Synthesis, structure, and extraction behavior of 4,5′,4″,5‴-tetra-*tert*-butyltetrabenzo-24-crown-8 †‡

Tatiana G. Levitskaia, Richard A. Sachleben, Jeffrey C. Bryan and Bruce A. Moyer *

Chemical and Analytical Sciences Division, Oak Ridge National Laboratory,
MS-6119/4500S, Oak Ridge, Tennessee 37831, USA

Received (in Cambridge, UK) 25th October 2000, Accepted 27th February 2001
First published as an Advance Article on the web 26th March 2001

Isomerically pure 4,5′,4″,5‴-tetra-*tert*-butyltetrabenzo-24-crown-8 was synthesized by a route that eliminates any need for isomer separation. Its structure was determined using single crystal X-ray diffraction methods. Since the observed saddle-shaped conformation of the crown ether is the same as previously reported for the closely related tetrabenzo-24-crown-8, the presence of the peripheral *tert*-butyl groups has no apparent effect on ring structure. This structure experiences few intermolecular interactions beyond London forces, suggesting it represents a low energy conformation. Liquid–liquid distribution behavior of $CsNO_3$ and $CsClO_4$ between water and 1,2-dichloroethane (1,2-DCE) containing 4,5′,4″,5‴-tetra-*tert*-butyltetrabenzo)-24-crown-8 was investigated. Equilibrium constants corresponding to the extraction of ion pairs and dissociated ions, formation of the caesium complex, and dissociation of the ion pairs in water-saturated 1,2-DCE at 25 °C were obtained from equilibrium modeling using the SXLSQI program. 4,5′,4″,5‴-Tetra-*tert*-butyltetrabenzo-24-crown-8 exhibits stronger caesium binding and a similarly low tendency towards ion-pairing, in comparison with the previously characterized isomeric 4,4′- and 4,5′-di-*tert*-octyltetrabenzo-24-crown-8 ethers.

Introduction

Research on crown ethers has been motivated by their remarkable ability to complex and transport alkali and alkaline-earth metal cations.[1] Historically, the features of the cyclic polyether ligands considered to be most important in determining binding strength are: number and type of donor atoms, dimensions of the cavity, presence of substituents on the donor ring, and degree of ligand preorganization.[1,2] Benzo-substituted crown ethers have received considerable attention due to the fact that they are more lipophilic than the corresponding unsubstituted crown ethers, are readily prepared from catechol,[3] and exhibit selectivity for complexation of alkali metal ions.[4]

Unfortunately, benzo-substituted crown ethers often suffer from limited solubility in solvents of low to moderate polarity, limiting their practical application.[5] The solubility properties of such macrocycles can be adjusted by the judicious addition of substituents to the periphery of the benzo group.[4–7] Addition of hydrocarbon groups generally increases the solubility of the crown ether in non-polar diluents.[4,5,7,8] A potential complication in the preparation of substituted benzo crown ethers, though, is the formation of positional isomers.[9] For example, alkylation of two opposing benzo groups on tetrabenzo-24-crown-8 results in a mixture of 4,4″ and 4,5″ positional isomers, and elaborate procedures are required to effect their separation.[10] Random monoalkylation of all four benzo groups on tetrabenzo-24-crown-8 would result in four isomers (Fig. 1). It is generally assumed that positional isomers exhibit similar metal ion complexation properties, although variable complexation and distribution behavior have been reported.[11] Additionally, the presence of multiple positional isomers interferes with physical and structural studies, such as single-crystal structure determination by X-ray diffraction and solution complexation studies by ^1H and ^{13}C NMR. Questions regarding reproducibility of results may also arise in that different batches of a compound containing positional isomers may not possess identical isomer distributions. Consequently, it is preferable to synthesize and study a single isomer.

Caesium complexation by tetrabenzo-24-crown-8 results in the formation of a structure exhibiting two clefts, which provide unique electronic and spatial environments suitable for the inclusion of additional species to saturate the Cs^+ coordination sphere and contribute to overall stability of the supramolecular assembly.[10,12,13] The considerable softness of the large charge-dispersed Cs^+ ion, as well as the topography of the clefts, creates a unique environment for 1,2-dichloroethane (1,2-DCE) solvent molecules to coordinate to Cs^+.[10] Liquid–liquid distribution studies using bis(*tert*-octylbenzo)dibenzo-24-crown-8 § in 1,2-DCE revealed that solvent inclusion in the clefts likely also occurs in solution, influencing the speciation and ion-pairing behavior of the cation complex.[10] Saturation of the Cs^+ inner coordination sphere by the crown ether and two 1,2-DCE solvent molecules leaves no open coordination sites for the anion, which is observed to reside in the second coordination sphere. As a result, Cs^+ complexes with tetrabenzo-24-crown-8 and its derivatives in 1,2-DCE exhibit unusually high stability and a low tendency towards ion-pairing.

As part of our investigation into the extraction properties of caesium-selective tetrabenzo-24-crown-8 ligands, we developed a synthesis of isomerically pure 4,5′,4″,5‴-tetra-*tert*-butyltetrabenzo-24-crown-8, determined its crystal structure, and analyzed its extraction behavior toward Cs^+ ion with nitrate and perchlorate counter-anions in 1,2-DCE. As part of these studies, we determined the caesium complex stability and the ion-pairing tendency of this new ligand. We were curious to

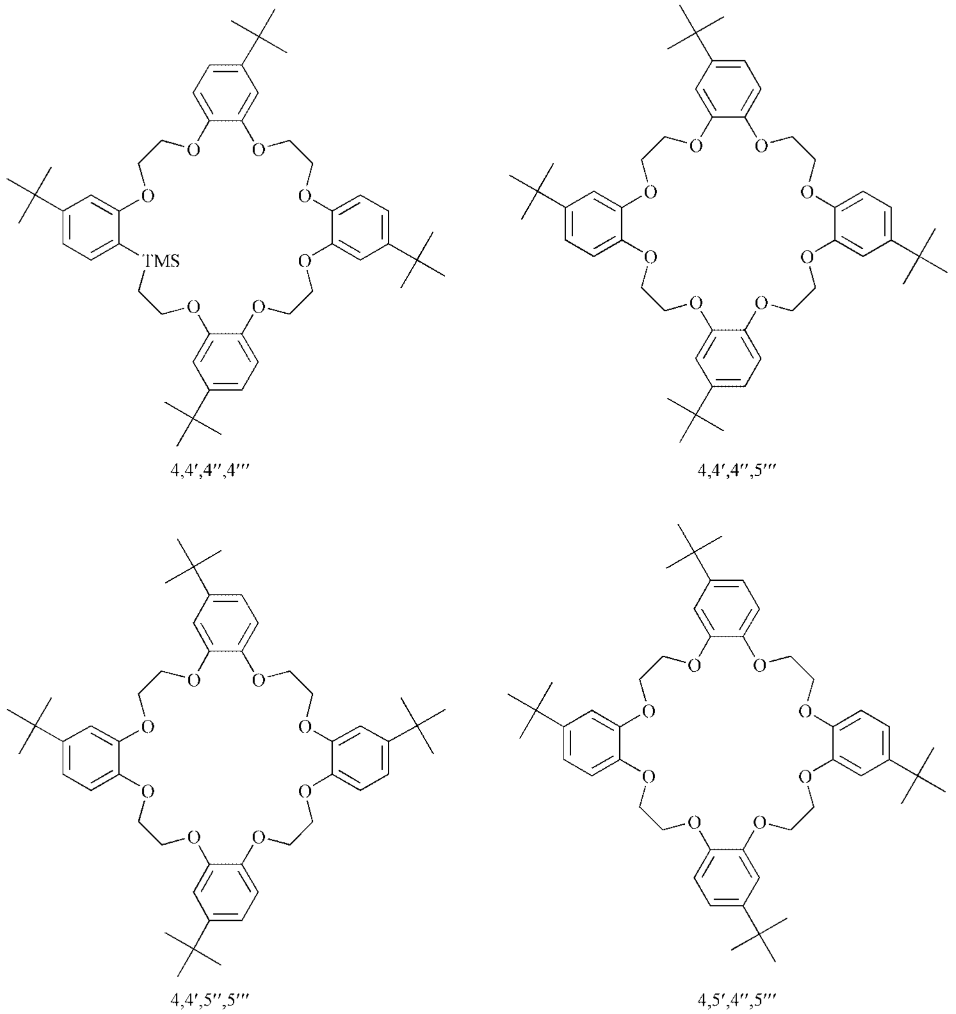
---

† This is the work of a contractor of the US Government under contract No. DE-AC05-00OR22725. Accordingly, the US Government retains a non-exclusive, royalty-free license to publish or reproduce the published form of this contribution, or allow others to do so, for the US Government purposes.

‡ The parameters used in SXLSQI modeling are available as supplementary data. For direct electronic access see http://www.rsc.org/suppdata/p2/b0/b008603g/

§ The IUPAC name for *tert*-octyl is 1,1,3,3-tetramethylbutyl.

DOI: 10.1039/b008603g



4,4′,4″,4‴ 4,4′,4″,5‴

4,4′,5″,5‴ 4,5′,4″,5‴

Fig. 1 Schematic representations of the four possible positional isomers of tetra-*tert*-butyltetrabenzo-24-crown-8.

understand how varying the alkyl substitution on the benzo rings would affect the complexation and transport properties of the ligand. For these purposes, we performed equilibrium modeling of the collected distribution data. The extraction constants thus obtained allowed calculation of the caesium complex stability and dissociation constants in water-saturated 1,2-DCE, which were then compared with those previously determined for the isomeric bis(*tert*-octylbenzo)dibenzo-24-crown-8 ligands.[10]

Results and discussion

Synthesis

As shown in Fig. 1, tetrakis(*tert*-butylbenzo)-24-crown-8 can exist as four regioisomers, depending on the relative orientation of the *tert*-butyl substituents. Upon complexing caesium, tetrabenzo-24-crown-8 adopts a saddle-shaped structure exhibiting two clefts formed by opposing pairs of benzo groups. Attachment of substituents, in this case *tert*-butyl, onto opposing benzo groups results in two possible relative orientations across the cleft, which can be viewed in terms of the symmetry operations necessary to interchange them. These two orientations require either reflection through a plane bisecting the cleft, referred to henceforth as σ, or rotation about a two-fold axis passing down the center of the cleft through the caesium ion, denoted as C_2. Since each tetrakis(*tert*-butylbenzo)-24-crown-8·Cs$^+$ complex contains two clefts, three possible structures result in the caesium complexes: $\sigma\sigma$, C_2C_2, and σC_2. Interestingly, two of the four regioisomers shown in Fig. 1 result in the C_2C_2 relationship; these are the 4,4′,4″,4‴ and the 4,5′,4″,5‴ isomers. The 4,4′,4″,5‴ isomer produces the σC_2 relationship, whereas the 4,4′,5″,5‴ isomer provides the $\sigma\sigma$ relationship. We chose to synthesize the 4,5′,4″,5‴ isomer since it could be obtained in a convergent manner, as shown in Scheme 1, from 1,2-bis(4′-*tert*-butylphenoxy)ethyl ether, readily obtained from 4-*tert*-butylphenol. It may be noted that tetrakis(*tert*-butylbenzo)-24-crown-8 is isomeric with the bis(*tert*-octylbenzo)-24-crown-8 studied previously by us[10] and discussed herein.

Crystallographic studies

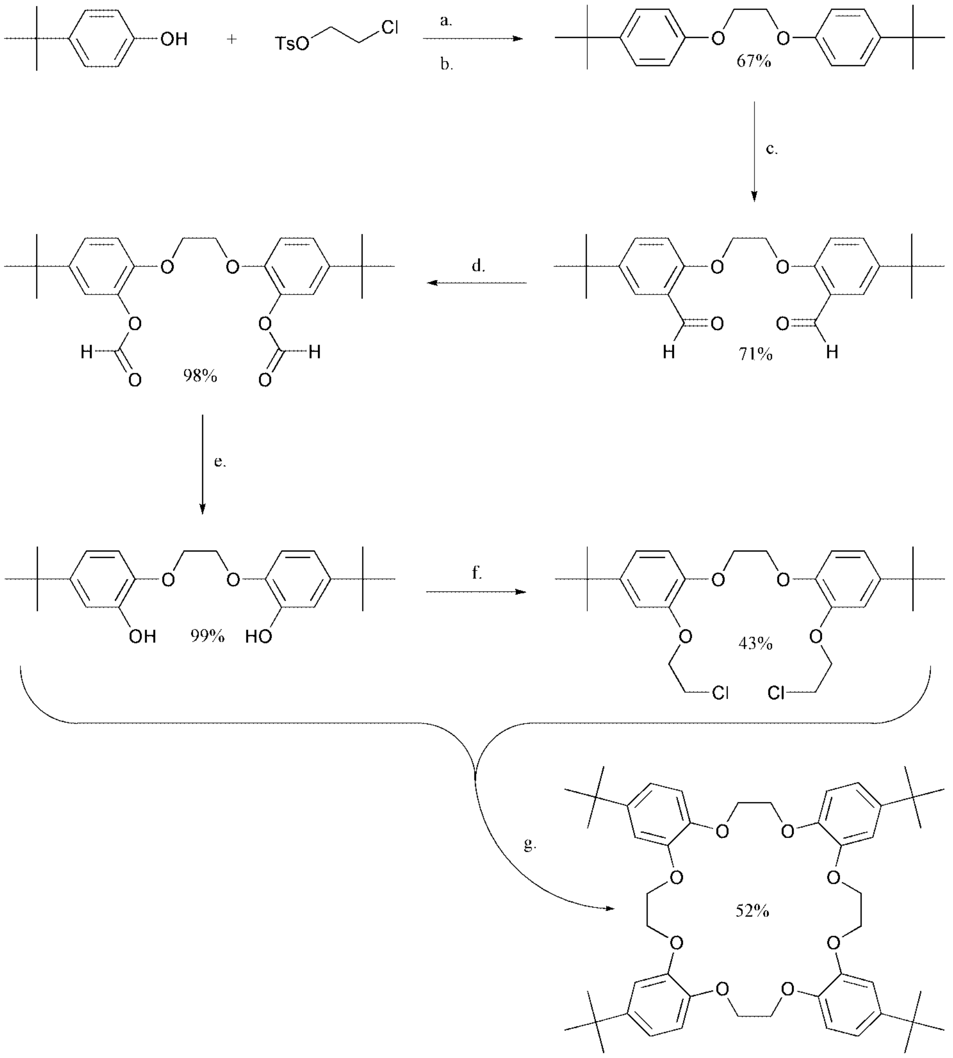
The structure of 4,5′,4″,5‴-tetra-*tert*-butyltetrabenzo-24-crown-8 is depicted in Fig. 2, affirming that the anticipated isomer was obtained. Only half of the molecule makes up the crystallographic asymmetric unit, the other half is generated through the crystallographic inversion center. The crown ether is collapsed in on itself, as is commonly observed in the structures of large, uncomplexed crown ethers.[9,14,15] Overall, the crown is relatively flat, and, as shown in Fig. 3, it stacks upon itself in the crystal lattice, roughly along the *a* axis, with an average inter-crown spacing of approximately 4.5 Å.

The crown conformation can be expressed in terms of the torsion angles around the ring,[16] starting with O1–C1–C2–O2, and leaving a space before each O–C–C–O torsion angle. The conformation observed here is: 0aa g$^+$ag$^+$ 0g$^+$(g$^+$) g$^-$ag$^+$ (Table 1), which is then repeated, albeit inverted, for the inversion symmetry-generated portion of the crown. The value of “(g$^+$)” refers to the C10–O4–C15–C16 torsion angle of 113.3(2)°, and is marked in parentheses because of its closeness to the intermediate value of 120°.[16] For binding, the pattern 0aa g$^\pm$aa should be repeated four times around the ring, as observed in

Table 1 Selected hydrogen bonding geometry (Å and °) and torsion angles (°) for 4,5′,4″,5‴-tetra-*tert*-butyltetrabenzo-24-crown-8

D–H···A	H···A	D···A	D–H···A
C8–H8B···O4	2.50	3.090(2)	118
C15–H15A···O3	2.54	2.994(2)	108
C16–H16B···O2^{i}	2.37	2.926(2)	114
C8–H8A···Cg2^{ii}	2.98	3.70	130
C16–H16A···Cg1^{iii}	2.71	3.48	135
O(1)–C(1)–C(2)–O(2)	0.2(2)	O(3)–C(9)–C(10)–O(4)	−4.3(2)
C(1)–C(2)–O(2)–C(7)	−175.59(14)	C(9)–C(10)–O(4)–C(15)	58.9(2)
C(2)–O(2)–C(7)–C(8)	−179.50(13)	C(10)–O(4)–C(15)–C(16)	113.26(15)
O(2)–C(7)–C(8)–O(3)	69.93(15)	O(4)–C(15)–C(16)–O(1)^{i}	−76.45(15)
C(7)–C(8)–O(3)–C(9)	172.19(12)	C(15)–C(16)–O(1)^{i}–C(1)^{i}	165.25(12)
C(8)–O(3)–C(9)–C(10)	67.90(18)	C(16)–O(1)^{i}–C(1)^{i}–C(2)^{i}	65.21(19)

Cg1 represents the centroid of C1–6 and Cg2 the centroid of C9–14. Symmetry codes *i* 2 − *x*, 2 − *y*, −*z*; *ii* *x* − 1, *y*, *z*; *iii* 1 − *x*, 2 − *y*, −*z*.



Scheme 1 a. K_2CO_3, CH_3CN; b. KI, K_2CO_3, DMF; c. Cl_2CHOCH_3, $TiCl_4$, CH_2Cl_2; d. mCPBA, CH_2Cl_2; e. $(C_2H_5)_3N$, CH_3OH; f. $TsOCH_2CH_2Cl$, K_2CO_3, acetone; g. KI, Cs_2CO_3, DMF.

the structures of Cs^+, Rb^+ and CH_3CN complexes of tetrabenzo-24-crown-8.[10,12,13]

The conformation observed here is the same as previously seen for the closely related tetrabenzo-24-crown-8.[14] Like its trimmed-down cousin, 4,5′,4″,5‴-tetra-*tert*-butyltetrabenzo-24-crown-8 experiences relatively short C–H···O intramolecular contact distances as a result of the crown ring's collapse. Some of these could be considered weak hydrogen bonds, although the C–H···O angles are generally quite small (Table 1).[17] Unlike tetrabenzo-24-crown-8, the tetra-*tert*-butyl structure presented here experiences very few intermolecular interactions beyond London forces. Two C–H···π hydrogen bonds are listed in Table 1, but no edge–face arene, or π-stacking is observed. This suggests that this crown conformation is likely a low-energy conformation.

Liquid–liquid distribution studies

Liquid–liquid distribution experiments using 4,5′,4″,5‴-tetra-*tert*-butyltetrabenzo-24-crown-8 were carried out to examine the question of the effect of alkyl substitution in comparison with the bis(*tert*-octylbenzo)-24-crown-8 isomers. The effect of varying the Cs^+ ion concentration in the aqueous phase at constant ligand concentration (10 mM in 1,2-DCE) on the Cs^+ ion

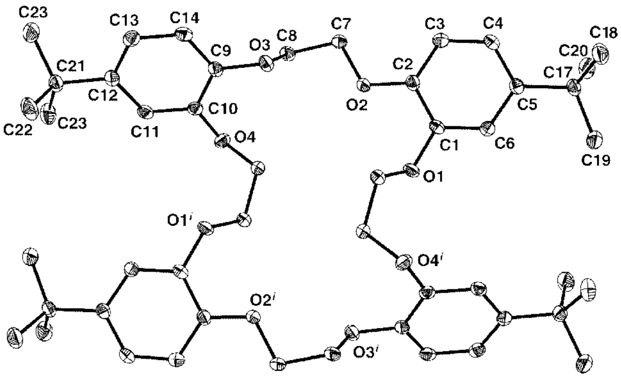


Fig. 2 ORTEP representation with 50% probability ellipsoids of 4,5′,4″,5‴-tetra-*tert*-butyltetrabenzo-24-crown-8. Hydrogen atoms are omitted for clarity. Symmetry code *i* 2 − *x*, 2 − *y*, −*z*.

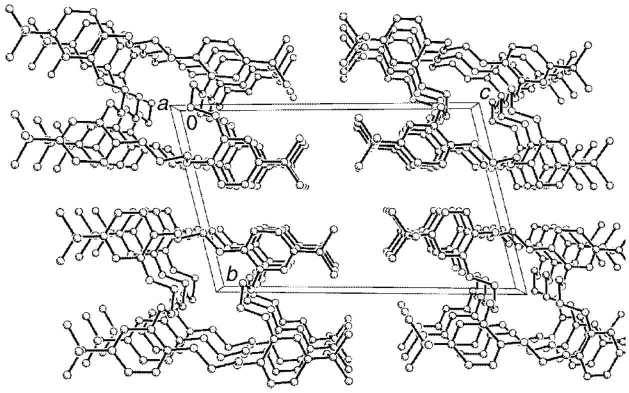


Fig. 3 Stacking diagram for 4,5′,4″,5‴-tetra-*tert*-butyltetrabenzo-24-crown-8. Atoms are represented by circles and hydrogen atoms are omitted for clarity.

distribution ratio between organic and aqueous phases is shown in Fig. 4. In general, the values of the Cs^+ ion distribution ratio ($D_{Cs} = [Cs]_{org}/[Cs]_{aq}$) observed with ClO_4^- are much greater than those obtained with NO_3^-, as expected since the more charge-dispersed ClO_4^- has a less positive standard Gibbs energy of partitioning between water and 1,2-DCE.[18] As seen in Fig. 4, the value of D_{Cs} remains relatively unchanged at lower concentrations of Cs^+. In view of the known behavior of similar systems,[7,10,19,20] it may be readily concluded that both $CsNO_3$ and $CsClO_4$ are extracted as dissociated ion pairs over a reasonably wide concentration range of complexed Cs^+ ion in 1,2-DCE. The onset of significant ion-pairing is indicated by the observed rise in slope as the aqueous caesium salt concentration increases. When significant loading of the extractant is achieved, values of D_{Cs} decrease. This effect is especially pronounced for $CsClO_4$, which loads the crown ether at lower aqueous concentrations of caesium salt due to its greater extractability into the organic phase.

Distribution data were fitted using the program SXLSQI[21] assuming simultaneous extraction of ion pairs and dissociated ions to obtain the values of log K_{ex} and log $K_{ex\pm}$ corresponding to the expected extractive processes given in eqns. (1) and (2).

$$Cs^+_{(aq)} + X^-_{(aq)} + crown_{(org)} \rightleftharpoons Cs(crown)X_{(org)} \quad K_{ex} \quad (1)$$

$$Cs^+_{(aq)} + X^-_{(aq)} + crown_{(org)} \rightleftharpoons Cs(crown)^+_{(org)} + X^-_{(org)} \quad K_{ex\pm} \quad (2)$$

Based on our previous studies of caesium complexation by tetrabenzo-24-crown-8 ligands both in solution and in the solid state,[10,12] formation of only a 1 : 1 caesium–crown ether complex was considered in the extraction model. Partitioning of 4,5′,4″,5‴-tetra-*tert*-butyltetrabenzo-24-crown-8 into the aqueous phase was neglected because of the high lipophilicity of this crown ether. To justify this assumption, the partition ratio from water to octan-1-ol was estimated by the group contribution method[22,23] giving log $P_{w\rightarrow oct} = 13.2$. Simple ion partitioning from water into 1,2-DCE was also neglected based on the results of control distribution experiments using an organic phase containing no crown ether. In the fitting, Pitzer parameters were employed to estimate aqueous-phase activity coefficients,[24] Hildebrand solubility parameters were employed to estimate the neutral contribution to nonideality of species in the organic phase,[23,25] and the Debye–Hückel treatment was used to estimate the electrostatic contribution to nonideality of ions in the organic phase.[21,24] All constants are thus corrected to infinite dilution. Parameters used in SXLSQI modeling are summarized in a table given in electronic supplementary information. The solubility parameter and molar volume of the 4,5′,4″,5‴-tetra-*tert*-butyltetrabenzo-24-crown-8 were estimated from the group-contribution method.[23] Excellent agreement between measured and calculated values of D_{Cs} (Fig. 4) and statistical agreement factors close to unity (Table 2) suggest that the observed extraction behavior is explained well by the chosen distribution model [based on simultaneous extraction processes given by eqns. (1) and (2)].

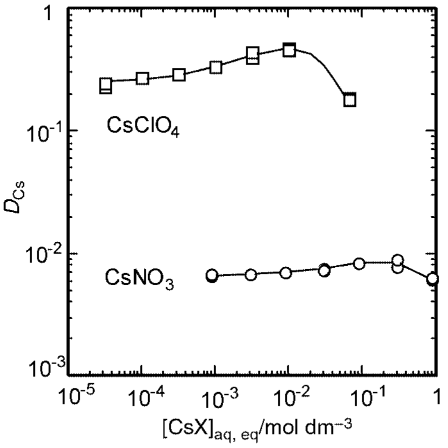


Fig. 4 Comparison of the calculated (solid line) and observed (symbols) caesium distribution ratios as a function of equilibrium aqueous-phase molarity of $CsNO_3$ or $CsClO_4$ employing a 10 mM solution of 4,5′,4″,5‴-tetra-*tert*-butyltetrabenzo-24-crown-8 in 1,2-DCE at 25 °C.

Examination of log K_{ex} and log $K_{ex\pm}$ values (Table 2) indicates that perchlorate gives approximately three orders of magnitude greater extractability of caesium than nitrate whether the anion is ion paired or dissociated. This implies that the discrimination of the anion by the caesium–crown complex cation is independent of the identity and relative location of the anion. In other words, the cleft formed by the crown ether as it envelops Cs^+ has no ability to recognize nitrate *versus* perchlorate. The same trend was observed with the isomeric bis(*tert*-octylbenzo)-dibenzo-24-crown-8 ligands studied previously (Table 2). From the tabulated values of log K_{ex} and log $K_{ex\pm}$, constants corresponding to the homogeneous processes of ion-pair dissociation (K_{diss}) and complex formation (K_f) in 1,2-DCE may be derived as described previously.[7,10,20] on the basis of eqns. (3) and (4). Taking the differences log $K_{ex}(NO_3^-)$ − log $K_{ex}(ClO_4^-)$

$$Cs(crown)X_{(org)} \rightleftharpoons Cs(crown)^+_{(org)} + X^-_{(org)} \quad K_{diss} \quad (3)$$

$$Cs^+_{(org)} + crown_{(org)} \rightleftharpoons Cs(crown)^+_{(org)} \quad K_f \quad (4)$$

and log $K_{ex\pm}(NO_3^-)$ − log $K_{ex\pm}(ClO_4^-)$ yields the constants corresponding to the exchange processes represented in eqns. (5) and (6).[10] Table 2 summarizes the log *K* values so

Table 2 Equilibrium constants for extractive reactions involving caesium complexes of tetrabenzo-24-crown-8 ligands in 1,2-dichloroethane at 25 °C[a]

Anion	log K_{ex} [eqn. (1)]	log $K_{ex\pm}$ [eqn. (2)]	log K_{diss} [eqn. (3)]	log K_f [eqn. (4)]	log K_{exch} [eqn. (5)]	log $K_{exch\pm}$ [eqn. (6)]	σ[b]
4,5′,4″,5″-Tetra-*tert*-butyltetrabenzo-24-crown-8[c]							
NO_3^-	0.54 ± 0.03	−2.39 ± 0.01	−2.93 ± 0.03	10.9 ± 0.2	3.13 ± 0.08	3.14 ± 0.02	1.02
ClO_4^-	3.67 ± 0.07	0.75 ± 0.02	−2.92 ± 0.07	11.1 ± 0.2			1.28
4,4″-Di-*tert*-octyltetrabenzo-24-crown-8[d]							
NO_3^-	0.14	−2.76	−2.88	10.5	3.09	3.00	
ClO_4^-	3.22	0.254	−2.98	10.6			
4,5″-Di-*tert*-octyltetrabenzo-24-crown-8[d]							
NO_3^-	0.30	−2.88	3.18	10.4	2.86	2.98	
ClO_4^-	3.16	0.104	−3.26	10.4			

[a] In the experiments, 1,2-DCE solutions of crown ether were equilibrated with equal volumes of aqueous $CsNO_3$ or $CsClO_4$ solutions at 25 ± 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. Uncertainties listed represent the standard error of fitting obtained directly (log K_{ex} and log $K_{ex\pm}$) or as propagated. The uncertainties for the values given for log K_f also include the uncertainties in the standard Gibbs energies of ion partitioning obtained from the literature. [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 $\sigma = [\Sigma w_i(Y_i - Y_{c,i})^2/(N_o - N_p)]^{\frac{1}{2}}$ where Y_i is the i-th 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. [c] This work. [d] Taken from ref. 10.

$$\mathrm{Cs(crown)NO_{3(org)} + ClO_4{}^-{}_{(aq)} \rightleftharpoons Cs(crown)ClO_{4(org)} + NO_3{}^-{}_{(aq)}} \quad K_{exch} \quad (5)$$

$$\mathrm{NO_3{}^-{}_{(org)} + ClO_4{}^-{}_{(aq)} \rightleftharpoons ClO_4{}^-{}_{(org)} + NO_3{}^-{}_{(aq)}} \quad K_{exch\pm} \quad (6)$$

derived. All the constants in Table 2 refer to water-saturated 1,2-DCE as the solvent.

The results support the conclusion that the tendency towards ion-pairing is low and that there is relative insensitivity to the nature of the anion. Namely, values of log K_{diss} are high and nearly equal (Table 2), within observed standard deviations, for both nitrate and perchlorate. Further, the observed values of log K_{diss} compare well with values calculated from ion-pair theory.[10] Such dissociation behavior can be explained by formation of ligand-separated ion pairs in 1,2-DCE with large interionic distance determined mainly by the bulky caesium–crown complex. This dissociation behavior is consistent with that previously observed for bis(*tert*-octylbenzo)dibenzo-24-crown-8 ligands in an analogous distribution study (Table 2), and with X-ray crystal structure results in which 1,2-DCE coordinates to caesium(tetrabenzo-24-crown-8) in preference to nitrate.[10] A similar solution structure is proposed for the 4,5′,4″,5‴-tetra-*tert*-butyltetrabenzo-24-crown-8–caesium complex in which the anion is excluded from the inner coordination sphere.

It may be seen from Table 2 that the observed values of log K_{exch} and log $K_{exch\pm}$ for ion pairs and dissociated ions are nearly equal within observed standard deviations. This result confirms that the caesium–crown complex does not exhibit any specific interaction with the counterion in 1,2-DCE and is unable to affect the natural discrimination between anions by the solvent. The same effect was demonstrated for the distribution studies of $CsNO_3$ and $CsClO_4$ using 4,5″- and 4,4″-di-*tert*-octyltetrabenzo-24-crown-8 extractants in 1,2-DCE (Table 2).

The values of log K_f derived from the extraction constants obtained using $CsNO_3$ and $CsClO_4$ agree, reflecting the expected independence of the complex stability constant on the nature of the counterion. The values of log K_f observed here are slightly higher than those (10.5) obtained for caesium complexes with 4,5″- and 4,4″-bis(*tert*-octylbenzo)dibenzo-24-crown-8 (Table 2). This increase of the complex stability can be readily attributed to higher binding strength of the tetra-*tert*-butyltetrabenzo-24-crown-8 due to the increased number of electron-donating alkyl substituents on the benzo groups. 4,5′,4″,5‴-Tetra-*tert*-butyltetrabenzo-24-crown-8 possesses four *tert*-butylbenzo groups attached to the crown ether moiety, whereas bis(*tert*-octylbenzo)dibenzo-24-crown-8 has two alkylated and two unsubstituted benzo groups. Subsequently, electron density on the donor oxygen atoms of tetrakis(*tert*-butylbenzo)-24-crown-8 is expected to be slightly higher and results in stronger interaction with the cationic guest.

Conclusions

4,5′,4″,5‴-Tetra-*tert*-butyltetrabenzo-24-crown-8 was synthesized by a route that ensures an isomerically pure product without the necessity for isomer separation. The structure of the crown ether was characterized by single crystal X-ray diffraction, showing that the conformation of the crown ether is unaffected by addition of four *tert*-butyl groups. Liquid–liquid distribution studies using 1,2-DCE as a diluent revealed that this ligand is a significantly stronger caesium extractant compared with the closely related 4,5″- and 4,4″-di-*tert*-octyltetrabenzo-24-crown-8 ethers, but the speciation behavior is otherwise quite similar. Improved solubility, strong caesium binding, low tendency towards ion-pairing, and a structure that excludes direct ion-pairing make this ligand an attractive candidate for caesium-selective complexation and transport in biphasic liquid systems.

Experimental

General

All reagents were obtained from commercial suppliers and used as received. The 3-chloroperoxybenzoic acid obtained from Aldrich Chemical Co. was stated to be of 57–86% purity. The caesium nitrate and caesium perchlorate (Johnson Matthey, 99.9%) salts were dried at 110 °C for at least 48 hours 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.[20] Aqueous solutions were prepared using distilled deionized water.

Synthesis

1,2-Bis(*p-tert*-butylphenoxy)ethane. A suspension of *p-tert*-butylphenol (50 g, 0.33 mol), 2-chloroethyl toluene-*p*-sulfonate (40 g, 0.17 mol), and K$_2$CO$_3$ (50 g, 0.36 mol) in acetonitrile (150 mL) was heated at reflux overnight (~18 h). Following addition of KI (1 g), K$_2$CO$_3$ (50 g, 0.36 mol) and DMF (300 mL), the mixture was heated at 80 °C for 24 hours, and then poured into water (500 mL) and allowed to cool to room temperature. The solid product was filtered, washed twice with 1 M NaOH (200 mL each), and recrystallized from methanol to obtain 37 g (0.11 mol, 67%) of 1,2-bis(*p-tert*-butylphenoxy)ethane. Mp 87–88 °C; δ_H 7.42 (4 H, d, *J* 8.9, H_Ar), 7.00 (4 H, d, *J* 8.9, H_Ar), 4.39 (4 H, s, CH_2), 1.41 (18 H, s, CH_3); δ_C 156.5, 143.8, 126.4, 114.3, 66.6, 34.2, 31.7.

1,2-Bis(2′-formyl-4′-*tert*-butylphenoxy)ethane. A solution of TiCl$_4$ (25 mL, 0.23 mol) in dichloromethane (100 mL) was added dropwise over 30 min to an ice-cold solution of 1,2-bis-(*p-tert*-butylphenoxy)ethane (33 g, 0.10 mol) and α,α-dichloromethyl methyl ether (25 mL, 0.27 mol) in dichloromethane (350 mL) under argon. Additional aliquots of TiCl$_4$ solution (3 × 5 mL, 0.14 mol) and α,α-dichloromethyl methyl ether (2 × 5 mL, 0.11 mol) were added alternately at 5 minute intervals. Ice-cold 1 M HCl (500 mL) was then added (cautiously), the phases were separated, and the organic phase washed sequentially with 1 M HCl (100 mL), saturated NaCl (200 mL), and saturated NaHCO$_3$ (200 mL) solutions. The organic phase was dried over Na$_2$SO$_4$ and evaporated *in vacuo*¶ to obtain 39 g (0.10 mol, 100%) of 1,2-bis(2′-formyl-4′-*tert*-butylphenoxy)ethane as an oil of sufficient purity for the next reaction. Recrystallization from cyclohexane gave pure 1,2-bis(2′-formyl-4′-*tert*-butylphenoxy)ethane (27 g, 71%). δ_H 10.35 (2 H, s, COH), 7.79 (2 H, d, *J* 2.6, H_Ar), 7.53 (2 H, dd, *J* 2.6, 8.7, H_Ar), 6.92 (2 H, d, *J* 8.7, H_Ar), 4.43 (4 H, s, CH_2), 1.25 (18 H, s, CH_3); δ_C 189.9, 159.0, 144.6, 133.3, 125.3, 124.8, 112.8, 67.4, 34.5, 31.5.

1,2-Bis(2′-formyloxy-4′-*tert*-butylphenoxy)ethane. Solid 3-chloroperoxybenzoic acid (25 g of 57–86% purity, ~82–124 mmol) was added in 5 g portions at 5 min intervals to a solution of 1,2-bis(2′-formyl-4′-*tert*-butylphenoxy)ethane (20 g, 52 mmol) in dichloromethane (150 mL). The resulting mixture was cooled in an ice bath and filtered. The filtrate was washed sequentially with 10% Na$_2$SO$_3$ (100 mL), 1 M NaOH (100 mL), and saturated NaHCO$_3$ (100 mL) solutions, dried over Na$_2$SO$_4$ and evaporated *in vacuo* to obtain 21 g (98%) of crude 1,2-bis(2′-formyloxy-4′-*tert*-butylphenoxy)ethane, which was used without further purification or characterization.

1,2-Bis(2′-hydroxy-4′-*tert*-butylphenoxy)ethane. A solution of crude 1,2-bis(2′-formyloxy-4′-*tert*-butylphenoxy)ethane (21 g, 51 mmol) in methanol (80 mL) containing triethylamine (1 mL) was heated at 55 °C for 20 minutes and then evaporated *in vacuo*. The residue was dissolved in dichloromethane (100 mL), washed sequentially with 1 M HCl (50 mL), saturated NaCl (50 mL), and saturated NaHCO$_3$ (50 mL) solutions, dried over Na$_2$SO$_4$ and evaporated *in vacuo* to obtain 18 g (99%) of a white solid. Recrystallization from methanol gave pure 1,2-bis(2′-hydroxy-4′-*tert*-butylphenoxy)ethane (12 g, 67%). Mp 129–130 °C; δ_H 7.03 (4 H, m, H_Ar), 6.87 (2 H, s, H_Ar), 5.77 (2 H, s, OH), 4.38 (4 H, s, CH_2), 1.30 (18 H, s, CH_3); δ_C 146.3, 145.8, 143.3, 116.9, 113.1, 112.9, 68.5, 34.5, 31.6.

1,2-Bis[2′-(2″-chloroethoxy)-4′-*tert*-butylphenoxy]ethane. A solution of 1,2-bis(2′-hydroxy-4′-*tert*-butylphenoxy)ethane (8.0 g, 20 mmol), 2-chloroethyl toluene-*p*-sulfonate (14 g, 60 mmol), and K$_2$CO$_3$ (15 g, 100 mmol) in acetone (150 mL) was heated at reflux overnight (~18 h), filtered, and evaporated *in vacuo*. The residue was dissolved in dichloromethane (50 mL), washed with water (50 mL), and passed through a silica gel (100 g) column. Elution with 5% ethyl acetate in hexanes gave 1,2-bis[2′-(2′-chloroethoxy)-4′-*tert*-butylphenoxy]ethane (4 g, 43%). Mp 173–174 °C; δ_H 7.01–6.92 (6 H, m, H_Ar), 4.37 (4 H, s, CH_2), 4.29 (4 H, t, *J* 6.0, CH_2), 3.79 (4 H, t, *J* 6.0, CH_2), 1.31 (18 H, s, CH_3); δ_C 147.9, 147.3, 145.4, 119.6, 115.1, 114.9, 70.6, 68.4, 42.5, 34.5, 31.7.

4,5′,4″,5‴-Tetra-*tert*-butyltetrabenzo-24-crown-8.‖ A mixture of 1,2-bis(2′-hydroxy-4′-*tert*-butylphenoxy)ethane (3.5 g, 9.8 mmol), 1,2-bis[2′-(2′-chloroethoxy)-4′-*tert*-butylphenoxy]ethane (4.0 g, 8.7 mmol), KI (~0.5 g), and Cs$_2$CO$_3$ (15 g, 46 mmol) in *N*,*N*-dimethylformamide (150 mL) was stirred at 65 °C overnight (~18 h). The mixture was evaporated *in vacuo*, dissolved in dichloromethane (100 mL) and washed once with 1 M HCl (100 mL) and three times with distilled water. The organic phase was dried over Na$_2$SO$_4$, passed through dry silica gel to remove phenolic impurities, and evaporated *in vacuo* to obtain 4.8 g (72%) of crude product. Recrystallization from hexanes gave pure 4,5′,4″,5‴-tetra-*tert*-butyltetrabenzo-24-crown-8 (3.5 g, 52%). Mp 173–174 °C; δ_H 7.05 (4 H, s, H_Ar), 6.95 (4 H, d, *J* 8.3, H_Ar), 6.85 (4 H, d, *J* 8.3, H_Ar), 4.35 (8 H, s, CH_2), 4.30 (8 H, s, CH_2), 1.29 (36 H, s, CH_3); δ_C 148.4, 147.6, 145.1, 119.1, 115.6, 114.6, 69.7, 68.1, 34.4, 31.6.

Crystal structure determination of 4,5′,4″,5‴-tetra-*tert*-butyltetrabenzo-24-crown-8**

The crystal structure reported here was determined by single crystal X-ray diffraction methods. Data collection and treatment of data were the same as previously described.[26]

Crystal data. C$_{48}$H$_{64}$O$_8$, $M = 769.0$, triclinic, $a = 5.8214(8)$, $b = 10.7769(19)$, $c = 17.258(3)$ Å, $\alpha = 76.083(14)$, $\beta = 82.120(12)$, $\gamma = 89.600(13)°$, $U = 1040.6(3)$ Å^3, $T = 100$ K, space group $P\bar{1}$ (no. 2), $Z = 1$, μ(Mo-Kα) = 0.082 mm^{-1}, 5827 reflections collected, 4533 independent ($R_\mathrm{int} = 0.023$) which were used in all calculations. The final $wR(F^2)$ was 0.137 (all data).

Liquid–liquid distribution experiments

Procedures. Equal volumes (0.5 mL each) of organic phase (10 mM solution of 4,5′,4″,5‴-tetra-*tert*-butyltetrabenzo-24-crown-8 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 3 min. To determine the Cs$^+$ ion distribution ratio, a fraction of each phase was removed and the activity of ^{137}Cs measured by gamma-radiometric techniques. The initial caesium salt concentration was varied in the ranges of 3×10^{-4} to 9×10^{-1} M and 3×10^{-5} to 6.8×10^{-2} M for CsNO$_3$ and CsClO$_4$ systems, respectively. Duplicate experiments were performed for every

---

¶ Note: the dichloromethane solution of 1,2-bis(2′-formyl-4′-*tert*-butylphenoxy)ethane may be used directly for the next reaction without evaporation or isolation.

‖ The IUPAC name for 4,5′,5″,5‴-tetra-*tert*-butyltetrabenzo-24-crown-8 is 1^4,6^4,11^5,16^4-tetra-*tert*-butyl-2,5,7,10,12,15,17,20-octaoxa-1,6,11,16(1,2)-tetrabenzenacycloicosaphane.

** CCDC reference number 152308. See http://www.rsc.org/suppdata/p2/b008603g/ for crystallographic data in CIF or other electronic format.

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 all data points.

Analysis. The caesium distribution from aqueous solutions to the 1,2-DCE phase was determined by gamma-counting techniques (^{137}Cs tracer) using a 3 inch NaI(Tl) crystal through-hole type detector (Packard Cobra Quantum Model 5003). Caesium distribution ratios D_{Cs}, defined as the ratio of total organic- and aqueous-phase caesium concentrations $[Cs]_{org}/[Cs]_{aq}$, were obtained directly as the ratio of background-corrected count rates per mL. In control experiments, no extraction within background was observed for 1,2-DCE (without crown ether) equilibrated with aqueous $CsNO_3$ or $CsClO_4$ solutions under the experimental conditions employed.

Data treatment. The caesium distribution ratios D_{Cs} were used as input by the solvent extraction modeling program SXLSQI.[21] Nonideality effects were taken into account by use of Pitzer parameters for aqueous ions, the Hildebrand–Scott treatment for non-ionic effects in the organic phase, and the Debye–Hückel treatment for electrostatic effects in the organic phase.[21,23–25,27,28] 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.[29] The solubility parameters and molar volumes of the ligand were estimated from group contributions.[23] Parameters used in the SXLSQI program are summarized in the electronic supplementary information.

Acknowledgements

This research was sponsored by the Division of Chemical Sciences, Geosciences, and Biosciences, Office of Basic Energy Sciences, US Department of Energy, under contract DE-AC05-00OR22725 with Oak Ridge National Laboratory, managed and operated by UT-Battelle, LLC.

References

1 J. S. Bradshaw, R. M. Izatt, A. V. Bordunov, C. Y. Zhu and J. K. Hathaway, in *Comprehensive Supramolecular Chemistry*, eds. J. L. Atwood, J. E. D. Davies, D. D. MacNicol, F. Vögtle and J.-M. Lehn, Pergamon, Oxford, 1996, vol. 1, p. 36; *Cation Binding by Macrocycles: Complexation of Cationic Species by Crown Ethers*, eds. Y. Inoue and G. W. Gokel, Marcel Dekker, New York, 1990, p. 111; L. F. Lindoy, *The Chemistry of Macrocyclic Ligand Complexes*, Cambridge University Press, Cambridge, 1990; G. Gokel, *Crown Ethers & Cryptands*, The Royal Society of Chemistry, Cambridge, 1991; B. G. Cox and H. Schneider, *Coordination and Transport Properties of Macrocyclic Compounds in Solution*, Elsevier, New York, 1992.

2 J.-M. Lehn, *Struct. Bonding* (*Berlin*), 1973, **16**, 1; A. V. Bajaj and N. S. Poonia, *Coord. Chem. Rev.*, 1988, **35**, 55; N. S. Poonia and A. V. Bajaj, *Chem. Rev.*, 1979, **79**, 389; D. W. McBride, Jr., R. M. Izatt, J. D. Lamb and J. J. Christensen, in *Inclusion Compounds*, eds. J. L. Atwood, J. E. D. Davies and D. D. MacNicol, Academic Press, New York, 1984, vol. 3, p. 571.

3 C. J. Pedersen, *J. Am. Chem. Soc.*, 1967, **89**, 7017.

4 W. J. McDowell, G. N. Case, J. A. McDonough and R. A. Bartsch, *Anal. Chem.*, 1992, **64**, 3013.

5 W. J. McDowell, *Sep. Sci. Technol.*, 1988, **23**, 1251; L. Tusek, P. R. Danesi and R. Chiarizia, *J. Inorg. Nucl. Chem.*, 1975, **37**, 1538.

6 R. M. Izatt, J. S. Bradshaw, S. A. Nielsen, J. D. Lamb, J. J. Christensen and D. Sen, *Chem. Rev.*, 1985, **85**, 271; R. M. Izatt, K. Pawlak, J. S. Bradshaw and R. L. Bruening, *Chem. Rev.*, 1991, **91**, 1721; T. B. Stolwijk, E. J. R. Sudölter and D. N. Reinhoudt, *Recl. Trav. Chim. Pays-Bas*, 1989, **108**, 103; W. J. McDowell, B. A. Moyer, G. N. Case and F. I. Case, *Solvent Extr. Ion Exch.*, 1986, **4**, 217; B. P. Hay, D. Zhang and J. R. Rustad, *Inorg. Chem.*, 1996, **35**, 2650.

7 R. A. Sachleben, Y. Deng, D. R. Bailey and B. A. Moyer, *Solvent Extr. Ion Exch.*, 1996, **14**, 995; Y. Deng, R. A. Sachleben and B. A. Moyer, *J. Chem. Soc.*, *Faraday Trans.*, 1995, **23**, 4215.

8 W. J. McDowell, G. N. Case and D. W. Aldrup, *Sep. Sci. Technol.*, 1983, **15**, 1483; T. B. Stolwijk, E. J. R. Sudölter and D. N. Reinhoudt, *J. Am. Chem. Soc.*, 1989, **111**, 6321.

9 R. A. Sachleben, J. C. Bryan, J. M. Lavis, C. M. Starks and J. H. Burns, *Tetrahedron*, 1997, **53**, 13567.

10 T. G. Levitskaia, J. C. Bryan, R. A. Sachleben, J. D. Lamb and B. A. Moyer, *J. Am. Chem. Soc.*, 2000, **122**, 554.

11 A. H. Bond, R. Chiarizia, V. J. Huber, M. L. Dietz, A. W. Herlinger and B. P. Hay, *Anal. Chem.*, 1999, **71**, 2757; M. L. Dietz, A. H. Bond, M. Clapper and J. W. Finch, *Radiochim. Acta*, 1999, **85**, 119.

12 J. C. Bryan, K. Kavallieratos and R. A. Sachleben, *Inorg. Chem.*, 2000, **39**, 1568; J. C. Bryan, R. A. Sachleben, G. J. Bunick and B. P. Hay, *Inorg. Chim. Acta*, 1999, **290**, 86.

13 G. G. Talanova, N. S. A. Elkarim, V. S. Talanov, R. E. Hanes, Jr., H.-S. Hwang, R. A. Bartsch and R. D. Rogers, *J. Am. Chem. Soc.*, 1999, **121**, 11281.

14 J. C. Bryan, G. J. Bunick and R. A. Sachleben, *Acta Crystallogr.*, *Sect. C: Cryst. Struct.*, 1999, **55**, 250.

15 J. C. Bryan, J. M. Lavis, B. P. Hay and R. A. Sachleben, *Acta Crystallogr.*, *Sect. C: Cryst. Struct.*, 2000, **56**, 391.

16 J. Dale, *Isr. J. Chem.*, 1980, **20**, 3.

17 T. Steiner, *Crystallogr. Rev.*, 1996, **6**, 1.

18 J. Czapkiewicz and B. Czapkiewicz-Tutaj, *J. Chem. Soc.*, *Faraday Trans. 1*, 1980, **76**, 1663.

19 I. M. Kolthoff, M. K. Chantooni and W.-J. Wang, *J. Chem. Eng. Data*, 1993, **38**, 556.

20 T. J. Haverlock, P. V. Bonnesen, R. A. Sachleben and B. A. Moyer, *J. Inclusion Phenom. Macrocyclic Chem.*, 2000, **36**, 21.

21 C. F. Baes, Jr., B. A. Moyer, G. N. Case and F. I. Case, *Sep. Sci. Technol.*, 1990, **25**, 1675; C. F. Baes, Jr., *SXLSQI, A Program for Modeling Solvent Extraction Systems*, Report ORNL/TM-13604, Oak Ridge National Laboratory, 1998; C. F. Baes, Jr., *Solvent Extr. Ion Exch.*, in the press.

22 B. A. Moyer, in *Comprehensive Supramolecular Chemistry*, ed. G. W. Gokel, Pergamon, Oxford, 1996, vol. 1, p. 377.

23 A. F. M. Barton, *CRC Handbook of Solubility Parameters and Other Cohesion Parameters*, CRC Press, Boca Raton, Florida, 1991.

24 K. S. Pitzer, in *Activity Coefficients in Electrolyte Solutions*, ed. K. S. Pitzer, CRC Press, Boca Raton, Florida, 1991, ch. 3.

25 E. J. Henley and J. D. Seader, *Equilibrium-Stage Separation Operation in Chemical Engineering*; John Wiley & Sons, New York, 1981.

26 J. C. Bryan, R. A. Sachleben, J. M. Lavis, M. C. Davis, J. H. Burns and B. P. Hay, *Inorg. Chem.*, 1998, **37**, 2749.

27 T. Konnecke, V. Neck, T. Fanghanel and J. I. Kim, *J. Solution Chem.*, 1997, **26**, 561.

28 C. F. Baes, Jr. and B. A. Moyer, *J. Phys. Chem. B.*, 1997, **101**, 6566.

29 F. J. Millero, in *Structure and Transport Processes in Water and Aqueous Solutions*, ed. R. A. Horne, John Wiley and Sons, New York, 1972, p. 519.