Solvent Extraction of Lanthanoid(III) Picrates with a Bis(crown ether): Enhanced Extractability through Double-sandwich Complexation†

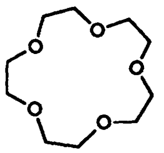
Yoshihisa Inoue,[*,a] **Kazuharu Nakagawa**[b] **and Tadao Hakushi**[c]
[a] *Department of Material Science, Himeji Institute of Technology, Kamigori, Hyogo 678-12, Japan*
[b] *Technical Center for Leather, Hyogo Prefectural Institute of Industrial Research, Nozato, Himeji 670, Japan*
[c] *Department of Applied Chemistry, Himeji Institute of Technology, Shosha, Himeji 671-22, Japan*

Solvent extractions of aqueous light lanthanoid(III) picrates (La–Gd) with 1,8-dioxooctamethylenebis(4′-benzo-15-crown-5) **4** were conducted at low ionic strength in the absence of dense background salts. Possessing two crown ether units, the bis(crown ether) gave much higher extractabilities for the lanthanoids than did the reference ligand, 4′-acetylbenzo-15-crown-5 **3**, or related ligands 15-crown-5 **1** and benzo-15-crown-5 **2**, although the profile of the relative cation-selectivity sequence became flat. Unexpectedly, quantitative solvent extraction studies revealed that the cation : ligand stoichiometry of the complex is not 1 : 1 but 1 : 2. This indicates that the enhanced extractabilities and the decreased cation selectivity arise not from the conventional intramolecular sandwich complexation but from the unique bimolecular double-sandwich complexation incorporating four crown ether units wrapping around a partially hydrated lanthanoid ion that has to be shielded effectively from the surrounding organic solvent molecules.

We have recently demonstrated that the solvent extraction of aqueous lanthanoid picrates with common crown ethers, 15-crown-5, 18-crown-6, and their benzo or cyclohexano derivatives, is characterized by much lower extractabilities than those for alkali- and alkaline-earth-metal picrates and, in particular, by an overwhelming preference for sandwich complexation, in spite of the apparent matching of the host cavity size and the diameter of the naked lanthanoid cation.[1–3] Both the low extractabilities and the preferential sandwich complexation observed are attributed to incomplete dehydration of trivalent lanthanoid ions upon extraction,[1] which necessitates more effective shielding of the partially hydrated ion through sandwich complexation by two ligand molecules in the organic phase. It was also shown that, although the effective diameter of the partially hydrated lanthanoid ion is much greater than that of the naked ion, the size-fit concept still holds in the sandwich complexation, resulting in distinctly different cation selectivities between 15-crown-5 and 18-crown-6 derivatives.[1–3]

In this context, it is an intriguing logical extension of the preceding work to examine a bis(crown ether) as a self-consistent ligand for unimolecular sandwich complexation, since the two crown ether units linked by an appropriate bridging chain have amply been shown to enhance dramatically the cation-binding abilities of the corresponding mono crown ether especially for medium- to large-sized cations.[4–11]

In the present study we synthesised a bis(benzo-15-crown-5) derivative **4**, in which two benzo-15-crown-5 units are linked by a 1,8-dioxooctamethylene chain, since this chain length has been shown to be most favourable for the complexation of potassium ion in methanol–water(8:2).[11] Its complexation behaviour with light lanthanoid ions, *i.e.* the cation-binding ability and the complexation stoichiometry, is evaluated by quantitative solvent extraction of aqueous lanthanoid(III) picrates, and the results are compared with those for the reference ligand, 4′-acetylbenzo-15-crown-5 **3**, and the related ligands 15-crown-5 **1** and benzo-15-crown-5 **2**.



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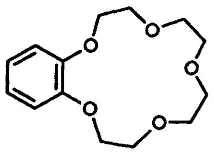

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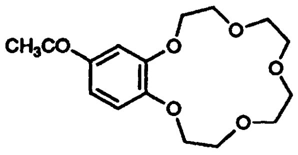

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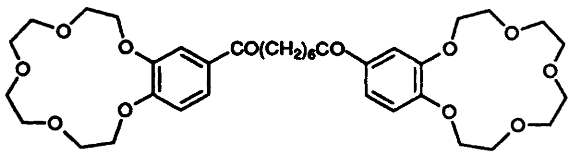

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Experimental

General.—Melting points were recorded on a Rigaku model 8075 differential thermal balance. Infrared spectra were obtained on a Bio-Rad FTS-40 spectrophotometer, ^{1}H NMR

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† Abbreviations:15-crown-5 = 1,4,7,10,13-pentaoxacyclopentadecane; 18-crown-6 = 1,4,7,10,13,16-hexaoxacyclooctadecane; benzo-15-crown-5 = 2,3,5,6,8,9,11,12-octahydro-1,4,7,10,13-benzopentaoxacyclopentadecine; 4′-acetylbenzo-15-crown-5 = 15-acetyl-2,3,5,6,8,9,11,12-octahydro-1,4,7,10,13-benzopentaoxacyclopentadecine; 1,8-dioxooctamethylenebis(4′-benzo-15-crown-5) = 1,8-bis(2,3,5,6,8,9,11,12-octahydro-1,4,7,10,13-benzopentaoxacyclopentadecin-15-yl)octane-1,8-dione.

Table 1 Solvent extraction of aqueous light lanthanoid picrates with crown ethers **1**–**4**

	Extractability (%)[b]						
Ligand	La^{3+}	Ce^{3+}	Pr^{3+}	Nd^{3+}	Sm^{3+}	Eu^{3+}	Gd^{3+}
1[c]	9.1	10.7	12.3	12.6	14.4	13.7	10.6
2[d]	8.5	11.0	13.2	13.6	15.6	14.2	10.8
3	5.7	6.7	8.1	7.5	8.8	8.9	6.4
4	18.2	18.1	21.4	20.6	19.6	22.0	19.4

[a] Extraction performed in dichloromethane–water system at 25.0 °C; [crown ether unit] = 60 mmol dm^{-3}, [picrate] = 3 mmol dm^{-3}. [b] Spectrophotometrically determined extractability of lanthanoid picrate extracted into the organic phase. [c] Ref. 1. [d] Ref. 2.

spectra on a JEOL JNM-GX400 instrument in [^{2}H]chloroform and electronic spectra on a Hitachi 228 spectrophotometer. Inductively coupled plasma (ICP) atomic emission analyses were performed on a Shimadzu GVM 100P instrument, which was calibrated for each lanthanoid as reported.[1,12]

Materials.—Commercially available picric acid (Nakarai), lanthanoid carbonates and oxides (Mitsuwa, Nakarai, Wako, or Rare Metallic Co.) were used without further purification. Lanthanoid picrates were prepared and purified as reported previously.[1,12] Deionized water and distilled dichloromethane were used throughout.

1,8-Dioxooctamethylenebis(4′-benzo-15-crown-5) **4** was synthesised in the reaction of benzo-15-crown-5 (Merck) with suberic acid (Nakarai) in polyphosphoric acid:[13] m.p. 138 °C (lit.,[13] 137–138 °C); IR (KBr) 3075, 2932, 2867, 1671, 1591, 1514, 1433, 1269, 1131, 1051 and 938 cm^{-1}; ^{1}H NMR δ 1.42 (m, 4 H), 1.73 (m, 4 H), 2.91 (t, 4 H, J = 7.3), 3.75 (m, 16 H), 3.92 (m, 8 H), 4.18 (m, 8 H), 6.85 (d, 2 H, J = 8.3), 7.50 (d, 2 H, J = 2.2) and 7.55 (dd, 2 H, J = 2.2, 8.3 Hz). 4′-Acetylbenzo-15-crown-5 **3** was obtained by the Williamson synthesis with 1,11-dichloro-3,6,9-trioxaundecane and 3,4-dihydroxyacetophenone which was prepared by the Fries rearrangement of catechol diacetate:[14] m.p. 97 °C (lit.,[14] 96–97 °C); IR (KBr) 3060, 2909, 2820, 1672, 1596, 1516, 1431, 1362, 1276, 1213, 1131, 1047 and 940 cm^{-1}; ^{1}H NMR δ 2.55 (s, 3 H), 3.75 (m, 8 H), 3.92 (m, 4 H), 4.19 (m, 4 H), 6.85 (d, 1 H, J = 8.5), 7.50 (d, 1 H, J = 2.0) and 7.55 (dd, 1 H, J = 2.0, 8.3 Hz).

Solvent Extraction.—The general procedures were analogous to those employed in previous studies.[1–3] The solvents, dichloromethane and water, were saturated with each other prior to use in order to prevent volume changes of both phases during extraction. Equal volumes (5 cm^3) of a dichloromethane solution of the bis(benzo-15-crown-5) **4** (15–45 mmol dm^{-3}) or acetylbenzo-15-crown-5 **3** (60–120 mmol dm^{-3}) and of an aqueous solution of lanthanoid picrate (3 mmol dm^{-3}) were introduced into an Erlenmeyer flask, which was stoppered and then shaken vigorously for 40 min in a Toyo incubator thermostatted at 25.0 ± 0.2 °C. The mixture was then allowed to stand for at least 2 h at that temperature in order to complete phase separation. Part (3 cm^3) of the dichloromethane phase was withdrawn and evaporated to dryness *in vacuo*. The residue was diluted with water–acetonitrile (1:2) to give a clear solution. The concentrations of picrate and lanthanoid were independently determined by photometric and ICP analyses, respectively, since the ligand-enhanced hydrolysis of light[3] and/or heavy[1,3,15] lanthanoids is known to occur in the absence of dense background salts. In the present case, both measurements gave practically the same extractabilities for all light lanthanoids employed, although the ICP analysis tended to give slightly higher values throughout the series.

In control runs, no detectable amounts of lanthanoid picrate were extracted into the organic phase in the absence of the ligand; the extractabilities were smaller than 0.1% for all lanthanoids.

Results and Discussion

Using bis(benzo-15-crown-5) **4** and the reference mono crown ether **3**, comparative solvent extractions of aqueous light lanthanoid picrates (3 mmol dm^{-3}) were first performed at a fixed ligand concentration: [crown ether unit] = 60 mmol dm^{-3}. The percent extractabilities obtained for the light lanthanoids are listed in Table 1, along with the corresponding data for their parent compounds, 15-crown-5 **1** and benzo-15-crown-5 **2**.

As can be seen from Table 1, acetylbenzo-15-crown-5 **3** shows substantially lower extractabilities for all light lanthanoids than do the parent ligands **1** and **2**, as a result of the well documented electronic effect of the acetyl group introduced.[16] By contrast, bis(benzo-15-crown-5) **4** appears to behave as intended, affording the highest extractabilities among the ligands ever examined under identical conditions.[1–3] From this result alone, the enhanced extractabilities observed would simply be ascribable to the conventional intramolecular sandwich complexation by two crown ether units.

For a more quantitative comparison of the cation-binding ability and the relative cation selectivity, the solvent extractions of aqueous lanthanoid picrates with ligands **3** and **4** were conducted at varying ligand concentrations. Quite unexpectedly, the quantitative solvent extraction revealed that not one but two molecules of **4** are involved in the lanthanoid picrate complex extracted into the organic phase.

As described previously,[1] the overall extraction equilibrium of an aqueous lanthanoid picrate (LnA_3) and n molecules of ligand (L) in the organic phase can be expressed as in equation (1). The extraction equilibrium constant (β_n) is given by equation (2) where the distribution ratio (D_{Ln}) of lanthanoid between the organic and aqueous phases is given by equation (3). Modification of equation (2) leads to (4).

$$Ln^{3+}(aq) + 3A^-(aq) + nL(org) \xrightleftharpoons{\beta_n} [LnL_nA_3](org) \quad (1)$$

$$\beta_n = D_{Ln}/[A^-]_{aq}^{\,3}[L]_{org}^{\,n} \quad (2)$$

$$D_{Ln} = [LnL_nA_3]_{org}/[Ln^{3+}]_{aq} \quad (3)$$

$$\log\{D_{Ln}/[A^-]_{aq}^{\,3}\} = n\log[L]_{org} + \log\beta_n \quad (4)$$

In order to determine the complexation stoichiometry (n) and the extraction equilibrium constants (β_n), quantitative extraction experiments on light lanthanoid (La–Gd) picrates at a fixed concentration (3 mmol dm^{-3}) were carried out with ligands **3** (60–120 mmol dm^{-3}) and **4** (15–45 mmol dm^{-3}). The results were analysed by equation (4). The log $\{D_{Ln}/[A^-]_{aq}^{\,3}\}$ values when plotted as a function of log $[L]_{org}$ gave a straight line of slope 2 in all cases, as exemplified in Fig. 1 for the extraction of cerium and samarium picrates with **4**. It is not anticipated but of great interest that not only the mono crown ether **3** but also the bis(crown ether) **4** predominantly form bimolecular sandwich complexes with lanthanum to gadolinium picrates over the entire range of ligand concentration employed.

The bimolecular extraction constant β_2 is obtained from the intercept of a plot of log $[L]_{org}$ *versus* log $\{D_{Ln}/[A^-]_{aq}^{\,3}\}$. The log β_2 values for ligands **3** and **4** are listed in Table 2, along with those reported for **1**[1] and **2**.[2] These values are plotted as functions of the reciprocal ionic radius (r^{-1}) of the lanthanoid[17] in Fig. 2. It is readily seen that, compared with the reference ligand **3** or the parents **1** and **2**, bis(benzo-15-crown-5) **4** possesses greatly improved cation-binding abilities but displays a poorer relative cation selectivity within the light lanthanoids.

All of the above observations on the complexation behaviour of ligand **4**, *i.e.* the preferential double sandwich complexation, the dramatic enhancement of extractability, and the flat profile

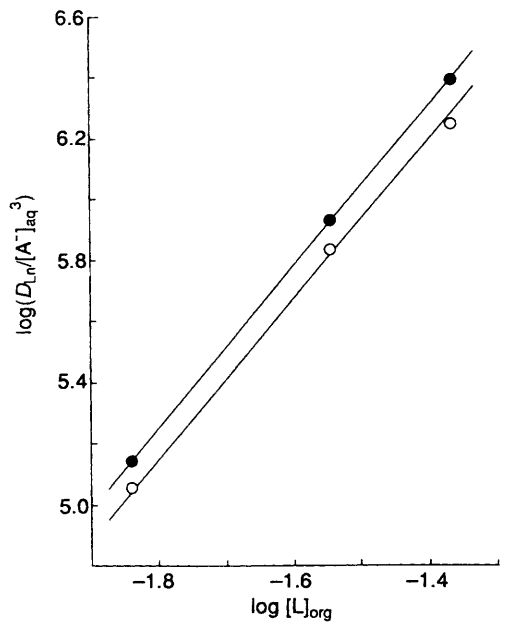


Fig. 1 Plots of $\log\{D/[A^-]_{aq}^3\}$ *versus* $\log[L]_{org}$ for the solvent extractions of cerium (○) and samarium (●) picrates with bis(benzo-15-crown-5) **4**; the slopes of the regression lines are 2

Table 2 Extraction equilibrium constants (β_2) for bimolecular sandwich complexation of lanthanoid picrates with crown ethers **1**–**4**[a]

	β_2						
Ligand	La^{3+}	Ce^{3+}	Pr^{3+}	Nd^{3+}	Sm^{3+}	Eu^{3+}	Gd^{3+}
1[b]	8.03	8.11	8.18	8.19	8.27	8.22	8.09
2[c]	7.71	7.88	8.02	8.04	8.12	8.06	7.87
3	7.45	7.58	7.65	7.60	7.77	7.71	7.51
4	8.83	8.83	8.97	8.94	8.91	9.00	8.89

[a] Determined in dichloromethane–water system at 25.0 °C. [b] Ref. 1. [c] Ref. 2.

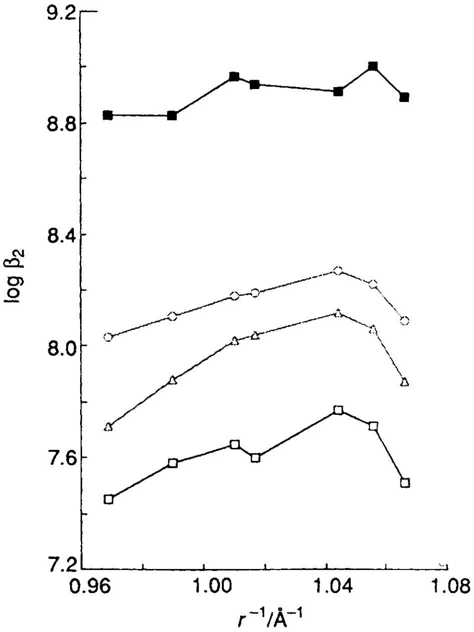
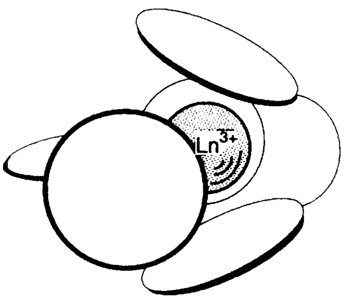


Fig. 2 Extraction equilibrium constants (β_2) for 1:2 sandwich complexation of lanthanoid picrates with 15-crown-5 **1** (○), benzo-15-crown-5 **2** (△), 4′-acetylbenzo-15-crown-5 **3** (□), and bis(benzo-15-crown-5) **4** (■) as a function of the reciprocal ionic radius (r^{-1}) of the lanthanoid; see Table 2 for the data



of the cation selectivity sequence, jointly suggest: (1) that the lanthanoid ions extracted are not completely dehydrated even with the bis(crown ether); (2) that these partially hydrated lanthanoid ions, possessing much larger effective ionic diameters than those of the naked ions, can be extracted into the organic phase only by forming a double-sandwich complex incorporating four crown ether units, as shown; and (3) that the poor relative cation selectivity is a natural consequence of the spatially less-defined three-dimensional cavity constructed by two unbound bis(crown ether) molecules. Probably, the 1,8-dioxooctamethylene bridge, though sufficiently long for the sandwich complexation of potassium ion,[10] is not long enough to provide an appropriate three-dimensional cavity to accommodate a partially hydrated lanthanoid ion through conventional intramolecular sandwich complexation. The most crucial driving force for this unique double-sandwich complexation seems to originate from the need for shielding effectively the partially hydrated lanthanoid ion from the surrounding organic solvents. Hence, a well designed bis(crown ether) possessing larger crown rings and a longer linking bridge is expected to give both much enhanced extractabilities and an excellent relative cation selectivity for the lanthanoids.

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