

No. 0803

Selective Separation of Lithium Ion by Self-Assembled Complexes

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Summary

In recent years, macrocyclic metal complexes have attracted increasing attention as a new class of molecular recognition agents. The complexes are often self-assembly formed and can be more easily synthesized than conventional organic macrocycles. However, little is known about their ability to extract metal ions. In this study, six kinds of macrocyclic arene-ruthenium trinuclear complexes bridged by 2,3-dioxypyridine ($[(\text{arene})\text{Ru}(\text{pyO}_2)]_3$; arene = *p*-cymene (1), 1,2,3-trimethylbenzene (2), 1,3,5-trimethylbenzene (3), 1,3,5-triethylbenzene (4), 1,2,4,5-tetramethylbenzene (5), hexamethylbenzene (6)) were synthesized and their extraction behavior for alkali metal ions was studied.

The complexes 2, 3, and 5, first synthesized in this study, were all self-assembly formed from $[(\text{arene})\text{RuCl}_2]_2$ and 2,3-dihydroxypyridine and obtained in high yield. Several counter anions (picrate, perchlorate, nitrate, and chloride) and solvents (dichloromethane, chloroform, and toluene) were examined for the extraction of Li^+ with 3; the highest extractability was observed when using picrate and dichloromethane. In the dichloromethane–water system, the complexes 1–5 were sufficiently stable, whereas 90% of 6 decomposed after 48 h of shaking. Therefore, the extractions of alkali metal picrates with dichloromethane solutions of 1–5 were investigated in detail. All the complexes exhibited high selectivity toward Li^+ . The extraction rate was fairly slow; for example, a shaking time of more than 24 h was required to attain equilibrium for 3 and 4. From equilibrium analysis, the extracted species were found to be ML^+A^- complexes (M^+ = alkali metal ion; L = macrocyclic complex; A^- = picrate ion), and the extraction equilibrium constants were determined. The Li^+/Na^+ selectivities of 2–5 were higher than that of a commercially available Li^+ -selective crown ether, 6,6-dibenzyl-14-crown-4, and the highest selectivity was found for 3 (Li^+/Na^+ separation factor = 1700). From molecular orbital calculations, it was revealed that the high selectivity of these complexes is caused by a steric hindrance of the arene ligands to the binding of an alkali metal ion on the central three oxygen atoms. Furthermore, extraction separation of Li^+ from artificial seawater to dichloromethane was examined using 3. Considerable amount of Na^+ was co-extracted under the condition that Li^+ was quantitatively extracted. However, by short-time shaking of the extracted solution with water, the Na^+ ion could be selectively removed into the water phase. Highly selective separation of Li^+ from seawater was successively achieved by such a simple solvent extraction method.