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Molecular Design of Crown Ethers. 3.[1] Extraction of Alkaline Earth and Heavy Metal Picrates with 14- to 17-Crown-5 and 17- to 22-Crown-6

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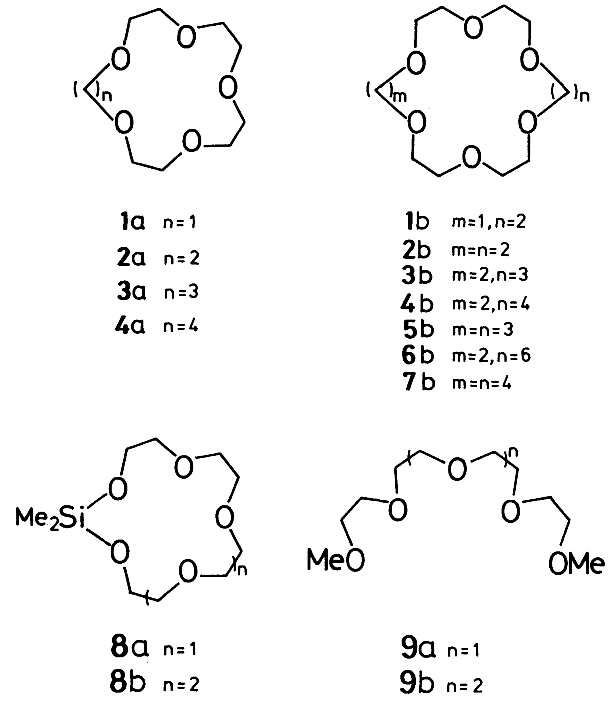
The solvent extraction of alkaline earth and heavy metal picrates with a series of ring-contracted and ring-enlarged crown ethers has been carried out in order to reveal the effects of methylene-chain length upon cation-binding ability. Compared with the parent 3*m*-crown-*m*, the ring-contracted crown ethers and their sila analogues possess limited extractabilities, often as low as those for the corresponding glymes. On the other hand, the ring-enlarged crown ethers, in general, show gradual, but not drastic, decreases in extractability for most cations with increasing methylene-chain length. Interestingly, the extractabilities for Ag^+, Tl^+, and Ba^{2+} do not decrease monotonously with ring expansion; in particular 16-crown-5 is a better extractant for Ag^+ than 15-crown-5 and even than 18-crown-6. These results are accounted for in terms of cavity size, conformation, and molecular symmetry of crown ethers. Effects of cation hydration upon extractability and the limitations of solvent extraction technique are also discussed.

Despite the extensive work on crown ether chemistry, the effect of methylene-chain length between two adjacent oxygen atoms of a crown ether upon its complexation ability has not been explored systematically until very recently. Recent investigations from this laboratory[2–4] have shown that, compared with common, symmetrical 3*m*-crown-*m* ethers (m=5,6), the ring-contracted and ring-enlarged ($3m+n$)-crown-*m* ethers (n=−1 to 4) exhibit drastic changes in cation-binding ability with alkali metal ions, endowing ($3m+n$)-crown-*m* characteristic cation-selectivities which are distinctly different from those for 3*m*-crown-*m*. It is interesting and significant that the introduction of extra methylene(s), which lower the crown ether's molecular symmetry, does not simply lead to monotonous decreases in complexation ability for all alkali cations but results in unequal decreases or even in an enhancement of cation-binding ability. 16-Crown-5, for example, possesses higher cation-binding ability and selectivity for Na^+ than 15-crown-5. More recently, Kimura *et al.*[5] have shown that, among 13- to 16-crown-4 derivatives, 14-crown-4 is most selective for Li^+ over any other alkali or alkaline earth metal ions. These selectivity shifts or enhancements caused by changing methylene-chain length between two adjacent oxygen atoms have been attributed to the changes in cavity size and/or conformation of the crown ether ring.[2–4]

In this paper, we report our results on the effects of ring contraction and ring enlargement upon cation-binding abilities for alkaline earth and heavy metal ions assessed by solvent extration studies. The extractabilities for alkali,[3,4] alkaline earth, and heavy metal ions are compared and discussed in terms of cavity size, conformation, and molecular symmetry of the crown ethers and also in terms of cation hydration energy. The limitations of solvent extraction as a method for evaluating complexation ability of crown ethers are also considered.



1a n=1
2a n=2
3a n=3
4a n=4

1b m=1,n=2
2b m=n=2
3b m=2,n=3
4b m=2,n=4
5b m=n=3
6b m=2,n=6
7b m=n=4

8a n=1
8b n=2

9a n=1
9b n=2

Chart 1.

Results

Solvent extractions from aqueous solutions (3.0×10^{-3} M† in salt) of alkaline earth and heavy metal picrates were performed at 25.0±0.1 °C with dichloromethane solutions (3.0×10^{-3} M in ligand) of a variety of symmetrical and less-symmetrical crown ethers and their acyclic analogues under the same conditions employed earlier for alkali metal picrates.[2–4] The % extractabilities (% *Ex*), defined as % picrate extracted into the organic phase, were measured twice and the average values are shown in Table 1; two independent measurements gave very close % *Ex* values with error of <0.5%. This equimolar condition has been employed,††

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† $1 M = 1 mol dm^{-3}$.

††Added in proof. E. Weber has indicated in a private communication that his group is going to employ the same equimolar condition to assess cation-binding ability of crown ethers. We propose that this condition is adopted widely for the facile assessment and that the results are accumulated for comparison.

Table 1. Solvent extraction of aqueous metal picrates[a]

Ligand	% Ex[b]					
	Ag^+	Tl^+	Mg^{2+}	Ca^{2+}	Sr^{2+}	Ba^{2+}
14-Crown-5 (**1a**)	0.8	1.1	0.5	0.5	0.5	1.5
Sila-14-crown-5 (**8a**)	0.3	1.6	<0.1	<0.1	<0.1	1.5
15-Crown-5 (**2a**)	26.7	29.2	0.7	1.5	8.0	25.3
16-Crown-5 (**3a**)	35.7	18.1	0.3	0.8	4.5	15.4
17-Crown-5 (**4a**)	13.8	7.8	0.7	0.7	0.9	2.1
Tetraglyme (**9a**)	0.2	1.0	<0.1	<0.1	0.2	1.3
17-Crown-6 (**1b**)	6.1	5.4	0.5	0.6	1.4	7.4
Sila-17-crown-6 (**8b**)	0.6	3.5	<0.1	<0.1	1.9	8.8
18-Crown-6 (**2b**)	31.3	73.2	2.5	26.2	69.0	75.8
19-Crown-6 (**3b**)	8.5	35.8	0.6	1.6	52.4	68.1
asym-20-Crown-6 (**4b**)	8.1	43.8	0.1	0.4	34.4	71.6
sym-20-Crown-6 (**5b**)	3.6	9.8	0.4	0.3	13.0	54.3
asym-22-Crown-6 (**6b**)	2.9	14.3	0.1	0.3	2.8	48.6
sym-22-Crown-6 (**7b**)	8.1	5.3	0.6	0.4	0.3	14.2
Pentaglyme (**9b**)	0.5	3.3	0.1	0.1	3.1	36.4

a) Temperature 25.0±0.1 °C; aqueous phase (10 mL): [picrate]=3.0×10^{-3} M; organic phase (CH_2Cl_2, 10 mL): [ligand]=3.0×10^{-3} M. b) Extractability defined as % picrate extracted into the organic phase.

Table 2. Extraction equilibrium constants (K_{ex})[a)] for 1 : 1 complexation of alkaline earth and heavy metal ions with some crown ethers[b)]

Ligand	log K_{ex}				
	Ag^+	Tl^+	Ca^{2+}	Sr^{2+}	Ba^{2+}
15-Crown-5 (**2a**)	5.00	5.08	6.49	7.26	<9.20[c)]
16-Crown-5 (**3a**)	5.25	4.63	6.16	7.02	7.74
17-Crown-5 (**4a**)	4.40	4.13	5.98	6.14	6.55
18-Crown-6 (**2b**)	5.09	6.71			
19-Crown-6 (**3b**)	4.24	5.28			
asym-20-Crown-6 (**4b**)	4.08	5.45	5.79	8.47	

a) Unit of K_{ex}: M^{-2} for monovalent and M^{-3} for divalent cations. b) Dichloromethane-water system at 25.0 °C. c) Least-square-means calculation gives a slope of 1.34 in this particular case, indicating the participation of 1:2 sandwitch type complex to some extent; the actual value K_{ex} value must be lower.

since the cation-selectivity sequence judged from the % Ex values coincides with that from the extraction equilibrium constants (K_{ex}).[2,3]

With selected combinations of crown ethers and mono- and divalent cations, the extraction equilibium constants (K_{ex}) and the complex stoichiometeries (n) for n:1 crown ether-cation complexes were also determined. The solvent extraction of a metal picrate MA_m (m=1 or 2) with n molecules of a crown ether (CE) is expressed by the following overall extraction equilibrium,

$$M_{aq}^{m+} + m\,A^-_{aq} + n\,CE_{org} \overset{K_{ex}}{\rightleftharpoons} [M(CE)_nA_m]_{org}$$

and the equilibrium constant (K_{ex}) is given by Eq. 1.

$$K_{ex} = \frac{D_M}{[A^-]^m_{aq}[CE]^n_{org}} \quad (1)$$

where

$$D_M = \frac{[M(CE)_nA_m]_{org}}{[M^{m+}]_{aq}} \quad (2)$$

Modification of Eq. 1 leads to the following equation.

$$\log(D_M/[A^-]^m_{aq}) = n\log[CE]_{org} + \log K_{ex} \quad (3)$$

Extraction studies were carried out under a variety of conditions to determine extraction equilibrium constant K_{ex} and complex stoichiometry n; [ligand]=0.5—5.0×10^{-3} M and [picrate]=3.0×10^{-3} M. As exemplified in Figure 1, in the most cases the plots of log (D_M/$[A^-]^m_{aq}$) *versus* log $[CE]_{org}$ gave straight lines with a slope (n) of unity, indicating that 15- to 17-crown-5 and 18- to 20-crown-6 form 1:1 crown ether-cation complexes under the conditions employed. The logK_{ex} values are given as intercepts of the straight lines; the results are listed in Table 2.

Discussion

Ring-contracted Crown Ethers 1 and 8. As can be seen from Table 1, all the ring-contracted crown ethers **1** and their sila analogues **8** possess extremely low extractabilities for the alkaline earth and heavy metal ions as compared with the symmetrical ligands 15-crown-5 (**2a**) and 18-crown-6 (**2b**), respectively. The extractabilities may more appropriately be compared with the corresponding glymes **9**. Similarly poor extraction ability has been previously reported in solvent extractions of alkali metal picrates with the same ring-contracted crown ethers **1** and **8**.[4,6] It was shown there that removal of a methylene group from a symmetrical crown ether results in nearly complete loss

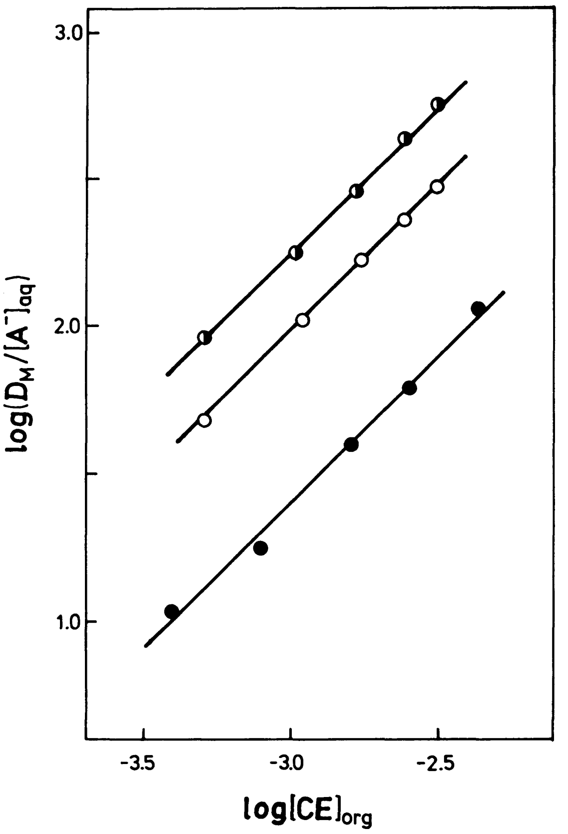

Fig. 1. Plots of log(D_M/[A^-]$_{aq}$) versus log[CE]$_{org}$ obtained in extraction experiments on 15- to 17-crown-5 **2a**(○), **3a**(◐), and **4a**(●) with silver picrate.

of complexing ability for most cations examined.

As has already been proposed in the extraction of alkali metal ions, the origin of the drastic reduction in cation-binding ability for alkaline earth and heavy metal ions is probably due not to diminished cavity size but to the conformational disorder induced by the ring contraction, since the removal of a methylene group does not reduce significantly the cavity size of crown ether and the replacement of the O–C–O linkage of **1** by a longer O–Si–O linkage to give **8** does not contribute to raise the extractability. Examinations of CPK space-filling molecular models also support the irregular spatial arrangement of the donor oxygen atoms; one of the five or six donor atoms cannot be accommodated in the plane of the remaining donor atoms, while the cavity sizes are *ca.* 1.7 Å for **1a**, **2a**, or **8a** and 2.5—2.6 Å for **1b**, **2b**, or **8b**. It is clear that, in this situation, one of the formal donor oxygen atoms no longer acts as an effective donor atom; this may be the major reason for the drastic decrease in the extractability of the ring contracted crown ethers **1** and **8**.

Ring-enlarged Crown Ethers 3—7. The introduction of extra methylene (s) at one or two transannular position (s) of the symmetrical 3*m*-crown-*m* gives ring-enlarged crown ethers. In general, these crown ethers of low symmetry, *i.e.* 16- and 17-crown-5 and 19- to 22-crown-6 possess lower % *Ex* or K_{ex} values for the cations examined in this study. This is also the case with the solvent extraction of alkali metal picrates with the same crown ethers.[3] For most cations, the % *Ex* or K_{ex} value decreases gradually or, in some cases, drastically with increasing methylene-chain length, although even the extremely enlarged 17-crown-5 **4a** and 22-crown-6 **6b**, **7b** are still the better ligands than the corresponding glymes **9**. Interestingly, the % *Ex* for Ba^{2+} is relatively insensitive to the ring expansion and therefore the less symmetrical crown ethers **3b**—**7b** exhibit higher Ba^{2+} selectivity than the parent 18-crown-6 **2b**. It is also noted that the highest selectivity for Ba^{2+} is given not by the crown ethers but by acyclic pentaglyme **9b**.

The major reason for the gradual decrease in % *Ex* or K_{ex} is certainly the lower symmetry, or in other words the less-favorable spatial arrangement of donor oxygen atoms, resulting from the ring expansion. In this context, the comparison of % *Ex* for the *asym*- and *sym*-isomers of 20- and 22-crown-6 is interesting. The % *Ex* values for *sym*-isomers **5b** and **7b** are considerably lower than those for *asym*-isomers **4b** and **6b** except for the complexation of Ag^+ with 22-crown-6. It may be concluded that, when the same number of methylene group is introduced into a crown ether, the double extension of methylene-chain length at the transannular positions giving a *sym*-crown ether is much more effective in diminishing cation-binding ability than the single extension giving an *asym*-crown ether. This is probably due to the greater deformation of spatial arrangement of donor atoms induced by the double, rather than single, extension of methylene-chain length.

Some exceptions to the gradation of % *Ex* or K_{ex} are seen at the same time in the extraction of Ag^+, Tl^+, and Ba^{2+}. In spite of the increased methylene-chain length, *asym*-20-crown-6 (cavity size 3.3 Å) exhibits somewhat higher % *Ex* values for Tl^+ (cation diameter 3.00 Å) and Ba^{2+} (2.72 Å) than 19-crown-6 (2.7 Å), although the % *Ex* values are considerably lower than those for the parent 18-crown-6. These irregular increases in % *Ex* may roughly be accounted for in terms of the size-fit concept[7]—relationship between relative sizes of cation and crown cavity; see Table 3 for these quantities.[8] A more remarkable result was obtained in the extraction of Ag^+ with 16-crown-5. In contrast to the monotonous decreases in % *Ex* or K_{ex} for the other cations, 16-crown-5 exhibits fairly higher % *Ex* and K_{ex} values for Ag^+ than the parent 15-crown-5 or even than 18-crown-6, preserving the 1:1 stoichiometry. This may be an exceptional case in which 18-crown-6 does not show the highest cation-binding ability, although Gokel *et al.*[9] have reported that 18-crown-6 shows the highest stability constants (K_s) for Na^+, K^+, NH_4^+, and Ca^{2+} in the homogeneous solution. This preferential extraction of Ag^+ by 16-crown-5 may originate from the "nesting" interaction in the 1:1 complex with Ag^+ as is the case with Na^+. It has been shown previously[2,3] that 16-

TABLE 3. CAVITY SIZE OF THE CROWN ETHERS AND CATION DIAMETER AND HYDRATION ENERGY ($-\Delta G^{h}_{H_2O}$) OF CATIONS

Ligand	Cavity diameter, Å[a]	Cation	Diameter, Å[b]	$-\Delta G^{h}_{H_2O}$, kcal/mol[c]
14-Crown-5 (**1a**)	1.7	Na^+	2.04	98
15-Crown-5 (**2a**)	1.7	K^+	2.76	81
16-Crown-5 (**3a**)	1.8	Rb^+	2.98	76
17-Crown-5 (**4a**)	2.0	Cs^+	3.40	68
17-Crown-6 (**1b**)	2.5	Ag^+	2.30	114
18-Crown-6 (**2b**)	2.6	Tl^+	3.00	82
19-Crown-6 (**3b**)	2.7	Mg^{2+}	1.44	454
asym-20-Crown-6 (**4b**)	3.3	Ca^{2+}	2.00	379
sym-20-Crown-6 (**5b**)	3.0	Sr^{2+}	2.32	340
asym-22-Crown-6 (**6b**)	3.4	Ba^{2+}	2.72	314
sym-22-Crown-6 (**7b**)	3.9			

a) Estimated by CPK molecular models. b) Reference 8b. c) Reference 13.

TABLE 4. EXTRACTABILITY (% *Ex*), EXTRACTION EQUILIBRIUM CONSTANT (K_{ex}), AND STABILITY CONSTANT (K_s) AT 25 °C FOR 15-crown-5 AND 18-crown-6

Ligand	Binding constant	Cation										Ref
		Na^+	K^+	Rb^+	Cs^+	Ag^+	Tl^+	Mg^{2+}	Ca^{2+}	Sr^{2+}	Ba^{2+}	
15-Crown-5	% *Ex*	13.2	14.3	9.6	3.3	26.7	29.2	0.7	1.5	8.0	25.3	a)
	log K_{ex}	4.52	4.40	4.29	3.74	5.00	5.08		6.49	7.26	<9.20	a)
		(≡1.0)	(0.97)	(0.95)	(0.83)	(1.11)	(1.12)					
	log K_s	3.48	3.77		2.18	3.62			2.18	2.63		b)
	(MeOH)	(≡1.0)	(1.08)		(0.63)	(1.04)						
	log K_s	0.70	0.74	0.62	0.8	0.94	1.23			1.95	1.71	c)
	(H_2O)	(≡1.0)	(1.06)	(0.89)	(1.14)	(1.34)	(1.76)					
18-Crown-6	% *Ex*	6.3	69.0	57.6	36.7	31.3	73.2	2.5	26.2	69.0	75.8	a)
	log K_{ex}	3.89	6.20	5.96	5.17	5.09	6.71					a)
		(0.63)	(≡1.0)	(0.96)	(0.83)	(0.82)	(1.08)					
	log K_s	4.36	6.06	5.32	4.79	4.58			3.86	5.5	7.04	b)
	(MeOH)	(0.72)	(≡1.0)	(0.88)	(0.79)	(0.76)						
	log K_s	0.80	2.03	1.56	0.99	1.50	2.27			2.72	3.87	c)
	(H_2O)	(0.39)	(≡1.0)	(0.77)	(0.49)	(0.74)	(1.11)					

a) This work and reference 3. b) Reference 12. c) Reference 11.

crown-5 possesses the highest extractability and selectivity for Na^+ among alkali metal ions, which is explained by the most favorable cavity size and orientation of the donor atoms for 1:1 complexation with Na^+, *i.e.* "nesting" interaction, and by the less-favorable "perching" interaction with the larger cations, K^+, Rb^+, Cs^+. The same situation may be attained in the 1:1 complex of 16-crown-5 with heavy metal ions. Taking into account of the axial development of hybrid orbital of silver ion originating from the d_z-s mixing,[10] Ag^+ (formal cation diameter 2.30 Å) is considered to be better accommodated in the cavity (1.8 Å) of 16-crown-5 than in the smaller cavity (1.7 Å) of 15-crown-5.

It is concluded that the cation-binding ability of the ring-enlarged crown ethers for monovalent cations is determined by a critical balance between the enlarged cavity size and the reduced molecular symmetry, although the cation selectivity is well accounted for in terms of the size-fit concept. It is also shown that the unfavorable effect of the conformational change induced by ring enlargement may be minimized or cancelled, in particular, with the size-fitted cations like Na^+ and Ag^+, but leads to the drastic decrease of extractability with the mismatched cations. This discriminating effect can be utilized as a tool to enhance the cation selectivity as demonstrated in the complexations of Na^+ and Ag^+ with 16-crown-5 and of Ba^{2+} with 19- to 22-crown-6.

Limitations of Solvent Extraction Technique. The solvent extraction of aqueous metal picrates has been employed as a facile method to assess cation-binding ability of crown ethers. However there may be some ambiguities with the binding ability assessed by this technique, since the extractability (% *Ex*) or extraction equilibrium constant (K_{ex}) would not necessarily be determined only by the cation-binding ability of ligand and the other factor might have a dominant effect.[9] In Table 4, the % *Ex* and K_{ex} values for 15-crown-5 and 18-crown-6 are compared with the corresponding stability constants (K_s) in homogeneous solution determined by the other investigators.[11,12] With monovalent cations, the K_{ex}, or % *Ex*, values parallel exactly the K_s values in methanol, indicating that the cation-binding ability and cation selectivity can be assessed quantitatively by the solvent extraction technique at least for monovalent cations.

Serious discrepancy is however found between the K_{ex} and K_s values for divalent cations. Thus the size-fit concept fails to explain the extractability trend for alkaline earth metal ions. This is most evident with

15- to 17-crown-5. As can be seen from Tables 1, 2, and 4, the K_{ex} or % Ex values for Mg^{2+} and Ca^{2+} are quite low for these ligands, although the cation diameters of these divalent cations (Mg^{2+} 1.44 Å, Ca^{2+} 2.00 Å)[8b] would fit in the cavity of 15-crown-5 (1.7 Å), 16-crown-5 (1.8 Å), or 17-crown-5 (2.0 Å). By contrast, the formally mismatched larger cations, *i.e.* Sr^{2+} and Ba^{2+}, are extracted more efficiently. These results strongly suggest that, in the solvent extraction of divalent cations, the extractability and cation-selectivity cannot be discussed by the size-fit concept alone and the other factor plays a primary role to determine the above quantities.

The major difference between the series of mono- and divalent cations is not the cation diameter but the energy of hydration. As listed in Table 3, the divalent cations possess much higher free energy of hydration ($\Delta G^\circ_{H_2O}$) than the monovalent ones; $-\Delta G^\circ_{H_2O}$ values are 68—114 kcal/mol* for the monovalent cations, while 314—454 kcal/mol for the divalent ones.[13] This does not immediately mean that the cation of higher hydration energy encounters greater difficulty upon complexation with a ligand, since the higher hydration energy also promises stronger interaction with the donor oxygen atoms of the ligand as well as water molecules. Indeed, judged from the K_s values obtained in homogeneous solutions (Table 4), the cation selectivities among the divalent cations appear to be accounted for in terms of the size-fit concept. The major difficulty for the divalent cations to be extracted into the organic phase may originate from the incomplete dehydration of the cation upon extraction. Iwachido *et al.*[14] have reported that the cation extracted into the organic phase in the form of 1:1 complex with a crown ether is not entirely dehydrated and the number of water molecule coextracted with a cation is much greater for the divalent than monovalent cations; for example, the hydration numbers for M^{n+}-dibenzo-18-crown-6 complex in nitrobenzene are: Na^+ 1.2; K^+-Cs^+ 0.1; Ca^{2+} 5.1; Sr^{2+} 4.9; Ba^{2+} 4.4. Therefore, although the organic phase and the crown ether reported are different from those used in this study, the discrepancy between the K_{ex} and K_s values for divalent cations probably ascribable to the higher barrier for the heavily hydrated complex to be extracted into the organic phase.

In conclusion, it is evident that the solvent extraction technique works well with monovalent cations to give appropriate K_{ex} or % Ex trends in accord with the K_s trends, but is inadequate as a metod to assess cation-binding ability and cation selectivity of crown ethers for di- and probably tri-valent cations.

Experimental

Material. *Crown ethers.* The ring-contracted crown ethers **1** were prepared by the method described by Kawakami *et al.*[6] Commercially available 3*m*-crown-*m* **2** (Nisso Co.) and sila crown ethers **8** (Petrarch Systems Inc.) were used without further purification. The ring-enlarged crown ethers **3**—**7** and glymes **9** were synthesized as reported previously.[3]

Metal Picrates. *Alkali metal picrates* were prepared from picric acid and the corresponding metal hydroxide as reported.[2–4]

Silver Picrate. Picric acid (4.1 g, 18 mmol) was dissolved in hot water (100 mL), to which silver oxide (2.0 g, 8.6 mmol) was added slowly and the mixture was stirred for additional 10 min at that temperature.[15] The precipitate formed upon cooling was recrystallized twice from ethanol and then once from water to give 0.6 g (20% yield) of silver picrate.

Thallium picrate was prepared from picric acid (3.4 g, 15 mmol) and thallium oxide (3.0 g, 7.1 mmol) in hot water according to the procedure described above. Recrystallization twice from water gave 2.5 g (81%) of thallium picrate.

Alkaline earth metal picrates were prepared from picric acid (4.6 g, 20 mmol) and the corresponding metal carbonate (10 mmol) in hot water according to the procedure described above.[16] Recrystallization twice from water gave 0.6 g (11%) of magnesium picrate, 0.9 g (15%) of calcium picrate, 0.9 g (14%) of strontium picrate, or 3.0 g (50%) of barium picrate. Magnesium, calcium, and strontium picrates were pentahydrates, and barium picrate was anhydrous salt.

Extraction Studies. The general procedures employed were similar to those described in previous papers.[2–4] The concentration of heavy metal picrate in the organic phase was determined from its absorption at 375 nm in a 1:1 mixture of dichloromethane and acetonitrile. The molar extinction coefficients at 375 nm of silver and thallium picrates are 18800 and 18900 $M^{-1} cm^{-1}$, respectively. The concentration of alkaline earth metal picrate in the organic phase was determined according to the procedure in the literature.[16] After the phase separation, 5 mL of the dichloromethane phase was withdrawn and evaporated to dryness, to which was added 5 mL of acetonitrile. After further dilution, if necessary, with acetonitrile, the picrate concentration in acetonitrile was determined from its absorption at 374 nm. The molar extinction coefficients at 374 nm for magnesium, calcium, strontium, and barium picrates are 29400, 29700, 29500, and 29000 $M^{-1} cm^{-1}$, respectively.

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