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Extraction Ability and Selectivity for Lithium Ion of Macrocyclic Trinuclear (Alkylbenzene)ruthenium(II) Complexes Bridged by 2,3-Pyridinediolato Ligands

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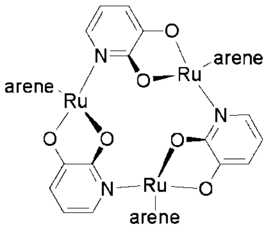
A series of macrocyclic trinuclear complexes of (η^6-alkylbenzene)ruthenium(II) bridged by 2,3-pyridinediolato ligands were synthesized and their liquid–liquid extraction properties for Li^+ and Na^+ were investigated at 25 °C. The alkylbenzenes used were *p*-cymene, 1,2,3-trimethylbenzene, 1,3,5-trimethylbenzene, 1,3,5-triethylbenzene, 1,2,4,5-tetramethylbenzene, and hexamethylbenzene. Most of the trinuclear complexes were stable for 48 h or more in a dichloromethane–water system. The extraction constants ($K_{ex} = [ML^+A^-]_o/([M^+][A^-][L]_o)$; M^+: alkali metal ion, L: trinuclear complex, A^-: counter anion (picrate), and o: organic phase (dichloromethane)) were determined from analysis of the extraction equilibria. Each trinuclear complex exhibited a larger K_{ex} value for Li^+ than for Na^+; particularly large separation factor, $SF = K_{ex}(Li^+)/K_{ex}(Na^+)$, was observed for the complexes of Ru(1,3,5-trimethylbenzene) ($SF = 1.7 \times 10^3$) and Ru(1,2,4,5-tetramethylbenzene) ($SF = 1.6 \times 10^3$). The extraction separation of Li^+ from seawater could be achieved by using the trinuclear complex of Ru(1,3,5-trimethylbenzene) with the aid of washing the organic phase with water to remove co-extracted Na^+.

Macrocyclic ligands like crown ethers and cryptands are important as neutral carriers of ions in some analytical and separation methods, such as ion-selective electrode potentiometry, liquid–liquid extraction, and membrane transport. Recently, some metal-containing macrocyclic compounds, which are similar in their structures and properties to crown ethers and called "metallacrowns," have attracted increasing attention in the field of supramolecular chemistry.[1–3] The metallacrowns are often formed by self-assembly at room temperature and therefore the synthesis is often easier than that of the organic macrocycles. It is also expected that the metallacrowns have some characteristic properties arising from the metal atoms in the frameworks.

The metallacrowns that we have interest in are macrocyclic trinuclear (η^6-arene)ruthenium(II) complexes, in which three 2,3-pyridinediolato ligands link three Ru(arene) units forming a macrocyclic structure like 12-crown-3. This type of metallacrowns was first reported by Severin and co-workers.[4] Some of the trinuclear complexes bind Li^+ and Na^+ selectively with three oxygen atoms arranging in the inner side of the ring, and the selectivity is very sensitive to the structure of the arene ligand.[5–7] These metallacrowns are electrically neutral and soluble in low polar organic solvents, opening the possibility of their application as neutral carriers for metal ions.[8]

We previously reported a study on the extraction equilibrium of alkali metal picrates with the trinuclear complexes of (η^6-*p*-cymene)ruthenium(II) **1** (Figure 1) and (η^5-pentamethylcyclopentadienyl)rhodium(III).[9] From comparison of the extraction ability of these complexes with that of 6,6-dibenzyl-14-crown-4[10] under the same experimental conditions, it was revealed that the Li^+/Na^+ selectivity of the trinuclear complexes is comparable to or higher than that of the commercially available Li^+-selective crown ether. In this study, we have further investigated the extraction properties of **2**–**6** (Figure 1) for Li^+ and Na^+. The trinuclear complexes, **1**–**6**, are similar in structure to each other but have different alkylbenzenes as their arene ligands. The complexes **2**, **3**, and **5** were first synthesized in this study. From analysis of the extraction equilibrium, the extraction ability and selectivity have been quantitatively evaluated and the extraction properties are discussed based on the geometric and electronic features of the complexes evaluated by DFT molecular calculations. The purpose of this study is to clarify the factors determining the selectivity and to find a complex having higher extractability and selectivity toward Li^+.



No.	arene
1	*p*-cymene
2	1,2,3-trimethylbenzene
3	1,3,5-trimethylbenzene
4	1,3,5-triethylbenzene
5	1,2,4,5-tetramethylbenzene
6	hexamethylbenzene

Figure 1. Structural formulas of macrocyclic trinuclear (η^6-arene)ruthenium(II) complexes.

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In addition, the extraction separation of Li^+ in seawater with one of the complexes has also been examined as an application. Although seawater contains Li^+ at 10^{-5} mol dm^{-3} level, the separation of Li^+ from seawater is very difficult because other metal ions such as Na^+ and Mg^{2+} are also present at much higher concentrations. Up to now, a number of studies have been reported on the separation of Li^+ from seawater by using inorganic absorbents[11–14] or ion-transport membranes containing organic ionophores.[15,16] However, there are only a few studies applying liquid–liquid extraction to the separation of Li^+ from seawater.[17,18]

Experimental

Reagents and Instruments. [{RuCl$_2$(*p*-cymene)}$_2$] (Aldrich, 98%), [{RuCl$_2$(hexamethylbenzene)}$_2$] (Tokyo Chemical Industry, 95%), and 1,2,4,5-tetramethylbenzene (Acros, 99%) were used as received. 1,2,3-Trimethylbenzene (Aldrich, 90%), 1,3,5-trimethylbenzene (Tokyo Chemical Industry, 97%), and 1,3,5-triethylbenzene (Tokyo Chemical Industry, 97%) were distilled under reduced pressure. 2,3-Pyridinediol (Tokyo Chemical Industry, 97%) was purified by vacuum sublimation at 150 °C. $LiCl\cdot H_2O$ (Merck, suprapur grade) and NaCl (Merck, 99.5%) were dried at 250 °C under vacuum. Aqueous solutions of lithium picrate and sodium picrate were prepared by neutralization of corresponding alkali metal hydroxide with picric acid in water. Water was distilled and further deionized with a Milli-Q Labo system (Millipore) just before use. All other chemicals were obtained from commercial sources as guaranteed-grade reagents and used without further purification.

Characterization of the complexes synthesized were carried out using a JEOL JNM-LA400 FT-NMR spectrometer, a JEOL JMS-AX500 mass spectrometer, and a Perkin-Elmer 2400 elemental analyzer at Chemical Analysis Center, Chiba University. UV–vis absorption spectra were recorded on a Beckman DU-640 spectrophotometer. Determination of metals was performed with a Hitachi Z-6100 polarized Zeeman flame atomic absorption spectrophotometer.

Preparation of Complexes. The synthetic experiments were conducted under nitrogen atmosphere and the solvents used were degassed by ultrasound just before use. The complexes **4** and **6** were synthesized according to the literature.[5] The other complexes were synthesized as follows.

[{RuCl$_2$(1,2,3-trimethylbenzene)}$_2$]: A mixture of [{RuCl$_2$(*p*-cymene)}$_2$] (1.31 g) and 1,2,3-trimethylbenzene (75 cm^3) was refluxed for 24 h. The brown precipitate was filtered off, washed with hexane, and dried under vacuum (yield: 0.537 g, 43%) ^{1}H NMR (400 MHz, CDCl$_3$, TMS): δ 2.04 (s, 6H, CH$_3$), 2.11 (s, 12H, CH$_3$), 5.26 (d, $^3J = 5.5$ Hz, 4H, CH), 5.53 (t, $^3J = 5.6$ Hz, 2H, CH).

[{RuCl$_2$(1,3,5-trimethylbenzene)}$_2$]: The product was obtained as a brown powder from [{RuCl$_2$(*p*-cymene)}$_2$] (1.34 g) and 1,3,5-trimethylbenzene (75 cm^3) in a similar manner as described for [{RuCl$_2$(1,2,3-trimethylbenzene)}$_2$] (1.12 g, yield 88%). ^{1}H NMR (400 MHz, DMSO-*d*$_6$, TMS): δ 2.14 (s, 18H, CH$_3$), 5.45 (s, 6H, CH).

[{RuCl$_2$(1,2,4,5-tetramethylbenzene)}$_2$]: A mixture of [{RuCl$_2$(*p*-cymene)}$_2$] (1.94 g) and 1,2,4,5-tetramethylbenzene (17.0 g) was heated to 196 °C with magnetic stirring for 24 h. After the melt was cooled, the solid was transferred on a glass filter and washed with hexane. The residual tetramethylbenzene was removed by vacuum sublimation at 80 °C. The solid was dissolved in dichloromethane and filtered. Evaporation of the filtrate solution gave an orange powder which was dried under vacuum (1.21 g, yield 62%). ^{1}H NMR (400 MHz, CDCl$_3$, TMS): δ 2.08 (s, 24H, CH$_3$), 5.01 (s, 4H, CH).

Trinuclear Complex 2: A suspension of [{RuCl$_2$(1,2,3-trimethylbenzene)}$_2$] (0.107 g), 2,3-pyridinediol (0.0408 g), Cs_2CO_3 (0.294 g) in methanol (8 cm^3) was stirred at room temperature for 1 h. After most of the solvent was evaporated, the residue was extracted with dichloromethane. The extract was filtered and washed twice with an equal volume of water. After evaporation, the residual dark brown crystalline material was dried under vacuum (0.0193 g, 15%). ^{1}H NMR (400 MHz, CDCl$_3$, TMS): δ 1.98 (s, 9H, CH$_3$), 1.99 (s, 9H, CH$_3$), 2.27 (s, 9H, CH$_3$), 5.11 (d, $^3J = 5.3$ Hz, 3H, CH, trimethylbenzene), 5.26 (d, $^3J = 5.6$ Hz, 3H, CH, trimethylbenzene), 5.56 (dd, $^3J = 5.5$ Hz, $^3J = 5.3$ Hz, 3H, CH, trimethylbenzene), 5.68 (dd, $^3J = 7.1$ Hz, $^3J = 6.3$ Hz, 3H, CH, dioxopyridine), 6.12 (dd, $^3J = 7.2$ Hz, $^4J = 1.7$ Hz, 3H, CH, dioxopyridine), 6.52 (dd, $^3J = 6.2$ Hz, $^4J = 1.6$ Hz, 3H, CH, dioxopyridine); ^{13}C NMR (100 MHz, CDCl$_3$, TMS): δ 12.93, 17.61, 17.71 (CH$_3$), 78.18, 78.76, 83.64, 86.40, 95.11, 95.25 ($Me_3C_6H_3$), 110.14, 113.91, 131.48, 156.95, 171.14 (dioxopyridine); MS (FAB+): (*m*/*z*): 992 [M]$^+$. Elemental analysis Calcd for $C_{42}H_{45}N_3O_6Ru_3\cdot CH_2Cl_2$: C, 48.00; H, 4.40; N, 3.91%. Found: C, 48.30; H, 4.30; N, 3.93%.

Trinuclear Complex 3: A suspension of [{RuCl$_2$(1,3,5-trimethylbenzene)}$_2$] (1.52 g), 2,3-pyridinediol (0.579 g), and Cs_2CO_3 (4.24 g) in methanol (130 cm^3) was stirred at room temperature for 1 h. After the solvent was evaporated, the residue was extracted with dichloromethane. The dichloromethane solution was filtered and washed twice with water, and then evaporated and dried under vacuum, leaving a dark brown powder (1.38 g, yield 74%). ^{1}H NMR (400 MHz, CDCl$_3$, TMS): δ 2.19 (s, 27H, CH$_3$), 4.75 (s, 9H, CH, trimethylbenzene), 5.68 (dd, $^3J = 7.1$ Hz, $^3J = 6.2$ Hz, 3H, CH, dioxopyridine), 6.09 (dd, $^3J = 7.2$ Hz, $^4J = 1.4$ Hz, 3H, CH, dioxopyridine), 6.66 (dd, $^3J = 6.3$ Hz, $^4J = 1.4$ Hz, 3H, CH, dioxopyridine); ^{13}C NMR (100 MHz, CDCl$_3$, TMS): δ 18.62 (CH$_3$), 73.7, 100.70 ($Me_3C_6H_3$), 109.90, 113.94, 132.90, 157.31, 171.00 (dioxopyridine); MS (FAB+): (*m*/*z*): 992 [M]$^+$. Elemental analysis Calcd for $C_{42}H_{45}N_3O_6Ru_3\cdot CH_2Cl_2$: C, 48.00; H, 4.40; N, 3.91%. Found: C, 48.18; H, 4.57; N, 4.02%.

Trinuclear Complex 5: A suspension of [{RuCl$_2$(1,2,4,5-tetramethylbenzene)}$_2$] (1.15 g), 2,3-pyridinediol (0.417 g), and Cs_2CO_3 (3.05 g) in methanol (100 cm^3) was stirred at room temperature for 1 h. After most of the solvent was evaporated, the residue was extracted with dichloromethane. The extract was filtered and washed twice with water, and then evaporated and dried under vacuum, leaving a brown powder (1.20 g, yield 86%). ^{1}H NMR (400 MHz, CDCl$_3$, TMS): δ 2.03 (s, 18H, CH$_3$), 2.18 (s, 18H, CH$_3$), 5.23 (s, 6H, CH, tetramethylbenzene), 5.65 (dd, $^3J = 7.1$ Hz, $^3J = 6.2$ Hz, 3H, CH, dioxopyridine), 6.09 (dd, $^3J = 7.1$ Hz, $^4J = 1.6$ Hz, 3H, CH, dioxopyridine), 6.51 (dd, $^3J = 6.4$ Hz, $^4J = 1.8$ Hz, 3H, CH, dioxopyridine); ^{13}C NMR (100 MHz, CDCl$_3$, TMS): δ 16.45, 16.47

(CH_3), 83.51, 89.70, 90.96 ($Me_4C_6H_2$), 110.04, 113.78, 131.25, 157.43, 171.36 (dioxopyridine); MS (FAB+): (*m/z*): 1034 $[M]^+$. Elemental analysis Calcd for $C_{45}H_{51}N_3O_6Ru_3 \cdot CH_2Cl_2$: C, 49.42; H, 4.78; N, 3.76%. Found: C, 49.43; H, 4.65; N, 3.67%.

Evaluation of Stabilities of Trinuclear Complexes. Equal volumes of a dichloromethane solution of a trinuclear complex (3×10^{-3} mol dm^{-3}) and water were placed in a centrifuge tube. The tube was mechanically shaken for a fixed time period at 250 strokes per min at 25 ± 0.2 °C. After the organic and aqueous phases were separated by centrifugation at 3000 rpm, aliquots of both phases were taken for measurements of UV–vis absorption spectra. In this and the following extraction experiments, degassing and nitrogen purging were not done.

Extraction of Alkali Metal Salts with Trinuclear Complexes. Equal volumes of an organic solvent solution of a trinuclear complex (6×10^{-4}–1×10^{-2} mol dm^{-3}) and an aqueous solution of an alkali metal salt (1×10^{-3}–1×10^{-2} mol dm^{-3}) were placed in a Teflon FEP centrifuge tube, where the Teflon ware was used to avoid contamination with sodium. The tube was mechanically shaken for a fixed time period at 25 ± 0.2 °C. The solvents and salts used were dichloromethane, toluene, and chloroform and chloride, nitrate, perchlorate, and picrate. After phase separation by centrifugation, the alkali metal concentration in each phase was determined as follows. The aqueous phase was directly subjected to atomic absorption spectrophotometry after addition of hydrochloric acid (final concentration, 0.05 mol dm^{-3}). For the organic phase, an aliquot of it was transferred into a beaker made of Teflon PFA and evaporated to dryness. A small amount of concentrated nitric acid was added into the beaker to decompose the trinuclear complex and the solution was re-evaporated to dryness. The residue was dissolved in 0.05 mol dm^{-3} hydrochloric acid and the alkali metal concentration was determined by atomic absorption spectrophotometry. The distribution ratio (*D*) of the alkali metal was calculated as the ratio of the molar concentration in the organic phase to that in the aqueous one. The recovery of the alkali metal from the two phases was generally quantitative. Blank extraction without the trinuclear complexes was negligibly small.

Molecular Calculations. The equilibrium geometries in vacuum of the trinuclear complexes **1**, **2**, **3**, and **5** and the Li^+ and Na^+ complexes of **1** and **3** were calculated using a hybrid DFT method, B3LYP[19–21] with the Gaussian 03 program package.[22] In the geometry optimization calculations, a 3-21G(d) standard basis set was applied for H, C, N, and O and a LANL2DZ effective core potential[23–25] for Ru. A single point energy calculation was performed on the optimized geometries using the B3LYP method with the 6-31G(d) (H, C, N, O) and LANL2DZ (Ru) basis sets. The charge distribution was evaluated by natural population analysis.[26]

Extraction of Li^+ from Artificial Seawater and Natural Seawater (Tentative Method). According to the Japanese Industrial Standards K2510,[27] artificial seawater was prepared by dissolving 24.5426 g NaCl, 11.1023 g $MgCl_2 \cdot 6H_2O$, 4.0895 g Na_2SO_4, 1.5384 g $CaCl_2 \cdot 2H_2O$, 0.6926 g KCl, 0.1998 g $NaHCO_3$, 0.1005 g KBr, 0.0303 g H_3BO_3, 0.0405 g $SrCl_2 \cdot 6H_2O$, and 0.0032 g NaF in 1 dm^3 water. LiCl (2.89×10^{-5} mol dm^{-3}, 1.23×10^{-3} g in 1 dm^3 water) was further dissolved in the artificial seawater. Natural seawater was collected at the coast of Chiba City (Japan), filtered through 0.45 µm membrane filter, and stored at 4 °C before use. The artificial or natural seawater, to which sodium picrate was added, were mechanically shaken with the dichloromethane solution of **3** in a FEP centrifuge tube in a volume ratio of 5:1 for 24 h at 25 ± 0.2 °C (the concentrations of **3** and sodium picrate are described in the following section). After centrifugation, a large portion of the organic phase was transferred into another centrifuge tube and shaken together with an equal volume of water for 15 min. This operation with water was repeated four times for the organic phase. The concentrations of Li, Na, K, Mg, and Ca in the organic phase were determined by atomic absorption spectrophotometry in a similar manner as described above.

Results and Discussion

Synthesis and Stabilities of Trinuclear Complexes. Similarly to the trinuclear complexes already known **1**, **4**, and **6**, the complexes **2**, **3**, and **5** were formed by self-assembly at room temperature from corresponding $[\{RuCl_2(arene)\}_2]$ and 2,3-pyridinediol. It was found from ^1H NMR and elemental analysis that all the trinuclear complexes obtained are adducts with dichloromethane (**2**, **3**, **5**, and **6**) or water (**4**).

The stabilities of the trinuclear complexes in a dichloromethane–water system at 25 °C were evaluated from measurements of their UV–vis absorption spectra. The wavelengths of maximum absorption and molar absorptivities in dichloromethane at 25 °C are as follows: 332 nm and 2.2×10^4 dm^3 mol^{-1} cm^{-1} for **1**;[9] 329 nm and 2.1×10^4 dm^3 mol^{-1} cm^{-1} for **2**; 333 nm and 2.4×10^4 dm^3 mol^{-1} cm^{-1} for **3**; 333 nm and 2.4×10^4 dm^3 mol^{-1} cm^{-1} for **4**; 331 nm and 2.3×10^4 dm^3 mol^{-1} cm^{-1} for **5**; 335 nm and 2.2×10^4 dm^3 mol^{-1} cm^{-1} for **6**. The spectra of **1**, **3**, and **4** were practically not changed during the shaking time of 48 h without degassing and nitrogen purging, showing that they are fairly stable and so hydrophobic that the distribution from the dichloromethane phase to the aqueous is negligible. The complexes **2** and **5** are a little less stable than **1**, **3**, and **4**; the absorbance of **2** and **5** in the dichloromethane phase decreased subsequently with the shaking time and reached 90–95% after 24 h shaking and ca. 80% after 48 h shaking. The absorbance of **6** decreased to 20% after 48 h shaking. The instability of **6** may be attributed to the steric hindrance between the adjacent bulky (hexamethylbenzene)Ru units, whereas the causes for the instability of **2** and **5** are not clear.

Extraction of Alkali Metal Picrates into Dichloromethane. The distribution ratio of Li^+ and Na^+ was measured as a function of shaking time at fixed concentrations of the alkali metal picrates (3×10^{-3} mol dm^{-3} (Li^+) or 1×10^{-2} mol dm^{-3} (Na^+)) and the trinuclear complexes (3×10^{-3} mol dm^{-3}). The shaking times required to obtain a constant distribution ratio of Li^+ were about 1 h for **1**[9] and **2**, 20 h for **3** and **4**, and 10 h for **5**; it was impossible to confirm the achievement of equilibrium for **6** owing to its decomposition. It follows from this that the extraction of Li^+ is relatively slow and the rate depends on the structure of the arene ligand in the trinuclear complex. The shaking time dependence of the

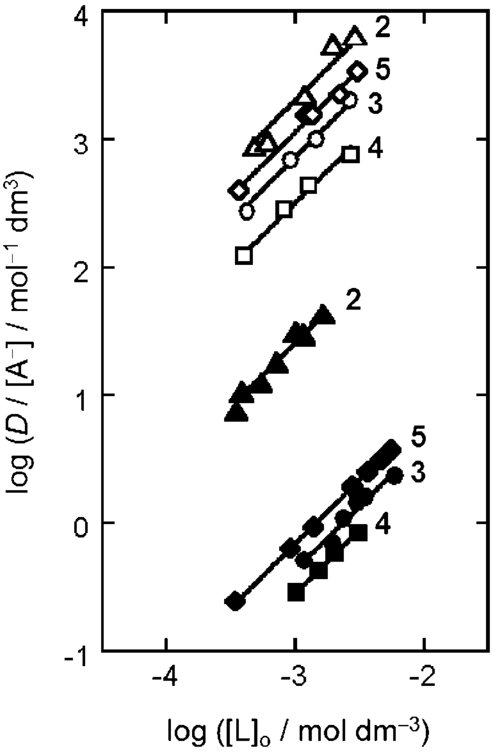

Figure 2. Plots of $\log(D/[\mathrm{A}^-])$ vs. $\log[\mathrm{L}]_o$ for the extraction system of lithium picrate (open symbols) and sodium picrate (filled symbols) with **2**, **3**, **4**, and **5** in CH_2Cl_2.

distribution ratio of Na^+ was similar to that of Li^+ with **1** and **2**, whereas the distribution ratio of Na^+ became constant in a shorter shaking time than that of Li^+ with **3**, **4**, and **5**. In the following extraction experiments, the shaking time was set to ensure the equilibrium (5 h for **2**, 24 h for **3** and **4**, and 10 h for **5**).

The extraction equilibrium of an alkali metal ion (M^+) with a trinuclear complex ligand (L) and a counter anion (A^-) can be considered as

$$\mathrm{M}^+ + \mathrm{A}^- + \mathrm{L}_o \rightleftharpoons \mathrm{ML}^+\mathrm{A}^-{}_o \qquad (1)$$

$$K_{ex} = [\mathrm{ML}^+\mathrm{A}^-]_o/([\mathrm{M}^+][\mathrm{A}^-][\mathrm{L}]_o) \qquad (2)$$

where ML^+A^- represents the ion pair of the ML^+ complex with A^-; the subscript "o" and the lack of a subscript refer to the organic and aqueous phases, respectively; K_{ex} is the extraction equilibrium constant. When the distribution ratio, D, of the alkali metal is approximately equal to $[\mathrm{ML}^+\mathrm{A}^-]_o/[\mathrm{M}^+]$, the following equation is derived from eq 2.

$$D/[\mathrm{A}^-] = K_{ex}[\mathrm{L}]_o \qquad (3)$$

The $[\mathrm{L}]_o$ value was calculated from the equation $[\mathrm{L}]_o = [\mathrm{L}]_t - [\mathrm{ML}^+\mathrm{A}^-]_o$ (the subscript "t" denotes the total concentration) because loss of the trinuclear complexes due to decomposition or distribution into the aqueous phase was negligibly small within the shaking time. The $[\mathrm{A}^-]$ value was obtained from $[\mathrm{A}^-] = [\mathrm{A}]_t - [\mathrm{ML}^+\mathrm{A}^-]_o$. The plots of $\log(D/[\mathrm{A}^-])$ vs. $\log[\mathrm{L}]_o$ are shown in Figure 2 for the extraction of Li^+ and Na^+ with the complexes **2**–**5**. All the plots give straight lines with slope 1 as expected from eq 3, proving that the alkali metal ions are extracted as ML^+A^-. The K_{ex} values determined are listed in Table 1.

Table 1. Equilibrium Constants for Extraction of Alkali Metal Picrates with Trinuclear Complexes in CH_2Cl_2 at 25 °C

Complex	K_{ex}/mol^{-2} dm^6 [a]	
	Li^+	Na^+
1[b]	$(5.3 \pm 1.6) \times 10^5$	$(3.2 \pm 0.2) \times 10^4$
2	$(1.9 \pm 0.3) \times 10^6$	$(2.6 \pm 0.3) \times 10^4$
3	$(7.3 \pm 0.6) \times 10^5$	$(4.3 \pm 0.3) \times 10^2$
4	$(3.2 \pm 0.3) \times 10^5$	$(2.80 \pm 0.05) \times 10^2$
5	$(1.13 \pm 0.09) \times 10^6$	$(6.9 \pm 0.1) \times 10^2$

a) Average and standard deviation calculated from the data in Figure 1. b) Ref. 9.

As shown by the K_{ex} values, all the complexes exhibit selectivity toward Li^+. The values of the Li^+/Na^+ separation factor, $SF = K_{ex}(\mathrm{Li}^+)/K_{ex}(\mathrm{Na}^+)$, are 17, 73, 1.7×10^3, 1.1×10^3, and 1.6×10^3 for **1**, **2**, **3**, **4**, and **5**, respectively. The complexes **3**, **4**, and **5** have extremely high selectivity toward Li^+. The complex having the largest K_{ex} value for Li^+ is **2**, but the Li^+/Na^+ selectivity of **2** is much lower than that of **3**, **4**, and **5**.

The complexes **2** and **3** are isomers having trimethylbenzenes as the arene ligands. These complexes are however very different in the extraction ability and the selectivity for Li^+ and Na^+. On the other hand, the complexes **3** and **4**, each of which has three methyl (**3**) or ethyl groups (**4**) at the same positions on the arene ligands, are similar in the extraction ability and the selectivity. It thus appears that the position of the alkyl groups on the arene ligands is a more important factor than the length of the alkyl groups.

The equilibrium geometries of **1**, **2**, **3**, and **5** obtained by the B3LYP calculations are shown in Figure 3. The alkali metal ions are expected to be captured by the trinuclear complexes on the central triangular oxygen atoms at the side of the arene ligands.[5] The radius of the cavity constructed by the central triangular oxygen atoms was calculated assuming the radius of O to be 0.136 nm.[28] The cavity radii and the average natural charges for the oxygen atoms are as follows: 0.043 nm and −0.645 for **1**; 0.042 nm and −0.640 for **2**; 0.045 nm and −0.650 for **3**; 0.045 nm and −0.665 for **5**. The cavity radius of **1** is in good agreement with 0.042 nm calculated from X-ray crystallographic data.[5] These values show that all the complexes are very similar both in the cavity size and the electron density on the oxygen atoms. On the other hand, as seen from Figure 3, there are large differences among the complexes in the structural effect of the arene ligands toward the central oxygen atoms. A comparison of the structures of the complexes having higher Li^+/Na^+ selectivity (**3** and **5**) with those of the others (**1** and **2**) shows that the oxygen atoms of the former complexes are more effectively shielded by the methyl groups of the arene ligands. The steric hindrance from the arene ligands on the oxygen atoms can be a cause for the high Li^+/Na^+ selectivity because the steric effect should be greater for the larger Na^+ ion (ionic radius[28] for coordination number 4: Li^+, 0.059 nm; Na^+, 0.099 nm). In Figure 4, the equilibrium geometries for the Li^+ and Na^+ complexes of **3** are shown as

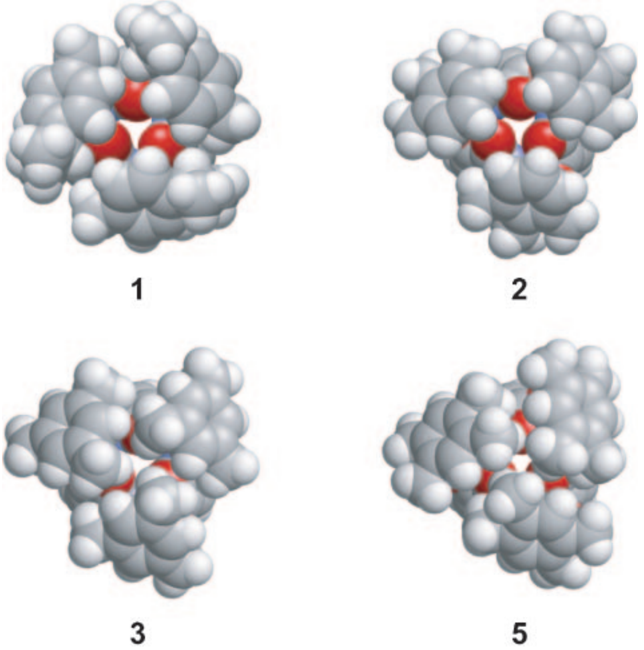

Figure 3. CPK representation of equilibrium geometries for **1**, **2**, **3**, and **5** obtained by DFT calculations (view along the C_3 axis).

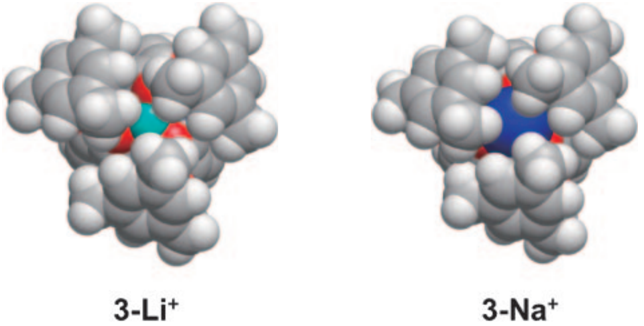

Figure 4. CPK representation of equilibrium geometries for the lithium and sodium complexes of **3** obtained by DFT calculations (view along the C_3 axis).

examples. The average distances between the three methyl groups which are directed to the center of the complex are 0.430, 0.447, and 0.496 nm for **3** (free), **3**-Li$^+$, and **3**-Na$^+$ complexes, respectively. These values clearly show that the steric strain caused by the alkali metal binding is greater for Na$^+$ than for Li$^+$. The geometries for the Li$^+$ and Na$^+$ complexes of **1** were also calculated; the average distances between the tertiary carbon atoms in the three isopropyl groups were 0.793, 0.816, and 0.819 nm for **1** (free), **1**-Li$^+$, and **1**-Na$^+$ complexes, respectively. In this case, no remarkable difference in the structure is observed for the Li$^+$ and Na$^+$ complexes.

The slow extraction rate observed for Li$^+$ with **3**, **4**, and **5** is also attributed to the steric hindrance from the arene ligands. However, the faster extraction of Na$^+$ with these trinuclear complexes than that of Li$^+$ was an unexpected result. Taking into account the fast reaction of Na$^+$ with **3**, **4**, and **5**, the Na$^+$ ion may not be captured by these trinuclear complexes in such a way as shown in Figure 4; for example, it is probable that Na$^+$ interacts weakly with the oxygen atoms on the opposite side of the triangular oxygen plane.

Table 2. Effects of Solvents and Counter Anions on Extraction of Li$^+$ and Na$^+$ with Complex **3** at 25 °C

Solvent	Anion	Alkali metal ion	K_{ex}/mol^{-2} dm^6 [a]	SF [b]
CH_2Cl_2	Picrate	Li$^+$	7.3×10^5	1.7×10^3
		Na$^+$	4.3×10^2	
	ClO_4^-	Li$^+$	4.3×10^2	3×10^1
		Na$^+$	1.7×10	
	NO_3^-	Li$^+$	2.1×10^2	8×10^1
		Na$^+$	2.7	
	Cl^-	Li$^+$	4.8	6
		Na$^+$	8×10^{-1}	
$CHCl_3$	Picrate	Li$^+$	4.8×10^5	2×10^3
		Na$^+$	2.6×10^2	
	ClO_4^-	Li$^+$	1.2×10^2	3×10^1
		Na$^+$	4.1	
	NO_3^-	Li$^+$	7.3×10	3×10^1
		Na$^+$	2.5	
	Cl^-	Li$^+$	3.0	3
		Na$^+$	1.1	
$C_6H_5CH_3$	Picrate	Li$^+$	4.0×10^5	8.3×10^2
		Na$^+$	4.8×10^2	
	ClO_4^-	Li$^+$	1.2×10^3	9.2×10^1
		Na$^+$	1.3×10	
	NO_3^-	Li$^+$	8.7×10^2	5.8×10^2
		Na$^+$	1.5	
	Cl^-	Li$^+$	4.0×10	5.0×10^1
		Na$^+$	8×10^{-1}	

a) Approximate value of the extraction constant calculated from distribution ratio measured at a single condition, except for the CH_2Cl_2–picrate systems. b) Separation factor for Li$^+$ over Na$^+$.

Effects of Solvents and Counter Anions. The liquid–liquid extraction experiments for Li$^+$ and Na$^+$ with **3** have been carried out using different organic solvents (dichloromethane, chloroform, and toluene) and counter anions (picrate, perchlorate, nitrate, and chloride). The volume ratio of the organic and aqueous phases, the shaking time, and the concentration of **3** were fixed at 1, 24 h, and 3.1×10^{-3} mol dm^{-3}, respectively, whereas the concentration of the alkali metal salts of different anions was changed according to the magnitude of the distribution ratio. For each system, the K_{ex} value was estimated from one datum of D at a given condition, assuming the extraction equilibrium expressed by eqs 1 and 2. The values of K_{ex} and SF are shown in Table 2. For all the organic solvents, the extraction ability of **3** for Li$^+$ decreases with a decrease of the anion size, i.e., picrate $\gg$ perchlorate $>$ nitrate $\gg$ chloride. This agrees with that observed for general ion pair extraction systems.[29,30] The solvent dependence of K_{ex} is as follows: dichloromethane $\approx$ chloroform $\approx$ toluene for picrate; toluene $>$ dichloromethane $>$ chloroform for the other anions. The extraction constant of an ion pair generally decreases with decreasing solubility parameter or E_T value of the extraction solvent, i.e., dichloromethane $>$ chloroform $>$ toluene.[29–31] Therefore, the solvent dependence of K_{ex} observed in the present study does not follow the general rule for ion pair

Table 3. Extraction Separation of Li from Artificial Seawater Using CH_2Cl_2 Solution of Complex **3** in the Presence of Sodium Picrate[a)]

	Li	Na	K	Mg	Ca
Initial artificial seawater					
[M][b)]	2.9×10^{-5}	0.48	1.0×10^{-2}	5.5×10^{-2}	1.0×10^{-2}
[M]/[Li][c)]	1	1.7×10^{4}	3.4×10^{2}	1.9×10^{3}	3.4×10^{2}
CH_2Cl_2 phase after extraction					
[M][b)]	4.9×10^{-5}	1.1×10^{-3}	9×10^{-6}	2.4×10^{-5}	not detected
[M]/[Li][c)]	1	2.2×10^{1}	2×10^{-1}	4.9×10^{-1}	≈ 0
CH_2Cl_2 phase after quadruplicate washing with water					
[M][b)]	4.1×10^{-5}	1.1×10^{-5}	1×10^{-6}	2×10^{-6}	not detected
[M]/[Li][c)]	1	2.7×10^{-1}	2×10^{-2}	5×10^{-2}	≈ 0

a) Experimental conditions are described in the text. b) Molar concentration of a metal ($mol\,dm^{-3}$).
c) Molar concentration of a metal relative to that of Li.

Table 4. Extraction Separation of Li from Natural Seawater Using CH_2Cl_2 Solution of Complex **3** in the Presence of Sodium Picrate[a)]

	Li	Na	K	Mg	Ca
CH_2Cl_2 phase after extraction					
[M][b)]	4.2×10^{-5}	9.5×10^{-4}	7.5×10^{-6}	1.4×10^{-5}	not detected
[M]/[Li][c)]	1	2.3×10^{1}	1.8×10^{-1}	3.3×10^{-1}	≈ 0
CH_2Cl_2 phase after quadruplicate washing with water					
[M][b)]	3.6×10^{-5}	1.2×10^{-5}	2×10^{-6}	2×10^{-6}	not detected
[M]/[Li][c)]	1	3.3×10^{-1}	6×10^{-2}	6×10^{-2}	≈ 0

a) Experimental conditions are described in the text. b) Molar concentration of a metal ($mol\,dm^{-3}$).
c) Molar concentration of a metal relative to that of Li.

extraction systems. The unexpectedly low extractability when using chloroform or dichloromethane may suggest a specific interaction (like hydrogen bonding) between the CH-acid solvent and the oxygen atoms of **3**, which gives a negative contribution to the complex formation of the alkali metal ion with **3**. This idea is consistent with the fact that most of the trinuclear complexes were obtained as adducts with dichloromethane in their synthesis. Among all the systems examined, the highest extractability for Li^+ and the highest Li^+/Na^+ selectivity were both found in the system using picrate and dichloromethane.

Extraction Separation of Li^+ from Seawater. We have examined extraction of Li^+ from artificial seawaters into a dichloromethane solution containing the complex **3** ($4.8 \times 10^{-3}\,mol\,dm^{-3}$). To the seawater, picrate anion ($1.0 \times 10^{-3}\,mol\,dm^{-3}$) was added as the sodium salt. The volume ratio of the organic phase to the seawater was 1/5. The molar concentrations of Li^+, Na^+, K^+, Mg^{2+}, and Ca^{2+} extracted into the organic phase are summarized in Table 3, where it was preliminarily confirmed that these metals were not detectably extracted without using the trinuclear complex. Under this condition, 34% of Li^+ in the artificial seawater was extracted with the complex **3**. Although the complex **3** has very high selectivity toward Li^+ as described above, the concentration of Na^+ co-extracted with Li^+ was 22-fold greater than that of Li^+ in the organic phase. This is because the initial concentration of Na^+ is much greater (1.7×10^4-fold) than that of Li^+ in the artificial seawater. Then we examined the stripping of Na^+ in the organic phase. The organic phase after the extraction was washed with deionized water, the volume of which was equal to that of the organic phase. The shaking time for the phase washing was 15 min. It was confirmed that in this shaking time, about 75% of Na^+ in the organic phase was back-extracted into water, whereas loss of Li^+ was only 4%; this supports the above-mentioned idea that the Li^+ and Na^+ ions are captured at different sites of the trinuclear complex. The Na^+ in the organic phase was effectively removed to water by repetition of the phase-washing operations; after the 4th washing, the concentration of Na^+ decreased to 1/3 of that of Li^+ in the organic phase. The concentrations of other metals (K, Mg, and Ca) remaining in the organic phase were 1/20 or less of that of Li^+.

In a similar manner, the separation of Li^+ from natural seawater was carried out. The concentration of **3** in the dichloromethane phase and that of sodium picrate in the seawater were 4.9×10^{-3} and $1.1 \times 10^{-3}\,mol\,dm^{-3}$, respectively. The results are summarized in Table 4. It is demonstrated that Li^+ in the natural seawater is successfully separated from other major metallic components by this simple liquid–liquid extraction method.

Conclusion

All the trinuclear (η^6-alkylbenzene)ruthenium(II) complexes bridged by 2,3-pyridinediolato ligands exhibit Li^+ selectivity in the liquid–liquid extraction. The most important factor governing the selectivity is steric hindrance of the arene ligands toward complexation of the alkali metal ion on the central three oxygen atoms of the trinuclear complex. The trinuclear complexes of Ru(1,3,5-trimethylbenzene) and Ru(1,2,4,5-tetramethylbenzene) have extremely high Li^+-selectivity; these arene ligands effectively shield the oxygen atoms with their methyl groups and hinder the interaction between the oxygen atoms and the alkali metal ions larger than Li^+. Particularly, the trinuclear complex of Ru(1,3,5-trimethylbenzene) is relatively stable even under atmospheric conditions and can be readily used as an extraction agent. However, the extraction rate for Li^+ is considerably slow when using the complex with high Li^+-selectivity.

By using the trinuclear complex of Ru(1,3,5-trimethylbenzene), Li^+ in seawater can be selectively extracted. Washing of the organic phase with water is effective to remove co-extracted Na^+. This fact also indicates that the Li^+ bound in the trinuclear complex is not easily released. Now we explore new complexes having faster and greater extractability and higher selectivity for Li^+.

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