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A Surprising Host−Guest Relationship between 1,2-Dichloroethane and the Cesium Complex of Tetrabenzo-24-crown-8

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Abstract: The structure of the complex [Cs(tetrabenzo-24-crown-8)(1,2-dichloroethane)$_2$](NO$_3$)·H$_2$O was shown by X-ray crystallography to involve an unprecedented bidentate coordination of two 1,2-dichloroethane solvent molecules to the Cs$^+$ cation via the four chlorine atoms. The coordination of the solvent molecules occurs within two clefts between facing benzo groups, one pair of benzo groups related to the other pair by an improper noncrystallographic 90° rotation. Resembling the seam on a tennis ball, the crown ether envelops the metal cation within a cagelike arrangement of eight crown ether oxygen atoms. Good geometric and electronic complementarity characterizes the apparent host−guest relationship between the cleft environment and the solvent molecules. The complete encapsulation of the cation by the crown ether and two solvent molecules explains well the speciation behavior observed in liquid−liquid extraction of CsNO$_3$ or CsClO$_4$ from aqueous solution to 1,2-dichloroethane solutions of the alkylated analogues 4,4″- or 4,5″-bis(*tert*-octylbenzo)dibenzo-24-crown-8. In the extraction process studied at 25 °C, simple 1:1 metal/crown complexes form in the solvent phase, as modeled by the program SXLSQI. The complex cation and counteranion are present both as ion-pairs, postulated to be ligand-separated ion-pairs as suggested by the crystal structure, and as dissociated ions. In agreement with a theoretical treatment of ion-pairing, the ion-pairs possess unusually low stability and exhibit no discrimination between the anions, largely ascribed to the large effective radius of the complex metal cation. Values of log K_f corresponding to the formation of the complex cations Cs[bis(*tert*-octylbenzo)-dibenzo-24-crown-8]$^+$ in 1,2-dichloroethane at 25 °C average 10.5 ± 0.2 for both positional isomers of the crown ether and for their 3:2 mixture. Overall, these results provide insight into the role of clefts as host environments for inclusion of neutral molecules and show how even solvent molecules with exceptionally weak donor−acceptor properties may participate in supramolecular assemblies. In addition, the results are unique in enabling a clear assessment of the effect of the encapsulation of the metal cation on the ion-pairing tendency of the metal complex and implications for anion selectivity.

Introduction

The focus of attention in research on crown ethers, cryptands, and calixarenes has traditionally been directed toward the relationship between the structure of the host molecule and its ability to bind and transport guest species, especially metal cations.[1−5] Major fundamental questions have dealt with the influence of substituent groups on conformational strain and how the resulting strain ultimately relates to selectivity and binding strength.[4] Less appreciated is the relationship between the function of the macrocycle and interactions of the complex with solvent molecules and counteranions.[3,6−8] As amply shown by the crystallographic record, the typical case entails a crown molecule incompletely saturating the coordination sphere of the metal cation, leaving room for additional coordination by solvent molecules, anions, or other crown molecules.[8−14] As is common

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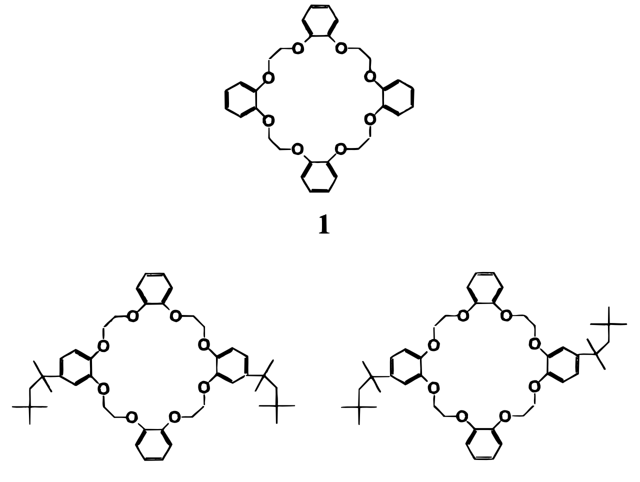

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$\mathbf{2}_{4,4'}$ $\mathbf{2}_{4,5'}$

Figure 1. Crown ethers used in this work: tetrabenzo-24-crown-8 (**1**), 4,4″-bis(*tert*-octylbenzo)dibenzo-24-crown-8 ($\mathbf{2}_{4,4''}$), and 4,5″-bis(*tert*-octylbenzo)dibenzo-24-crown-8 ($\mathbf{2}_{4,5''}$).

for alkali and alkaline earth cations, the interaction of the additional ligands with the cation tends to be electrostatically based (hard−hard), and oxygen atoms represent the most common donor.[8−11] Occasionally, the space occupied by the solvent molecule or anion is sufficiently well defined as to suggest a host−guest relationship.[11,14,15] Approaches to the enhancement of such a host−guest relationship have been reported for the case wherein the metal cation is fairly electropositive or has some tendency toward covalency in its interaction with donor molecules.[16] Such complex hosts offer clefts and cavities for the guest species based upon strong donor−acceptor interactions, and the cation is generally not readily dissociable from its primary ligand.

We recently reported that the crystalline cesium complex of tetrabenzo-24-crown-8 (**1**) (Figure 1) features a cagelike arrangement of the eight oxygen donor atoms of the crown ether about the Cs^+ ion, where the connectivity of these oxygen atoms follows the pattern of the seam on a tennis ball.[14] This structure orients opposing pairs of benzo groups so as to create two clefts large enough to host *p*-dioxane molecules. At one side of each cleft resides the charge-diffuse Cs^+ ion, which may be easily dissociated or replaced with another metal ion (e.g., Rb^+ ion). The intriguing question arises as to the nature of the clefts in the complex $[Cs(\mathbf{1})]^+$ and how the features of this host environment contribute to the overall stability of the supramolecular assembly of cation, crown, and guests residing in the clefts. In this regard, the structures of the cleft sites may be expected to depend on the particular metal ion bound by the crown ether, implying a degree of allosteric control over the affinity and selectivity of the clefts for guest species. In turn, the guest species occupying the clefts may be expected to influence the affinity and selectivity of the crown ether in the complexation and transport of metal cations.

We have now structurally characterized a crystalline complex of tetrabenzo-24-crown-8 (**1**) that exhibits unprecedented metal−solvent interactions between Cs^+ ion and 1,2-dichloroethane (1,2-DCE). The apparent inclusion of 1,2-DCE molecules within the clefts affords a unique opportunity to gain insight into the above questions as well as into the nature of solvation by molecules possessing weak solvation properties. With sufficient polarity ($\epsilon = 10.4$)[17] to dissolve some electrolytes, 1,2-DCE is a widely used solvent in electrochemistry, liquid−liquid extraction chemistry, organic synthesis, and physical solution chemistry, where it is taken to be a model "noncoordinating" solvent. Having zero donor number and zero Kamlet−Taft H-bond acceptor and donor parameters, 1,2-DCE possesses at best feeble donor−acceptor properties.[17] Not surprisingly, no crystallographic examples of coordination of 1,2-DCE and other halocarbons such as chloroform and dichloromethane to alkali and alkaline earth metals have been reported. Nevertheless, solvation of the alkali metals by such solvents is significant, judging by the available thermodynamic and physical data.[18] Accordingly, theoretical models of ion solvation have for decades assumed that neighboring solvent molecules around a solute ion must possess a degree of immobilization in order to account for observed non-Bornian solvation thermodynamic properties.[19] In the case of chloroform[20] and 1,2-DCE,[21] molecular dynamics calculations for selected alkali metal ions support this view. Crystal structures showing coordination of halocarbons,[22] in particular 1,2-DCE,[23,24] 1,2,3-trichloropropane,[25] and dichloromethane[26] molecules, to transition and post-transition metals provide definitive evidence for the ability of these solvent molecules to function as ligands.

The present crystallographic study is essential in understanding how the structure of the supramolecular assembly of **1**, Cs^+ ion, and two 1,2-DCE molecules observed in the solid-state translates into identifiable consequences in solution behavior. In our own studies of liquid−liquid systems,[27−32] 1,2-DCE has

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been an ideal water-immiscible solvent in that its mild polarity supports partial dissociation of univalent ion-pairs. This enables convenient analysis of the interaction of anions with metal−ion complexes, an aspect of extraction behavior that has been poorly understood.[3] In the specific case reported here, the clefts capture 1,2-DCE molecules as seemingly unlikely guests, remarkably to the exclusion of the counteranion. Experiments were therefore designed to elucidate speciation and ion-pairing effects in the extraction of two salts, cesium nitrate and perchlorate, by **1**. Owing to the limited solubility of **1** in 1,2-DCE, however, it was necessary to employ an alkylated analogue, bis(*tert*-octylbenzo)dibenzo-24-crown-8 (**2**), which was prepared as pure 4,4″ ($\mathbf{2}_{4,4''}$) and 4,5″ ($\mathbf{2}_{4,5''}$) isomers (Figure 1). The alkylated derivatives made it possible to collect sufficient cesium distribution data at 25 °C to permit equilibrium modeling, yielding the predominant species and the corresponding extraction constants corrected to infinite dilution. This then allowed the calculation of the constants for binding of Cs^+ ion by both isomers of **2** in homogeneous 1,2-DCE solution and for ion-pairing of the complex cations with the two anions. Finally, a theoretical model for ion-pairing was shown to correlate the organic phase dissociation constants with the interionic distances obtained from the crystal structure, supporting the proposition that, in solution, 1,2-DCE occupies the clefts in preference to the anion, as it does in the solid state.

Experimental Section

Materials. All chemicals were used as supplied. Tetrabenzo-24-crown-8 (**1**) was prepared using a literature method.[33] Bis(*tert*-octylbenzo)dibenzo-24-crown-8 (**2**) was prepared as a mixture of 4,4″ and 4,5″ positional isomers ($\mathbf{2}_{4,4''}$ and $\mathbf{2}_{4,5''}$, respectively) as described previously.[28] The isomers $\mathbf{2}_{4,4''}$ and $\mathbf{2}_{4,5''}$ were separated by column chromatography followed by fractional crystallization from acetone. The cesium nitrate and cesium perchlorate (Johnson Matthey, 99.9%) salts were dried at 110 °C for at least 48 h before use. HPLC grade 1,2-dichloroethane (Sigma-Aldrich) was purified by passage through activated alumina followed by distillation. The radiotracer ^{137}Cs was received as $^{137}CsCl$ in 1 M HCl (Amersham) and converted to a neutral aqueous solution of $^{137}CsNO_3$ by ion exchange as described previously.[31] Aqueous solutions were prepared using distilled deionized water.

X-ray Structure Determination for [Cs(tetrabenzo-24-crown-8)-(1,2-DCE)$_2$](NO$_3$)·H$_2$O (3). Crystals were prepared by adding 21 mg (0.11 mmol) of $CsNO_3$ in 0.22 mL of H_2O to 60 mg (0.11 mmol) of tetrabenzo-24-crown-8 in 10 mL of 1,2-DCE/MeOH (5:1) and allowing the mixed solvent to slowly evaporate. A clear plate, measuring $0.29 \times 0.36 \times 0.61$ mm^3, was mounted on a glass fiber. Data were obtained at −100 °C using a Nonius CAD4 diffractometer. A total of 11 004 reflections were collected ($2\theta \le 54°$, $+h, \pm k, \pm l$; $2\theta \le 30°$, $-h, \pm k, \pm l$). The data were averaged over $\bar{1}$ symmetry ($R_{int} = 3.1\%$). Both 1,2-DCE ligands are disordered and are modeled over two sites, nearly superposed. Additionally, two oxygen atoms on the nitrate ion are disordered over two sites, and a lattice water molecule is apparently disordered over five sites. All nitrate N−O bonds and O···O 1,3-distances are restrained to be approximately equal with chemically equivalent distances. Each nitrate orientation is also restrained to be planar. The thermal ellipsoids of atoms in disordered molecules refine with unusual elongation, possibly due to unresolved disorder. As a result, the oxygen atoms on the lattice water molecule, the minor components of the disordered 1,2-DCE ligands, and C36 were refined isotropically. All other atoms associated with disordered groups were restrained to have U_{ij} values similar to those of atoms bound to them, or atoms within 0.7 Å. Each H atom was placed in a calculated position, refined using a riding model, and given an isotropic displacement parameter equal to 1.2 times the equivalent isotropic displacement parameter of the atom to which it is attached. Calculations were carried out using XCAD4[34] (data reduction), SHELXTL[35] (structure solution/refinement, and molecular graphics), and PLATON[36] (structure analysis). A summary of crystallographic data is given in Table 1, and selected bond lengths and angles are given in Table 2. Complete tabulations of crystallographic data are available as Supporting Information.

Table 1. Summary of Crystallographic Data for **3**

chemical formula	$C_{36}H_{42}Cl_4CsNO_{12}$
a, Å	13.355(3)
b, Å	13.465(3)
c, Å	13.642(4)
α, deg	90.67(2)
β, deg	104.65(2)
γ, deg	117.44(2)
V, Å^3	2082.9(8)
Z	2
formula weight	955.4
space group	$P\bar{1}$ (No. 2)
T, °C	−100
λ, Å	0.710 73
ρ_{calcd}, g cm^{-3}	1.52
μ, cm^{-1}	12.0
R^a	0.061
w$R2^b$	0.182

[a] $R = (\sum||F_o| - |F_c||)/\sum|F_o|)$, based on $F_o^2 > 2\sigma F_o^2$. [b] $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum w(F_o^2)^2\}^{1/2}$.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for **3**

Cs−O$_{crown}$ (range)	3.245(4)−3.375(4)
Cs−O$_{crown}$ (average)^a	3.29(5)
Cs−centroid(O$_{crown}$)^c	0.13
Cs−Cl (range)^b	3.456(3)−3.638(5)
Cs−Cl (average)^{a,b}	3.55(6)
Cl1−Cs−Cl2^b	57.6(1)
Cl3−Cs−Cl4^b	57.0(3)
O−C$\overset{...}{-}$C−O (range)^d	0.1(7)−1.0(7)
O−CH$_2$−CH$_2$−O (range)^d	69.0(6)−70.9(5)

[a] Uncertainties quoted for averaged bond lengths are *σ* values based on statistical distributions. [b] Only values for the major disorder components are presented. [c] The calculated centroid of the eight ether oxygen atoms. [d] Absolute values of torsion angles are presented.

Procedures. For the extraction experiments, bis(*tert*-octylbenzo)-dibenzo-24-crown-8 (**2**) as mixed or pure isomers was used. Equal volumes (0.5−0.75 mL each) of organic phase (solution of crown ether in 1,2-DCE) and aqueous phase (aqueous solution of $CsNO_3$ or $CsClO_4$ spiked with ^{137}Cs tracer) were equilibrated in 2-mL vials by repeated inversion on a Glass-Col laboratory rotator in a thermostated air box at 25 ± 0.2 °C for 2 h. Subsequently, the samples were centrifuged at 4000 rpm for 5 min. To determine the Cs^+ ion distribution ratio, a fraction of each phase was removed and the activity of ^{137}Cs measured by *γ* radiometric techniques. In general, experiments entailed variation of crown ether concentration at fixed initial aqueous salt concentration or variation of the aqueous salt concentration at fixed crown ether concentration. For the $CsNO_3/\mathbf{2}_{4,5''}$ system, 58 data points were collected in the following ranges: 5×10^{-5} M $\le [\mathbf{2}_{4,5''}]_{initial} \le 0.1$ M and $1 \times 10^{-4} \le [CsNO_3]_{initial} \le 0.933$ M. For the $CsClO_4/\mathbf{2}_{4,5''}$ system, 48 data points were collected in the following ranges: 4×10^{-5} M $\le [\mathbf{2}_{4,5''}]_{initial}$

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$\leq$ 0.1 M and $2 \times 10^{-5} \leq [\mathrm{CsClO_4}]_{\mathrm{initial}} \leq 0.0653$ M. Less extensive data sets of 18−20 data points were subsequently collected for systems involving the $\mathbf{2}_{4,4''}$ isomer or mixed isomers, in which the initial cesium salt concentration was varied at fixed crown ether concentration. Duplicate experiments were performed for every data point. For proper weighting of the data in SXLSQI modeling (see below), experimental precision for each data point was estimated from a combination of replicate determinations, volumetric error, and counting precision. From these considerations, the precision was taken to be constant at ±3% for most of the data points, unless either counting statistics or agreement between duplicates dictated assignment of greater precision error up to ±15%. The largest error was obtained when organic-phase total cesium concentration fell below ca. 3×10^{-7} M.

Analysis. The cesium distribution from aqueous solutions to 1,2-DCE phase was determined by γ counting techniques (^{137}Cs tracer) using a 3″ NaI(Tl) crystal through-hole type detector (Packard Cobra Quantum model 5003). Cesium distribution ratios D_{Cs} were defined as the ratio of total organic- and aqueous-phase Cs concentrations $[\mathrm{Cs}]_{\mathrm{org}}/[\mathrm{Cs}]_{\mathrm{aq}}$ and were obtained directly as the ratio of background-corrected count rates per milliliter. In control experiments, no extraction within background was observed for 1,2-DCE (no crown ether) equilibrated with aqueous $\mathrm{CsNO_3}$ or $\mathrm{CsClO_4}$ solutions under the experimental conditions employed.

Data Treatment. The cesium distribution ratios D_{Cs} were used as input by the solvent extraction modeling program SXLSQI.[30,31,37,38] Nonideality effects were taken into account by use of Pitzer parameters for aqueous ions, the Hildebrand−Scott treatment for nonionic effects in the organic phase, and the Debye−Hückel treatment for electrostatic effects in the organic phase.[30,37−43] All constants are thus corrected to infinite dilution. The program converts the molar concentration to the molality scale employed in the Pitzer treatment using Masson coefficients.[44] The solubility parameters and molar volumes of the ligands were estimated from group contributions.[42] Parameters used in the SXLSQI program are summarized in Table 3.

Table 3. Parameters Used in SXLSQI[29] Modeling

Masson Coefficients[a]

ion	V_0 (cm^3 mol^{-1})	S_V* (cm^3 L$^{1/2}$ mol$^{-3/2}$)
$\mathrm{Cs^+}$	21.29	1.393
$\mathrm{ClO_4^-}$	44.38	−0.057
$\mathrm{NO_3^-}$	29.33	0.543

Pitzer Parameters[b]

interaction	$\beta^{(0)}$	$\beta^{(1)}$	α
$\mathrm{Cs^+}$−$\mathrm{ClO_4^-}$	−0.1652[c]	−0.150[c]	2.0[c]
$\mathrm{Cs^+}$−$\mathrm{NO_3^-}$	−0.0758[d]	−0.0669[d]	2.0[d]

Other Parameters

species	V_0[e] (cm^3 mol^{-1})	δ[h] (J$^{1/2}$ cm$^{-3/2}$)
1,2-DCE	79.4[f]	20.3[f]
2	713.2[g]	19.01[g]
$\mathrm{Cs^+}$	21	14.0[i]
$\mathrm{ClO_4^-}$	44	25.8[i]
$\mathrm{NO_3^-}$	29	25.8[i]

[a] Masson coefficients allow the aqueous density to be estimated for molality−molarity interconversions. Values were taken from ref 44. [b] Pitzer parameters allow aqueous-phase ionic activity coefficients to be estimated. [c] Values were taken from ref 41. [d] Taken from ref 40. [e] Molar volume of the species in the organic phase. Values for the inorganic ions were taken to be approximately equal to V_0. [f] Taken from ref 42. [g] Estimated according to group contributions as described in ref 42. [h] Hildebrand solubility parameters were used in estimation of the activity coefficients of organic-phase species. The solubility parameter of a complex was taken as the volume-weighted average of the solubility parameters of its constituents. For example, $\delta = (V_M\delta_M + V_B\delta_B)/(V_M + V_B)$.[43] [i] Taken from ref 43.

Results and Discussion

Crystal Structure. Crystallization of tetrabenzo-24-crown-8 with $\mathrm{CsNO_3}$ from a 1,2-DCE/MeOH/$\mathrm{H_2O}$ solvent mixture yields large, clear plates of $[\mathrm{Cs(tetrabenzo\text{-}24\text{-}crown\text{-}8)(1,2\text{-}DCE)_2}](\mathrm{NO_3})\cdot\mathrm{H_2O}$ (**3**). As may be seen in Figure 2, the crown ether organizes itself in a cagelike structure about the cation, with the crown ether backbone resembling the seam on a tennis ball. This orients alternating pairs of benzo groups so as to face one another, one pair related to the other by a noncrystallographic improper 90° rotation. Because of the positioning of the two pairs of benzo groups, the complex features two clefts, each occupied by a 1,2-DCE molecule coordinated in bidentate fashion through the chlorine atoms.

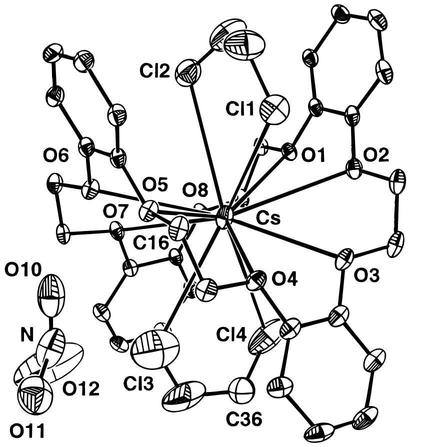

Figure 2. ORTEP drawing (30% probability ellipsoids) of [Cs(tetrabenzo-24-crown-8)(1,2-dichloroethane)$_2$](NO$_3$)·H$_2$O (**3**). The isotropically refined atom (C36) is represented as a sphere. Minor disorder components and hydrogen atoms are omitted for clarity.

This rare example of a crystallographic characterization of 1,2-DCE binding to a metal ion is unique for alkali metal cations. The only X-ray structural precedents that demonstrate 1,2-DCE coordination to a metal ion are for silver or thallium ions with bulky, very weakly bonding anions.[23,24] The Cs−Cl distances cover a broad range [2.98(2)−3.83(2) Å for all disorder components] and should be interpreted only qualitatively since both 1,2-DCE ligands are disordered and are not perfectly modeled. This disorder likely reflects the weak binding strength of the 1,2-DCE ligand. However, the Cs−Cl distances observed in **3** are all shorter than the sum of the van der Waals radii of $\mathrm{Cs^+}$ (2.15 Å)[45] and Cl (1.75 Å)[46] and are comparable with $\mathrm{M^+}$−Cl distances for the published 1,2-DCE complexes with $\mathrm{Ag^+}$ and $\mathrm{Tl^+}$ ions after the differences in metal ion radii are considered.[23,24]

Whereas bond distances and angles involving atoms from the 1,2-DCE ligands need to be interpreted cautiously owing to their disorder, comparison of average values observed here to those

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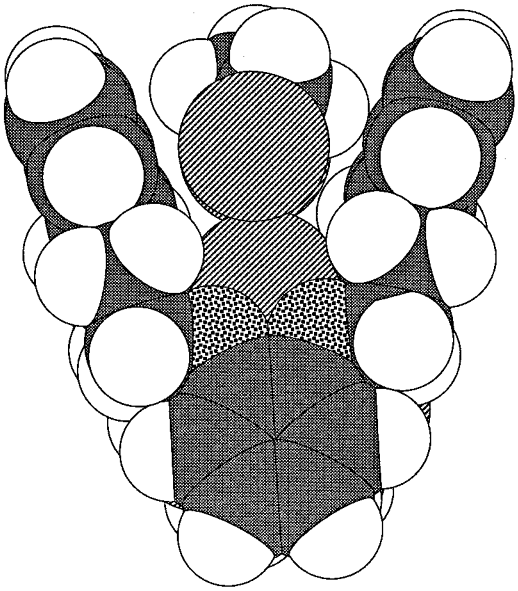

Figure 3. Space-filling drawing of [Cs(tetrabenzo-24-crown-8)(1,2-dichloroethane)$_2$](NO$_3$)$\cdot$H$_2$O (**3**). Lattice species and minor disorder components are omitted for clarity.

previously reported is worth considering. The average values quoted here are weighted according to the occupancy factor of the ligand or ligand fragment, primarily to downweight the least chemically reasonable values, obtained from the 17% occupied fragment containing C34A and Cl2A. The average bite angle (Cl−Cs−Cl) in **3** is 55°, much lower than that observed in the silver complexes (75−78°)[23] or the thallium structure (65°).[24] The Cl−C−C−Cl torsion angle is also smaller at 56° (65−70° for Ag$^+$,[23] 69° for Tl$^+$,[24]) and 62° in the free ligand.[47] While these numbers suggest that 1,2-DCE is bound more tightly in this structure, they may also reflect the steric requirements of the cleft, as suggested in the space-filling diagram of the structure (Figure 3). For example, Cl1 has only 3.05 and 3.21 Å separating it from H atoms (H7A and H16B, respectively) on either side of the cleft.

It is remarkable that the nitrate anion is excluded from the Cs coordination sphere in preference to 1,2-DCE, when it would appear that there is no obvious steric reason for it to be excluded from the cleft created by the crown ether. In a similar complex of KSCN with bisnaphthopyridino-21-crown-7, a cleft between two facing naphtho groups acts as a host for the SCN$^-$ anion.[15] In the present case, comparison of the size and electronic topography of the narrow nitrate anion with those of the wider and diverging cleft suggests less ideal host−guest complementarity. On the other hand, 1,2-DCE is more electronically favored to reside in the clefts, as five of its slightly electropositive hydrogen atoms (out of 14 total on all disorder components of both 1,2-DCE ligands) are within 3.2 Å of an arene ring centroid (H···ring distances range from 2.64 to 2.94 Å), allowing interaction with the π-clouds of the opposing arene rings. It may be noted that the crystallographic record shows many examples of both inner-sphere and outer-sphere association of anions with univalent and divalent cations complexed with crown ethers.[48,49] Inner-sphere coordination is favored with charge-dense cations, such as Li$^+$, Na$^+$, and Ca^{2+}, whereas solvent molecules, especially water, tend to displace the anion from the inner sphere of crown ether complexes of more charge-diffuse cations.[49] Thus, it must be concluded that the charge-diffuse Cs$^+$ cation together with the complementary host environment in the present case allows the weak ligand 1,2-DCE guest molecule to take precedence over coordination by the nitrate anion.

The nitrate is not completely excluded from bonding interactions, though. Its oxygen atoms experience several contacts with crown hydrogen atoms that are very close to or slightly smaller than the sum of their van der Waals radii. Only one of these interactions has directionality appropriate for a hydrogen bond of appreciable strength[50] (H16A···O10 = 2.57 Å, C16−H16A···O10 = 143.7(4)°). Not surprisingly, it involves the only well-ordered oxygen atom on the nitrate anion.

Liquid−Liquid Distribution. Isomeric mixtures of alkylated dibenzo crown ethers are commonly employed in solution studies of crown ethers, based on the assumption that the positional isomers exhibit essentially the same complexation properties. Although not yet experimentally justified to our knowledge, this assumption would seem to be reasonable because of the minor differences in extraction observed on alkylation of various benzo-crown compounds with *tert*-butyl and *tert*-octyl groups.[27,28,30,32] The fact that positional isomers of **2** have different symmetry, and thus slightly different physical properties, allowed the separation of $\mathbf{2}_{4,4''}$ and $\mathbf{2}_{4,5''}$ by a combination of column chromatography and fractional crystallization. Both isomers of **2** showed high solubility in 1,2-DCE.

According to the concept of lipophilicity parameters[51] as previously discussed in the context of crown ethers,[3,30,52] **1** and **2** should be highly lipophilic. Estimates from group contributions (viz., 4 veratrole units × 1.329 + 0 or 2 *tert*-octyl units × 4.00)[3] give $\log P_{\rm oct} = 5.3$ for **1** and $\log P_{\rm oct} = 13.3$ for **2**, where P is the partition ratio for the crown ether from water to an immiscible organic solvent, and the subscript denotes 1-octanol. Since the value of $\log P$ tends to be even higher for 1,2-DCE than for 1-octanol,[3,53] these estimates indicate that the aqueous-phase concentration of **2** in the distribution experiments to be described below may be taken as negligible for the purpose of analysis of organic-phase speciation.

The extraction behavior of the individual isomers $\mathbf{2}_{4,4''}$ and $\mathbf{2}_{4,5''}$ and their respective 3:2 mixture at 25 °C was characterized by systematic variation of the organic-phase extractant and aqueous-phase CsNO$_3$ or CsClO$_4$ concentrations. Figure 4 shows the effect of aqueous-phase Cs$^+$ concentration on the Cs$^+$ distribution ratio $D_{\rm Cs}$ using the $\mathbf{2}_{4,5''}$ isomer at constant concentration in 1,2-DCE. (See Supporting Information for similar plots, Figures 6S and 7S, corresponding respectively to the $\mathbf{2}_{4,4''}$ isomer and the 3:2 $\mathbf{2}_{4,4''}$:$\mathbf{2}_{4,5''}$ isomeric mixture.) Qualitatively, the perchlorate salt of cesium yields significantly stronger extraction than the nitrate salt, in accord with the expected bias[54] in favor of the less charge-dense anion.[3] In the case of $\mathbf{2}_{4,5''}$, another experiment was performed with variable ligand concentration in the organic phase at constant aqueous Cs$^+$ ion concentration. Defined as the ratio of the total organic-phase

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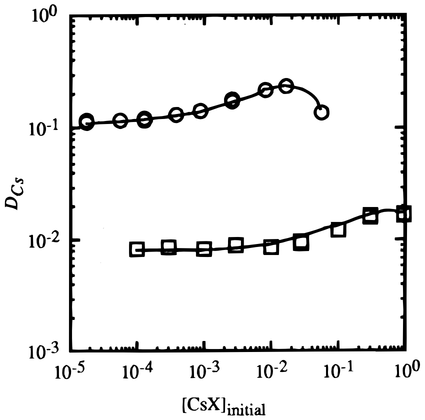

Figure 4. Comparison of calculated (solid line) and observed (symbols) cesium distribution ratios as a function of equilibrium aqueous-phase molarity of (□) $CsNO_3$ and (○) $CsClO_4$ employing respectively 0.05 and 0.01 M 4,5″-bis(*tert*-octylbenzo)dibenzo-24-crown-8 ($\mathbf{2}_{4,5''}$) solutions in 1,2-DCE at 25 °C.

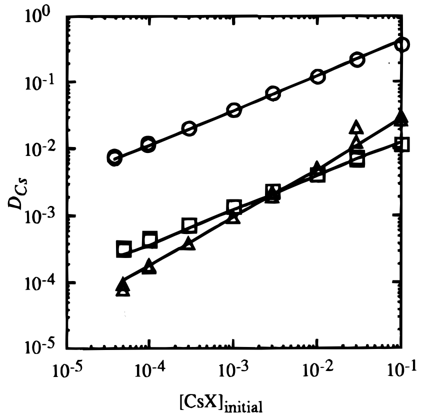

Figure 5. Comparison of calculated (solid line) and observed (symbols) cesium distribution ratios as a function of equilibrium organic-phase molarity of 4,5″-bis(*tert*-octylbenzo)dibenzo-24-crown-8 ($\mathbf{2}_{4,5''}$) in 1,2-DCE at 25 °C. Initial aqueous-phase $CsNO_3$ concentrations were 0.003 (□) and 0.3 M (△), and the initial aqueous-phase $CsClO_4$ concentration was 0.0003 M (○).

cesium concentration to the initial organic-phase crown ether concentration, the loading of the crown ether by $CsNO_3$ reached 0.26; maximum loading of the crown ether by $CsClO_4$ was 0.80. Logarithmic plots of D_{Cs} vs organic-phase ligand concentration are nearly linear, with slopes of 0.76 ± 0.02 for $CsNO_3$ and 0.502 ± 0.002 for $CsClO_4$ (Figure 5). As discussed in detail below, the different slopes reflect the expected effect of partial dissociation of the anion from the complex cation,[30] which is apparently nearly complete for perchlorate under the conditions of Figure 5.

For purposes of detailed equilibrium analysis, the systems studied offered simplicity by including only four components: water, cesium salt, 1,2-DCE, and crown ether. The low mutual solubility of water and 1,2-DCE was neglected in the treatment to follow, and as just discussed, the scant distribution of the crown ethers to the aqueous phase was also neglected. Since the diluent alone extracts the cesium salts feebly, as shown in control experiments in the present work and in work reported earlier,[30] essentially all of the cesium present in the organic phase may be presumed to be in the form of crown ether complexes.

Based on the crystal structure performed in this work and the wealth of data reported on the extraction of alkali metal salts by crown ethers,[1−3,30] it was expected that the liquid−liquid distribution behavior of **1** and **2** would reflect the formation of a simple 1:1 metal/crown organic-phase complex. The extraction of cesium salt (CsX) by a crown ether (B) to give a neutral 1:1:1 ion-pair complex may be represented by the following equilibrium:

$$Cs^+(aq) + X^-(aq) + B(org) \rightleftharpoons CsBX(org) \qquad (1)$$

The corresponding equilibrium constant can be expressed as

$$K_{ex} = [CsBX]_{org} y_{CsBX} / \{[B]_{org} y_B [Cs^+]_{aq}^2 y_{\pm,aq}^2\} \qquad (2)$$

where square brackets denote molarity, $y_{\pm,aq}$ is the mean molar activity coefficient for aqueous CsX, and y_B and y_{CsBX} are respectively the molar activity coefficients of B and CsBX in the organic phase. Since CsX is the only electrolyte in the system, $[Cs^+]_{aq} = [X^-]_{aq}$. Further, if CsBX is assumed to be the only organic-phase product species, the cesium distribution ratio D_{Cs} may then be written

$$\log D_{Cs} = \log K_{ex} + \log(y_B y_{\pm,aq}^2 / y_{CsBX}) + \log [B]_{org} + \log [Cs^+]_{aq} \qquad (3)$$

In a diluent with sufficiently high dielectric constant that the CsBX complex becomes significantly dissociated in the organic phase, the extraction equilibrium giving the complex cation CsB^+ must be taken into account.[3,30,55] The corresponding equilibrium relationships analogous to eqs 1−3 become

$$Cs^+(aq) + X^-(aq) + B(org) \rightleftharpoons CsB^+(org) + X^-(org) \qquad (4)$$

$$K_{ex\pm} = [CsB^+]_{org}^2 y_{\pm,org}^2 / \{[B]_{org} y_B [Cs^+]_{aq}^2 y_{\pm,aq}^2\} \qquad (5)$$

$$\log D_{Cs} = {}^1/_2 \log K_{ex\pm} + {}^1/_2 \log(y_B y_{\pm,aq} / y_{\pm,org}^2) + {}^1/_2 \log [B]_{org} \qquad (6)$$

where $[CsB^+]_{org} = [X^-]_{org}$. Equation 6 applies to the case of complete dissociation in the organic phase.

For a state of partial dissociation of the complex ion-pair CsBX in the organic phase, the dissociation equilibrium becomes of interest:

$$CsBX(org) \rightleftharpoons CsB^+(org) + X^-(org) \qquad K_{diss} \qquad (7)$$

The value of log K_{diss} is readily obtained from log $K_{ex\pm}$ and log K_{ex} via the relation

$$\log K_{diss} = \log K_{ex\pm} - \log K_{ex} \qquad (8)$$

Typical values of K_{diss} for polyether complexes of Cs^+ ion with several anions in 1,2-DCE at 25 °C lie in the range from 6×10^{-6} to 6×10^{-4} M^{-1}.[30,31] Since it may be shown that the total concentration of a weak electrolyte at 50% dissociation is $2K_{diss}$, it may be appreciated that a state of partial dissociation of the organic-phase complex ion-pair exists under typical experimental conditions (viz., Figures 4 and 5). Accordingly, by increasing the aqueous-phase CsX concentration over a sufficiently wide range, it becomes possible to cause the degree of dissociation to vary from high to low. Concomitantly, the observed behavior of log D_{Cs} shifts from that predicted by eq 6 to that predicted by eq 3, ultimately allowing one to extract the values of log $K_{ex\pm}$, log K_{ex}, and log K_{diss} by appropriate analysis.

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Table 4. Equilibrium Constants for Extractive Reactions Involving Cesium Complexes of Bis(*tert*-octylbenzo)dibenzo-24-crown-8 (**2**) in 1,2-Dichloroethane[a]

ligand	anion	log K_{ex} (eq 3)	log $K_{ex\pm}$ (eq 6)	log K_{diss} (eq 8)	log K_f (eq 17)	log K_{exch} (eq 10)	log $K_{exch\pm}$ (eq 11)	σ^b
$\mathbf{2}_{4,4''}$	NO_3^-	0.14 ± 0.03	−2.76 ± 0.01	−2.88 ± 0.04	10.5 ± 0.2	3.09 ± 0.04	3.00 ± 0.01	1.11
	ClO_4^-	3.22 ± 0.02	0.254 ± 0.005	−2.98 ± 0.02	10.6 ± 0.2			0.71
$\mathbf{2}_{4,5''}$	NO_3^-	0.30 ± 0.02	−2.88 ± 0.02	−3.18 ± 0.03	10.4 ± 0.2	2.86 ± 0.04	2.98 ± 0.02	2.27
	ClO_4^-	3.16 ± 0.03	0.104 ± 0.007	−3.26 ± 0.03	10.4 ± 0.2			1.32
3:2 mixture of $\mathbf{2}_{4,4''} + \mathbf{2}_{4,5''}$	NO_3^-	0.33 ± 0.05	−2.77 ± 0.02	−3.10 ± 0.05	10.5 ± 0.2	3.00 ± 0.06	3.00 ± 0.02	1.96
	ClO_4^-	3.34 ± 0.03	0.24 ± 0.01	−3.10 ± 0.03	10.5 ± 0.2			1.45

[a] In the experiments, 1,2-DCE solutions of **2** were equilibrated with equal volumes of aqueous $CsNO_3$ or $CsClO_4$ solutions at 25.0 ± 0.2 °C. See text for definitions of each constant according to the indicated equation. Values of log K_{ex} and log $K_{ex\pm}$ were determined from the computer modeling. All others were derived from them. [b] The goodness of fit for a particular model to the given data set is quantified by the *agreement factor* σ, defined according to the least-squares criterion as $\sigma = [\sum w_i(Y_i - Y_{c,i})^2/(N_o - N_p)]^{1/2}$, where Y_i is the ith experimentally observed quantity (i.e., D_{Cs}), $Y_{c,i}$ is the corresponding quantity calculated from the model being tested, w_i is the weighting factor defined as the reciprocal of the square of the estimated uncertainty of Y_i, N_o is the number of observations, and N_p is the number of adjustable parameters (i.e., log K values). The value of σ will approach unity when the error of fitting is equal to the estimated experimental error; values less than unity are interpreted as experimental precision being better than the estimated precision.

The distribution behavior shown in Figures 4 and 5 may thus be readily interpreted in terms of the two equilibria defined in eqs 1 and 4. In Figure 4, the value of log D_{Cs} levels off as the aqueous CsX concentration decreases. This is expected since eq 6 predicts that log D_{Cs} becomes independent of the aqueous-phase CsX concentration when the free organic-phase ions are predominant over ion-pairs. In the other direction, with increasing aqueous-phase CsX concentration, eq 3 predicts that log D_{Cs} should tend to a slope of 1, whence formation of the organic-phase ion-pair complex CsBX predominates. Both curves in Figure 4 do, in fact, exhibit regions of increasing slope. However, in the case of $CsClO_4$, onset of loading leads to a maximum in the curve, whereupon the concentration of free organic-phase crown ether concentration ($[B]_{org}$) begins to decrease significantly. In the case of $CsNO_3$, the maximum occurs at higher aqueous salt concentration. Regarding the dependence of log D_{Cs} on organic-phase crown ether concentration under low-loading conditions, slopes of 1.0 and 0.5 are respectively predicted according to eq 3 (complete ion-pairing) or eq 6 (complete ion-pair dissociation). Under the conditions examined, Figure 5 shows that the organic-phase complex is predominantly dissociated (slope = 0.502 ± 0.002) in the $CsClO_4$ system and partially dissociated in the $CsNO_3$ system (slope = 0.76 ± 0.02).

For a more rigorous testing of the equilibrium model, the data shown in Figures 4, 5, 6S, and 7S were fit using the program SXLSQI,[30,31,37,38] assuming simultaneous formation of ion-pair complexes CsBX and ions CsB^+ and X^- in the organic phase. For this model, the program automatically solves the pair of conservation-of-mass equations corresponding to crown ether and cesium salt subject to the equilibrium conditions defined in eqs 2 and 5. Iteration to minimize the weighted sum of the squares of the residuals between observed and calculated D_{Cs} values leads to refinement of the initial estimates of log K_{ex} and log $K_{ex\pm}$. By accounting for nonideality of species in both phases (see Experimental Section), the program corrects these constants to the state of infinite dilution. The results are summarized in Table 4.

Based on the qualitative agreement between the model (curves) and data (points) shown in Figures 4 and 5 and on the statistical agreement factors given in Table 4, it may be seen that the simple equilibrium scheme involving formation of the complex cation CsB^+ and ion-pair CsBX adequately describes the observed behavior. By comparison, dibenzo- and dicyclohexano-21-crown-7 ethers also formed these species plus the higher complexes CsB_2^+ and CsB_2X.[30] Such higher complexes apparently cannot be detected with the tetrabenzo-24-crown-8 ethers examined here, because significant systematic deviation (as an underprediction) would otherwise be seen in Figure 5 with increasing concentration of **2**. The absence of higher complexes in the present case follows logically from the efficient encapsulation of the metal cation by the ligand and two solvent molecules and from the relative inflexibility and steric bulk of the four benzo substituents on the crown ring. It may also be noted that the relative placement of the two *tert*-octyl groups has little if any effect on the extraction constants.

The observed dissociation behavior strongly suggests that the extraction complexes in the systems examined form ligand-separated ion-pairs. It may be noted that the tabulated values of log K_{diss} are much higher than the reported values for the dissociation of nitrate from 1:1 complexes of Cs^+ with dibenzo-, bis(alkylbenzo)-, and dicyclohexano-21-crown-7 ethers (log K_{diss} = −5.1 to −4.4)[30] and with calix[4]arene-bis(*tert*-octylbenzo-crown-6) (log K_{diss} = −3.7)[31] in 1,2-DCE at 25 °C. Each of these complexes entails at least one open coordination site accessible to the anion. For the complex $[Cs(\text{dicyclohexano-21-crown-7})_2](NO_3)$, the ion-pair dissociates even more readily (log K_{diss} = −3.2) under the same conditions and presumably has no open coordination sites available to the anion.[30] In general, the ion-pairing tendency in polyether complexes of a given metal cation decreases with increasing polyether size, as the coordination sphere of the metal cation becomes progressively saturated by the crown ether and less available to the anion.[3,30,31] Moreover, despite the significant difference in anion radii (r_- = 0.196[54] and 0.250[18] nm for NO_3^- and ClO_4^-, respectively), the log K_{diss} values given in Table 4 for nitrate are essentially identical to the values given for perchlorate. Both of these observations suggest that the Cs^+ cation is completely encapsulated, excluding the anion from the inner coordination sphere. This interpretation is consistent with the X-ray crystal structure results discussed above, which show the coordination of Cs^+ cation within a cage of eight oxygen atoms from the crown ether and four chlorine atoms from the two 1,2-DCE molecules in the clefts. Thus, we propose that the structure of the complex in the solid state persists in solution and that the clefts exhibit no tendency to act as a host for either NO_3^- or ClO_4^- in competition with 1,2-DCE molecules.

This model of ligand-separated ion-pairs receives support from a theoretical treatment,[56] which when evaluated at 25 °C gives the contact ion-pair association constant according to the

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Table 5. Estimation of the Dissociation Constant log K_{Diss} from Contact Ion-Pair Theory[a]

anion	a (nm)	r_+ (nm)	r_- (nm)	basis	log K_{diss} calcd	log K_{diss} obsd
NO_3^-	0.709[b]			crystal[b]	−3.27	−2.88 to −3.18
	0.769	0.573[c]	0.196	thermochem.	−3.11	
ClO_4^-	0.813	0.573[c]	0.240	thermochem.	−3.02	−2.98 to −3.26

[a] Calculations employed eq 9 in the text, using a relative permittivity of 10.36.[17] [b] The interionic distance a was taken directly from the X-ray structural results in this work. [c] The cationic radius was estimated as 0.573 nm from the molar volume of the complex $[\mathrm{Cs}(\mathbf{1})\cdot 2(1{,}2\text{-DCE})]^+$, estimated to be 640.9 cm^3 mol^{-1} from the sum of molar volumes of Cs$^+$ ion (Table 3), 1,2-DCE,[42] and **1**, where the molar volume of **1** was obtained from group contributions.[42]

simple analogue form,

$$K_{\mathrm{A}} = 2.522a^3 \exp\left[\frac{56.05|Z_+Z_-|}{\epsilon a}\right] \tag{9}$$

where a is the interionic distance in nanometers, ϵ is the relative permittivity, and Z is the ionic charge. Table 5 summarizes the estimation of log K_{diss} from eq 9, using log $K_{\mathrm{diss}} = -\log K_{\mathrm{A}}$, and its comparison with the observed values from the extraction experiments. It may be seen that the theory closely predicts the ion-pair dissociation constants, whether the interionic distance is based on the actual crystallographic measurement in the solid state (the shortest Cs···N separation) or on thermochemical radii. At the large distances involved, the theory dictates that the value of log K_{diss} should be rather insensitive to interionic distance. For example, given the actual oblong shape of the cationic complex $[\mathrm{Cs}(\mathbf{1})(1{,}2\text{-DCE})_2]^+$ viewed as a space-filling model calculated from the crystal structure, the interionic distance of a ligand-separated contact ion-pair with either anion may be expected to vary in the wide range 0.65−0.80 nm. However, this range corresponds to log K_{diss} values in the relatively narrow range −3.5 to −3.0. This places into perspective the virtual equality of the log K_{diss} values observed for nitrate and perchlorate. However, as the cationic radius decreases, the value of log K_{diss} decreases rapidly, more so for nitrate than for perchlorate. Accordingly, in the absence of other ligands, direct coordination of the anions to the Cs$^+$ cation would be expected from eq 9 to result in differentiation of the anions: log $K_{\mathrm{diss}} = -5.55$ (nitrate) or −5.00 (perchlorate).

From the foregoing, it may be understood why perchlorate gives approximately 3 orders of magnitude greater extractability of cesium than nitrate whether the anion is ion-paired or dissociated. Taking the differences log $K_{\mathrm{ex}}(\mathrm{ClO_4^-}) - \log K_{\mathrm{ex}}(\mathrm{NO_3^-})$ and log $K_{\mathrm{ex}\pm}(\mathrm{ClO_4^-}) - \log K_{\mathrm{ex}\pm}(\mathrm{NO_3^-})$ gives the constants corresponding to the following hypothetical exchange processes, respectively:

$$\mathrm{CsBNO_3(org) + ClO_4^-(aq) \rightleftharpoons CsBClO_4(org) + NO_3^-(aq)} \qquad \log K_{\mathrm{exch}} \tag{10}$$

$$\mathrm{NO_3^-(org) + ClO_4^-(aq) \rightleftharpoons ClO_4^-(org) + NO_3^-(aq)} \qquad \log K_{\mathrm{exch}\pm} \tag{11}$$

Table 4 gives the values of log K_{exch} and log $K_{\mathrm{exch}\pm}$ so derived. Note that log $K_{\mathrm{exch}\pm}$ should be independent of the cation and crown ether and can be predicted from independently reported constants via the expression

$$\log K_{\mathrm{exch}\pm} = [\Delta G^\circ_{\mathrm{p}}(\mathrm{NO_3^-}) - \Delta G^\circ_{\mathrm{p}}(\mathrm{ClO_4^-})]/2.303RT \tag{12}$$

where $\Delta G^\circ_{\mathrm{p}}$ is the standard Gibbs energy of partitioning of the indicated anion from water to 1,2-DCE at 25 °C. The experimental values of log $K_{\mathrm{exch}\pm}$ agree well with the predicted value of 2.93 obtained using reported $\Delta G^\circ_{\mathrm{p}}$ values based on the tetraphenylarsonium tetraphenylborate (TATB) assumption.[57] The good agreement supports the reliability of the SXLSQI modeling results. Toward understanding the effect of ion-pairing on anion selectivity more quantitatively, one may express the standard Gibbs energy of exchange corresponding to eq 10 by the following:

$$\Delta G^\circ_{\mathrm{exch}} = \Delta G^\circ_{\mathrm{diss}}(\mathrm{NO_3^-}) + \Delta G^\circ_{\mathrm{exch}\pm} - \Delta G^\circ_{\mathrm{diss}}(\mathrm{ClO_4^-}) \tag{13}$$

It follows that

$$\log K_{\mathrm{exch}} = \log K_{\mathrm{diss}}(\mathrm{NO_3^-}) + \log K_{\mathrm{exch}\pm} - \log K_{\mathrm{diss}}(\mathrm{ClO_4^-}) \tag{14}$$

Since the difference log $K_{\mathrm{diss}}(\mathrm{NO_3^-}) - \log K_{\mathrm{diss}}(\mathrm{ClO_4^-})$ is estimated from eq 9 to be on the order of −0.1, the ion-pairing practically does not change the natural anion discrimination by the solvent.

Finally, for purposes of comparison of the Cs$^+$ ion complexation by **2** to that with other crown ethers, it is useful to estimate the formation constant K_{f} corresponding to the homogeneous complexation process in water-saturated 1,2-DCE:

$$\mathrm{Cs^+(org) + B(org) \rightleftharpoons CsB^+(org)} \qquad K_{\mathrm{f}} \tag{15}$$

The following relation was used to derive log K_{f}:

$$\log K_{\mathrm{f}} = \log K_{\mathrm{ex}\pm} + [\Delta G^\circ_{\mathrm{p}}(\mathrm{Cs^+}) + \Delta G^\circ_{\mathrm{p}}(\mathrm{X^-})]/2.303RT \tag{16}$$

where $\Delta G^\circ_{\mathrm{p}}(\mathrm{Cs^+})$ and $\Delta G^\circ_{\mathrm{p}}(\mathrm{X^-})$ are the standard Gibbs energies of partitioning of the indicated ions between water and 1,2-DCE at 25 °C. For the Cs$^+$, $\mathrm{NO_3^-}$, and $\mathrm{ClO_4^-}$ ions, values of $\Delta G^\circ_{\mathrm{p}}$ were taken as 41.7,[55] 33.9,[57] and 17.2[57] kJ mol^{-1}, respectively (TATB assumption). Note that these values of $\Delta G^\circ_{\mathrm{p}}$ refer to the *partition* process between mutually saturated water and 1,2-DCE, as opposed to values of $\Delta G^\circ_{\mathrm{tr}}$ (standard Gibbs energies of transfer) that refer to the hypothetical *transfer* process between pure water and 1,2-DCE. The derived values of log K_{f} given in Table 4 agree well, confirming the expected independence on the nature of the anion and the positional isomerism of the crown ether.

Among the simple crown ethers, **2** is the strongest ligand reported to date for Cs$^+$ ion in 1,2-DCE, though it is still 2 orders of magnitude weaker than the calix[4]arene-crown-6 ethers.[31] The complexation strengths of representative crown ethers in water-saturated 1,2-DCE at 25 °C (log K_{f} values in parentheses) follow the order: dibenzo-24-crown-8 (8.5)[58] ∼ dibenzo-21-crown-7 (8.5)[30] < dicyclohexano-21-crown-7 (9.3)[30] < dibenzo-30-crown-10 (9.4)[58] < 18-crown-6 (10.2)[55] < **2** (10.5) < calix[4]arene-bis(*tert*-octylbenzo-crown-6) (12.3).[31] Despite the inductive electron-withdrawing effect of the benzo groups, **2** bests dibenzo-24-crown-8 by 2 orders of magnitude. In a qualitative survey, both extraction strength and selectivity toward CsNO$_3$ were found to follow the order dibenzo-24-crown-8 < tribenzo-24-crown-8 < tetrabenzo-24-crown-8 (**1**).[28] Since an increasing number of benzo groups on a large crown

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(58) Samec Z.; Papoff, P. *Anal. Chem.* **1990**, *62*, 1010.

ether does not consistently lead to the same order (i.e., di- < tri- < tetra-), it has been pointed out that the resulting order must follow from an interplay between inductive and ligand-strain effects.[32] Molecular mechanics calculations earlier showed that the cagelike binding conformation of tetrabenzo-24-crown-8 enjoys a relatively low strain upon incorporation of a Cs^+ cation.[14] Assuming that this favorable conformation is highly populated in solution would well explain the favorable complexation strength of **1** among the simple crown ethers.

Conclusions

The structure of [Cs(tetrabenzo-24-crown-8)(1,2-DCE)$_2$](NO$_3$) (**3**) provides a rare glimpse of 1,2-DCE as a ligand and the first structural characterization of this ligand with an alkali metal ion. Binding of 1,2-DCE even occurs in competition with the nitrate anion. This recognition reflects the unique steric and electronic environment afforded by the two clefts formed within the Cs(tetrabenzo-24-crown-8)$^+$ complex. Liquid−liquid distribution experiments agree well with the picture presented by the crystallographic results. Namely, the distribution results strongly suggest that, in solution, the anions are relegated to the outer coordination sphere of the Cs^+ cation, apparently owing to effective competition for coordination by 1,2-DCE molecules. The key extraction properties include ease of dissociation of the anion (NO_3^- or ClO_4^-) from the complex cation Cs(tetrabenzo-24-crown-8)$^+$, the equivalence of their ion-pair dissociation constants within experimental error, the agreement of the ion-pair dissociation constants with the theory of contact ion-pairs, and the lack of selectivity in the derived anion-exchange constants for the ion-pairs. The extraction data revealed that 4,4″ and 4,5″ positional isomers of bis(*tert*-octylbenzo)dibenzo-24-crown-8 (**2**) exhibit essentially equal binding strength toward the Cs^+ cation.

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Supporting Information Available: Figure 6S, comparing calculated and observed cesium distribution coefficients as a function of initial aqueous-phase concentrations of $CsNO_3$ and $CsClO_4$ employing 0.01 M 4,4″-bis(*tert*-octylbenzo)dibenzo-24-crown-8 ($\mathbf{2}_{4,4''}$) in 1,2-DCE at 25 °C; Figure 7S, comparing calculated and observed cesium distribution coefficients as a function of initial aqueous-phase concentrations of $CsNO_3$ and $CsClO_4$ employing 0.01 M bis(*tert*-octylbenzo)dibenzo-24-crown-8 (**2**) as a 3:2 mixture of its respective 4,4″ and 4,5″ isomers in 1,2-DCE at 25 °C; and additional crystallographic details, including tables of positional and thermal parameters (PDF). X-ray crystallographic data, in CIF format, are also available. This material is available free of charge via the Internet at http:pubs.acs.org.

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