Synthesis and Co-ordination Chemistry of a Novel Bis(Benzo Crown Ether) Substituted Calix[4]arene that can Simultaneously Complex Cations and Anions†

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New calix[4]arene compounds substituted at the lower rim by four (L^3) or two (L^6) benzo-15-crown-5 (2,3,5,6,8,9,11,12-octahydro-1,4,7,10,13-benzopentaoxacyclopentadecine) groups respectively have been prepared. Proton NMR co-ordination studies with sodium and potassium cations in deuteriated acetonitrile revealed that L^3 forms $L^3{\cdot}5M^+$ ($M^+ = Na^+$ or K^+) solution stoichiometric complexes consisting of an alkali-metal cation bound in each of the four crown ether moieties and one occupying the tetraamide lower-rim cavity. Compound L^6 complexes K^+, Ba^{2+} and NH_4^+ exclusively at the crown ether binding sites in a 1 : 1 intramolecular sandwich stoichiometric fashion. A crystal-structure determination of $[KL^6][I_3]$ has been carried out. Although neither L^3 nor L^6 co-ordinates anions the potassium and ammonium complexes $[ZL^6]PF_6$ ($Z = K^+$ or NH_4^+) form 1 : 1 complexes with Cl^-, NO_3^-, HSO_4^- and $H_2PO_4^-$. Stability constant evaluations have shown that the strongest anion complexes are produced with $H_2PO_4^-$ and HSO_4^-.

Designing new ditopic[1] ligands for the simultaneous complexation of anionic and cationic guest species is a new area of co-ordination chemistry of interest to the selective extraction and/or transportation of metal salts across lipophilic membranes. Recently crown ether moieties have been combined with Lewis-acidic boron,[2] polyamines[3] and uranyl centres[4] to produce multifunctional receptors capable of complexing alkali-metal halide and potassium dihydrogenphosphate salts.

Calixarenes[5] are attractive supramolecular building blocks on which to attach additional ligating units. For example lower-rim ester,[6] amide[6] and crown ether[7] functionalised calixarenes have been shown to co-ordinate Group 1 metal cations selectively. As a result of our own anion co-ordination chemical investigations we have discovered the vital importance of favourable amide (CONH) hydrogen-bonding interactions for recognising anionic guest species[8] and have recently adapted this knowhow to produce the first examples of calixarene-containing anion receptors.[9] Combining amide groups with calixarenes and crown ethers will create novel multidentate receptors capable of co-ordinating anions and cations.‡ This paper reports the syntheses and co-ordination chemistry of new heteroditopic calix[4]arene compounds which contain lower-rim amide-linked benzo-15-crown-5 (2,3,5,6,8,9,11,12-octahydro-1,4,7,10,13-benzopentaoxacyclopentadecine) units tailored to complex cationic guests at the crown ether recognition sites and simultaneously create a unique calix[4]arene lower-rim cavity in close proximity to the positive centre to bind anions *via* favourable electrostatic and amide–hydroxyl hydrogen-bonding interactions (Fig. 1).

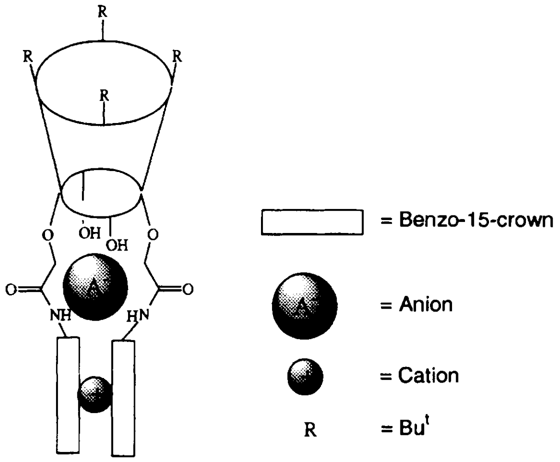

Fig. 1 Schematic representation of the simultaneous co-ordination of a cation and an anion by a lower rim benzo crown ether substituted calix[4]arene ligand

Experimental

Solvent and Reagent Purification.—Where necessary solvents and reagents were purified prior to use and stored under an atmosphere of nitrogen. Thionyl chloride was treated with triphenyl phosphite and then distilled under nitrogen. Acetone was dried by distillation from fresh calcium sulfate. Diethyl ether and tetrahydrofuran (thf) were distilled from sodium using benzophenone as an indicator. Distillation from calcium hydride was used to purify dichloromethane whilst toluene was dried by distillation from sodium. Acetonitrile was pre-dried over class 4 Å molecular sieves (4–8 mesh) and then distilled from calcium hydride.

5,11,17,23-Tetra-*tert*-butyl-25,26,27,28-tetrakis(chlorocarbonylmethoxy)calix[4]arene(L^1),[11] 4′-aminobenzo-15-crown-5-(L^2)[12] and 5,11,17,23-tetra-*tert*-butyl-25,27-bis(chlorocarbonylmethoxy)-26,28-dihydroxycalix[4]arene (L^5)[13] were prepared according to literature methods.

Instrumental Methods.—The NMR spectra and titrations were performed on a Brüker AM 300 instrument; ^1H NMR spectra were recorded at 300 MHz and ^{13}C spectra at 75.42

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

‡ Whilst this work was in progress Reinhoudt and co-workers[10] reported FAB mass spectrometric evidence of a uranyl calix[4]arene receptor co-ordinating NaH_2PO_4.

MHz. Microanalyses were carried out by the Inorganic Chemistry Laboratory Microanalysis Service. Ultraviolet experiments were performed on a Perkin-Elmer Lambda 6 UV/VIS spectrometer. Fast atom bombardment (FAB) mass spectra were recorded by the EPSRC Mass Spectrometry Service at Swansea.

Ligand Syntheses.—*Tetrakis*(*benzo*-15-*crown*-5) *substituted calix*[4]*arene* L^3. The *p-tert*-butylcalix[4]arene tetrakis(acid chloride) L^1 (0.72 g, 0.75 mmol) was dissolved in dry dichloromethane (40 cm^3) and added to a solution of 4′-aminobenzo-15-crown-5 (1.00 g, 3.19 mmol) and triethylamine (0.38 g, 3.76 mmol) in CH_2Cl_2 (50 cm^3). The resulting mixture was stirred at room temperature for 12 h and washed with dilute acid and water. After drying over magnesium sulfate the solvent was removed *in vacuo* to give a brown solid. This crude product was washed with hot methanol and recrystallised from dichloromethane–hexane to give an off-white powder (0.90 g, 62% yield) (Found: C, 65.35; H, 7.15; N, 2.80. $C_{108}H_{136}N_4O_{28}$ requires C, 66.30; H, 7.25; N, 2.90%). Mass spectrum (FAB): *m*/*z* 1941 [M^+ − H], 1965 [M + Na$^+$], 2073 [M + Cs$^+$]. NMR ($CDCl_3$): ^{1}H, δ 1.10 (s, 36 H, Bu^t), 3.27 (d, 4 H, H$_{eq}$ of calixarene CH_2), 3.70–4.02 (m, 64 H, crown CH_2CH_2), 4.57–4.61 (m, 12 H, H$_{ax}$ of calixarene CH_2 and OCH_2COH), 6.67 (d, 4 H, NHC_6H_3, 6.80 (s, 8 H, calixarene arene), 7.00 (d, 4 H, NHC_6H_3), 7.56 (s, 4 H, NHC_6H_3), 9.16 (s, 4 H, NH); ^{13}C, δ 31.36 (Me_3C), 32.00 (calixarene CH_2), 33.92 (Me_3C) 68.61, 69.41, 69.64, 70.39, 70.53, 70.87, 71.02 (crown CH_2), 75.22 (OCH_2), 78.30 (aromatic C), 107.39, 113.34, 114.47, 125.83 (aromatic CH), 131.65, 132.81, 145.79, 146.02, 149.22, 153.49 (aromatic C), 166.34 (C=O).

Tetraveratrole substituted calix[4]*arene* L^4. An analogous synthetic procedure to that above using 4 equivalents of 4-aminoveratrole and L^1 gave L^4 as a white solid in 74% yield (Found: C, 71.00; H, 7.5; N, 3.75. $C_{84}H_{100}N_4O_{16}$ requires C, 70.70; H, 7.10; N, 3.95%). Mass spectrum (FAB): *m*/*z* 1444 [M + Na$^+$]. NMR ($CDCl_3$): ^{1}H, δ 1.10 (s, 36 H, Bu^t), 3.31 (d, 4 H, H$_{eq}$ of calixarene CH_2), 3.66 (s, 12 H, OMe), 3.76 (s, 12 H, OMe), 4.63 (d, 4 H, H$_{ax}$ of calixarene CH_2), 4.68 (s, 8 H, OCH_2CO), 6.59 [d, 4 H, $C_6H_3(OMe)_2$], 6.83 (s, 8 H, calixarene aromatic H), 6.94 [dd, 4 H, $C_6H_3(OMe)_2$], 7.28 [s, 4 H, $C_6H_3(OMe)_2$], 8.98 (s, 4 H, NH); ^{13}C, δ 31.33 (Me_3C), 32.00 (calixarene CH_2), 33.91 (Me_3C), 55.72 (OMe), 55.96 (OMe), 75.20 (OCH_2), 105.68, 111.30, 113.02, 125.70 (aromatic CH), 130.93, 132.77, 146.18, 148.95, 150.13, 153.29 (aromatic C), 166.30 (C=O).

Bis(*benzo*-15-*crown*-5) *substituted calix*[4]*arene* L^6. The *p-tert*-butylcalix[4]arene bis(acid chloride) L^5 (1.54 g, 1.92 mmol) was dissolved in dry dichloromethane (40 cm^3) and added to a solution of 4′-aminobenzo-15-crown-5 (1.35 g, 4.31 mmol) and triethylamine (0.6 g, 5.90 mmol) in CH_2Cl_2 (20 cm^3). After stirring for 12 h at room temperature the reaction mixture was washed with dilute acid and water. Drying over magnesium sulfate and removal of the solvent *in vacuo* gave a yellow solid which was purified by recrystallisation from dichloromethane–hexane to give L^6 (1.54 g, 65% yield) (Found: C, 70.30; H, 7.55; N, 2.45. $C_{76}H_{96}N_2O_{16}$ requires C, 70.45; H, 7.60; N, 2.15%). Mass spectrum (FAB): *m*/*z* 1296 [M + H], 1318 [M + Na$^+$], 1428 [M + Cs$^+$]. NMR ($CDCl_3$): ^{1}H, δ 1.09 (s, 18 H, Bu^t), 1.28 (s, 18 H, Bu^t), 3.51 (d, 4 H, H$_{eq}$ of calixarene CH_2), 3.77 (s, 16 H, crown CH_2CH_2), 3.80 (t, 8 H, CH_2), 3.98 (t, 4 H, OCH_2CH_2O), 4.13 (t, 4 H, OCH_2CH_2O), 4.15 (d, 4 H, H$_{ax}$ of calixarene CH_2), 4.59 (s, 4 H, OCH_2CO), 6.73–6.86 (m, 4 H, NHC_6H_3), 7.00 (s, 4 H, calixarene aromatic H), 7.12 (s, 4 H, calixarene aromatic H), 7.30 (d, 2 H, NHC_6H_3), 8.13 (s, 2 H, OH), 10.14 (s, 2 H, NH); ^{13}C, δ 31.00, 31.62 (Me_3C), 32.27 (calixarene CH_2), 33.98, 34.23 (Me_3C), 68.56, 69.67, 69.80, 70.60, 70.73, 71.14 (crown CH_2), 74.79 (CH_2O), 106.22, 111.27, 114.88 (aromatic CH), 125.80 (aromatic C), 126.45, 127.22 (aromatic CH), 132.00, 132.23, 143.61, 148.44, 148.87, 149.23, 149.37 (aromatic C), 164.92 (C=O).

[KL^6]PF$_6$. Compound L^6 (0.70 g, 0.54 mmol) was dissolved in a minimum of dichloromethane and methanol (1 cm^3) added. A solution of excess KPF_6 in methanol was added whereupon a pale yellow solid precipitated which was collected and washed with methanol to give the required complex (0.61 g, 76% yield) (Found: C, 61.25; H, 6.40; K, 2.60; N, 1.90. $C_{76}H_{96}F_6KN_2O_{16}P$ requires C, 61.70; H, 6.70; K, 2.65; N, 1.90%). Mass spectrum (FAB): *m*/*z* 1334 [M], 1372 [M + K$^+$]. ^{1}H NMR ($CDCl_3$) δ: 0.93 (s, 18 H, Bu^t), 1.31 (s, 18 H, Bu^t), 3.44 (d, 4 H, H$_{eq}$ of calixarene CH_2), 3.75–3.95 (br m, 32 H, crown CH_2CH_2), 4.25 (d, 4 H, H$_{ax}$ of calixarene CH_2), 4.63 (s, 4 H, OCH_2CO), 6.50 (d, 4 H, NHC_6H_3), 6.80 (br s, 6 H, NHC_6H_3 and calixarene aromatic H), 7.14 (s, 4 H, calixarene aromatic H), 7.68 (s, 2 H, OH), 9.42 (s, 2 H, NH).

[NH$_4$L^6]PF$_6$. This complex was prepared in an analogous fashion to the potassium complex above using NH_4PF_6. Yield 62% (Found: C, 62.45; H, 6.75; N, 3.00. $C_{76}H_{100}F_6N_3O_{16}P$ requires C, 62.60; H, 7.05; N, 2.90%). ^{1}H NMR (CD_2Cl_2) δ: 1.13 (s, 18 H, Bu^t), 1.25 (s, 18 H, Bu^t), 3.35 (d, 4 H, H$_{eq}$ of calixarene CH_2), 3.73–4.00 (br m, 32 H, crown CH_2CH_2), 4.28 (d, 4 H, H$_{ax}$ of calixarene CH_2), 4.63 (s, 4 H, OCH_2CO), 6.57–6.64 (m, 4 H, NHC_6H_3), 7.08 (s, 4 H, calixarene aromatic H), 7.14 (s, 4 H, calixarene aromatic H), 7.61 (s, 2 H, NHC_6H_3), 7.86 (s, 2 H, OH), 9.47 (s, 2 H, NH).

Crystal-structure Determination of [KL^6][I$_3$].—Crystal data for [KL^6][I$_3$] are given in Table 1, together with refinement details. Data were collected with Mo-Kα radiation using the MARresearch image plate system. The crystal was positioned at 75 mm from the image plate, 95 frames were measured at 2° intervals with a counting time of 2 min. Data analysis was carried out with the XDS program.[14] The structure was then solved by direct methods with the SHELXS 86 program.[15] All non-hydrogen atoms were refined with anisotropic thermal parameters apart from those belonging to the *tert*-butyl groups. These were affected to some extent by positional disorder

Table 1 Crystal data and structure refinement for [KL^6][I$_3$]

	[KL^6][I$_3$]·0.75EtOH
Empirical formula	$C_{77.5}H_{96.5}I_3KN_2O_{16.75}$
M	1743.9
T/K	293(2)
Wavelength/Å	0.710 70
Crystal system	Monoclinic
Space group	$P2_1/c$
a/Å	23.157(8)
b/Å	15.831(8)
c/Å	25.706(8)
β/°	113.25(1)
U/Å^3	8659(6)
Z	4
D_c/Mg m^{-3}	1.338
μ/mm^{-1}	1.190
F(000)	3550
Crystal size/mm	0.20 × 0.15 × 0.10
θ range for data collection/°	2.70–25.17
hkl ranges	−27 to 27, 0 to 16, −30 to 30
Reflections collected	21 625
Independent reflections(R_{int})	12 643 (0.0515)
Refinement method	Full-matrix least-squares on F^2
Data, parameters	12 643, 846
Goodness to fit on F^2	1.049
Weighting scheme	$w = 1/[\sigma^2(F_o)^2 + (aP)^2 + bP]$, where $P = [\max(F_o^2, 0) + 2F_c^2]/3$, $a = 0.18$, $b = 22.1$
Final R^1 and wR^2 indices [$I > 3\sigma(I)$]	0.094, 0.345
(all data)	0.166, 0.405
Largest difference peak and hole/e Å^{-3}	1.087, −0.873

Table 2 Atomic coordinates ($\times 10^4$) for $[KL^6][I_3]\cdot 0.75EtOH$

Atom	*x*	*y*	*z*
I(1)	1 377(1)	7 914(1)	1 204(1)
I(2)	123(1)	8 553(1)	419(1)
I(3)	2 543(1)	7 236(1)	1 959(1)
K	−642(3)	10 472(3)	−3 554(2)
C(11)	3 905(9)	9 325(16)	163(9)
C(12)	4 315(13)	8 787(22)	421(12)
C(13)	4 268(15)	8 136(22)	832(16)
C(14)	3 665(18)	8 207(23)	873(14)
C(15)	3 190(11)	8 743(17)	576(11)
C(16)	3 331(11)	9 311(16)	229(8)
C(17)	2 644(10)	8 772(15)	712(8)
C(21)	2 573(10)	9 479(13)	1 022(9)
C(22)	2 949(7)	9 562(15)	1 628(8)
C(23)	2 995(12)	10 148(22)	1 981(7)
C(24)	2 646(10)	10 867(18)	1 731(9)
C(25)	2 270(11)	10 897(13)	1 149(10)
C(26)	2 257(10)	10 229(14)	814(8)
C(27)	1 916(9)	11 700(17)	884(10)
C(31)	2 336(12)	12 392(16)	813(12)
C(32)	2 526(17)	13 059(20)	1 265(15)
C(33)	2 944(18)	13 661(19)	1 306(15)
C(34)	3 164(13)	13 598(20)	899(16)
C(35)	2 994(13)	12 997(18)	445(12)
C(36)	2 575(9)	12 364(12)	446(10)
C(37)	3 344(13)	12 905(18)	90(12)
C(41)	3 828(11)	12 223(19)	192(11)
C(42)	4 357(12)	12 340(20)	724(13)
C(43)	4 766(13)	11 659(18)	933(9)
C(44)	4 635(10)	10 874(17)	583(10)
C(45)	4 159(10)	10 800(15)	101(9)
C(46)	3 738(11)	11 461(16)	−113(10)
C(47)	4 012(10)	10 026(17)	−194(9)
O(250)	1 890(6)	10 242(9)	227(5)
C(251)	1 244(9)	9 891(17)	49(8)
C(252)	1 070(11)	9 675(14)	−547(7)
O(253)	1 450(8)	9 524(13)	−768(7)
N(254)	450(8)	9 554(13)	−795(7)
C(255)	64(11)	9 376(12)	−1 377(7)
C(256)	−558(12)	9 296(16)	−1 523(9)
C(257)	−944(13)	9 174(18)	−2 088(10)
C(258)	−703(15)	9 137(17)	−2 491(9)
C(259)	−51(13)	9 185(14)	−2 335(10)
C(260)	330(9)	9 337(11)	−1 771(7)
O(261)	−1 049(10)	9 032(17)	−3 052(7)
C(262)	−1 705(16)	9 022(21)	−3 231(10)
C(263)	−1 917(15)	8 863(19)	−3 873(9)
O(264)	−1 732(11)	9 598(12)	−4 136(8)
C(265)	−1 739(21)	9 413(21)	−4 688(9)
C(266)	−1 152(36)	8 870(23)	−4 670(19)
O(267)	−712(13)	9 423(13)	−4 456(8)
C(268)	−84(23)	9 064(23)	−4 396(13)
C(269)	401(20)	9 579(23)	−4 144(12)
O(270)	515(10)	9 781(12)	−3 577(7)
C(271)	855(16)	9 140(22)	−3 194(11)
C(272)	787(15)	9 301(25)	−2 649(10)
O(273)	117(10)	9 173(13)	−2 774(6)
O(450)	3 221(7)	11 433(11)	−597(6)
C(451)	3 261(11)	11 787(19)	−1 089(10)
C(452)	2 616(11)	11 887(19)	−1 533(10)
O(453)	2 533(8)	12 161(16)	−2 003(8)
N(454)	2 147(9)	11 658(13)	−1 372(7)
C(455)	1 501(10)	11 699(12)	−1 691(8)
C(456)	1 109(10)	11 606(14)	−1 419(7)
C(457)	521(15)	11 528(14)	−1 684(10)
C(458)	230(9)	11 626(12)	−2 280(7)
C(459)	607(12)	11 715(12)	−2 559(7)
C(460)	1 234(11)	11 735(14)	−2 280(8)
O(461)	−400(8)	11 631(13)	−2 629(6)
C(462)	−856(11)	11 617(14)	−2 392(9)
C(463)	−1 481(19)	11 809(28)	−2 846(17)
O(464)	−1 600(8)	11 245(14)	−3 254(7)
C(465)	−2 124(15)	11 442(25)	−3 771(12)
C(466)	−1 931(14)	12 077(21)	−4 097(11)
O(467)	−1 487(8)	11 623(10)	−4 277(7)
C(468)	−1 259(13)	12 137(19)	−4 622(11)
C(469)	−794(12)	11 639(18)	−4 736(10)
O(470)	−240(8)	11 489(10)	−4 247(5)
C(471)	191(13)	12 104(17)	−4 035(9)
C(472)	644(12)	11 909(18)	−3 481(8)
O(473)	311(7)	11 813(11)	−3 136(5)
O(150)	2 856(8)	9 915(12)	−119(6)
O(350)	2 406(8)	11 780(12)	21(6)
C(100)	4 761(17)	7 561(24)	1 140(16)
C(101)	4 994(22)	7 096(29)	776(19)
C(102)	4 561(21)	6 988(26)	1 480(18)
C(103)	5 310(20)	8 049(33)	1 544(21)
C(200)	3 364(11)	10 110(17)	2 608(9)
C(201)	4 008(12)	9 900(30)	2 730(17)
C(202)	3 083(16)	9 484(20)	2 846(13)
C(203)	3 346(20)	10 943(19)	2 848(16)
C(300)	3 101(17)	14 325(23)	1 751(15)
C(302)	2 512(20)	14 691(33)	1 739(24)
C(301)	3 452(20)	14 994(24)	1 632(18)
C(303)	3 431(25)	13 950(35)	2 307(15)
C(400)	5 254(15)	11 618(23)	1 497(13)
C(401)	5 029(24)	11 035(31)	1 842(18)
C(402)	5 340(21)	12 426(24)	1 808(16)
C(403)	5 838(16)	11 324(36)	1 508(20)
O(500)	−2 055(21)	11 049(30)	1 460(18)
C(501)	−2 541(35)	11 188(49)	1 452(30)
C(502)	−2 468(44)	10 291(70)	1 763(39)

though we were unable to find a suitable model to describe this. Some atoms in one crown, around C(266), had high thermal motion in one direction, but again a satisfactory disordered model could not be found and atoms were therefore refined anisotropically. Hydrogen atoms bonded to carbon and nitrogen were included in geometric positions. The two hydrogen atoms bonded to oxygen at the bottom of the cone could not be located in a Fourier-difference map and were therefore not included in subsequent refinement. Methyl groups were refined as rigid groups. An ethanol molecule was refined with an occupancy of 0.75. The structure was then refined using SHELXL 93.[16] No absorption correction was applied. All calculations were carried out on a Silicon Graphics R4000 Workstation at the University of Reading. The final coordinates are given in Table 2, important dimensions in Table 3 and torsion angles in Table 4. Details of the intramolecular hydrogen bonds are given in Table 5.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Co-ordination Studies.—^{1}H *NMR titrations.* In a typical titration 5×10^{-6} mol of receptor was dissolved in deuteriated acetonitrile (0.50 cm^3) and placed in an NMR tube. A solution of cation ($NaClO_4$ or KPF_6) tetrabutylammonium anion salt to be used was made up in acetonitrile such that 50 μl of solution contained 1 equivalent of guest (typically 5×10^{-4} mol in 0.50 cm^3 of acetonitrile). After each addition of guest, the NMR tube was inverted to ensure mixing of the solutions.

UV titrations. Ultraviolet titrations were generally performed in dry acetonitrile. A 1.20×10^{-5} mol dm^{-3} solution of receptor was used and 3.00 cm^3 of it transferred to the UV solution cell. The guest solution was prepared such that 50 μl contained 1 equivalent of anion or cation. The cell contents were mixed thoroughly between additions and care was taken to avoid solvent evaporation.

Results and Discussion

Ligand Syntheses.—The condensation of the calix[4]arene tetrakis(acid chloride) (L^1)[11] with 4 equivalents of 4′-aminobenzo-15-crown-5 (L^2)[12] in dry dichloromethane containing excess triethylamine gave a crude product which was purified by recrystallisation from dichloromethane–hexane to give a white powder (L^3) in 62% yield (Scheme 1). The tetraveratrole calix[4]arene derivative L^4 was prepared in 74% yield, using an analogous procedure, from L^1 and 4 equivalents of 4-aminoveratrole. Reaction of the calix[4]arene bis(acid chloride) (L^5)[13] with 2 equivalents of L^2 in the presence of triethylamine afforded the new calix[4]arene bis(crown ether) derivative L^6 as a white solid in 65% yield (Scheme 2). All of the new ligands were characterised by ^1H, ^{13}C NMR, fast atom bombardment mass spectrometry and elemental analyses (see Experimental section).

Table 3 Bond lengths (Å) and angles (°) for $[KL^6][I_3]\cdot 0.75EtOH$

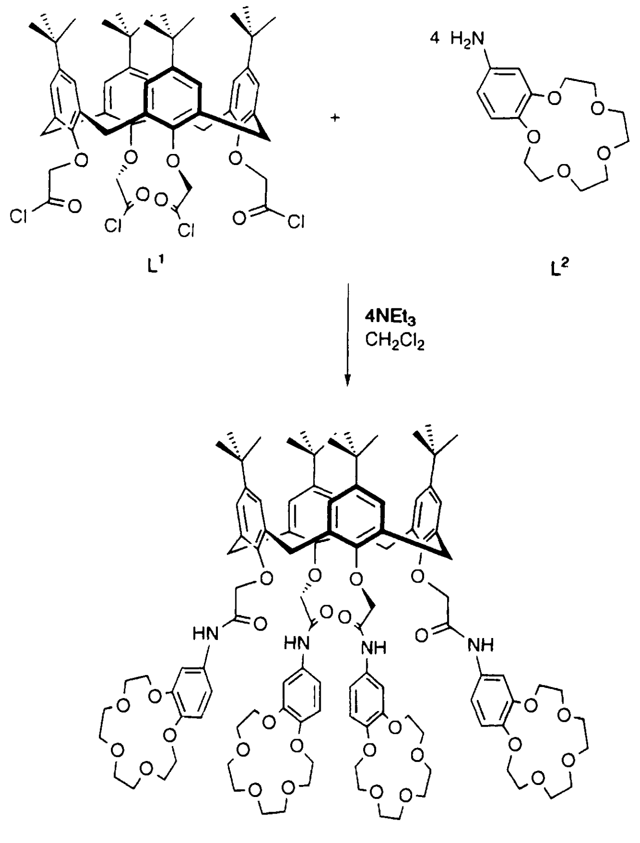
Iodide anion			
I(1)–I(3)	2.841(3)	I(1)–I(2)	2.984(2)
I(3)–I(1)–I(2)	177.34(7)		
Potassium co-ordination sphere			
K–O(264)	2.75(2)	K–O(464)	2.89(2)
K–O(467)	2.78(2)	K–O(270)	2.92(2)
K–O(267)	2.80(2)	K–O(273)	2.93(2)
K–O(470)	2.82(2)	K–O(473)	2.94(2)
K–O(461)	2.88(2)	K–O(261)	2.95(2)
O(264)–K–O(467)	73.4(6)	O(267)–K–O(273)	88.5(6)
O(264)–K–O(267)	60.7(7)	O(470)–K–O(273)	125.2(6)
O(467)–K–O(267)	92.4(6)	O(461)–K–O(273)	90.7(5)
O(264)–K–O(470)	114.0(5)	O(464)–K–O(273)	115.5(5)
O(467)–K–O(470)	61.6(5)	O(270)–K–O(273)	56.1(5)
O(267)–K–O(470)	75.0(5)	O(264)–K–O(473)	163.4(6)
O(264)–K–O(461)	127.5(6)	O(467)–K–O(473)	90.0(5)
O(467)–K–O(461)	89.5(5)	O(267)–K–O(473)	121.3(6)
O(267)–K–O(461)	171.7(7)	O(470)–K–O(473)	55.4(4)
O(470)–K–O(461)	98.8(5)	O(461)–K–O(473)	50.6(4)
O(264)–K–O(464)	73.8(6)	O(464)–K–O(473)	98.1(5)
O(467)–K–O(464)	59.3(5)	O(270)–K–O(473)	73.5(5)
O(267)–K–O(464)	132.2(7)	O(273)–K–O(473)	95.5(5)
O(470)–K–O(464)	114.0(6)	O(264)–K–O(261)	57.7(6)
O(461)–K–O(464)	55.2(5)	O(467)–K–O(261)	122.4(6)
O(264)–K–O(270)	117.0(7)	O(267)–K–O(261)	88.8(6)
O(467)–K–O(270)	130.0(5)	O(470)–K–O(261)	163.7(6)
O(267)–K–O(270)	61.0(7)	O(461)–K–O(261)	97.0(5)
O(470)–K–O(270)	70.5(5)	O(464)–K–O(261)	78.4(6)
O(461)–K–O(270)	112.0(5)	O(270)–K–O(261)	100.0(6)
O(464)–K–O(270)	166.3(5)	O(273)–K–O(261)	50.7(6)
O(264)–K–O(273)	101.1(6)	O(473)–K–O(261)	136.0(4)
O(467)–K–O(273)	173.0(6)		

Table 4 Intramolecular hydrogen bonds [distances (Å), angles (°)] in $[KL^6][I_3]\cdot 0.75EtOH$

O(150) ··· O(450)	2.970	O(350) ··· O(250)	2.854
O(250) ··· O(150)	2.764	O(450) ··· O(350)	2.958
N(454) ··· O(350)	3.394	H(454) ··· O(350)	2.643
N(454)–H(454) ··· O(350)	146.6		

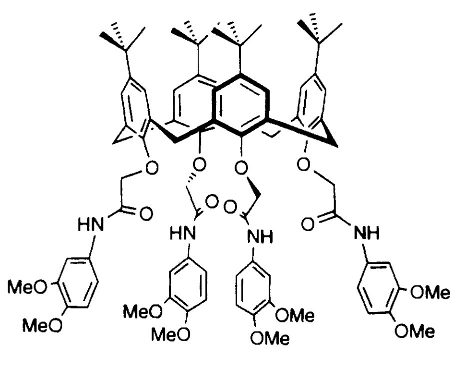
Table 5 Torsion angles (°) for $[KL^6][I_3]\cdot 0.75EtOH$

	$n = 2$	$n = 4$
O(*n*50)–C(*n*51)–C(*n*52)–N(*n*54)	−164.4	2.2
O(*n*73)–C(*n*59)–C(*n*58)–O(*n*61)	4.1	1.2
C(*n*59)–C(*n*58)–O(*n*61)–C(*n*62)	−177.0	−174.5
C(*n*58)–O(*n*61)–C(*n*62)–C(*n*63)	−178.0	168.1
O(*n*61)–C(*n*62)–C(*n*63)–O(*n*64)	−65.2	58.1
C(*n*62)–C(*n*63)–O(*n*64)–C(*n*65)	162.9	−168.0
C(*n*63)–O(*n*64)–C(*n*65)–C(*n*66)	−76.1	78.4
O(*n*64)–C(*n*65)–C(*n*66)–O(*n*67)	−68.9	68.4
C(*n*65)–C(*n*66)–O(*n*67)–C(*n*68)	−179.5	178.1
C(*n*66)–O(*n*67)–C(*n*68)–C(*n*69)	−175.8	175.9
O(*n*67)–C(*n*68)–C(*n*69)–O(*n*70)	63.3	−67.7
C(*n*68)–C(*n*69)–O(*n*70)–C(*n*71)	81.1	−76.5
C(*n*69)–O(*n*70)–C(*n*71)–C(*n*72)	−164.4	167.2
O(*n*70)–C(*n*71)–C(*n*72)–O(*n*73)	65.7	−60.6
C(*n*71)–C(*n*72)–O(*n*73)–C(*n*59)	172.4	−172.5
C(*n*72)–O(*n*73)–C(*n*59)–C(*n*58)	174.4	−179.6

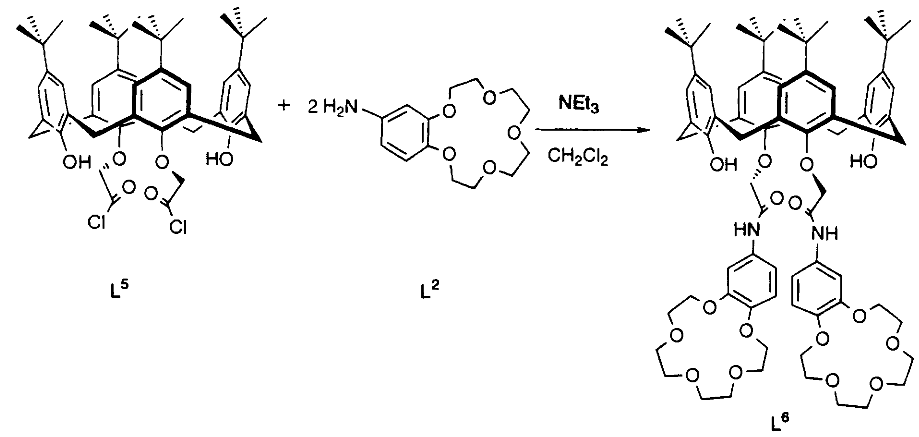


L3

Scheme 1



L4



Scheme 2

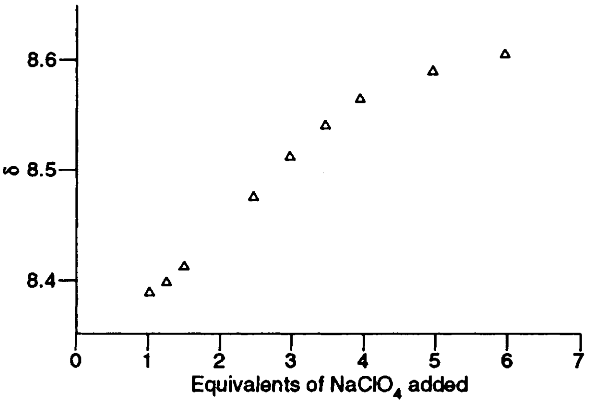


Fig. 2 Proton NMR titration curves of L^3 and $NaClO_4$ in CD_3CN solution, δ is the shift of the aryl crown ether protons

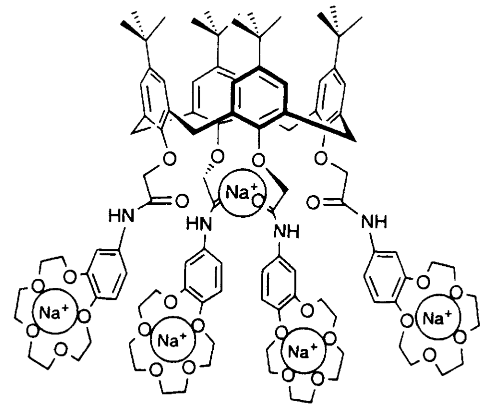


Fig. 3 Proposed solution structure of the sodium polymetallic complex of L^3

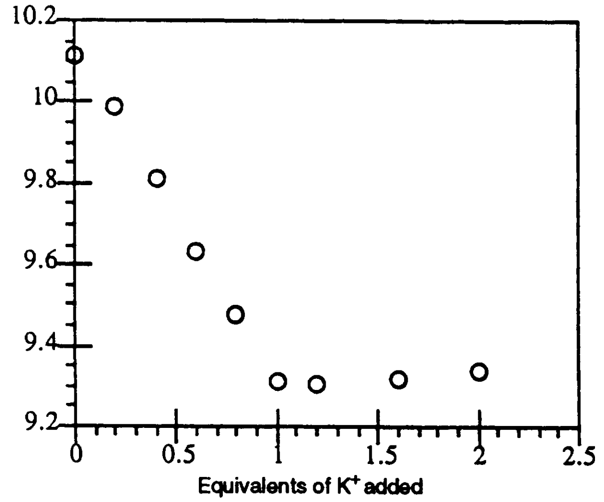


Fig. 4 Proton NMR titration curves of the shift of the amide NH proton of L^6 upon addition of potassium cations

Metal Cation Co-ordination Studies.—Proton NMR spectroscopy was used to investigate the solution co-ordination chemistry of L^3, L^4 and L^6 towards alkali-metal cations. The stepwise addition of sodium perchlorate to deuteriated acetonitrile solutions of L^3 and L^4 led to the evolution of a new set of proton resonances at the expense of the respective free ligand's absorptions which disappeared completely after 1 equivalent of Na^+ had been added, suggesting the formation of a kinetically stable complex on the NMR time-scale. It is noteworthy that in the case of L^3 the amide and methylene protons of the calixarene are most affected by the alkali-metal complexation with the crown ether protons being relatively unperturbed ($\Delta\delta \leqslant 0.05$ ppm), suggesting they are not initially involved in the metal–cation binding process. Although further addition of Na^+ to L^4 led to no subsequent change in the ^1H NMR spectrum, suggesting a 1 : 1 stoichiometric complex, the addition of up to 4 more equivalents of Na^+ to L^3 produced significant shifts in the crown ether protons (Fig. 2). This is consistent with Na^+ binding to each of the crown ether moieties, after the tetraamide lower-rim cavity of the calixarene is occupied by one sodium cation (Fig. 3). Analogous ^1H NMR titration experiments with KPF_6 gave similar results with one K^+ initially being bound and additional potassium cations complexing at the crown ether recognition sites.

In contrast to L^3, ^1H NMR titrations of L^6 with K^+, Ba^{2+} and NH_4^+ cations revealed exclusive complexation at the crown ether recognition sites with the resulting titration curves all indicating 1 : 1 complex stoichiometry (Fig. 4), suggestive of the well known intramolecular sandwich complexation with two benzo-15-crown-5 units.[17] Attempts were made using the computer program EQNMR[18] to estimate stability constants from the ^1H NMR titration data. Unfortunately the complexes are so strong in acetonitrile that only a semi-quantitative estimate of the value of log $K > 4$ could be determined. However, UV titrations at much lower ligand concentrations in acetonitrile with L^6 and potassium cations enabled a quantitative stability constant to be calculated. Monitoring the intensity changes of the ligands electronic absorption at $\lambda = 350$ nm produced a titration curve suitable for SPECFIT[19] analysis. The calculated stability constant value of log K (4.61 ± 5%) for K^+ implies that a relatively strong complex exists in acetonitrile solution. Proton NMR solution binding studies with sodium perchlorate implied a 2 : 1 $Na^+ : L^6$

stoichiometry in which one sodium cation binds in each crown ether.

Potassium and ammonium complexes of L^6 were isolated *via* the addition of an excess of the respective hexafluorophosphate salt to methanol–dichloromethane solutions of the bis(benzo-15-crown-5) substituted calix[4]arene. Elemental analyses and fast atom bombardment mass spectrometry confirmed the 1 : 1 stoichiometry ($[ZL^6]PF_6$, $Z = K^+$ or NH_4^+), as evidenced by solution co-ordination investigations.

X-Ray Structural Investigation of $[KL^6][I_3]$.—Crystals of the potassium complex of L^6 suitable for X-ray structural investigation were serendipitously grown from an aqueous methanolic solution of the ligand in the presence of potassium iodide and iodine.

The structure of the potassium complex is shown in Fig. 5. There are two O–H ⋯ O bonds around the bottom of the calixarene cone and in addition one of the NH groups is directed towards an oxygen atom at 3.39 Å. The other NH moiety is directed away from the cavity, as the O(calix)–C–C–N linkage is *trans*, rather than the usual *cis*. The reason for this must be to facilitate the formation of the potassium bis(crown ether) complex. The two phenyl rings intersect at an angle of 12.0° and are significantly displaced so that the distance between centroids is 4.71 Å.

The potassium ion is sandwiched between the two bis(benzo-15-crown-5) units with K ⋯ O distances ranging from 2.75 to 2.95 Å which is well within the normal limits for such contacts. There are several examples of potassium ions sandwiched between two 15-crown-5 ligands[20–23] with similar distances. As is apparent from the torsion angles in Table 4, the conformations of the two 15-membered crowns are similar but of opposite sign.

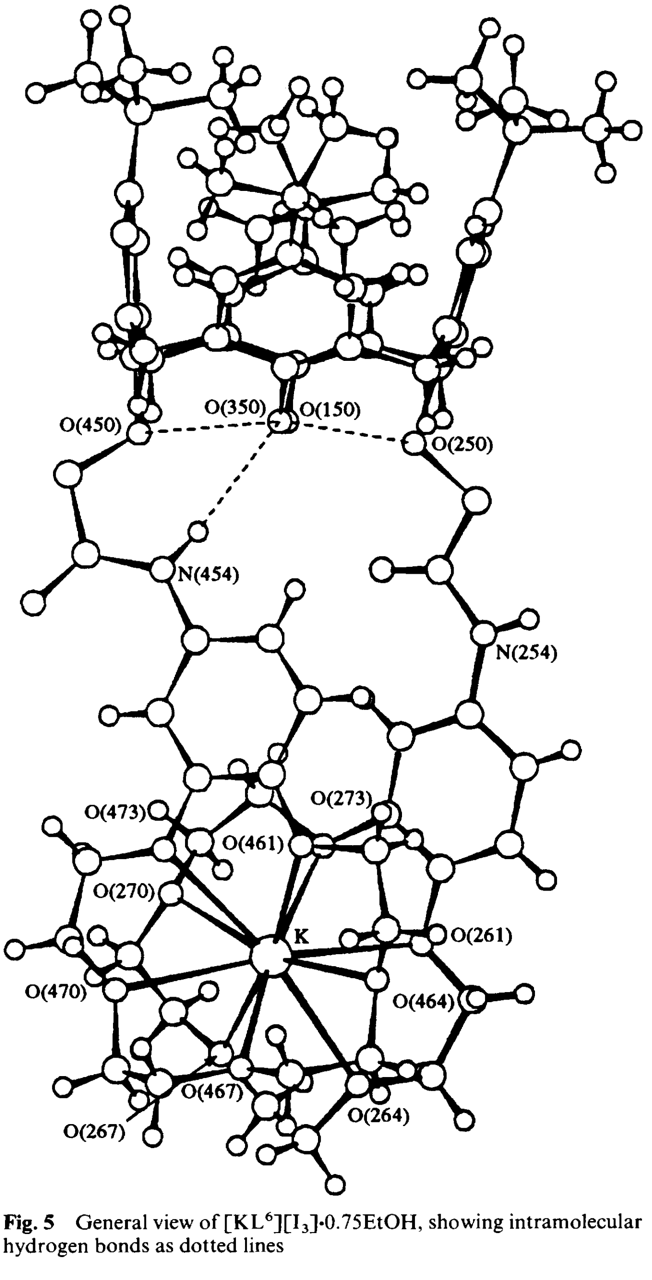


Fig. 5 General view of $[KL^6][I_3]\cdot 0.75EtOH$, showing intramolecular hydrogen bonds as dotted lines

Anion Co-ordination Studies.—Proton NMR titration experiments of the tetrabutylammonium chloride and hydrogensulfate anion salts with L^3, L^4 and L^6 gave little evidence of complexation with maximum shifts of the respective ligand's protons of only $\leqslant 0.05$ ppm. Unfortunately the unexpected strength of Na^+ and K^+ co-ordination at the amide lower rim of L^3 negated the undertaking of analogous anion ^1H NMR titration experiments in the presence of these metal cations. However anion titration experiments with the potassium and ammonium complexes of L^6 in deuteriated acetonitrile solutions gave evidence of 1 : 1 stoichiometric anion recognition with Cl^-, NO_3^-, HSO_4^- and $H_2PO_4^-$ through perturbations of amide and methylene protons in the lower-rim vicinity of the calix[4]arene ligand. For example, substantial downfield shifts of the amide protons of up to $\Delta\delta = 1.5$ ppm were observed with chloride anions (Fig. 6). Stability constants were determined using EQNMR[18] analysis from the resulting titration curves and are reported in Table 6. The stability constant values suggest the strongest complexes are formed with $H_2PO_4^-$ and HSO_4^-. This may be attributable to the calix[4]arene appended bis(crown ether) intramolecular sandwich K^+ or

Table 6 Anion stability constant data for potassium and ammonium complexes of L^6

Complex	Anion	K^a/dm^3 mol^{-1}
$[KL^6]PF_6$	Cl^-	3500
$[KL^6]PF_6$	NO_3^-	1300
$[NH_4L^6]PF_6$	NO_3^-	1800
$[KL^6]PF_6$	HSO_4^-	5600
$[NH_4L^6]PF_6$	HSO_4^-	6400
$[KL^6]PF_6$	$H_2PO_4^-$	$> 10^4$ [b]
$[NH_4L^6]PF_6$	$H_2PO_4^-$	$> 10^4$ [b]

[a] Determined in CD_3CN; errors $\geqslant 15\%$. [b] Complexes with $H_2PO_4^-$ too strong to be accurately determined so an estimate is given.

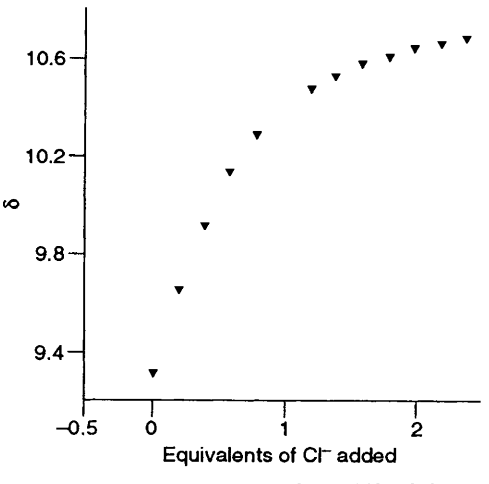


Fig. 6 Proton NMR titration curves of the shift of the amide NH protons of $[KL^6]^+$ upon addition of chloride anions

NH_4^+ complex relatively rigidifying the hydrogen-bonding arrangement of two amides and two hydroxyl protons creating a unique pseudo-tetrahedral cavity of complementary topology for either tetrahedrally shaped anionic guest species.

Conclusion

The synthesis of new tetra- and bis-(benzo-15-crown-5) substituted calix[4]arene ligands has been accomplished. Proton NMR sodium and potassium cation co-ordination investigations in deuteriated acetonitrile suggest the tetrakis(crown) calix[4]arene derivative L^3 forms $L^3{\cdot}5M^+$ ($M^+ = Na^+$ or K^+) solution stoichiometric complexes in which an alkali-metal cation binds in each of the four crown ether moieties after the tetraamide lower-rim cavity of the calix[4]arene is occupied by one metal cation. In contrast the bis(crown) calix[4]arene ligand L^6 complexes the cations K^+, Ba^{2+} and NH_4^+ exclusively at the crown ether recognition sites in a 1 : 1 intramolecular sandwich stoichiometric fashion. A crystal-structure determination of a 1 : 1 potassium complex of L^6 supports the proposed solution complex structures. Proton NMR titration anion co-ordination studies gave no evidence for either L^3 or L^6 to bind anions. However analogous anion complexation experiments with the potassium and ammonium complexes $[ZL^6]PF_6$ ($Z = K^+$ or NH_4^+) suggested the 1:1 stoichiometric binding of Cl^-, NO_3^-, HSO_4^- and $H_2PO_4^-$ anions in the lower-rim vicinity of the calix[4]arene ligand. Stability constant evaluations implied that the strongest complexes were formed with the tetrahedrally shaped $H_2PO_4^-$ and HSO_4^- anionic guest species, which may complement the unique pseudo-tetrahedral amide and hydroxyl hydrogen-bond arrangement of the lower-rim calix[4]arene cavity of L^6.

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