Synthesis and Complexation Properties of a Novel Potassium-selective Trisanisyl Bis(benzo-crown ether)

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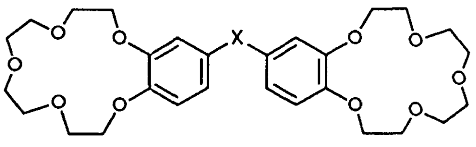
The condensation of 2,2′2″-trimethoxy-5,5′,5″-trimethyl-1,1′:3′,1″-terphenyl-3,3″-di(carbonyl chloride) (**2**) with two equivalents of 4-aminobenzo-15-crown-5 (15-amino-2,3,5,6,8,9,11,12-octahydro-1,4,7,10,13-benzopentaoxacyclopentadecine) (**3**) gave a novel bis(crown ether) (**4**) containing a rigid preorganised trisanisyl chain backbone. Titrations of this new host with alkali-metal cations and the ammonium ion monitored by ^{13}C n.m.r. spectroscopy suggested that the benzo crown ether moieties alone provided the co-ordinating sites for the cationic guests, forming a 1 : 2 [(**4**) : M^+] complex with sodium ions, while potassium, rubidium, and ammonium ions formed 1 : 1 intramolecular sandwich complexes. The association constants (K/dm^3 mol^{-1}) of the bis(crown ether) (**4**) with picrate salts of potassium (7.93 × 10^6), rubidium (0.19 × 10^6), caesium (0.03 × 10^6), and ammonium (0.02 × 10^6) in $CDCl_3$ were measured by deuteriochloroform–water extraction and spectroscopic techniques, indicating a high degree of selectivity for potassium over the other cations [$K(K^+)/K(Rb^+) = 42$, $K(K^+)/K(Cs^+) = 264$, and $K(K^+)/K(NH_4^+) = 397$]. This result is in agreement with fast-atom-bombardment mass spectrometric competition experiments.

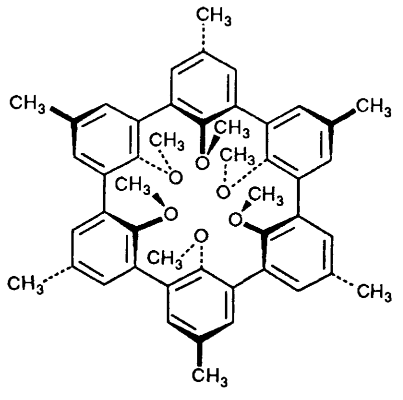
The observation[1] that the potassium cation forms a 1:2 stoicheiometric complex with benzo-15-crown-5 (2,3,5,6,8,9,11,-12-octahydro-1,4,7,10,13-benzopentaoxacyclopentadecine) has resulted in the synthesis of macrocyclic polyether ligand systems known as the bis(crown ethers). These compounds contain two crown ether subunits linked together by a single bridge (X) which can simply be a hydrocarbon chain,[2–5] alkene,[6] azo unit,[7] or even a metallocene redox centre.[8] Due to the co-operative effect of the two crown ether rings, bis(crown ethers) have been shown to exhibit remarkable selectivity for alkali-metal cations, forming 1:1 cation:bis(crown ether) intramolecular sandwich complexes with alkali-metal cations larger than the hole size of the respective crown ether unit. This change in selectivity has been termed the 'bis crown effect'.[9]

The rigid trisanisyl unit has been successfully used to construct preorganised spherand host molecules such as (**1**) which display the highest selectivities and stability constants known for certain alkali-metal cations.[10,11] The combination of the trisanisyl chain with two crown ether units would produce a novel bis(crown ether) expected to show a greater complexing ability and degree of selectivity towards particular alkali-metal cations over the monocyclic crown ether analogue, as a result of both the preorganised[10] nature of the trisanisyl moiety and the 'bis crown effect'.[9] This paper describes the synthesis, complexation studies including cation extraction and association-constant determinations, and fast-atom-bombardment (f.a.b.) competition selectivity investigations of one such bis(crown ether) (**4**).

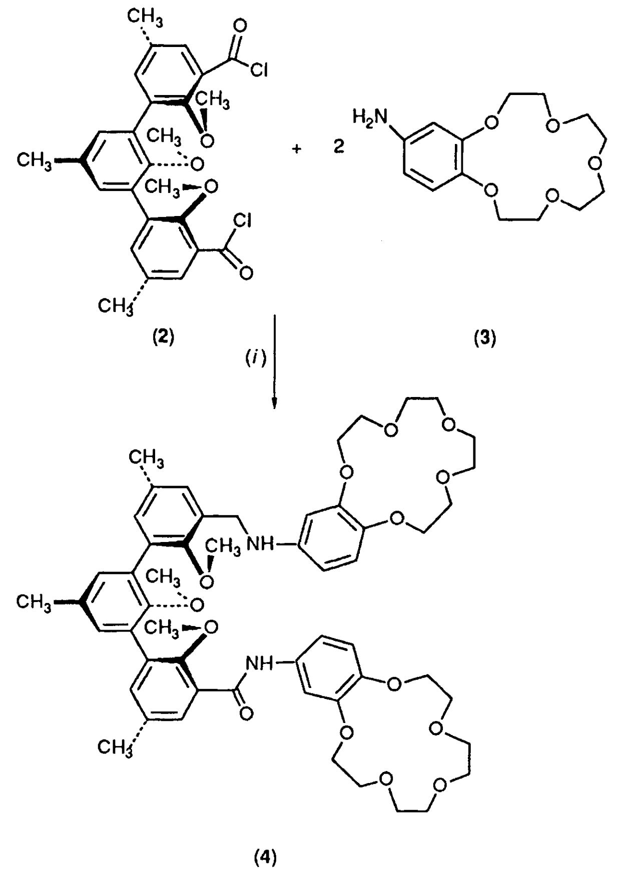
Results and Discussion

Synthesis.—The condensation of diacid chloride (**2**)[12] with 2 mol of 4-aminobenzo-15-crown-5 (15-amino-2,3,5,6,8,9,11,12-octahydro-1,4,7,10,13-benzopentaoxacyclopentadecine) (**3**)[13] in the presence of triethylamine and a catalytic amount of 4-dimethylaminopyridine (dmap) gave, after column chromatography [alumina, dichloromethane–methanol (98:2)], the new bis(crown ether) (**4**) in 60% yield (Scheme 1). The analogous condensation of (**2**) with 2 mol of 3,4-dimethoxyaniline (**5**) gave 'model' compound (**6**) in 51% yield (Scheme 2). The structure of (**4**) and (**6**) were characterised by i.r., ^{1}H and ^{13}C n.m.r., f.a.b. mass spectroscopy, and elemental analyses (see Experimental section).

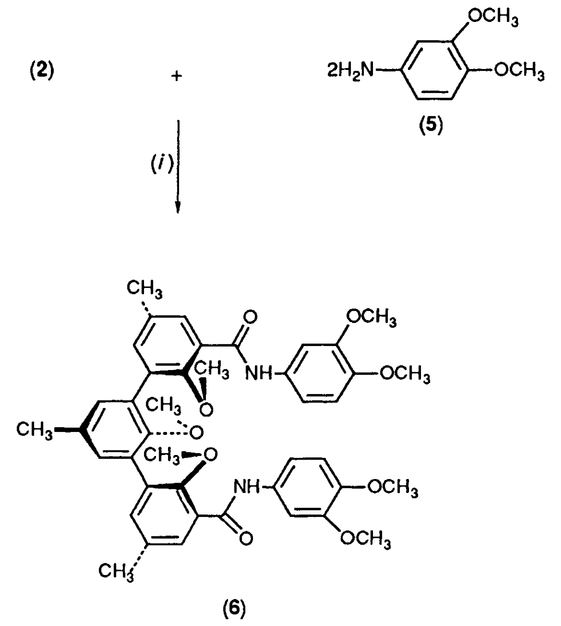



(**1**)

Complexation Studies.—Alkali metal and ammonium cations. Bis(crown ether) (**4**) contains two types of binding sites which may be suitable for complexing alkali-metal or ammonium cations. First, the macrocyclic crown ether moieties may complex a small cation within each ring, or act co-operatively to form an intramolecular sandwich complex in which a larger



Scheme 1. (*i*) $N(CH_2CH_3)_3$, dmap



Scheme 2. (*i*) $N(CH_2CH_3)_3$, dmap

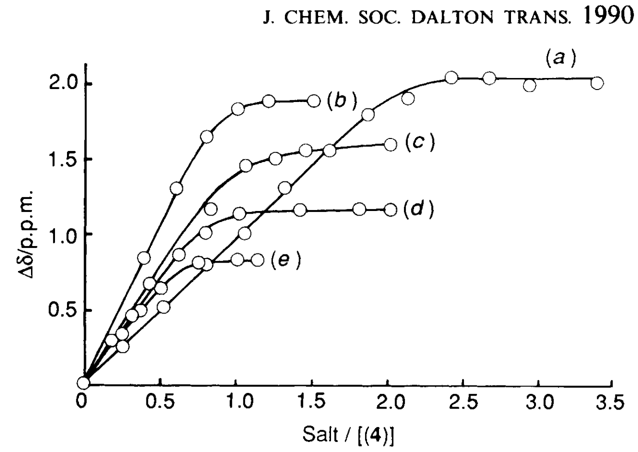


Figure 1. ^{13}C N.m.r. titration curves of compound (**4**) with (*a*) Na^+, (*b*) K^+, (*c*) Rb^+, (*d*) NH_4^+, and (*e*) Cs^+

Table 1. Stoicheiometry of cationic complexes with compound (**4**)

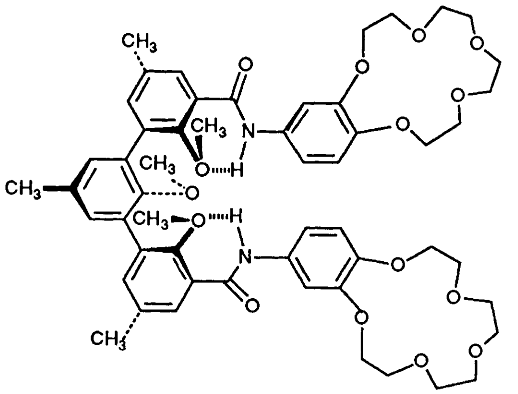
Guest species (G^+)	Stoicheiometry Host (**4**):G^+	Ionic diameter of G^+ [19] (Å)
Na^+	1:2	1.94
K^+	1:1	2.66
Rb^+	1:1	2.94
Cs^+	Unclear*	3.34
NH_4^+	1:1	2.86

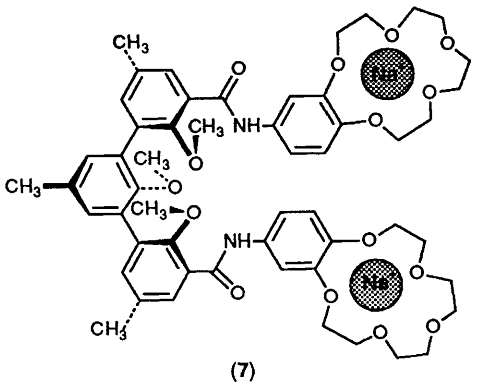
* Precipitation problems; titration curve indicates solution complex of stoicheiometry between 2:1 and 1:1.

cation is co-ordinated by oxygen donor atoms from both rings. In the case of the sandwich complexes it may be possible for a second cation to be complexed at the site of the trisanisyl unit, stabilised by donation of electron density from the anisole and amido oxygens. Alternatively, cationic complexation could occur at the trisanisyl binding site alone. To elucidate the solution co-ordination properties, ^{13}C n.m.r. spectroscopy[14] was used to determine the stoicheiometry of the complexes formed between (**4**) and alkali-metal cations Na^+, K^+, Rb^+, and Cs^+ and the ammonium cation.

The stepwise addition of a concentrated solution of sodium tetraphenylborate in deuteriated acetonitrile, or potassium, rubidium, caesium, or ammonium nitrate in deuterium oxide, to a dilute deuteriated acetonitrile solution of compound (**4**) led to considerable upfield shifts of the resonances of the OCH_2CH_2O carbons of the host. Negligible shifts were observed with compound (**6**) under identical experimental conditions. Plots of the $\Delta\delta$ of the most downfield crown ether carbon *versus* [Salt]/[(**4**)] (Figure 1) gave the stoicheiometries listed in Table 1. A control experiment in which a deuteriated acetonitrile solution of (**4**) was titrated with deuterium oxide produced a negligible effect on the OCH_2CH_2O carbons, confirming that the addition of the guest cation was responsible for the observed changes in the chemical shifts.

It is noteworthy that the chemical shifts of the anisole carbons of host (**4**) were found to remain constant during these titrations, suggesting that complexation involving electron-density donation from the anisole oxygens to the cationic guest species was not occurring. This may be due to the steric crowding at this binding site, as suggested from a Corey–Pauling–Koltun (C.P.K.) model, or the poor electron-donor properties of the anisole oxygen atoms compared to the crown ether oxygens. Cram *et al.*[15] have demonstrated the poor electron-donor properties of the anisole oxygens by showing that an acyclic array of six anisole rings is a very poor co-ordinating ligand for lithium and sodium cations, in sharp contrast to the preorganised macrocyclic spherand analogue (**1**). Intramolecular hydrogen bonding between an oxygen anisole and the adjacent amide linkage to form a 'six-membered ring' as illustrated, as well as unfavourable mutual electrostatic repulsion of cations bound at both sites, may also play roles in preventing complexation at the trisanisyl moiety.





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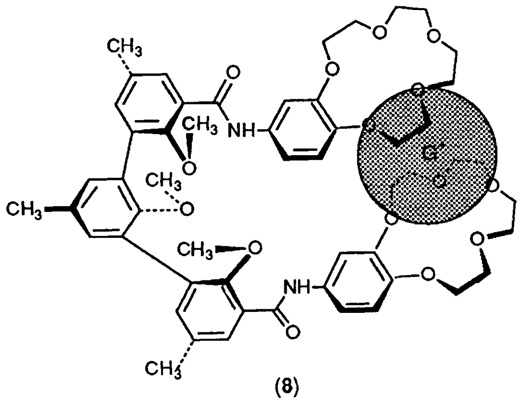
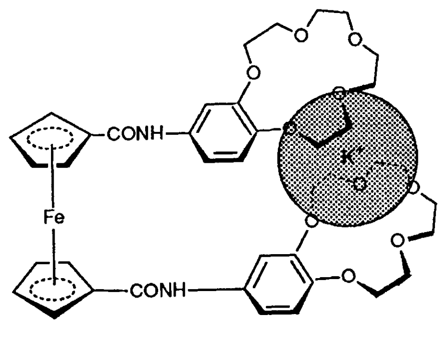


(8)

$G^+ = K^+, Rb^+, Cs^+, \text{ or } NH_4^+$



(9)

Table 2. Percentage of picrate salts extracted

Picrate salt	Percentage extracted		
	Host (4)[a]	Benzo-15-crown-5[b]	4-Methylbenzo-15-crown-5[b]
K^+	51.6 ± 1.5	14.2	22.3
Rb^+	13.0 ± 1.6	11.2	13.0
Cs^+	3.5 ± 0.7	7.7	3.5
NH_4^+	2.05 ± 0.7	—	—

[a] Mean ± standard deviation of four experiments. [b] Initial ratio of crown in organic phase (dichloromethane):cation in aqueous phase was 5:1.[9]

The titration results in Table 1 suggest that the stoicheiometry of the complexes formed with the crown ether rings of host (**4**) depends on the size of the cationic guest. A sodium cation is complexed by each of the benzo-15-crown-5 rings to give a 1:2 (**4**):Na^+ complex (**7**). Larger cations such as K^+, Rb^+, and NH_4^+ form 1:1 complexes (**8**), indicating that the benzo-15-crown-5 moieties are able to lie approximately cofacial to one another and act co-operatively to form intramolecular sandwich complexes. This suggestion is supported by our recent report of the *X*-ray crystal structure of a 1:1 intramolecular sandwich complex formed between K^+ and a ferrocene bis(benzo-15-crown-5) ligand (**9**).[16] An *X*-ray crystal structure of a sandwich complex between NH_4^+ and benzo-15-crown-5 has also been described.[17]

The titration with the larger caesium cation gave a curve implying a solution complex of stoicheiometry (**4**):Cs^+ between 2:1 and 1:1. Detrimental precipitation problems were encountered as the caesium salt was added and so little significance can be attributed to this particular titration result.

Cation Extraction Studies.—The ability of compounds (**4**) and (**6**) to extract potassium, rubidium, caesium, or ammonium picrates from an aqueous into a chloroform layer was determined by measuring the electronic absorbance of the organic phase at 375 nm, following the procedure devised by Cram.[18] The extractions were initiated with an equal number of moles of (**4**) in the chloroform layer and picrate salt in the aqueous layer, on the basis that 1:1 complexes were formed between the host and cationic guest in each case. This assumption was supported for K^+, Rb^+, and NH_4^+ by the ^{13}C n.m.r. titration results described earlier. Caesium was also assumed to form a 1:1 complex, in spite of an unsatisfactory ^{13}C n.m.r. titration, on the precedence of the 1:1 complexes detected between hydrocarbon-linked bis(benzo-15-crown-5) ethers and caesium by other workers.[9]

The percentage of individual picrate salts extracted into the organic phase by compound (**4**) is shown in Table 2. The results obtained from analogous extraction experiments using benzo-15-crown-5 and 4-methylbenzo-15-crown-5[9] are included within this table for comparison. Control experiments with (**6**) revealed that virtually no extraction of all four picrate salts into the organic phase took place, confirming that complexation of the cationic guest only takes place at the crown ether binding sites of (**4**)

The association constants (*K*), equation (1) (G = guest,

$$[G^+pic^-]_{CDCl_3} + [H]_{CDCl_3} \overset{K}{\rightleftharpoons} [G^+H\cdot pic^-]_{CDCl_3} \qquad (1)$$

H = host), and free energies of association (ΔG°) for the formation of 1:1 complexes of (**4**) with potassium, rubidium, caesium, and ammonium picrate were subsequently calculated, using the experimental extraction data, according to Cram's method[18] and the results are presented in Table 3.

The association data indicate that compound (**4**) forms 1:1

Table 3. Association constants (K) and free energies of association (ΔG°) for the formation of 1:1 complexes of compound (**4**) with picrate salts; 1 cal = 4.184 J

Picrate salt	$10^6\ K$/dm^3 mol^{-1}	$-\Delta G^\circ$/kcal mol^{-1}
K^+	7.93	9.41
Rb^+	0.19	7.20
Cs^+	0.03	6.11
NH_4^+	0.02	5.96

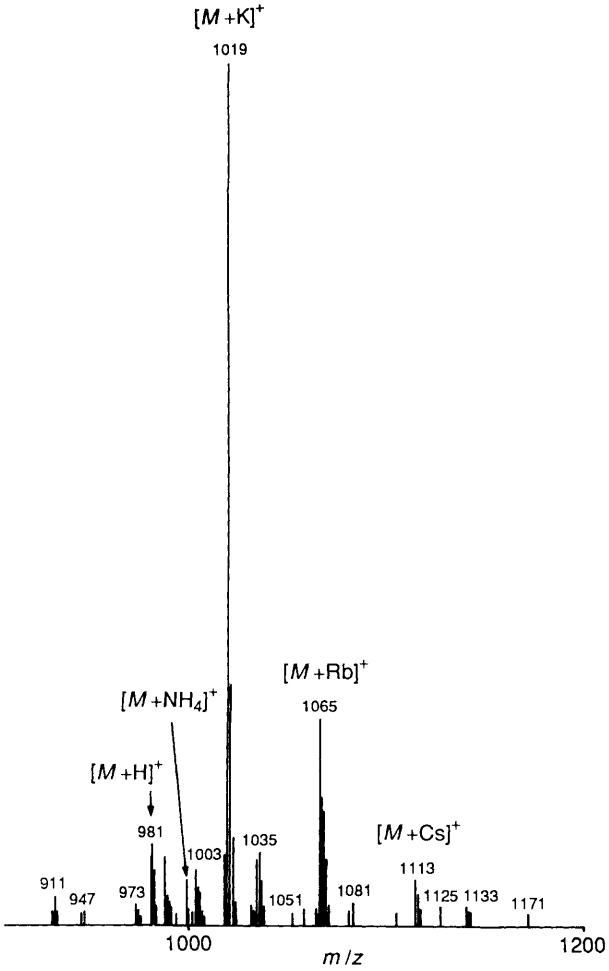


Figure 2. F.a.b. mass spectrum of compound (**4**) + K^+, Rb^+, Cs^+, NH_4^+, and Ag^+ (primary scan)

complexes with the respective cations in order of decreasing stability $K^+ > Rb^+ > Cs^+ \approx NH_4^+$. The decrease in free energy of association as the Group 1A metal cations increase in size is probably predominantly a steric effect. Host (**4**) possesses a rigid preorganised backbone and C.P.K. models suggest a well defined cavity exists between the cofacial amido benzo-15-crown-5 units of optimal spatial dimensions[19] for the K^+ guest cation. The ammonium ion is of similar size to potassium and yet exhibits relatively weak binding with (**4**). This result suggests that the formation of four tetrahedrally arranged hydrogen bonds between NH_4^+ and the crown ether donor atoms is less favourable than the non-directional spherical binding utilised by the alkali-metal cations. It is noteworthy that the rigid trisanisyl linking group of compound (**4**) appears to improve significantly the degree of selectivity for potassium over rubidium $[K(K^+)/K(Rb^+) = 42]$ and caesium $[K(K^+)/K(Cs^+) = 264]$ when compared to the mono(benzo-15-crown-5) hosts and bis crown ethers containing more flexible hydrocarbon bridging units.[9]

F.A.B. Mass Spectrometry Competition Experiments.—F.a.b. mass spectrometry has been used as a semiquantitative technique to study the selectivity of monocyclic[20] and bis(crown ethers)[8,16] for Group 1A metal cations in competition experiments. An experiment in which compound (**4**) (5×10^{-3} mol dm^3, 0.5 cm^3 acetonitrile) was mixed with an aqueous solution of potassium, rubidium, caesium, ammonium, and silver nitrates (each at 5×10^{-3} mol dm^{-3}, 0.5 cm^3), using 3-nitrobenzyl alcohol as the matrix, gave the spectrum shown in Figure 2.

This experiment indicates an order of selectivity $K^+ \gg Rb^+ > Cs^+ \approx NH_4^+$ (a silver complex was not detected), in agreement with the thermodynamic values described in the previous section. A control experiment with compound (**6**) did not detect the formation of any complexes with these cations. In comparison, the metallocene bis(crown ether) (**9**) exhibits exclusive selectivity for potassium over sodium and caesium during similar f.a.b. competition experiments.[16]

Conclusion

Novel bis(crown ether) (**4**), in which two benzo-15-crown-5 units are linked by a rigid trisanisyl chain, has been shown to form a 1:2 host:cation complex with sodium ions and 1:1 complexes with potassium, rubidium, and ammonium ions at the crown ether binding sites. No evidence for binding of these cations at the potential trisanisyl co-ordinating site was found. The host (**4**) exhibits a high degree of selectivity towards potassium ions ($K = 7.93 \times 10^6$ dm^3 mol^{-1}) compared to rubidium ($K = 0.19 \times 10^6$ dm^3 mol^{-1}) $[K(K^+)/K(Rb^+) = 42]$, caesium ($K = 0.03 \times 10^6$ dm^3 mol^{-1}) $[K(K^+)/K(Cs^+) = 264]$, and ammonium ($K = 0.02 \times 10^6$ dm^3 mol^{-1}) $[K(K^+)/K(NH_4^+) = 397]$ ions, in agreement with the results of f.a.b. competition experiments.

The trisanisyl chain of (**4**) may in future be made more attractive to binding cationic species by reducing the amide linking groups to amines, which would undoubtedly improve the donor properties of the nitrogen atoms and decrease the steric crowding at this potential binding site. Alkaline-earth-metal cations may be complexed at this new ligating unit following the precedent recently set by Reinhoudt and co-workers[21] of a new dinuclear macrocyclic ligand complexing barium ions at a binding site largely based on a trisanisyl chain.

Experimental

Solvent and Reagents Pretreatment.—Where necessary, solvents were purified by distillation prior to use. The following drying agents and conditions were used before distillation; acetonitrile was distilled from CaH_2, dichloromethane from P_2O_5, hexane and diethyl ether from sodium, toluene and tetrahydrofuran (thf) from sodium using benzophenone as the indicator, dimethylformamide (dmf) under reduced pressure from $MgSO_4$, and thionyl chloride from triphenyl phosphite.

Unless otherwise stated, commercial grade chemicals were used without further purification.

Methods.—Melting points were recorded on a Gallenkamp apparatus in open capillaries and are uncorrected. Literature values for known compounds are quoted in parentheses. Infrared spectra were obtained on a Perkin-Elmer 297 instrument (4 000—600 cm^{-1}) as KBr discs, n.m.r. spectra on JEOL FX-90Q, GX-270, and Bruker WH400 instruments using tetramethylsilane as internal standard ($\delta = 0$). Mass spectra and f.a.b. spectra were recorded on a Kratos MS80 RF mass spectrometer; the latter used an argon primary beam and 3-nitrobenzyl alcohol as the matrix. The u.v.–visible spectra were recorded on a Shimadzu u.v.-240 spectrophotometer. All elemental analyses were performed at the University of Birmingham.

Syntheses.—*2,2′,2″-Trimethoxy-5,5′,5″-trimethyl-1,1′:3′,1″-terphenyl-3,3″-di(carbonyl chloride)* (**2**). Compound (**2**) was prepared from the corresponding diacid by a method modified from that outlined by Cram and co-workers.[12] The diacid [12] (0.2 g, 0.44 mmol) was placed in a flask, and flushed with nitrogen. Thionyl chloride (10 cm^3, 0.14 mol) was added, and the resulting dark brown mixture was stirred at 25 °C for 2 h; during this time the diacid gradually dissolved and the solution lightened in colour. Dry toluene (30 cm^3) was added, and the solution was evaporated under reduced pressure. This procedure was repeated twice. The product was used directly in the preparation of compounds (**4**) and (**6**), i.r.: 1 780 cm^{-1} (C=O stretch).

4-Aminobenzo-15-crown-5 (**3**) was prepared according to literature procedures.[13]

2,2′,2″-Trimethoxy-5,5′,5″-trimethyl-3,3″-bis[N-*(2,3,5,6,-8,9,11,12-octahydro-1,4,7,10,13-benzopentaoxacyclopentadecin-16-yl)carbamoyl*]-*[1,1′:3′,1″-terphenyl]* (**4**). Diacid chloride (**2**) (0.2 g, 0.44 mmol) was dissolved in dry toluene (50 cm^3) and transferred to a pressure-equalising dropping funnel (100 cm^3). This solution was added, over 1 h, to a stirred solution of compound (**3**) (0.25 g, 0.88 mmol), triethylamine (0.12 cm^3, 0.88 mmol), and 4-dimethylaminopyridine (0.03 g, 0.25 mmol) in dry toluene (50 cm^3) under nitrogen. The mixture was then stirred at room temperature for 16 h, and refluxed for a further 4 h, before the solvent was removed *in vacuo*. The residue was shaken with dichloromethane and water. The organic layer was washed with water, LiOH solution (50 cm^3, 2 mol dm^{-3}), and dilute hydrochloric acid (50 cm^3, 2 mol dm^{-3}), and then dried ($MgSO_4$), filtered, and evaporated to dryness. The light brown residue was purified by column chromatography on alumina, flushing the column first with dichloromethane, then eluting the product with dichloromethane–methanol (98:2, v/v). Finally, the oily product was triturated with hexane to solidify it, filtered, and dried *in vacuo* to give (**4**) as a cream powder (0.26 g, 60% yield) (Found: C, 65.9; H, 6.5; N, 2.7. Calc. for $C_{54}H_{64}N_2O_{15}$: C, 66.1; H, 6.6; N, 2.9%), m.p. 109—111 °C, *m/z* 981, i.r. 1 670 cm^{-1} (C=O stretch). N.m.r. ($CDCl_3$): ^1H, δ 2.41 (9 H, s, CH_3), 3.23 (3 H, s, inner OCH_3), 3.60 (6 H, s, outer OCH_3), 3.75 (16 H, s, OCH_2CH_2O), 3.89—3.91 (8 H, m, OCH_2CH_2O), 4.12—4.14 (4 H, m, OCH_2CH_2O), 4.19—4.21 (4 H, m, OCH_2CH_2O), 6.85 (2 H, d, *J* 8.6, aryl H), 6.99 (2 H, dd, *J* 2.4, 8.6, aryl H), 7.18 (2 H, s, aryl H), 7.30 (2 H, d, *J* 2.0, aryl H), 7.62 (2 H, d, *J* 2.4, aryl H), 8.02 (2 H, d, *J* 1.8 Hz, aryl H), and 9.84 (2 H, br s, NH); ^{13}C, δ 20.66 (CH_3), 60.98 (inner OCH_3), 61.60 (outer OCH_3), 68.83, 69.43, 69.64, 70.39, 70.55, 70.92, 70.99 (OCH_2CH_2O), 107.26, 112.45, 114.85, 126.02, 131.36, 131.75, 131.93, 132.62, 133.19, 134.24, 135.69, 143.60, 145.69, 149.37, 153.14, 153.42 (aryl C), and 163.07 (C=O).

3,3″-Bis(*3,4-dimethoxyphenylcarbamoyl*)*-2,2′,2″-trimethoxy-5,5′,5″-trimethyl-1,1′:3′,1″-terphenyl* (**6**). The procedure for the preparation of compound (**6**) was as that described for (**4**), but replacing (**3**) with 3,4-dimethoxyaniline (**5**); 51% yield (Found: C, 69.0; H, 6.1; N, 3.2. Calc. for $C_{42}H_{44}N_2O_9$: C, 70.0; H, 6.2; N, 3.9%), m.p. 76—80 °C, *m/z* 721, i.r. 1 660 cm^{-1} (C=O stretch). N.m.r. ($CDCl_3$): ^1H δ 2.43 (9 H, s, CH_3), 3.26 (3 H, s, inner OCH_3), 3.63 (6 H, s, outer OCH_3), 3.89 (6 H, s, OCH_3), 3.94 (6 H, s, OCH_3), 6.85 (2 H, d, *J* 8.7, aryl H), 7.04 (2 H, dd, *J* 2.5, 8.7, aryl H), 7.21 (2 H, s, aryl H), 7.33 (2 H, d, *J* 2.2, aryl H), 7.65 (2 H, d, *J* 2.5, aryl H), 8.05 (2 H, d, *J* 1.7 Hz, aryl H), and 9.84 (2 H, br s, NH); ^{13}C, δ 20.78 (CH_3), 55.99, 56.19 (OCH_3), 61.10 (inner OCH_3), 61.71 (outer OCH_3), 105.32, 111.53, 112.05, 126.19, 131.49, 131.85, 132.08, 132.18, 133.31, 134.32, 135.78, 145.90, 149.15, 153.29, 153.54 (aryl C), and 163.26 (C=O).

^{13}C *N.M.R. Titration Experiments*.—The experimental procedure consisted of measuring Δδ as a function of the concentration of the guest salt while the concentration of the host (**4**) was kept constant. In a typical experiment compound (**4**) (0.08 mmol) was dissolved in CD_3CN (3 cm^3) and the resulting solution transferred to a ^{13}C n.m.r. tube (10 mm). The ^{13}C n.m.r. chemical shifts were measured *versus* tetramethylsilane as internal standard after sequential additions [10 cm^3 (0.12 equivalent)] of $NaBPh_4$ (in CD_3CN), KNO_3, $RbNO_3$, $CsNO_3$, and NH_4NO_3 (in D_2O) respectively. Titration curves were obtained by plotting Δδ of the most downfield crown ether carbon *versus* [Salt]/[(**4**)], see Figure 1.

Determination of the Percentage Extraction of Picrate Salts by Hosts (**4**) *and* (**6**).—This procedure was similar to that reported by Cram and co-workers.[18]

Deuteriated chloroform and deionised water were used throughout these experiments for reasons of purity. All operations were conducted at room temperature. The absorbances were measured at 375 nm, and the picrate salts were prepared previously according to the method of Coplan and Fuoss [22] and dried under vacuum before use. The absorption coefficient (ε) for each picrate salt in CH_3CN was determined in the concentration range 10^{-6}—10^{-4} mol dm^{-3} from the gradients of plots of absorbance against concentration.

Aqueous solutions were prepared which were 0.015 mol dm^{-3} in the picrate of K^+, Rb^+, Cs^+, and $NH_4{}^+$. Into a plastic centrifuge tube (with cap) (1.5 cm^3) was transferred the appropriate picrate solution (0.5 cm^3), and a previously prepared 0.015 mol dm^{-3} solution (0.5 cm^3) of host (**4**) or (**6**) in $CDCl_3$. The tubes were centrifuged for 30 s in an Eppendorf centrifuge 5412, then shaken for 10 min by a Stuart flask shaker, before being centrifuged for 30 s. A 20-μl aliquot of each organic phase was then carefully removed with a microlitre syringe, and transferred to volumetric flasks (5 cm^3) which were brought to the mark with CH_3CN. The absorbance of each sample was then determined, and the percentage extractions and association data were calculated as described by Cram and co-workers.[18]

Acknowledgements

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