

# Extraction Selectivities of Crown Ethers for Alkali Metal Cations: Differences between Single-Species and Competitive Solvent Extractions

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**Separation factor values for pairs of alkali metal cations determined in competitive solvent extractions of alkali metal picrates from aqueous solutions into chloroform by a variety of benzo- and cyclohexano-group-containing crown ethers vary significantly from extrapolations based upon the results of single-species extraction experiments. For almost all of the crown ether–alkali metal cation combinations examined, the separation factor values are greater for competitive solvent extraction. In view of the unexpected results for sodium picrate extraction by dibenzo-24-crown-8, the solid-state structure of the isolated complex was determined.**

Due to their unique capabilities for the selective complexation of alkali metal cations, crown ethers (CEs) have been widely utilized for the separation of these metal ion species.<sup>1</sup> For potential practical applications, the behavior of these macrocyclic ionophores in solvent extraction from aqueous solutions containing mixtures of different alkali metal cations is important. Extraction selectivities of CEs for alkali metal cations depend on the compositions and stabilities of the complexes which they form with the metal salts in the two-phase extraction systems. In the simplest cases, when CEs bind only one metal cation per ligand molecule, their separation efficiencies may be determined by comparing the extraction constants values for different alkali metal cations. However, the composition of the alkali metal complexes formed by macrocyclic ligands may vary with the cation identity, especially when the size of the metal ion is incompatible with that of the CE cavity.<sup>2</sup> This makes comparison of the corresponding extraction constants impossible. Also, the determination of alkali metal cation extraction constants for CEs may be difficult, particularly when the ligands are mixtures of isomers that possess

different metal binding abilities, such as cyclohexano-CEs.<sup>3</sup> Therefore, the capability of a CE for separating metal ion species is most often assessed from metal ion distribution ratios determined in either single-species or competitive alkali metal salt extractions.

It has often been assumed that selectivities based upon extrapolations made from single-species extraction data will closely resemble the competitive behavior. However, dramatic selectivity changes between single-species and competitive processes have been reported for closely related metal ion transport across liquid membranes by macrocyclic ionophores.<sup>4</sup> To the best of our knowledge, comparable studies of selectivities in single-species and competitive solvent extractions of alkali metal cations by CEs have not appeared in the literature.

We now provide a systematic comparison of the separating abilities of a wide variety of 18- to 24-membered benzo- and cyclohexano-group-containing CEs **1–12** (Chart 1) in single-species and competitive extractions of alkali metal salts, mostly picrates, from aqueous solutions into chloroform. In view of the unexpected results for NaPic extractions with dibenzo-24-crown-8 (**3**), the solid-state structure of the isolated complex was determined by X-ray diffraction.

## EXPERIMENTAL SECTION

**Reagents.** Dibenzo-CEs **1–3** and dicyclohexano-CEs (mixed isomers) **5** and **6** are commercially available compounds. The known<sup>5</sup> *unsym*-dibenzo-18-crown-6 (**4**) and the polybenzo-CEs **7–10** were obtained in improved yields as will be described elsewhere.<sup>6</sup> *sym*-Tricyclohexano-18-crown-6 (**11**) and *sym*-tricyclohexano-21-crown-7 (**12**), both as mixtures of isomers, were synthesized by the procedure provided below. By a similar procedure with the reaction carried out for 20 h at 65 °C, dibenzo-21-crown-7 (**2**) was hydrogenated to give the corresponding dicyclohexano-21-crown-7 (**6**) in 97% yield, which is appreciably higher than that obtained by the reported procedure with RuO<sub>2</sub> catalyst.<sup>5</sup>

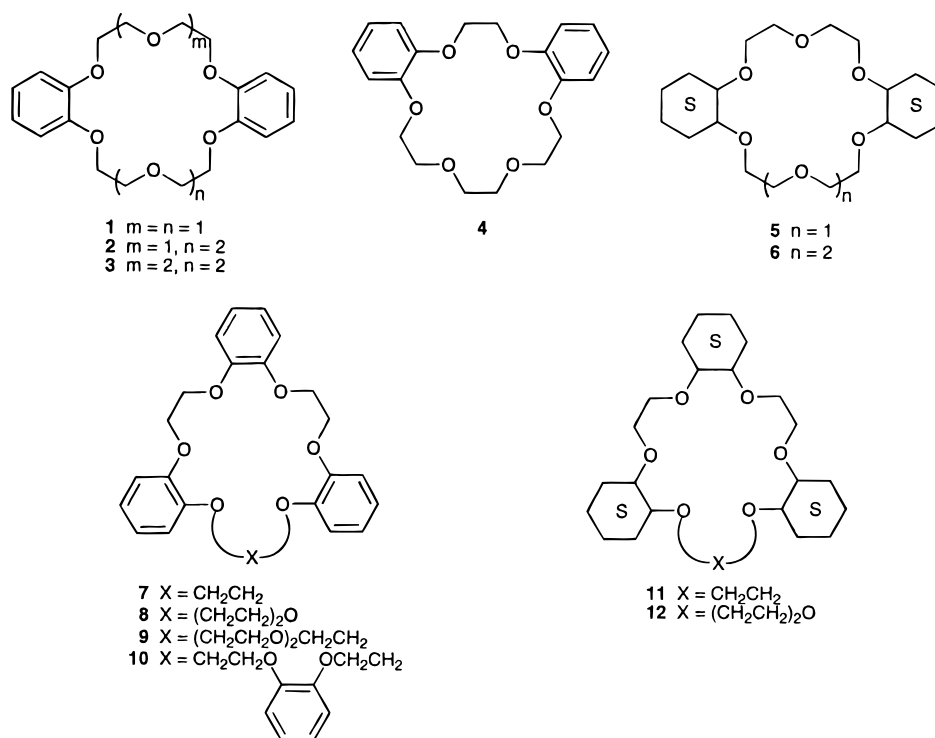
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Chart 1



**Synthesis of Tricyclohexanocrown Ethers 11 and 12.** A mixture of 4.65 mmol of the corresponding tribenzo-CE **7** or **8**, 1.00 g of 5% Rh on alumina catalyst, and 1.00 g of acetic acid in 500 mL of 1-butanol was subjected to 500–600 psi of hydrogen at 95 °C for 10 days. The reaction mixture was filtered and evaporated in vacuo. The residue was chromatographed on a short alumina column with EtOAc as eluent to afford the desired product as a colorless oil. Compound **11** was produced in 96% yield.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  0.90 (s, 1H), 1.07–2.10 (m, 24H), 3.35–4.00 (m, 18H). IR (film): 3470 ( $\text{H}_2\text{O}$ ), 1101 (C–O)  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{24}\text{H}_{42}\text{O}_6 \cdot 0.4\text{H}_2\text{O}$ : C, 66.45; H, 9.94. Found: C, 66.46; H, 9.76. Compound **12** was obtained in 99% yield.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  1.08–2.10 (m, 24H), 2.20 (s, 2H,  $\text{H}_2\text{O}$ ), 3.45–3.90 (m, 16H). IR (film): 3492 ( $\text{H}_2\text{O}$ ), 1102 (C–O)  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{26}\text{H}_{46}\text{O}_7 \cdot \text{H}_2\text{O}$ : C, 63.91; H, 9.90. Found: C, 63.92; H, 9.73.

**Synthesis of NaPic-3.** A 0.030 M solution of **3** in  $\text{CHCl}_3$  was stirred magnetically with an excess of solid NaPic for 24 h. The mixture was filtered, and the separated solid was washed on the filter with boiling  $\text{CHCl}_3$ . The combined  $\text{CHCl}_3$  filtrate and washing were evaporated in vacuo, and the resultant solid was recrystallized from  $\text{CH}_2\text{Cl}_2$ – $\text{CH}_3\text{OH}$  (5:1).

**Procedure for Single-Species Solvent Extraction of Alkali Metal Salts with CEs 1–12.** Single-species alkali metal picrate extraction was conducted with 2.00 mL of an aqueous solution containing 5.00 mM alkali metal picrate and 50.0 mM of the corresponding alkali metal chloride as a spike and 2.00 mL of a 5.00 mM  $\text{CHCl}_3$  solution of the CE in a 15-mL, metal-free plastic centrifuge tube. The tube was agitated for 4 min with a vortex mixer and centrifuged for 4 min to ensure complete phase separation. After back-extraction from the separated  $\text{CHCl}_3$  layer into deionized  $\text{H}_2\text{O}$  (at least three consecutive stripping treatments were performed to ensure the completeness of back-extraction), the metal cation concentration in the combined aqueous stripping

solutions was determined by ion chromatography with a Dionex DX-120 ion chromatograph. Three independent extraction experiments were conducted for each combination of CE and alkali metal salt.

When KPic was extracted with **7**, precipitation of the extraction complex was observed in the organic phase. Similarly, precipitates formed in the single-species extractions of RbPic and CsPic with **10**.

For a single-species alkali metal iodide extraction experiment, 2.00 mL of an aqueous solution containing 0.50 M alkali metal iodide and 2.00 mL of a 10.0 mM solution of the CE in  $\text{CHCl}_3$  were utilized. Other aspects of the extraction, back-extraction, and determination of the alkali metal cation concentrations in the stripping solution were the same as described above.

**Procedure for Competitive Solvent Extraction of Alkali Metal Salts with CEs 1–12.** Competitive alkali metal picrate extraction was conducted with 2.00 mL of an aqueous solution containing lithium, sodium, potassium, rubidium, and cesium picrates (1.00 mM in each, and 10.0 mM in each chloride as a spike) and 2.00 mL of a 1.00 mM  $\text{CHCl}_3$  solution of the CE. Extraction, back-extraction, and determination of the alkali metal cation concentrations in the stripping solution were performed in the same manner as given above for single-species extractions of alkali metal picrates.

After the competitive alkali metal picrate extractions with **7** and **10** were completed and the initial organic and aqueous phases separated, yellow precipitates formed in the organic layers. The precipitates were filtered, washed with  $\text{CHCl}_3$ , and dried in vacuo. Samples of each solid were boiled in a small amount of concentrated  $\text{HNO}_3$ . The resultant solutions were diluted with deionized  $\text{H}_2\text{O}$ , and the alkali metal cation concentrations were determined by ion chromatography. The precipitate obtained from the competitive alkali metal picrate extraction with **7** was found to

contain only  $K^+$ , and that obtained with **10** contained  $Cs^+$  and  $Rb^+$  in a 3.5:1 ratio.

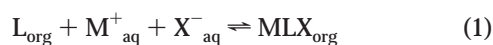
Competitive alkali metal iodide extraction was performed with 2.00 mL of an aqueous solution which was 0.50 M in each of the alkali metal iodides and 2.00 mL of a 10.0 mM solution of the CE in  $CHCl_3$ . Extraction, stripping, and determination of the alkali metal cation concentrations in the stripping solution were performed in the same manner as given above for single-species extractions of alkali metal iodides.

Relative to the other alkali metal cations, the amounts of extracted  $Li^+$  were too small for accurate determination of separation factors involving  $Li^+$  in the competitive extractions of alkali metal picrates and iodides.

**X-ray Data Collection, Structure Determination, and Refinement.** A yellow single crystal obtained by slow air evaporation of a  $CH_2Cl_2$ – $CH_3OH$  solution of NaPic-**3** was mounted on a fiber and transferred to the goniometer of a Siemens CCD area detector-equipped platform diffractometer. A stream of cold nitrogen gas was used to cool the crystal to  $-100\text{ }^\circ\text{C}$  during data collection. The data collection, reduction, absorption correction, and structure solution and refinement were carried out with the Siemens software products SMART, SAINT, SADABS, and SHELXTL, respectively. Unit cell data were determined by a global refinement of several thousand reflections within the data collection range. The space group was determined using systematic absences and subsequent solution and successful refinement of the structure (to distinguish between centric and acentric choices). Refinement was full-matrix, least-squares of  $F^2$ . A summary of data collection parameters is given in Table 1S in the Supporting Information.

## RESULTS AND DISCUSSION

**Extraction Equilibria and Separation Factors for Single-Species and Competitive Extraction of Alkali Metal Salts with CEs.** Interaction of a CE with an alkali metal salt in a two-phase solvent extraction system to form a 1:1 metal ion-to-ligand complex is represented by eq 1,



where the subscripts org and aq refer to the organic and aqueous phases, respectively. The equilibrium constant for this reaction (the extraction constant,  $K_{\text{ex}}$ ) is given by eq 2,

$$K_{\text{ex}} = [MLX]_{\text{org}} / [L]_{\text{org}} [M^+]_{\text{aq}} [X^-]_{\text{aq}} \quad (2)$$

where  $[MLX]_{\text{org}}$ ,  $[L]_{\text{org}}$ ,  $[M^+]_{\text{aq}}$ , and  $[X^-]_{\text{aq}}$  are the equilibrium concentrations of the indicated species in the organic and aqueous solutions. The distribution ratio,  $D_M$ , of the metal salt between the organic and aqueous phases is given by eq 3.

$$D_M = [MLX]_{\text{org}} / [M^+]_{\text{aq}} \quad (3)$$

From single-species extractions performed for two different alkali metal cations under the same conditions (i.e., the same ligand and anion and the same total concentrations of the ligand and metal salt), the separation factor,  $(\alpha_{M_1, M_2})_{\text{single}}$ , of the CE for

$M_1^+$  over  $M_2^+$  is determined as a ratio of  $D_{M_1}$  and  $D_{M_2}$ , as described by the equation,

$$(\alpha_{M_1, M_2})_{\text{single}} = D_{M_1} / D_{M_2} = K_{\text{ex } 1} [L]_{\text{org } 1} / K_{\text{ex } 2} [L]_{\text{org } 2} \quad (4)$$

where  $K_{\text{ex } 1}$  and  $K_{\text{ex } 2}$  are extraction constants and  $[L]_{\text{org } 1}$  and  $[L]_{\text{org } 2}$  are the equilibrium CE concentrations in the organic phases for the extractions of  $M_1X$  and  $M_2X$ , respectively.

For competitive extraction of  $M_1X$  and  $M_2X$  under the same conditions, the equilibrium CE concentration is determined by both complexation reactions. Therefore,  $[L]_{\text{org } 1} = [L]_{\text{org } 2} = [L]_{\text{org}}$ , and eq 4 converts into

$$(\alpha_{M_1, M_2})_{\text{comp}} = K_{\text{ex } 1} / K_{\text{ex } 2} \quad (5)$$

From comparison of eqs 4 and 5, it follows that separation factors determined by single-species and competitive extractions of alkali metal salts by a CE will differ, except for the special case in single-ion extractions when  $[L]_{\text{org } 1} = [L]_{\text{org } 2}$ , which requires that  $K_{\text{ex } 1} = K_{\text{ex } 2}$ . Otherwise, the greater the difference between  $K_{\text{ex } 1}$  and  $K_{\text{ex } 2}$ , the greater will be the difference between the CE selectivity factors in single-species and competitive extractions because  $[L]_{\text{org } 1}$  will not be equal to  $[L]_{\text{org } 2}$ . Under competition conditions, extraction of the metal ion which forms the most stable complex with the CE into the organic phase should suppress extraction of the other metal ion species. If so, the  $(\alpha_{M_1, M_2})_{\text{comp}}$  value will be larger than the corresponding  $(\alpha_{M_1, M_2})_{\text{single}}$  value.

In the treatment provided above, we have taken into consideration only the simplest (and most commonly encountered) case in which 1:1 metal ion-to-ligand extraction complex stoichiometries are involved. If the stoichiometry of the extraction complex varies as the alkali metal cation is changed, separation factors for single-species and competitive extractions will have more complicated relationships which will not be discussed further here.

**Selectivities of CEs 1–12 for Alkali Metal Picrates in Single-Species and Competitive Solvent Extractions.** To probe the potential differences in selectivities for single-species and competitive solvent extractions of alkali metal cations by a CE, we have performed solvent extractions of five alkali metal picrates (LiPic, NaPic, KPic, RbPic, and CsPic) present in aqueous solution individually and as an equimolar mixture into chloroform with CEs **1–12**. Values of the separation factors,  $\alpha_{M_1, M_2}$ , calculated for pairs of alkali metal cations as  $D_{M_1} / D_{M_2}$  are presented in Tables 1–3 for substituted 18-crown-6, 21-crown-7, and 24-crown-8 compounds, respectively.

The data contained in Tables 1–3 unequivocally demonstrate that, for all of the CEs examined, the selectivities determined from the single-species and competitive extraction experiments are different, regardless of the cavity size, the number of oxygens in the macrocyclic ring, and the type of substituents. In almost every case, competitive extraction from the mixture of alkali metal picrates provides more selective metal ion separation by the CE than would be predicted from the results of single-species extractions, i.e.,  $(\alpha_{M_1, M_2})_{\text{comp}} > (\alpha_{M_1, M_2})_{\text{single}}$ . The most impressive example is the increase of  $K^+$  selectivity over the other alkali metal cations on going from single-species to competitive alkali metal picrate extraction for the two cyclohexano-group-containing, 18-membered CE extractants, *sym*-dicyclohexano-18-crown-6 (**5**) and

Table 1. Separation Factor Values Determined for Pairs of Alkali Metal Cations in Single-Species and Competitive Extraction of Alkali Metal Picrates from Aqueous Solution into Chloroform with 18-Membered Benzo- and Cyclohexano-Group-Containing CEs

CE	extraction type	$\alpha_{K,M}$			
		M = Li	M = Na	M = Rb	M = Cs
1	single-species	68	17	1.5	3.4
	competitive	<i>a</i>	43	3.2	13
4	single-species	25	6.4	1.5	2.3
	competitive	<i>a</i>	27	3.9	8.5
5	single-species	60	3.0	1.2	1.7
	competitive	<i>a</i>	84	4.3	25
7	single-species	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>
	competitive	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>
11	single-species	10	2.1	1.1	1.4
	competitive	<i>a</i>	22	3.6	22

<sup>a</sup> The separation factor could not be determined accurately due to negligible LiPic extraction. <sup>b</sup> The selectivity factor could not be determined accurately due to precipitation of the KPic-7 complex in the organic phase.

Table 2. Separation Factor Values Determined for Pairs of Alkali Metal Cations in Single-Species and Competitive Extraction of Alkali Metal Picrates from Aqueous Solution into Chloroform with 21-Membered Benzo- and Cyclohexano-Group-Containing CEs

CE	extraction type	$\alpha_{Rb,M}$			
		M = Li	M = Na	M = K	M = Cs
2	single-species	14	13	1.5	1.0
	competitive	<i>a</i>	14	2.4	0.9
6	single-species	72	3.2	1.3	1.0
	competitive	<i>a</i>	11	1.5	1.0
8	single-species	>100	66	1.2	1.6
	competitive	<i>a</i>	31	1.5	3.3
12	single-species	14	3.0	1.3	1.0
	competitive	<i>a</i>	4.8	1.2	1.2

<sup>a</sup> The separation factor could not be determined accurately due to negligible LiPic extraction.

*sym*-tricyclohexano-18-crown-6 (11) (Table 1). For 5, the  $\alpha_{K,Na}$ ,  $\alpha_{K,Rb}$ , and  $\alpha_{K,Cs}$  values determined for competitive extraction are 28, 3.6, and 15 times greater, respectively, than those calculated from the results of single-species extraction experiments. Similarly, the separation factors for KPic over NaPic, RbPic, and CsPic determined for 11 increase 10, 3.3, and 16 times, respectively, on going from single-species to competitive extraction. It should also be noted that, even though the single-species experiments gave appreciable extraction of LiPic for CEs 1–12, the levels of LiPic transferred into the organic phases for competitive extractions of the five alkali metal picrates were too small for ( $\alpha_{M,Li}$ )<sub>comp</sub> values to be determined accurately.

It has been shown that the identity of the anion may influence the selectivity for alkali metal cation extraction by CEs.<sup>7</sup> To determine if the anion identity is a causative factor for the difference between the selectivity of single-species and competitive extractions, we compared the results from single-species versus competitive extraction of alkali metal picrates with tricyclohexano-

Table 3. Separation Factor Values Determined for Pairs of Alkali Metal Cations in Single-Species and Competitive Extraction of Alkali Metal Picrates from Aqueous Solution into Chloroform with 24-Membered Benzo- and Cyclohexano-Group-Containing CEs

CE	extraction type	$\alpha_{Cs,M}$			
		M = Li	M = Na	M = K	M = Rb
3	single-species	72	14	2.2	1.2
	competitive	<i>a</i>	9.2	3.5	2.4
9	single-species	26	12	1.5	1.0
	competitive	<i>a</i>	29	6.1	2.8
10	single-species	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>
	competitive	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>

<sup>a</sup> The separation factor could not be determined accurately due to negligible LiPic extraction. <sup>b</sup> The selectivity factors could not be determined accurately due to precipitation of CsPic-10 and RbPic-10 complexes in the organic phase.

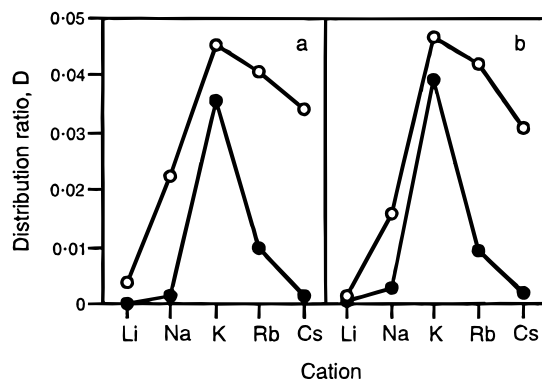


Figure 1. Variation of the alkali metal ion distribution ratios for single-species (○) and competitive (●) extractions of alkali metal a) picrates and b) iodides into chloroform by tricyclohexano-18-crown-6 (11).

18-crown-6 (11) with the corresponding data for the solvent extraction of alkali metal iodides by the same CE. Distribution ratios of alkali metal ions for extractions of alkali metal picrates and iodides by 11 are presented in Figure 1. From the graphs, it can be seen that the changes in K<sup>+</sup> selectivity for this CE in single-species and competitive solvent extraction are nearly identical for alkali metal picrates and iodides.

Of the variety of CE–alkali metal picrate extraction systems examined, only two exhibited decreases in the separation factor value on going from single-species to competitive solvent extraction. Both exceptions are observed for the large cavity size CEs in their separations of the larger alkali metal cations, Rb<sup>+</sup> and Cs<sup>+</sup>, from Na<sup>+</sup>. Thus, for *sym*-dibenzo-24-crown-8 (3), lower selectivity for Cs<sup>+</sup> over Na<sup>+</sup> is noted for competitive extraction of alkali metal picrates than that calculated from the results of the corresponding single-ion extraction experiments (Table 3). Similar behavior is observed with the tribenzo-21-crown-7 8, for which the  $\alpha_{Rb,Na}$  value is lower in competitive alkali metal picrate extraction (Table 2). In contrast, the  $\alpha_{Cs,K}$  and  $\alpha_{Cs,Rb}$  values for 3 and the  $\alpha_{Rb,K}$  and  $\alpha_{Rb,Cs}$  values for 8 follow the general tendency to increase on going from single-species to competitive extraction of alkali metal picrates.

It is suggested that the decrease in the  $\alpha_{Cs,Na}$  and  $\alpha_{Rb,Na}$  values for 3 and 8, respectively, when the single-species extractions results are compared with competitive alkali metal picrate extrac-

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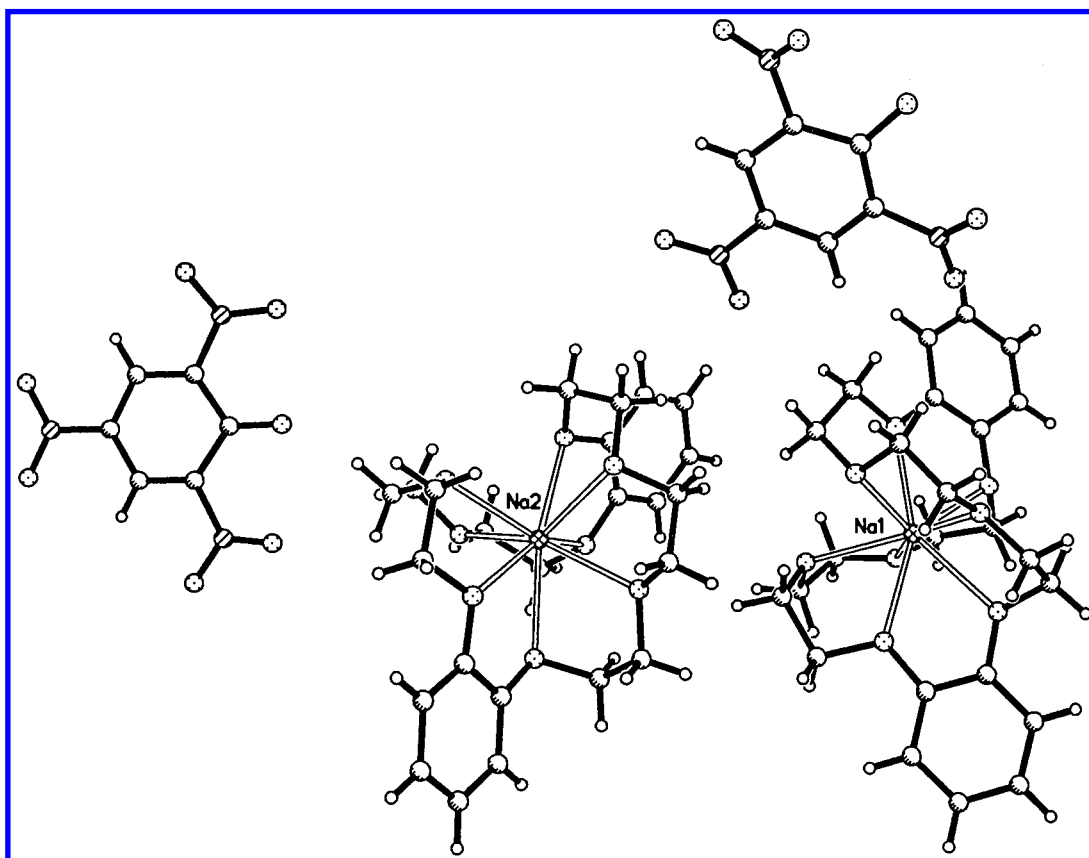


Figure 2. Crystal structure of the NaPic complex of dibenzo-24-crown-8 (**3**).

tions may result from a change of the NaPic extraction complex stoichiometry due to differing conditions for the complexation process. For single-species extraction of NaPic from aqueous solution into  $\text{CH}_2\text{Cl}_2$  by **3**, the data indicate the presence of complexes with different stoichiometries with a preference for the 2:1 metal ion-to-ligand complex.<sup>8</sup> Also, for sodium salts with inorganic anions, **3** exhibits a dual-mode behavior by coordinating either one or two  $\text{Na}^+$  per CE molecule in the complex.<sup>9</sup> To gain better insight into the stoichiometry expected for complexation of  $\text{Na}^+$  by **3**, the solid-state structure of NaPic-**3** was determined by X-ray diffraction. In this structure (Figure 2), coordination of one  $\text{Na}^+$  per ligand is clearly evident. It is interesting to note that the crystal structure of this complex is quite different from that reported for the sodium 2-nitrophenolate complex with **3**, in which two  $\text{Na}^+$  are encapsulated within the crown ether cavity, with the anion bridging the pair of cations.<sup>9,10</sup> These results demonstrate that, under differing conditions, either one or two  $\text{Na}^+$  may be complexed within the cavity of **3**.

Under the conditions for single-species extraction of NaPic by **3**, in which the initial concentrations of the NaPic and CE are comparable, formation of a 1:1 ligand-to-metal ion complex may be anticipated. However, when the same CE interacts with all five of the alkali metal picrates present in the aqueous solution, there is a deficiency of the ligand compared to the NaPic concentration, and the probability for formation of a complex involving two  $\text{Na}^+$  per molecule of extractant may increase. Thus, we suggest that a

change of the extraction complex stoichiometry from 1:1 to 1:2 may be responsible for the observed decrease of the  $\alpha_{\text{Cs,Na}}$  value for **3** on going from single-species to competitive alkali metal picrate extraction.

A similar situation may be responsible for the anomalous selectivity behavior of **8**, even though no literature data are available which indicate that **8** may bind two  $\text{Na}^+$  per CE molecule.

For two of the CEs, *sym*-tribenzo-18-crown-6 (**7**) and *sym*-tetrabenzo-24-crown-8 (**10**), determination of the separation factors was impossible for both single-species and competitive extractions of alkali metal picrates due to precipitation of the complexes from the organic phase (see Experimental Section). With **7**, selective precipitation of the KPic complex is observed. In single-species extractions with **10**, precipitates were formed for both RbPic and CsPic. The solid which was separated from the organic phase after competitive alkali metal picrate extraction with **10** contained only  $\text{Cs}^+$  and  $\text{Rb}^+$  (3.5:1).

**Crystal Structure of NaPic-3.** Crystallographic parameters for the complex of dibenzo-24-crown-8 (**3**) with NaPic are summarized in Table 1. In the two similar, but crystallographically distinct 1:1 complex species, the large-ring, flexible ligand completely encapsulates  $\text{Na}^+$ , as shown in Figure 2. The cavity formed by the eight ring oxygen atoms of **3** is highly distorted and three-dimensional. The eight coordination sites of  $\text{Na}^+$  are occupied by CE oxygen atoms, which does not permit association of the  $\text{Pic}^-$  in the primary coordination sphere. The  $\text{Pic}^-$  anions stack face-to-face in the unit cell (see Supporting Information). A more detailed discussion of the structure of the NaPic-**3** complex is provided in the Supporting Information.

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The flexible crown ether **3** coordinates Na<sup>+</sup> in two ways. The two unique crown ether molecules in the structure adopt different geometries, and, indeed, each unique Na<sup>+</sup> exists in a different eight-coordinate geometry. These results support the argument that **3** can extract Na<sup>+</sup> in either a 1:1 or 2:1 metal ion-to-ligand stoichiometry.

## CONCLUSIONS

Systematic comparison of separation factor values determined for the series of CEs **1–12** in single-species and competitive solvent extractions of alkali metal picrates show that these values may be significantly different. In most cases, higher selectivity is obtained in competitive extractions than for selectivities calculated from the results of single-species extractions. Replacement of alkali metal picrates with iodides demonstrated that the anion identity is not responsible for the observed selectivity differences for CEs in single-species and competitive alkali metal salt extractions.

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## SUPPORTING INFORMATION AVAILABLE

Ball-and-stick representations and atom numbering schemes for molecules A and B and the unit cell; Tables summarizing crystallographic parameters, atomic coordinates and equivalent displacement parameters, torsion angles, bond lengths and angles, anisotropic displacement parameters, and hydrogen coordinates and isotropic displacement parameters; and a further discussion of the solid-state structure of the NaPic-**3** complex (19 pages). See any current masthead page for ordering information.

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