

# Solvent Extraction of Rare Earth Metals With Crown Ethers

Lin-Mei Tsay, Jeng-Shang Shih\* and Shaw-Chii Wu\*

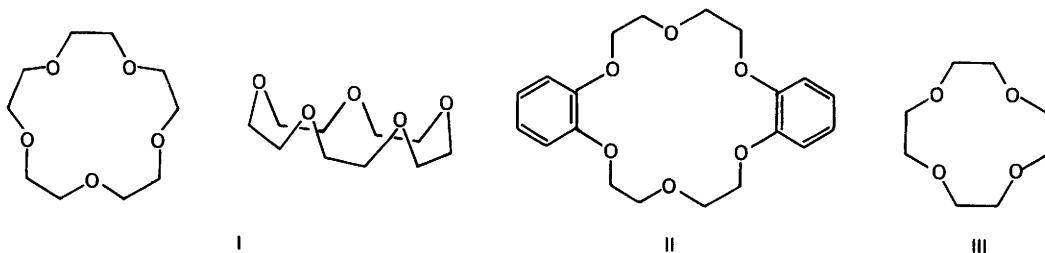
Department of Chemistry, National Taiwan Normal University of Taipei, Taiwan 117, Republic of China

Crown ethers, such as 15-crown-5, 12-crown-4 and dibenzo-18-crown-6, were used to extract individual rare earth ions from aqueous solutions containing picrate into nitrobenzene solution. The rare earth metal ion europium(III) is extracted as a 2:1 crown-ion sandwich complex with 12-crown-4, but as a 1:1 complex with both 15-crown-5 and dibenzo-18-crown-6. From studies of picric acid concentration effects on complexation, the extracted species of  $\text{Eu}(\text{NO}_3)_3$  with 15-crown-5 and dibenzo-18-crown-6 are  $\text{Eu}[(15\text{-crown-5})\text{-(picrate)}_2(\text{NO}_3)]$  and  $\text{Eu}[(\text{dibenzo-18-crown-6})(\text{picrate})_2(\text{NO}_3)]$ , respectively, but  $\text{Eu}[(12\text{-crown-4})_2(\text{picrate})_3]$  is formed with 12-crown-4. The extraction of rare earth ions showed that  $\text{Tb}^{3+}$ ,  $\text{Eu}^{3+}$ ,  $\text{Gd}^{3+}$ ,  $\text{Nd}^{3+}$  and  $\text{Yb}^{3+}$  can be easily extracted using 15-crown-5; however, the extraction of  $\text{Ce}^{4+}$ ,  $\text{Sm}^{3+}$ ,  $\text{Dy}^{3+}$  and  $\text{Lu}^{3+}$  is more difficult.

**Keywords:** Rare earth metals; solvent extraction; crown ethers

It has been demonstrated that macrocyclic polyethers can behave as highly selective complexing agents for cations<sup>1-5</sup> and are of potential significance in the separation of ions using solvent extraction procedures. Solvent extraction methods can not only be applied in the separation of ions, but can also provide information concerning the nature of the complex formed between the ion and the ligand. Extractions of alkali metal ions with crown ethers have been extensively studied,<sup>6-9</sup> but there are very few reports on the extraction with crown ethers of transition metal ions and rare earths. The complexation of rare earth ions by crown ethers has been little studied until recently<sup>10-20</sup> and rare earth-crown ether complexes have been isolated.<sup>10,16,19,20</sup> In general, rare earth ions can form 1:1 or 2:1 crown to ion complexes with 12-crown-4,<sup>16,19,20</sup> but only 1:1 complexes with 15-crown-5 and 18-crown-6.<sup>10</sup> Rare earth metals have similar chemical properties and are difficult to separate from each other. Because crown ethers showed unusual sensitivity to the size of the metal ion, rare earth ions with reasonable difference in their sizes may be separated from each other or from other transition-metal ions by extraction with crown ethers.

In this work, rare earth metals were extracted with 15-crown-5 (I), dibenzo-18-crown-6 (II) and 12-crown-4 (III) ethers. This work has provided information about the relative stabilities of rare earth-crown ether complexes and presented evidence for the formation of a rare earth-12-crown-4 ether sandwich complex.



## Experimental

### Reagents

All reagents except the following were of analytical-reagent grade. Crown ethers, 15-crown-5 and 12-crown-4, were obtained from E. Merck. Dibenzo-18-crown-6 was synthesised

\* To whom correspondence should be addressed.

as described by Pedersen.<sup>1</sup> Rare earth oxides were obtained from Fluka and picric acid and nitrobenzene from E. Merck. The mixture of radioisotopes  $^{152}\text{Eu}$  and  $^{154}\text{Eu}$  was prepared from the irradiation of  $\text{Eu}_2\text{O}_3$  with  $1 \times 10^{13} \text{ n cm}^{-2}$  thermal neutrons in a nuclear reactor at the Nuclear Research Institute in Taiwan. All rare earth nitrates were prepared from the dissolution of rare earth oxides in nitric acid.

### Apparatus

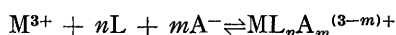
The total radioactivity of the mixture of europium isotopes  $^{152}\text{Eu}$  and  $^{154}\text{Eu}$  was measured with a sodium iodide scintillation counter. Concentrations of other rare earth ions were determined with a Spectrametrics SMI-III DC plasma emission spectrometer.

### Procedure

The rare earth ions in 10 ml of aqueous solution containing 10 mg  $\text{ml}^{-1}$  of picric acid were extracted with 0.1 g of a given crown ether in 10 ml of nitrobenzene. The concentration of the rare earth ions used was in the range 0.6–40 p.p.m. The mixed solution was shaken at room temperature for 30 min for extraction.

### Theory

The distribution coefficient ( $D$ ) of the extraction



is given by the following equation:

$$D = \frac{\sum [\text{M}^{3+}]_{\text{org}}}{\sum [\text{M}^{3+}]_{\text{aq}}} = \frac{[\text{ML}_n\text{A}_m^{(3-m)+}]_{\text{org}}}{[\text{M}^{3+}]_{\text{aq}} + [\text{ML}_n^{3+}]_{\text{aq}}} \quad (1)$$

where  $\text{M}^{3+}$ , L and A are the rare earth ion, crown ether and picrate ion, respectively. For the extraction of alkali metal ions with crown ethers,<sup>9</sup> we can assume that for a large excess of  $\text{A}^-$ , most of the  $\text{ML}_n^{3+}$  ions readily form the complex  $[\text{ML}_n^{3+}][\text{A}^-]$ , which can be extracted into the organic phase, thus  $[\text{ML}_n^{3+}]_{\text{aq}}$  may be considered much smaller than  $[\text{M}^{3+}]_{\text{aq}}$  and  $D$  becomes

$$D = \frac{[\text{ML}_n\text{A}_m^{(3-m)+}]_{\text{org}}}{[\text{M}^{3+}]_{\text{aq}}} \quad (2)$$

under equilibrium conditions. The partition of L between organic solvent and water is given by

$$\text{L}_{\text{aq}} \rightleftharpoons \text{L}_{\text{org}}; K_d = \frac{[\text{L}]_{\text{org}}}{[\text{L}]_{\text{aq}}} \quad (3)$$

Complex formation in aqueous solution is expressed by

$$\text{M}^{3+} + n\text{L}_{\text{aq}} \rightleftharpoons \text{ML}_n^{3+}; K_f = \frac{[\text{ML}_n^{3+}]_{\text{aq}}}{[\text{M}^{3+}][\text{L}]_{\text{aq}}^n} \quad (4)$$

Extraction of the complex from the aqueous phase into the organic phase is given by

$$\text{ML}_n^{3+}_{\text{aq}} + m\text{A}_{\text{aq}}^- \rightleftharpoons \text{ML}_n\text{A}_m^{(3-m)+}; K_{\text{ex}} = \frac{[\text{ML}_n\text{A}_m^{(3-m)+}]_{\text{org}}}{[\text{ML}_n^{3+}]_{\text{aq}}[\text{A}^-]_{\text{aq}}^m} \quad (5)$$

By combining equations (2), (3), (4) and (5), we obtain

$$D = \frac{K_{\text{ex}}K_f[\text{L}]_{\text{org}}^n[\text{A}^-]_{\text{aq}}^m}{K_d^n} \quad (6)$$

When the volumes of organic and aqueous solutions are the same, the initial concentration of crown ethers  $[\text{L}_0]$  can be expressed by

$$[\text{L}_0] = [\text{L}]_{\text{org}} + [\text{L}]_{\text{aq}} \quad (7)$$

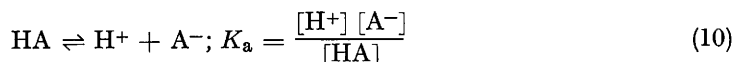
Further, by insertion of equation (3) into equation (7), the following relationship can be obtained:

$$\frac{[L]_{\text{org}}}{[L_0]} = \frac{K_d}{1 + K_d} \quad (8)$$

Hence, by substitution of equation (8) into equation (6):

$$D = \frac{K_{\text{ex}} K_f [L_0]^n [A^-]^m}{(1 + K_d)^n} \quad (9)$$

In the extraction, picric acid (HA) dissociates according to the equation



Under the conditions  $\text{HA} \gg \text{M}^{3+}$  and  $[\text{H}^+] = [\text{A}^-]$

$$[\text{A}^-] = (K_a [\text{HA}])^{\frac{1}{2}} \quad (11)$$

and equation (9) becomes

$$D = \frac{K_a^{m/2} K_{\text{ex}} K_f [L_0]^n [\text{HA}]^{m/2}}{(1 + K_d)^n} \quad (12)$$

and

$$\text{Log} D = \log \frac{K_{\text{ex}} K_f K_a^{m/2}}{(1 + K_d)^n} + \frac{m}{2} \log [\text{HA}] + n \log [L_0] \quad (13)$$

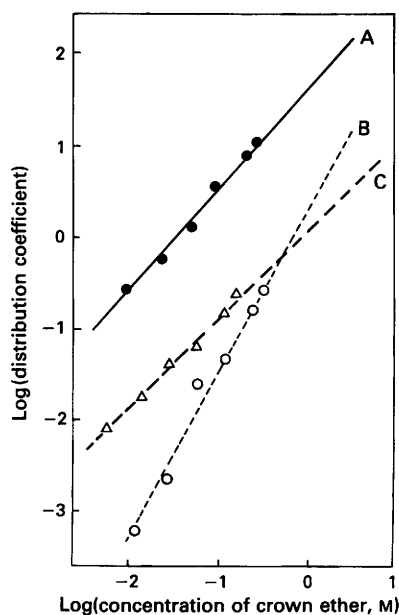


Fig. 1. Effect of crown ether concentration on the extraction of  $\text{Eu}^{3+}$  ions [ $0.588 \mu\text{g ml}^{-1}$  of  $\text{Eu}(\text{NO}_3)_3$  and  $10 \text{ mg ml}^{-1}$  of picric acid]. A, 15-Crown-5, slope = 1.12; B, 12-crown-4, slope = 1.83; and C, dibenzo-8-crown-6, slope = 1.07.

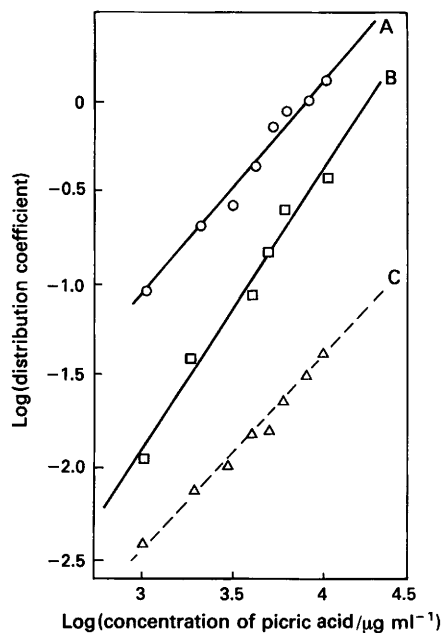


Fig. 2. Effect of picric acid concentration on the extraction of  $\text{Eu}^{3+}$  ions with various crown ethers [ $0.1 \text{ g}$  of crown ether and  $0.588 \mu\text{g ml}^{-1}$  of  $\text{Eu}(\text{NO}_3)_3$ ]. A, 15-Crown-5, slope = 1.16; B, 12-crown-4, slope = 1.43; and C, dibenzo-8-crown-6, slope = 1.10.

## Results and Discussion

It is reasonable to predict that rare earth ions can form stronger complexes and be easily extracted by 15-crown-5 ether because 15-crown-5 has the most suitable cavity size (0.85–1.1 Å)<sup>21</sup> to fit a rare earth ion with the size 0.85–1.06 Å,<sup>22</sup> while dibenzo-18-crown-6 (1.3–1.6 Å or 12-crown-4 (0.65–0.70 Å) ethers are either too big or too small for rare earth ions. This is shown in Fig. 1, where, for a given concentration of crown ether, Eu<sup>3+</sup> is more readily extracted with 15-crown-5 than 12-crown-4 or dibenzo-18-crown-6. Fig. 1 also shows the linear relationship between distribution coefficient ( $\log D$ ) and crown ether concentration ( $\log[L_0]$ ), which is

TABLE I

EFFECTS OF VARIOUS ORGANIC ACIDS ON THE EXTRACTION OF Eu<sup>3+</sup> IONS WITH 15-CROWN-5

A 0.1-g mass of 15-crown-5 in 10 ml of nitrobenzene was used and each acid contained 10 mg ml<sup>-1</sup> of the individual acid and 0.588 µg ml<sup>-1</sup> of Eu(NO<sub>3</sub>)<sub>3</sub> in 10 ml of aqueous solution.

Acid	$D$	$\log D$
Picric .. ..	1.29	0.11
Tartaric .. ..	$3.00 \times 10^{-3}$	-2.52
Citric .. ..	$2.96 \times 10^{-2}$	-1.53
Acetic .. ..	$3.46 \times 10^{-3}$	-2.46
Oxalic .. ..	$3.38 \times 10^{-2}$	-1.47
Sebacic .. ..	$2.99 \times 10^{-3}$	-2.52

in agreement with equation (13). Equation (13) shows that when the concentration of picric acid (HA) remains constant, the graph of  $\log D$  against  $\log[L_0]$  must give a straight line with slope  $n$ . From the  $n$  value, the structure of extracted species (*e.g.*, EuL<sub>*n*</sub><sup>3+</sup>) can be elucidated. The slopes of the graphs in Fig. 1 seem to indicate that the Eu<sup>3+</sup> ion can form 1:1 (crown ether - Eu<sup>3+</sup>) complexes with 15-crown-5 and dibenzo-18-crown-6, but forms a 2:1 sandwich complex with 12-crown-4.

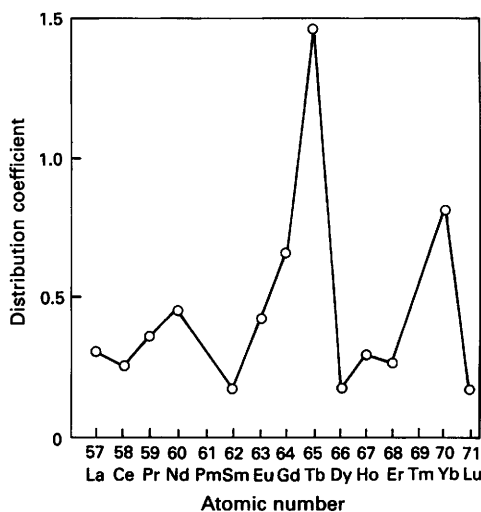


Fig. 3. Graph of distribution coefficients ( $D$ ) versus atomic numbers of rare earth ions extracted by 15-crown-5 (0.1 g of 15-crown-5 in 10 ml of nitrobenzene was used to extract the individual rare earth, 40 µg ml<sup>-1</sup>, in an aqueous solution containing 10 mg ml of picric acid).

In addition, according to equation (13), the picric acid concentration  $[HA]$  should affect the extraction. As shown in Fig. 2, at constant concentration of crown ether, the graph of picric acid concentration ( $\log[HA]$ ) *versus* the distribution coefficient ( $\log D$ ) gives a straight line for each ether. The  $m$  values obtained from the slopes of the graphs (*i.e.*, slope =  $m/2$ ) seem to indicate that the extraction species of  $Eu^{3+}$ , as  $Eu[(\text{crown ether})_n(\text{picrate})_m]$  with 15-crown-5 and dibenzo-18-crown-6 may be  $Eu[(15\text{-crown-5})(\text{picrate})_2(\text{NO}_3)]$  and  $Eu[(\text{dibenzo-18-crown-6})(\text{picrate})_2(\text{NO}_3)]$  but  $Eu[(12\text{-crown-4})_2(\text{picrate})_3]$  with 12-crown-4. Besides picric acid, some other organic acids were also tried for the extraction. However, as shown in Table I, picric acid is the best, which may be due to its higher dissociation constant (0.42 M) or the stronger tendency of the picrate anion to form an ion pair with the complexed cation than other organic acids of interest.

The extraction of individual rare earth ions with 15-crown-5 was investigated. The graph of  $D$  *versus* the atomic number of rare earth ions is shown in Fig. 3. The extractions of rare earth ions showed that  $Tb^{3+}$ ,  $Eu^{3+}$ ,  $Gd^{3+}$ ,  $Nd^{3+}$  and  $Yb^{3+}$  can be most easily extracted with 15-crown-5, but the extraction is difficult for  $Ce^{4+}$ ,  $Sm^{3+}$ ,  $Dy^{3+}$  and  $Lu^{3+}$ . A similar trend was found in the study of the adsorption of the rare earth ion with a synthetic adsorbent of 15-crown-5 with phosphomolybdic acid - polyacrylamide.<sup>23</sup> In general, heavier rare earth ions always have stronger complexing abilities with ligands owing to their greater ionic potentials (charge/radius). However, the complexing behaviour of an ion with a crown ether depends not only on the ionic potential but also the relative size of the ion and cavity of the crown ether ring. As shown in Fig. 3, the  $Tb^{3+}$  ion is the easiest rare earth ion to be extracted. There is not, however, enough evidence to show whether this is due to the best fit of the  $Tb^{3+}$  ion into the cavity of the 15-crown-5 ether; the actual reason is still not understood and further study is necessary.

TABLE II

EFFECT OF THE PRESENCE OF OTHER TRANSITION METAL IONS ON THE EXTRACTION OF THE  $Eu^{3+}$  ION

Added cation (B), 10 p.p.m.	Concentration of B/mm	$D$	$\Delta D$	$I_p^*$
( $Eu^{3+}$ )† .. ..	—	1.29( $D_0$ )	—	—
$Ni^{2+}$ .. ..	0.169	1.28	0.01	0.0002
$Co^{2+}$ .. ..	0.169	1.20	0.09	0.0016
$Ag^+$ .. ..	0.093	1.23	0.06	0.0019
$Cu^{2+}$ .. ..	0.157	1.17	0.12	0.0023
$Fe^{3+}$ .. ..	0.178	1.11	0.18	0.0031
$Zn^{2+}$ .. ..	0.154	1.02	0.27	0.0053
$Cd^{2+}$ .. ..	0.089	1.02	0.27	0.0092
$Th^{4+}$ .. ..	0.043	1.15	0.14	0.0098
$UO_2^{2+}$ .. ..	0.042	1.07	0.22	0.0158
$Hg^{2+}$ .. ..	0.055	0.84	0.45	0.0247
$Pb^{2+}$ .. ..	0.048	0.87	0.42	0.0265

\*  $[Eu^{3+}] = 0.0039$  M.

† No added cation.

The presence of other metal ions always affects the extraction of a metal ion. Table II shows the effect of the addition of 10 p.p.m. of some transition metal ions on the extraction of the  $Eu^{3+}$  ion with 15-crown-5. The interference of other metal ions in the extraction of  $Eu^{3+}$  ions can be expressed by  $I_p$ , which is defined as  $I_p = (\Delta D/D_0)/([B]/[Eu^{3+}])$ , where  $\Delta D = D_0 - D$  and  $D$  and  $D_0$  are the distribution coefficients in aqueous solutions of  $Eu^{3+}$  ions with and without other metal ions (B), respectively;  $[B]$  and  $[Eu^{3+}]$  are concentrations of ion B and  $Eu^{3+}$ . From the definition of  $I_p$ , an  $I_p$  of  $>0.5$  means that crown ether prefers the added cation to the  $Eu^{3+}$  ion; an  $I_p < 0.5$  indicates that the  $Eu^{3+}$  ion is the most easily extracted. In Table II it can be seen that transition metal ions only have small effects; only  $Pb^{2+}$  and  $Hg^{2+}$  show slightly larger effects (*i.e.*, larger  $I_p$ ,  $I_p > 0.02$ ), which may be the result of the similar size of  $Pb^{2+}$  (0.94 Å) and of  $Hg^{2+}$  (0.93 Å) to the  $Eu^{3+}$  ion (0.95 Å).

The authors express their appreciation to the Institute of Nuclear Energy Research in Taiwan and the National Science Council of the Republic of China for its support in this work.

## References

1. Pedersen, C. J., *J. Am. Chem. Soc.*, 1967, **89**, 7017.
2. Christensen, J. J., Eatough, D. J., and Izatt, R. M., *Chem. Rev.*, 1974, **74**, 351.
3. Izatt, R. M., and Christensen, J. J., *Editors*, "Synthetic Multidentate Macrocyclic Compounds," Academic Press, New York, 1978.
4. Kolthoff, I. M., *Anal. Chem.*, 1979, **51**, 1R.
5. Izatt, R. M., and Christensen, J. J., *Editors*, "Progress in Macrocyclic Chemistry," Wiley-Interscience, New York, 1979.
6. Frensdorff, H. K., *J. Am. Chem. Soc.*, 1971, **93**, 4684.
7. Kopolow, I., and Smid, J., *Macromolecules*, 1973, **6**, 135.
8. Fernado, L. A., Miles, M. L., and Bown, L. H., *Anal. Chem.*, 1980, **52**, 1115.
9. Sekine, T., and Hasegawa, Y., *Bull. Chem. Soc. Jpn.*, 1978, **51**, 645.
10. King, R. B., and Heckley, P. R., *J. Am. Chem. Soc.*, 1974, **96**, 3118.
11. Deserrenx, J. F., Renard, A., and Duyckaerts, G., 1977, **39**, 1587.
12. Gansow, O. A., Kansar, A. R., Triplett, K. M., Weaver, M. J., and Yee, E. L., *J. Am. Chem. Soc.*, 1977, **99**, 7087.
13. Desereux, J. F., *Bull. Cl. Sci. Acad. R. Belg.*, 1978, **64**, 814.
14. Caton, G. A., Harman, M. E., Hart, F. A., Hawkes, G. E., and Moss, G. P., *J. Chem. Soc., Dalton Trans.*, 1978, 181.
15. Bunzli, J. C., and Wessner, D., *Helv. Chim. Acta*, 1978, **61**, 1454.
16. Desereux, J. F. and Duyckaerts, G., *Inorg. Chim. Acta*, 1979, **35**, L313.
17. Oanh, H. T., *Inorg. Chim. Acta*, 1979, **32**, L33.
18. Ciampolini, M., and Nardi, N., *Inorg. Chim. Acta*, 1979, **32**, L9.
19. Bunzli, J. C., and Wessner, D., *Inorg. Chim. Acta*, 1980, **44**, L55.
20. Bunzli, J. G., Oanh, H. T., and Gillet, B., *Inorg. Chim. Acta*, 1981, **53**, L219.
21. Pedersen, C. J., and Frensdorff, H. K., *Angew. Chem., Int. Ed. Engl.*, 1972, **11**, 16.
22. Templeton, D. H., and Dauben, C. H., *J. Am. Chem. Soc.*, 1954, **76**, 5237.
23. Tsai, M. L., Shih, J. S., and Wu, S. C., unpublished work.

Received February 2nd, 1983

Accepted April 26th, 1983