of buffer solution, pH = 6.0) and the receiving phase was
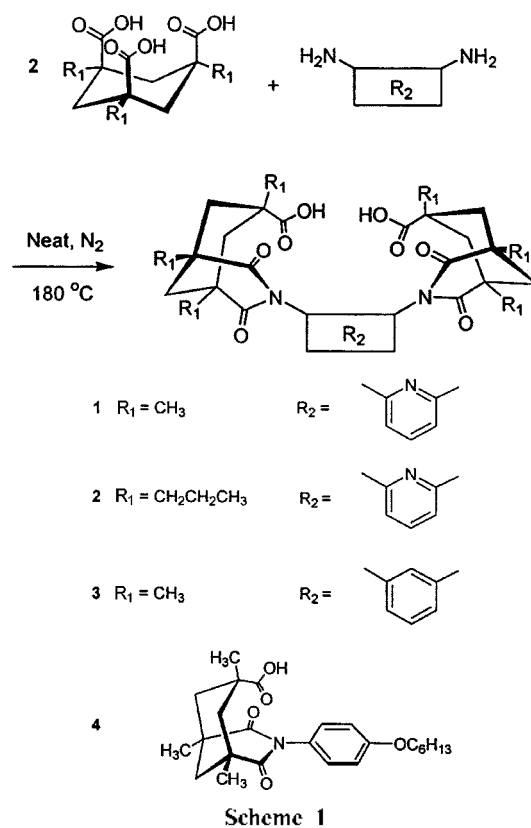
Scheme 1

an acidic solution of HNO₃ (0.1 M, 5 mL). After 1 day of transport, the concentration of transported metal ions in the receiving phase was determined by the inductively coupled plasma atomic emission spectroscopy (ICP-AES).

The preliminary transport experiments suggest that the ionophore **1** showed pronounced transport selectivity toward Hg²⁺ among the surveyed metal ions. So, we performed a systematic evaluation of the Hg²⁺ selective transport behavior of the carrier **1** employing various combination of metal ion mixtures (Table 1). Table 1 shows the consistent transport selectivity of **1** toward Hg²⁺ ions over other surveyed metal ions. Among the heavy metal ions, the selectivity pattern is Hg²⁺ >> Pb²⁺ > Cd²⁺ and the selectivity toward Hg²⁺ over Pb²⁺ and Cd²⁺ was found to be 31.5 and larger than 250, respectively. In competition with alkaline earth metal ions, the carrier **1** still exhibited high preference toward Hg²⁺ ion with a trivial selectivity toward Ca²⁺ ions among the alkaline earth metal ions. Another interesting thing is the lower affinity of the carrier for most of the transition metal ions tested. In the competitive transport with the transition metal ions, the carrier **1** exhibited only a small transport selectivity toward Cu²⁺ ions. For alkali metal ions, preliminary experi-

Table 1. Transport of Metal Ions by Kemp's Triacid-based Ionophore 1 and 4[a]

Ionophore	Transport rates (× 10^{-8} mol/h)											Selectivity		
	Hg^{2+}	Cd^{2+}	Pb^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}	Mg^{2+}	Ca^{2+}	Sr^{2+}	Ba^{2+}	Hg^{2+}/Pb^{2+}	Hg^{2+}/Ca^{2+}	Hg^{2+}/Cu^{2+}
1	3.41													
1	2.52	–[b]	0.08	–[b]	–[b]	0.11	–[b]					31.5		22.9
1	2.20	–[b]	0.19					0.02	0.10	–[b]	–[b]	11.6	22.0	
1	2.17	–[b]	0.08	–[b]	–[b]	0.08	0.04	0.02	0.03	–[b]	–[b]	27.1	72.3	27.1
4	1.44	–[b]	0.87	–[b]	–[b]	0.38	0.13					1.7		3.8

[a]Transport conditions : Source phase: 5 mmol of metal acetates in 5.0 mL of NaOAc HOAc buffer (pH 6). Membrane phase: 0.075 mmol of carrier in 15 mL of CHCl$_3$. Receiving phase: 5.0 mL of 0.1M HNO$_3$. [b]Less than 0.01 × 10^{-8} mol/h.

Table 2. Transport of metal ions by Kemp's triacid-based ionophore 2[a]

Transport rates (× 10^{-8} mol/h)											Selectivity		
Hg^{2+}	Cd^{2+}	Pb^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}	Mg^{2+}	Ca^{2+}	Sr^{2+}	Ba^{2+}	Hg^{2+}/Pb^{2+}	Hg^{2+}/Ca^{2+}	Hg^{2+}/Cu^{2+}
2.80													
2.51	–[b]	0.03	–[b]	–[b]	0.03	0.04					83.7		83.7
2.44	–[b]	0.04					0.02	0.09	–[b]	–[b]	61.0	27.1	
2.45	–[b]	0.03	–[b]	–[b]	0.04	–[b]	–[b]	0.04	–[b]	–[b]	81.7	61.3	61.3

[a]Transport conditions: same as in Table 1. [b]Less than 0.01 × 10^{-8} mol/h.

ments confirmed that almost no transport was observed under the present competitive experimental conditions. The transport results suggest that the selective and efficient transport behaviors toward Hg^{2+} ions of the carrier **1** under the present experiment condition.

The structural characteristic of the carrier **1** as a Hg^{2+}-selective ionophore is further evidenced by the results with the mono-Kemp's triacid derivative **4**. The transport efficiency of **1** is much higher than the control compound **4** having only one Kemp's triacid moiety in the molecular framework. In addition, the selectivity of **4** toward Hg^{2+} was not so good due to the increased transport efficiency toward Pb^{2+} and Cu^{2+} ions.

To evaluate the effects of lipophilicity of the carrier, the more lipophilic propyl analog **2** was employed for the transport experiments (Table 2). The propyl analog exhibited similar transport behavior compared with the methyl analog **1**; the carrier **2** showed high selectivity toward Hg^{2+} ions among heavy metal ions and inefficient transports of other surveyed transition metal ions as well as alkaline earth metal ions. This observation suggests that, under the transport condition of source phase of pH 6, the methyl analog **1** seems to have sufficient lipophilicity to act as an efficient carrier.

However, as can be seen from the Table 2, the fluxes of **2** for other ions are more or less diminished, that results in moderate enhancement of the Hg^{2+} selectivity of the propyl analog. The benzene analog of the carrier **3** has also been tested as a reference to elucidate the effects of the structural variation of the aromatic spacer group on the transport (Table 3). The pyridine moiety of **1** and **2** definitely provides extra binding site of basic nitrogen atom to the guest metal ions, which might augment the stabilization of the complexed metal ions. In fact, carrier **3** exhibited significantly decreased transport rate for Hg^{2+} ions, that suggests the nitrogen atom of the pyridine ring of **1** and **2** provides extra beneficial contribution to the overall ionophoric properties as a carrier.

The selective ionophoric properties of the carrier **1** toward Hg^{2+} ions were further supported by the standard ^{13}C NMR titration experiments. Upon addition of 1 equiv of Hg(OAc)$_2$, the chemical shifts of the pyridine moiety of the carrier **1** shifted significantly downfield in CD$_3$CN/CDCl$_3$ (8 : 2, v/v) mixed solution ($\Delta\delta$ = 1.17 ppm, 1.51 ppm, and 1.78 ppm, for *ortho*-, *meta*- and *para*-carbon, respectively). In contrast to this, the changes in ^{1}H NMR chemical shifts are relatively small and the *para*-H of the pyridine ring shifted only 0.077 ppm downfield upon addition of 1 equiv

Table 3. Transport of metal ions by Kemps triacid-based ionophore 3[a]

Transport rates (× 10^{-8} mol/h)											Selectivity		
Hg^{2+}	Cd^{2+}	Pb^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}	Mg^{2+}	Ca^{2+}	Sr^{2+}	Ba^{2+}	Hg^{2+}/Pb^{2+}	Hg^{2+}/Ca^{2+}	Hg^{2+}/Cu^{2+}
1.98													
1.82	–[b]	0.03	–[b]	–[b]	0.03	–[b]					60.7		60.7
1.84	0.02	0.08					0.02	0.14	–[b]	–[b]	23.0	13.1	
1.71	–[b]	0.03	–[b]	–[b]	0.05	–[b]	–[b]	0.06	–[b]	–[b]	57.0	28.5	34.2

[a]Transport conditions : same as in Table 1. [b]Less than 0.01 × 10^{-8} mol h.

of Hg^{2+} in the same mixed solvent.

In conclusion, competitive transport experiments of cleft-type ionophores having two convergent carboxylic acids showed that they are efficient carriers for the transport of Hg^{2+} ions through chloroform liquid membrane. They showed high selectivity toward Hg^{2+} over other heavy metal ions, transition metal ions, alkaline earth metal ions, as well as alkali metal ions. These observations suggest that the compounds **1-3** can be successfully employed as carriers for the removal of toxic Hg^{2+} ions in suitable wastewater treatment systems.

Experimental Section

Kemp's triacid (trimethyl-1,3,5-cyclohexanetricarboxylic acid), its propyl analog, and 2,6-diaminopyridine were purchased from Aldrich Co. 2,6-Diaminopyridine was purified by passing through a short-plug of silica gel column with THF just before the reaction. Compounds **1** and **2** were prepared following the reported procedure.[11] ^1H NMR (300 MHz) and ^{13}C NMR (75 MHz) spectra were obtained by a Varian Gemini 2000 Spectrometer. ICP-AES was performed on a Jovin Yvon JY-24. FAB-MS measurements were performed on an Autospec (Micromass) mass spectrometer.

Synthesis of Phenylenediamine Derivative 3. A mixture of *m*-phenylenediamine (100 mg, 0.92 mmol) and Kemp's triacid (478 mg, 1.85 mmol) was heated in neat at 180 °C for 2 h under inert N_2 atmosphere. After cooling, the reaction mixture was dissolved in excess CH_2Cl_2 (250 mL) and washed with 1 M HCl (250 mL). The organic phase was evaporated under reduced pressure and crystallized from CH_2Cl_2/MeOH to yield colorless crystals of **3** (279 mg). Yield, 55%; mp: 254 °C; ^1H NMR (CDCl$_3$) δ 7.45 (t, $J = 8.1$ Hz, 1H), 6.98 (dd, $J = 8.1$ and 2.1 Hz, 2H), 6.84 (t, $J = 2.1$ Hz, 1H), 2.83 (d, $J = 13.5$ Hz, 4H), 2.15 (d, $J = 13.2$ Hz, 2H), 1.48 (d, $J = 13.2$ Hz, 2H), 1.33 (s, 18H), 1.26 (d, $J = 14.1$ Hz, 4H); FAB MS (*m*-NBA) for $C_{30}H_{37}N_2O_8$ [M+H]$^+$ calcd 553.3, found 553.6.

Transport Experiments. Stock solutions were prepared by dissolving metal acetates in acetate buffer (NaOAc/HOAc) at pH 6.0. Competitive transport experiments were performed through chloroform liquid membrane by means of U-type tube (i.d. = 1.5 cm) at 25 °C. Source phase was a mixture of metal acetates (1.0 mM each) in 5 mL of acetate buffer (pH 6). Membrane phase was 0.075 mmol of the carrier in 15 mL of chloroform. Receiving phase was an acidic solution of 0.1 M HNO_3 (5 mL). The chloroform phase was magnetically stirred at a constant speed of 200 rpm (tachometer). After 1 day of transport, the amounts of transported metal ions in the receiving phase were determined by means of ICP-AES technique.

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