Synthesis and Positive Cooperativity in Cation Binding of New Podand Possessing Tropolonoids at Both Terminals of Oligoethylene Glycol

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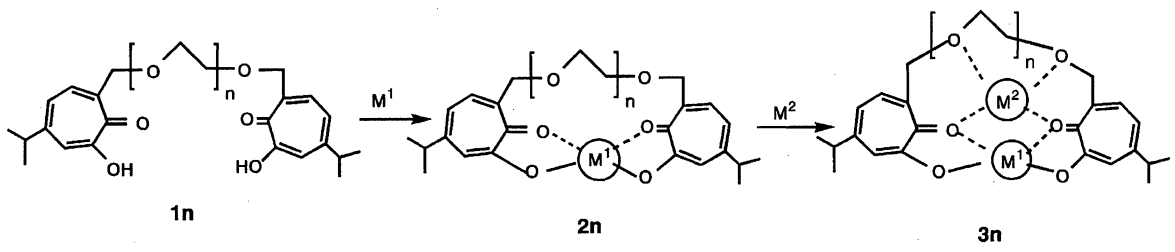
The oligoethylene glycol derivatives having tropolonoid moieties at both terminals were synthesized. The diethylene to pentaethylene glycol derivatives formed Zn complex in an intramolecular fashion, which extracted metal picrates from the aqueous solution. The larger cooperativity was observed in the extractions of alkaline earth metal ions as compared with those of alkaline metal ions.

For the purpose of a biological device to control enzymatic functions, studies on the cooperative binding of two metal ions in a molecule have attracted much interest.[1,2] It is reasonably expected that oligoethylene glycol derivatives **1*n*** having tropolonoid moieties at both terminals is a good podand for the cooperative binding of two different types of metal ions. Since tropolonoid is an excellent chelating agent toward various metal ions, binding of an additional metal ion (M^2) may be possible after formation of clathrate compound **2*n*** by chelation of **1*n*** with M^1 ion as shown in Scheme 1. Here we report the synthesis of **1*n*** and its cooperative binding properties toward metal ions.

4-Isopropyl tropolone (2-hydroxy-4-isopropylcycloheptatrienone, Hinokitiol) **4** was selectively converted to 7-chloromethylhinokitiol **6** by the known procedure,[3] i. e., sequential treatments of potassium salt of **4** with 37% aq HCHO solution at 60 °C to 7-hydroxymethylhinokitiol **5** (91%) followed by chlorination (86% yield) with thionyl chloride and pyridine. Introduction of two 4-isopropyl-7-tropolonylmethyl groups at both terminals of oligoethylene glycol was achieved by stepwise reactions. When **6** was treated with large excess of oligoethylene glycol in the presence of $NaHCO_3$, monoether **7*n*** (n=1—5) was obtained in high yields (91—97%). The remaining terminal hydroxyl group of **7*n*** was etherified to give the objectives **1*n*** (n=1—5) in moderate yields (70—90%) when **7*n*** (n=1—5) was reacted with **6** in the presence of $NaHCO_3$ and $MgSO_4$. Since the coupling reaction of **6** and **7*n*** accompanied the formation of bis(4-isopropyl-7-tropolonyl)methyl ether **8**, addition of $MgSO_4$ is essential. The objectives **1*n*** (n=1—5) were purified by converting the reaction mixture into the corresponding dipivalate ester **1*n*** ($OCOCMe_3$ instead of OH) followed by silica gel column chromatography and then hydrolysis with KOH. Coupling of **5** and **6** under the same conditions afforded the bisether **8**.

When **1*n*** (n=2—5) was stirred with equimolar amounts of Zn(II) acetate in chloroform solution at room temperature, Zn complex was obtained in quantitative yields. The mass spectra indicate the formation of a 1:1 complex. By Zn complex formation, the 3-proton of the tropolone nucleus of **1*n*** shifted to downfield (0.2 ppm) while the remaining protons on the tropolone nucleus including isopropyl and 7-methylene groups showed upfield shifts in the ^1H NMR spectra. The Zn complex formation caused the remarkable downfield shifts of carbons at 1, 2 and 3 positions of



Scheme 1.

the tropolone nucleus of **1*n*** in the ^{13}C NMR spectra. These data are in agreement with structures **9**—**12**, in which Zn is coordinated by two hinokitiol moieties in an intramolecular fashion (Scheme 2). The treatment of 5-isopropyltropolone with Zn(II) acetate furnished the corresponding Zn complex **13**, which exhibited the similar properties in its NMR spectra. In the cases of **8** and **1*n*** (n=1), the Zn complexes are almost insoluble in organic solvents and hence the structures remained unclarified.

By using chloroform solution of Zn complexes **9**—**13**, extraction of metal picrate from the aqueous phase was examined by UV spectroscopies. An example was shown in Fig. 1. By shaking the chloroform solution of Zn complex **11** with aqueous Ba^{2+} picrate solution, the absorbance at 338 nm of **11** (solid line) increased with slight change of the position of absorption maximum at 341 nm (dotted line) in the UV spectra. Since Ba^{2+} picrate shows the absorption maximum at 357 nm in aqueous solution, the net increase of the absorbance may be due to Ba^{2+} picrate extracted with **11** from aqueous to the chloroform solutions. When the Ba^{2+} picrate complex of **11** in chloroform solution was shaken with water, the gross spectrum (dashed line) was almost identical with the original Zn complex **11**, indicating the back-extraction of Ba^{2+} picrate into the aqueous solution. The UV spectrum of the aqueous solution was identical with that of metal picrate. By the back-extraction, 95% of the picrate ion was transfered to the aqueous solution. Although the reason of slight difference between solid and dashed lines is obscure, a possibility of partial exchange of Zn^{2+} and Ba^{2+} during the extraction work is not completely ruled out.

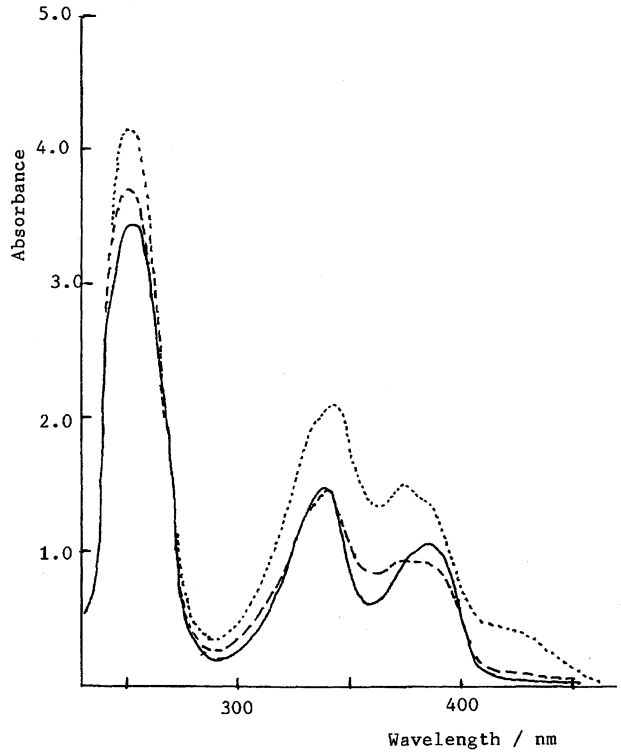
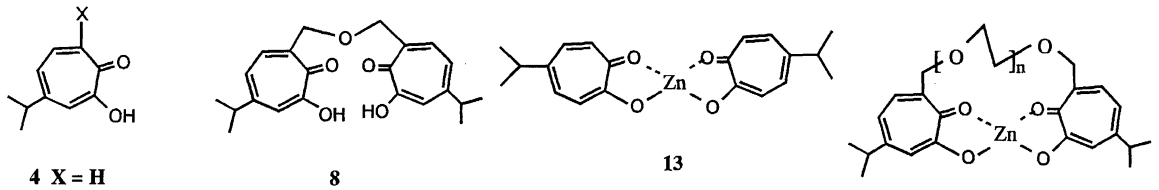


Fig. 1. UV spectra in $CHCl_3$ solutions. Zn complex **11** (solid line): after extraction of Ba^{2+} picrate from aqueous phase with **11** (dotted line): after back-extraction of Ba^{2+} picrate complex of **11** with water (dashed line).

The partition coefficients (K) of metal picrates between the chloroform and aqueous phases were determined as shown in Table 1.[4] Partition coefficients (K) were obtained from $K=([Pic]_i-[Pic]_f)/[Pic]_f$, $[Pic]_i$ and $[Pic]_f$ being picrate concentrations in the aqueous phase before and after the partition, respectively. The K values of both alkaline and alkaline earth metal ions depend on the concentration of host solution, increasing linearly by the concentration increase. As added in Table 1, the Zn complex **13** of 5-isopropyl tropolone was inert and showed no extractability of metal ion when contacted with aqueous solution of the corresponding metal picrate. In addition, the partition coefficients

Table 1. Partition Coefficients ($K\times100$) of Alkaline and Alkaline Earth Metal and Ammonium Ions with 0.075 mM $CHCl_3$ Solution of Zn Complexes

Hosts	Li^+	Na^+	K^+	Rb^+	Cs^+	NH_4^+	Ca^{2+}	Sr^{2+}	Ba^{2+}
9	0.7	3.0	9.0	5.0	2.2	0.6	25.9	31.2	26.7
10	0.9	2.8	10.4	13.3	13.6	10.2	59.0	80.1	85.1
11	2.5	1.3	6.4	5.5	3.5	1.5	8.5	15.3	115.0
12	0.0	0.2	1.8	2.3	2.3	1.4	0.9	12.6	34.2
13	—	—	0.0	—	0.0	—	0.0	—	0.0
1*n* (n=3)	0.2	0.0	0.0	—	—	—	3.9	0.0	0.0



4 X = H
5 X = CH_2OH
6 X = CH_2Cl
7 X = $CH_2[OCH_2CH_2]_nOH$

8

13

9 n = 2
10 n = 3
11 n = 4
12 n = 5

Scheme 2.

were negligible when **1***n* ($n=3$) was used in the free form. These results clearly indicate the formation of inclusion compounds corresponding to **3***n* ($M^1=Zn$; M^2=metal ion), that is, the cooperativity is essential in the sense that the extraction of metal picrates takes place only with the assistance of chelation with Zn ion. It should be pointed out that the oligoethylene glycoxy chain of Zn complexes **9**—**12** is essential since **13** showed no extractability of M^2 ion. For comparison of extractability under the same conditions, partition coefficients using typical crown ethers were measured as summarized in Table 2.[5] It is of interest to note that the cooperativity of Zn complexes **9**—**12** depends largely on the kinds of metal ion. When M^2 are bivalent alkaline earth metal ions, K values are larger than those of the typical crown ethers, exhibiting a gross correlation between ionic diameters and the cavity size. In the meanwhile, K values and selectivities are both smaller when M^2 are monovalent alkaline metal ion as compared with those of the typical crown ethers. Although the exact reason is unclear at present, the two hinokitiol moieties of the Zn complexes **9**—**12** may essentially concern with the large K values and selectivities of the bivalent metal ions. It is noteworthy that dibutyl stannio complexes **2***n* ($M^1=SnBu_2$; $n=2$—5), prepared from **1***n* by the action of dibutyltin oxide in quantitative yields, showed almost negligible extractability of alkali metal ion, indicating the different cooperativity of **2***n* between Zn and Bu_2Sn species.

Experimental

Unless otherwise noted, ^1H NMR and ^{13}C NMR spectra were recorded on solutions in $CDCl_3$ with $SiMe_4$ as an internal standard with JEOL FX-90Q spectrometer. Chemical shifts are reported in δ-units, and J-values are in Hz. The mass spectra were measured with Hitachi M-80 spectrometer. The measurements include EIMS (electron ionization) and FABMS (fast atom bombardment) mass spectrometries. UV spectra were measured with Hitachi U 3210 spectrometer with water or chloroform as solvent. Column chromatographic purification was carried out on using Kiesel gel 60, Art 7734 (70—230 mesh) or Nacalai Tesque Cosmosil 140C-18 OPN. Water applied in the experiments was purified with Advantec GS-200 distillation apparatus. All the tropolonoid compounds excepting **5** (mp 63 °C) and **6** (mp 71 °C) were obtained as pale yellow oil.

Oligoethylene Glycol Monoethers 7*n* **(n=1—5).** A mixture of 7-chloromethylhinokitiol **6** (271 mg), ethylene glycol (4 ml), and anhydrous $NaHCO_3$ (128 mg, 1.2 molar amount) in CH_2Cl_2 (1.3 ml) was stirred at room temperature for 21 h. The mixture was poured into 0.5 M aq HCl solution (1 M=1 mol dm^{-3}) and extracted with CH_2Cl_2. The CH_2Cl_2 solution was washed with brine, dried over Na_2SO_4 and evaporated to give 2-[(4-isopropyl-7-tropolonyl)methoxy]ethanol **7***n* ($n=1$) (294 mg, 97%). By the similar reactions with oligoethylene glycol $H(OCH_2CH_2)_nOH$, **7***n* ($n=2$, 95%), ($n=3$, 94%), ($n=4$, 96%), and ($n=5$, 98%) were prepared.

Oligoethylene Glycol Bisethers 1*n* **(n=1—5).** After a mixture of **7***n* ($n=5$) (92 mg, 0.22 mmol), anhydrous $MgSO_4$ (2.0 g), 7-chloromethylhinokitiol **6** (94 mg, 2 molar amounts) and $NaHCO_3$ (37 mg, 2 molar amounts) in CH_2Cl_2 (5 ml) was stirred at room temperature for 2 d, **6** (94 mg, 2 molar amounts) and $NaHCO_3$ (37 mg, 2 molar amounts) were additionally supplied and the stirring was continued for further 2 d. The mixture was poured into 0.5 M aq HCl solution and extracted with CH_2Cl_2. After washing with brine and drying over Na_2SO_4, the CH_2Cl_2 solution was evaporated to give the crude product. To the resultant crude product (255 mg) in THF (10 ml) were added *N*,*N*-diisopropylethylamine (1.5 ml, 20 molar amounts) and pivaloyl chloride (0.8 ml, 15 molar amounts) at −78 °C. The cooling bath was removed after 30 min stirring and the stirring was continued for 15 h by raising gradually the temperature to room temperature. The reaction mixture was poured into aqueous $NaHCO_3$ solution and extracted with ether. The ether solution was successively washed with aqueous $NaHCO_3$ and then brine and dried over Na_2SO_4. Evaporation of the solvent and column chromatography with SiO_2 (60 g) (hexane–AcOEt=10 : 1) afforded pivalate of **1***n* ($n=5$) ($OCOCMe_3$ instead of OH; 114 mg, 68%) in addition to pivalates of **8** (76 mg) and **5** (40 mg). By the similar reactions, pivalates of **1***n* ($OCOCMe_3$ instead of OH) ($n=1$, 82%), ($n=2$, 91%), ($n=3$, 71%), and ($n=4$, 74%) were prepared. Similarly, stirring a mixture of **5** (246 mg, 1.27 mmol), **6** (404 mg, 1.5 molar amount), $MgSO_4$ (3.8 g, 25 molar amounts) and $NaHCO_3$ (181 mg, 1.7 molar amount) in CH_2Cl_2 (9 ml) for 15 h at room temperature afforded the bisether **8** (280 mg, 60%).

Hydrolysis of Pivalates of 1*n* **(n=1—5).** After the pivalate of **1***n* ($n=5$) (27 mg) in 2 M KOH–MeOH (3 ml) was stirred for 3 min at room temperature, the mixture was poured into 0.2 M aq HCl and extracted with ether. The ether solution was washed with brine and dried over Na_2SO_4. Evaporation of the volatile materials furnished pure **1***n* ($n=5$) (20 mg, 97%). By the similar treatment, the rest of the pivalates of **1***n* ($n=1$—4) provided pure **1***n* ($n=1$—4) in almost quantitative yield. If necessary, the purification can be achieved by reversed phase column chro-

Table 2. Partition Coefficients ($K\times100$) of Alkaline and Alkaline Earth Metal and Ammonium Ions with 0.075 mM $CHCl_3$ Solution of Crown Ethers

Hosts	Li^+	Na^+	K^+	Rb^+	Cs^+	NH_4^+	Ca^{2+}	Sr^{2+}	Ba^{2+}
12-c-4	0.3	0.0	0.0	0.4	0.0	0.2	0.0	0.0	0.0
15-c-5	0.1	48.9	3.4	2.2	0.4	0.8	0.3	0.4	0.1
18-c-6	1.8	21.8	310.5	292.2	83.7	355.6	4.9	30.5	2.6
DB-18-c-6[a]	0.0	3.1	154.2	69.8	15.9	37.6	0.0	0.3	0.0

a) Dibenzo-18-c-6.

matography with CH_3CN–H_2O=10 : 1.

Zn Complex Formation. A mixture of bisether **1*n*** (*n*=3) (34 mg) and $Zn(OAc)_2$ (16.3 mg, 1.0 molar amount) in $CHCl_3$ (30 ml) was stirred at room temperature for 23 h. After filtration, volatile materials were removed to afford Zn complex **10** (44 mg). By the similar reactions, Zn complexes **9**, **11**, **12**, and **13** were prepared in quantitative yield.

^{n}Bu$_2$Sn Complex Formation of Oligoethylene Glycol Bisethers. A mixture of bisether **1*n*** (*n*=4) (50 mg) and ^{n}Bu$_2$SnO (23 mg, 1 molar amount) in benzene (18 ml) was stirred at 80 °C for 18 h. After filtration, the benzene solution was evaporated to give ^{n}Bu$_2$Sn complex **2*n*** (M^1=^{n}Bu$_2$Sn, *n*=4) (71 mg). Similarly, **1*n*** (*n*=3 and 5) afforded the corresponding ^{n}Bu$_2$Sn complexes **2*n*** (M^1=^{n}Bu$_2$Sn, *n*=3 and 5) in quantitative yields.

7*n* (*n*=1): ^{1}H NMR δ=7.75 (1H, d, J=9.7 Hz), 7.37 (1H, d, J=1.8 Hz), 7.04 (1H, dd, J=1.8, 9.7 Hz), 4.74 (2H, s), 3.82 (2H, t, J=5.7 Hz), 3.78 (2H, t, J=5.7 Hz), 2.92 (1H, sept, J=7.2 Hz), 1.28 (6H, d, J=7.2 Hz); ^{13}C NMR δ=172.0 (s), 166.5 (s), 158.7 (s), 136.6 (s), 136.0 (d), 125.9 (d), 119.7 (d), 72.4 (t), 70.1 (t), 61.7 (t), 38.5 (d), 23.2×2 (q). Found (EIMS): *m/z* 238.1197. Calcd for $C_{13}H_{18}O_4$: M, 238.1205.

1*n* (*n*=1): ^{1}H NMR δ=7.84 (2H, d, J=10.8 Hz), 7.36 (2H, d, J=1.8 Hz), 7.04 (2H, dd, J=1.8, 10.8 Hz), 4.78 (4H, s), 3.77 (4H, s), 2.92 (2H, sept, J=7.2 Hz), 1.29 (12H, d, J=7.2 Hz); ^{13}C NMR δ=171.8×2 (s), 166.7×2 (s), 158.5×2 (s), 136.3×2 (s), 136.3×2 (d), 126.0×2 (d), 119.8×2 (d), 70.7×2 (t), 70.0×2 (t), 38.7×2 (d), 23.4×4 (q). Found (EIMS): *m/z* 414.2028. Calcd for $C_{24}H_{30}O_6$: M, 414.2042.

7*n* (*n*=2): ^{1}H NMR δ=7.79 (1H, d, J=9.9 Hz), 7.36 (1H, d, J=1.8 Hz), 7.06 (1H, dd, J=1.8, 9.9 Hz), 4.75 (2H, s), 3.56—3.86 (8H, m), 2.92 (1H, sept, J=7.2 Hz), 1.28 (6H, d, J=7.2 Hz); ^{13}C NMR δ=171.5 (s), 166.5 (s), 158.1 (s), 136.0 (s), 135.8 (d), 125.6 (d), 119.6 (d), 72.4 (t), 70.3 (t), 70.1 (t), 69.6 (t), 61.4 (t), 38.2 (d), 23.0×2 (q). Found (EIMS): *m/z* 282.1465. Calcd for $C_{15}H_{22}O_5$: M, 282.1467.

1*n* (*n*=2): ^{1}H NMR δ=7.82 (2H, d, J=9.9 Hz), 7.36 (2H, d, J=1.8 Hz), 7.03 (2H, dd, J=1.8, 9.9 Hz), 4.78 (4H, s), 3.81 (8H, s), 2.92 (2H, sept, J=7.2 Hz), 1.27 (12H, d, J=7.2 Hz); ^{13}C NMR δ=171.8×2 (s), 166.6×2 (s), 158.4×2 (s), 136.3×2 (s), 136.3×2 (d), 126.0×2 (d), 119.7×2 (d), 71.0×2 (t), 70.7×2 (t), 69.8×2 (t), 38.6×2 (d), 23.4×4 (q). Pivalate: Found (FABMS): *m/z* 627.3528. Calcd for $C_{36}H_{50}O_9$+H: M, 627.3533.

9: ^{1}H NMR δ=7.40—7.80 (4H, m), 6.83 (2H, bd, J=9.9 Hz), 4.66 (4H, bs), 3.66 (8H, bs), 2.74 (2H, br), 1.28 (12H, bd, J=6.7 Hz); ^{13}C NMR δ=176.1×2 (s), 174.6×2 (s), 159.5×2 (s), 137.3×2 (s), 135.6×2 (d), 125.3×2 (d), 124.6×2 (d), 71.4×2 (t), 70.9×2 (t), 70.5×2 (t), 38.8×2 (d), 23.7×4 (q). Found (EIMS): *m/z* 520. Calcd for $C_{26}H_{32}O_7Zn$: M, 520.

7*n* (*n*=3): ^{1}H NMR δ=7.84 (1H, d, J=9.9 Hz), 7.38 (1H, d, J=1.8 Hz), 7.08 (1H, dd, J=1.8, 9.9 Hz), 4.77 (2H, s), 3.58—3.85 (12H, m), 2.94 (1H, sept, J=7.2 Hz), 1.30 (6H, d, J=7.2 Hz); ^{13}C NMR δ=171.9 (s), 166.7 (s), 158.4 (s), 136.4 (s), 136.4 (d), 125.9 (d), 119.9 (d), 72.7 (t), 70.8×3 (t), 70.6 (t), 69.9 (t), 61.8 (t), 38.6 (d), 23.4 (q). Found (EIMS): *m/z* 326.1723. Calcd for $C_{17}H_{26}O_6$: M, 326.1729.

1*n* (*n*=3): ^{1}H NMR δ=7.79 (2H, d, J=10.5 Hz), 7.33 (2H, d, J=1.8 Hz), 7.04 (2H, dd, J=1.8, 10.5 Hz), 4.72 (4H, s), 3.78 (8H, s), 3.74 (4H, s), 2.90 (2H, sept, J=7.0 Hz), 1.26 (12H, d, J=7.0 Hz); ^{13}C NMR δ=171.9×2 (s), 166.8×2 (s), 158.4×2 (s), 136.4×2 (s), 136.4×2 (d), 126.1×2 (d), 119.9×2 (d), 71.0×2 (t), 70.8×4 (t), 70.0×2 (t), 38.8×2 (d), 23.5×4 (q). Pivalate: Found (FABMS): *m/z* 671.3813. Calcd for $C_{38}H_{54}O_{10}$+H: M, 671.3813.

10: ^{1}H NMR δ=7.67 (2H, d, J=10.8 Hz), 7.52 (2H, s), 6.84 (2H, d, J=10.8 Hz), 4.65 (4H, s), 3.64 (12H, s), 2.74 (2H, sept, J=7.0 Hz), 1.13 (12H, d, J=7.0 Hz); ^{13}C NMR δ=176.2×2 (s), 174.6×2 (s), 159.3×2 (s), 136.9×2 (s), 135.6×2 (d), 125.4×2 (d), 124.4×2 (d), 71.1×4 (t), 70.8×2 (t), 70.5×2 (t), 38.8×2 (d), 23.8×4 (q). Found (EIMS): *m/z* 564. Calcd for $C_{28}H_{36}O_8Zn$: M, 564.

7*n* (*n*=4): ^{1}H NMR δ=7.82 (1H, d, J=9.9 Hz), 7.36 (1H, d, J=1.8 Hz), 7.06 (1H, dd, J=1.8, 9.9 Hz), 4.74 (2H, s), 3.52—3.82 (16H, m), 2.92 (1H, sept, J=7.2 Hz), 1.28 (6H, d, J=7.2 Hz). Found (EIMS): *m/z* 370.1989. Calcd for $C_{19}H_{30}O_7$: M, 370.1992.

1*n* (*n*=4): ^{1}H NMR δ=7.81 (2H, d, J=10.8 Hz), 7.36 (2H, d, J=1.8 Hz), 7.04 (2H, dd, J=1.8, 10.8 Hz), 4.73 (4H, s), 3.76 (8H, s), 3.72 (8H, s), 2.92 (2H, sept, J=7.2 Hz), 1.29 (12H, d, J=7.2 Hz); ^{13}C NMR δ=171.6×2 (s), 166.3×2 (s), 158.1×2 (s), 136.3×2 (s), 136.1×2 (d), 125.9×2 (d), 119.6×2 (d), 70.7×4 (t), 70.5×4 (t), 70.0×2 (t), 38.5×2 (d), 23.3×4 (q). Pivalate: Found (FABMS): *m/z* 715.4058. Calcd for $C_{40}H_{58}O_{11}$+H: M, 715.4057.

11: ^{1}H NMR δ=7.67 (2H, d, J=10.8 Hz), 7.52 (2H, s), 6.85 (2H, d, J=10.8 Hz), 4.67 (4H, s), 3.64 (16H, s), 2.76 (2H, sept, J=7.0 Hz), 1.16 (12H, d, J=7.0 Hz); ^{13}C NMR δ=176.2×2 (s), 173.8×2 (s), 159.3×2 (s), 137.3×2 (s), 136.8×2 (d), 125.2×2 (d), 124.2×2 (d), 70.8×6 (t), 70.4×4 (t), 38.8×2 (d), 23.8×4 (q). Found (FABMS): *m/z* 631.1871. Calcd for $C_{30}H_{40}O_9Zn$+Na: M, 631.1861.

7*n* (*n*=5): ^{1}H NMR δ=7.78 (1H, d, J=10.8 Hz), 7.37 (1H, d, J=1.8 Hz), 7.06 (1H, dd, J=1.8, 10.8 Hz), 4.77 (2H, s), 3.48—3.84 (20H, m), 2.93 (1H, sept, J=7.2 Hz), 1.29 (6H, d, J=7.2 Hz); ^{13}C NMR δ=171.7 (s), 166.5 (s), 158.4 (s), 136.3 (s), 136.3 (d), 126.0 (d), 119.8 (d), 72.5 (t), 70.7×8 (t), 69.8 (t), 61.8 (t), 38.6 (d), 23.4×2 (q). Found (EIMS): *m/z* 414.2238. Calcd for $C_{21}H_{34}O_8$: M, 414.2253.

1*n* (*n*=5): ^{1}H NMR δ=7.80 (2H, d, J=9.9 Hz), 7.34 (2H, d, J=1.8 Hz), 7.04 (2H, dd, J=1.8, 9.9 Hz), 4.72 (4H, s), 3.74 (8H, s), 3.68 (8H, s), 3.64 (4H, s), 2.91 (2H, sept, J=7.2 Hz), 1.27 (12H, d, J=7.2 Hz); ^{13}C NMR δ=171.5×2 (s), 166.3×2 (s), 158.1×2 (s), 136.0×2 (s), 136.0×2 (d), 125.8×2 (d), 119.5×2 (d), 70.5×10 (t), 69.6×2 (t), 38.4×2 (d), 23.2×4 (q). Pivalate: Found (FABMS): *m/z* 759.4319. Calcd for $C_{42}H_{62}O_{12}$+H: M, 759.4315.

12: ^{1}H NMR δ=7.72 (2H, bd, J=10.8 Hz), 7.52 (2H, bs), 6.88 (2H, bd, J=10.8 Hz), 4.65 (4H, bs), 3.66 (20H, s), 2.76 (2H, sept, J=7.0 Hz), 1.16 (12H, bd, J=7.0 Hz); ^{13}C NMR δ=175.4×2 (s), 173.4×2 (s), 159.1×2 (s), 136.5×2 (s), 135.6×2 (d), 124.6×4 (d), 70.8×8 (t), 70.4×4 (t), 38.7×2 (d), 23.7×4 (q). Found (EIMS): *m/z* 652. Calcd for $C_{32}H_{44}O_{10}Zn$: M, 652.

13: ^{1}H NMR δ=7.44 (4H, d, J=12.5 Hz), 7.19 (4H, d, J=12.5 Hz), 2.79 (2H, sept, J=7.0 Hz), 1.17 (d, J=7.0 Hz); ^{13}C NMR δ=177.0×4 (s), 146.8×2 (s), 136.6×4 (d), 126.8×4 (d), 37.4×2 (d), 24.0×4 (q). Found (EIMS): *m/z* 390. Calcd for $C_{20}H_{22}O_4Zn$: M, 390.

Measurements of Partition Coefficients. Chloroform solution (20 ml) containing 0.075 mM host was vigorously shaken for 5 min with an aqueous solution (10 ml)

containing 0.15 mM metal or ammonium picrate and the corresponding MCl at 1.0 M. The UV spectrum of the picrate solution showed the λ_{max} at 357 nm, the absorbance of which corresponds to $[Pic]_i$. After standing for 5 min, absorbance at λ 357 nm of the aqueous phase was measured and termed as $[Pic]_f$. The UV spectra indicate that the partition equilibrium of metal picrate between chloroform and aqueous solutions reaches within 2 min shaking. The partition coefficients of typical crown ethers described in Table 2 were determined by the same conditions using 20 ml of chloroform solution containing 0.075 mM host crown ethers.

Extraction and Back-Extraction of Ba^{2+} Picrate with Zn Complex 11. Chloroform solution (20 ml) containing Zn complex **11** (0.075 mM) was shaken for 5 min with an aqueous solution (10 ml) containing Ba^{2+} picrate (0.15 mM) and $BaCl_2$ (1.0 M). The initial aqueous solution shows λ_{max} at 357 nm (abs. 2.21). After standing for 5 min, the aqueous phase was separated, showing λ_{max} at 357 nm (abs. 1.03). The UV spectrum of the chloroform solution was shown in Fig. 1 (dotted line). The chloroform solution was shaken with distilled water (10 ml) for 5 min. After standing for 5 min and then separating two phases, the chloroform solution was again shaken with distilled water (10 ml). The absorbances at 357 nm of the first and second aqueous phases were 0.97 and 0.15, respectively. The UV spectra in $CHCl_3$ of the original Zn complex **11** and that obtained after first back-extraction were shown with solid and dashed lines in Fig. 1.

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