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Rare-earth-metal solvent extraction with calixarene phosphates

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Several phosphate esters in which calixarenes act as either uni- or bi-dentate ligands towards P^V have been investigated as solvent-extraction agents for the rare-earth metals (La to Lu, excluding Pm, plus Y). Extraction of picrate salts into dichloromethane, ethyl acetate and tributyl phosphate–hexane (1 : 1) is considerably enhanced by some of these esters but in no case is any marked selectivity exhibited, although some features of the observed extraction patterns suggest ways in which the molecular design of such extractants may be improved. Crystal structure determinations on two phosphate esters in which the calixarene unit is bidentate indicate that the relatively poor metal-ion binding abilities of these ligands may be a consequence of a preferred orientation of the phosphoryl donor groups in which they diverge from the macrocyclic ring. A crystal structure determination on the 2 : 1 complex of tetrakis-*O*-(diethoxyphosphoryl)-*p*-*tert*-butylcalix[4]arene and lanthanum picrate (2,4,6-trinitrophenolate) shows that a convergent array of phosphoryl donor groups can form in such cases where the functional groups are flexible. This does not, however, appear to lead to a particular enhancement of stability, as the complex readily dissociates into a 1 : 1 species in solution.

The highly lipophilic nature of metal-ion complexes of many calixarenes indicates a potential for use in solvent extraction, especially where the particular calixarene may give rise to some extraction selectivity, and this prospect has been investigated in a variety of systems.[1–5] The results of this work and of related investigations of ion transport through hydrophobic membranes have indeed given rise to the possibility of significant practical applications of calixarenes.[1,6] Our earlier studies of the co-ordination chemistry of the rare-earth metals and simple (phenolic) calixarenes[7–15] were in part motivated by an intent to use the calixarenes in solvent extraction of these metals but it was soon apparent that the insolubility of rare-earth-metal hydroxides under conditions where appreciable deprotonation of a readily available species such as *p*-*tert*-butylcalix[8]arene (4,11,18,25,32,39,46,53-octa-*tert*-butyl[1$_8$]metacyclophane-7,14,21,28,35,42,49,56-octol) was achievable mitigated against any such application. Nonetheless, the nature of the complexes isolated from non-aqueous solutions showed that the stability depended markedly on the calixarene ring size and that at least with *p*-*tert*-butylcalix[8]arene there was some variation in stability across the rare-earth-metal series.[11,16] Also interesting was the fact that the elements uranium and thorium, commonly undesired contaminants of rare-earth minerals, readily formed complexes for which, in the case of uranyl ion at least, the dependence of stability on calixarene ring size was quite different to that for the rare-earth metals.[17,18]

Phosphorus-containing extractants, of which tri-*n*-butyl phosphate is perhaps best known,[19] have well established use in lanthanide (rare earth) and actinide extraction, especially from acidic media, where the phosphoryl oxygen remains an active donor site despite the possibility of protonation. With the objective of using this donor ability in an array of variable but potentially controllable stereochemistry, we have evaluated the use of several calixarene phosphates as neutral rare-earth extractants and report the results of this work herein. To provide some understanding of important aspects of the co-ordination chemistry involved, we have also determined the crystal structures of two calixarene phosphates and a bis(ligand) complex of lanthanum(III).

Experimental

Reagents and instrumentation

The *p*-*tert*-butylcalix[*n*]arenes (n = 4, 6 or 8) were prepared[20–23] and debutylated[24] (n = 6, 8 only) by literature procedures. *p*-*tert*-Butyldihomooxacalix[4]arene was isolated as a side product of the *p*-*tert*-butylcalix[8]arene synthesis.[14,17,23] Tetrakis-*O*-(diethoxyphosphoryl)-*p*-*tert*-butylcalix[4]arene (cone and partial cone forms) and *O*-diethoxyphosphoryl-O^2,O^3-ethoxyphosphoryl-*p*-*tert*-butylcalix[4]arene were prepared as described previously.[25] *p*-*tert*-Butylcalix[4]arene pyrophosphate[26] was obtained on pyrolysis of any of these three compounds and the 1,2; 3,4-dibridged phosphate esters are described below. O^1,O^3-bis(diethoxyphosphoryl)-*p*-*tert*-butylcalix[4]arene,[27] O^1,O^3-dibenzyl-*p*-*tert*-butylcalix[4]arene,[28] hexa-*O*-methylcalix[6]arene[24] and octa-*O*-methylcalix[8]arene[24] were prepared by literature methods. *p*-(1,1,3,3-Tetramethylbutyl)calix[*n*]arenes (n = 4 or 8) were prepared from *p*-(1,1,3,3-tetramethylbutyl)phenol by literature methods[20,29] while the hexamer (n = 6) was obtained as a mixture with these two oligomers by following the preparative method for *p*-*tert*-butylcalix[6]arene.[22] It was isolated by chromatography and its identity confirmed by dealkylation to give calix[6]arene.

Rare-earth-metal picrate dodecahydrates, $Ln(pic)_3 \cdot 12H_2O$ (Hpic = 2,4,6-trinitrophenol), were prepared as described elsewhere.[30] Dichloromethane, ethyl acetate and tributyl phosphate were purified by conventional procedures.[31] Diethyl chlorophosphate,[32] butyl dichlorophosphate[33] and chloromethyl octyl ether[34] were prepared by literature methods.

Nuclear magnetic resonance spectra were recorded using Bruker AM300 and ARX500 instruments, UV/VIS spectra using a Hewlett-Packard 8452A diode-array spectrophotometer. Phosphorus was analysed using ICPAES (inductively coupled plasma atomic emission spectroscopy) on an ARL 3520 instrument, C, H, N and S on a LECO 932 CHNS Analyser housed at the Chemistry Centre of Western Australia.

Syntheses

Calixarene phosphorylation reactions were in the main carried

out using basically the phase-transfer catalysis (PTC) method of Goren and Biali,[35] in which the calixarene in dichloromethane is treated with a large excess of a halogeno phosphate ester in the presence of concentrated aqueous sodium hydroxide and a tetrabutylammonium halide as phase-transfer catalyst. This is referred to in the following as the GB method, and where it has been applied only important details of the product-isolation procedures are given.

Tetrakis-*O*-(diethoxyphosphoryl)-*p*-(1,1,3,3-tetramethylbutyl)calix[4]arene. *p*-(1,1,3,3-Tetramethylbutyl)calix[4]arene was treated with diethyl chlorophosphate by the GB method and the organic phase separated, dried (Na_2SO_4) and evaporated, leaving a high-boiling orange oil (≈ 10 cm^3) containing calixarene and unreacted diethyl chlorophosphate/diethylphosphoric acid. Water (15 cm^3) was added giving a white, sludgy precipitate which was recrystallized from methanol–water and then light petroleum (b.p. = 40–60 °C) to give glistening white crystals (2.42 g, 55%), m.p. 201–203 °C (Found: C, 64.1; H, 8.6; P, 8.6. $C_{76}H_{124}O_{16}P_4$ requires C, 64.4; H, 8.8; P, 8.75%). NMR ($CDCl_3$, 298 K): ^{1}H (300.13 MHz), δ 0.62 [36 H, s, $C(CH_3)_3$], 1.09 [24 H, s, $C(CH_3)_2$], 1.25 (24 H, td, $POCH_2CH_3$, $^3J_{HH}$ = 7.0, $^4J_{HP}$ = 0.7), 1.51 (8 H, s, CH_2), 3.24, 4.80 [8 H, AB q, RCH_2R (R = aryl) $^2J_{HH}$ = 13.6], 4.07–4.27 (16 H, m, $POCH_2CH_3$) and 6.85 (8 H, s, H of R); ^{13}C (75.47 MHz), δ 16.22 (d, $POCH_2CH_3$, $^3J_{CP}$ = 6.5), 31.12 (s, RCH_2R), 31.28, 31.65 [2 s, $(CH_3)_2$, $(CH_3)_3$], 32.29, 37.91 (2 s, quaternary C), 57.26 (s, CH_2), 64.57 (d, $POCH_2CH_3$, $^2J_{CP}$ = 5.7), 126.24 (s, *m*-C of R), 133.51 (s, *o*-C of R), 142.76 (d, RO, $^2J_{CP}$ = 8.1 Hz) and 145.78 (s, *p*-C of R); ^{31}P (121.50 MHz), δ −4.12 (s).

Tetrakis-*O*-(diethoxyphosphoryl)-*p*-*tert*-butyldihomooxacalix[4]arene. *p*-*tert*-Butyldihomooxacalix[4]arene was treated with diethyl chlorophosphate by the GB method and the organic phase separated, washed with a saturated NaCl solution (100 cm^3), dried ($MgSO_4$) and evaporated, giving a pale yellow oil. Water (30 cm^3) was added, precipitating a white solid which was collected and the water evaporated under reduced pressure to leave a pale yellow foam which was dissolved in boiling light petroleum (25 cm^3). On cooling to room temperature a white solid precipitated (1.89 g). The filtrate was taken to dryness and the residue recrystallized from light petroleum (10 cm^3) to give 0.43 g of the white compound (2.32 g, 61%), m.p. 157–158 °C (Found: C, 59.7; H, 7.8; P, 10.3. $C_{61}H_{94}O_{17}P_4$ requires C, 59.9; H, 7.75; P, 10.15%). NMR ($CDCl_3$, 298 K): ^{1}H (300.13 MHz), δ 0.90, [18 H, s, $C(CH_3)_3$], 1.19 [18 H, s, $C(CH_3)_3$], 1.24 (6 H, td, $POCH_2CH_3$, $^3J_{HH}$ = 7.0, $^4J_{HP}$ = 1.1), 1.29 (6 H, td, $POCH_2CH_3$, $^3J_{HH}$ = 7.0, $^4J_{HP}$ = 1.1), 1.32 (6 H, td, $POCH_2CH_3$, $^3J_{HH}$ = 7.0, $^4J_{HP}$ = 1.0), 1.34 (6 H, td, $POCH_2CH_3$, $^3J_{HH}$ = 7.0, $^4J_{HP}$ = 1.1), 3.29, 4.90 (2 H, AB q, RCH_2R, $^2J_{HH}$ = 14.2), 3.32, 4.85 (4 H, AB q, RCH_2R, $^2J_{HH}$ = 14.9), 3.43, 4.83 (4 H, AB q, RCH_2R, $^2J_{HH}$ = 14.3), 4.06–4.29 (16 H, m, $POCH_2CH_3$), 6.66, 7.03 (4 H, AB q, H of R, $^2J_{HH}$ = 2.3), 7.08, 7.09 (4 H, AB q, H of R, $^2J_{HH}$ = 3.2); ^{13}C (75.47 MHz), δ 16.14 (d, $POCH_2CH_3$, $^3J_{CP}$ = 6.9), 16.29 (d, $POCH_2CH_3$, $^3J_{CP}$ = 7.1), 30.48, 30.97 (2 s, RCH_2R), 31.36 [s, $(CH_3)_3$], 34.15 (s, quaternary C), 64.62, 64.66 (2 d, $POCH_2CH_3$, $^2J_{CP}$ = < 0.5), 68.27 (s, RCH_2O), 123.41, 126.20, 126.41 (3 s, *m*-C of R), 130.86, 132.33, 133.38 (3 s, *o*-C of R), 142.38, 143.16 (2 d, RO, $^2J_{CP}$ = 7.8, 9.0 Hz), 146.80, 147.03 (2 s, *p*-C of R); ^{31}P (121.50 MHz), δ −3.65 and −4.23 (2 s).

Octakis-*O*-(diethoxyphosphoryl)-*p*-*tert*-butylcalix[8]arene. *p*-*tert*-Butylcalix[8]arene was treated with diethyl chlorophosphate by the GB method and the organic phase separated, washed with NaCl (75 cm^3), dried ($MgSO_4$) and evaporated, leaving a high-boiling yellow oil containing phosphorylated calixarene and unreacted diethyl chlorophosphate/diethylphosphoric acid. The oil was dissolved in methanol and water added to reprecipitate an oil, which was dissolved in diethyl ether (100 cm^3), washed twice with water (100 cm^3), and the organic phase dried ($MgSO_4$) and evaporated, giving an off-white foam. Crystallization from methanol–water gave 0.81 g (29%) of a fine white precipitate. The compound was also prepared using tetraethylammonium bromide as phase-transfer catalyst and isolated as described above to give 1.85 g (70%) of fine white crystals, m.p. 137–140 °C (Found: C, 60.3; H, 7.6; P, 10.4. $C_{120}H_{184}O_{32}P_8$ requires C, 60.4; H, 7.75; P, 10.4%). NMR ($CDCl_3$, 298 K): ^{1}H (500.14 MHz), δ 1.06 [120 H, br s, $C(CH_3)_3$, $POCH_2CH_3$], 4.05 (32 H, vbr s, $POCH_2CH_3$), 4.25 (16 H, br s, RCH_2R) and 7.01 (16 H, s, H of R); ^{13}C (125.76 MHz), δ 15.87 (d, $POCH_2CH_3$, $^3J_{CP}$ = 6.7), 31.22 [s, $(CH_3)_3$], 31.40 (s, RCH_2R), 34.10 (s, quaternary C), 64.36 (d, $POCH_2CH_3$, $^2J_{CP}$ = 5.7), 126.52 (s, *m*-C of R), 131.60 (s, *o*-C of R), 145.19 (d, RO, $^2J_{CP}$ = 7.8 Hz) and 147.22, (s, *p*-C of R); ^{31}P (202.46 MHz), δ −4.63 (s).

Octakis-*O*-(diethoxyphosphoryl)-*p*-(1,1,3,3-tetramethylbutyl)calix[8]arene. *p*-(1,1,3,3-Tetramethylbutyl)calix[8]arene was treated with diethyl chlorophosphate by the GB method and the organic phase separated, washed with NaCl (50 cm^3), dried ($MgSO_4$) and the solvent evaporated. Water (50 cm^3) was added to the residue forming a light brown solid (1.48 g, still slightly wet). Boiling methanol (50 cm^3) was added to the solid and the small amount of insoluble material filtered off and discarded. The methanol filtrate was reduced to a volume of 10 cm^3, water (3 cm^3) added, and the solution allowed to cool, resulting in a white precipitate which was filtered off to give 0.76 g (64%) of white crystals, m.p. 163–165 °C (Found: C, 64.2; H, 8.9; P, 8.9. $C_{152}H_{248}O_{32}P_8$ requires C, 64.4; H, 8.8; P, 8.75%). NMR (298 K): ^{1}H (500.14 MHz, $CDCl_3$), δ 0.68 [72 H, s, $C(CH_3)_3$], 1.14 [48 H, s, $C(CH_3)_2$], ≈1.3 (48 H, br s, $POCH_2CH_3$), 1.58 (16 H, s, CH_2), 4.0 (32 H, br s, $POCH_2CH_3$), ≈4.2 (16 H, br s, RCH_2R) and ≈7.1, (16 H, vbr s, H of R) at 328 K all peaks slightly sharper, with the methylene peak at ≈4.2 sharpening the most; (C_5D_5N), δ 0.86 [72 H, s, $C(CH_3)_3$], ≈1.2 (48 H, br m, $POCH_2CH_3$), 1.42 [48 H, s, $C(CH_3)_2$], 1.80 (16 H, s, CH_2), 4.25 (32 H, br s, $POCH_2CH_3$), 4.8, 5.4 (16 H, 2 br s, RCH_2R) and ≈7.7 (16 H, vbr s, H of R); (363 K) δ 0.92 [72 H, s, $C(CH_3)_3$], 1.25 (48 H, t, $POCH_2CH_3$, $^3J_{HH}$ = 7.0, $^4J_{HP}$ < 0.5), 1.42 [48 H, s, $C(CH_3)_2$], 1.86 (16 H, s, CH_2), 4.22–4.28 (32 H, m, $POCH_2CH_3$), 4.79 (16 H, s, RCH_2R) and 7.50 (16 H, s, H of R); ^{13}C (125.76 MHz, $CDCl_3$), δ 15.94, (br s, $POCH_2CH_3$), 31.86, 32.06 [2 s, $(CH_3)_2$, $(CH_3)_3$], 31.51 (s, RCH_2R), 32.30, 38.12 (2 s, quaternary C), 56.68 (s, CH_2), 64.39 (s, $POCH_2CH_3$), 127.30 (br s, *m*-C of R), 131.38 (s, *o*-C of R), 145.31 (s, RO) and 146.57 (br s, *p*-C of R); (C_5D_5N), δ 15.69 (d, $POCH_2CH_3$, $^3J_{CP}$ = 5.6); 31.54, 32.05 (2 s, CH_3), 31.95, 37.94 (2 s, quaternary C), 56.54 (s, CH_2), 62.80 (d, $POCH_2CH_3$, $^2J_{CP}$ = 6.4 Hz), 127.11 (s, *m*-C of R), 131.57 (s, *o*-C of R) and 145.89 (br s, *p*-C of R, RO); ^{31}P (202.46 MHz, $CDCl_3$), δ −5.03 (s).

1,2-μ-3,4-μ′-Di(*n*-butoxyphosphoryl)-*p*-*tert*-butylcalix[4]arene, '*exo-exo*' A and '*exo-endo*' B isomers. Using a procedure based on the GB method, a solution of 50% NaOH (100 cm^3) was added dropwise to a stirred solution of *p*-*tert*-butylcalix[4]arene (2.00 g, 3.08 mmol), butyl dichlorophosphate (10 cm^3) and tetrabutylammonium bromide (0.2 g, 0.62 mmol) in dichloromethane (200 cm^3). After 6 h of heating at reflux the solution was cooled to room temperature, the organic phase separated, washed (NaCl), dried (Na_2SO_4) and the solvent evaporated, leaving a white solid. Thin-layer chromatography of the solid (toluene–ethyl acetate, 9:1) showed it to be a mixture of two compounds. Flash chromatography of the solid (toluene–ethyl acetate, 19:1) gave 0.40 g (17%) of the '*exo-exo*' calixarene **A** and 0.20 g (9%) of the '*exo-endo*' calixarene **B**.

Isomer **A**: m.p. 263–264 °C (Found: C, 70.4; H, 7.8; P, 6.9. $C_{52}H_{70}O_8P_2$ requires C, 70.55; H, 7.95; P, 7.00%). NMR ($CDCl_3$, 298 K): ^1H (500.14 MHz), δ 1.02 (6 H, t, $POCH_2CH_2CH_2CH_3$, $^3J_{HH}$ = 7.4), 1.10 [36 H, s, $C(CH_3)_3$], 1.48–1.56 (4 H, m, $POCH_2CH_2CH_2CH_3$), 1.94–2.00 (4 H, m, $POCH_2CH_2CH_2CH_3$), 3.34, 4.55 (4 H, AB q, RCH_2R, $^2J_{HH}$ = 14.2), 3.46, 5.19 (4 H, AB q, RCH_2R, $^2J_{HH}$ = 15.7), 4.42–4.48 (4 H, m, $POCH_2CH_2CH_2CH_3$), 6.777 (4 H, br s, H of R) and 6.784 (4 H, br s, H of R); ^{13}C (125.76 MHz), δ 13.76 (s, $POCH_2CH_2CH_2CH_3$), 18.69 (d, $POCH_2CH_2CH_2CH_3$, $^4J_{CP}$ = 1.6), 29.16, 37.56 (2 s, RCH_2R), 31.25 [s, $(CH_3)_3$], 32.73 (d, $POCH_2CH_2CH_2CH_3$, $^3J_{CP}$ = 2.4), 33.89 (s, quaternary C), 69.75 (d, $POCH_2CH_2CH_2CH_3$, $^2J_{CP}$ = 5.0), 125.22, 127.27 (2 s, *m*-C of R), 129.58 (s, *o*-C of R), 130.82 (d, *o*-C of R, $^3J_{CP}$ = 7.6), 146.45 (d, RO, $^2J_{CP}$ = 2.6 Hz), 146.45, 146.49 (2 s, *p*-C of R); ^{31}P (202.46 MHz), δ −4.36 (s).

Isomer **B**: m.p. 246–248 °C (Found: C, 70.6; H, 8.1; P, 6.9%). NMR ($CDCl_3$, 298 K): ^1H (500.14 MHz), δ 0.76, (3 H, t, $POCH_2CH_2CH_2CH_3$, $^3J_{HH}$ = 7.4), 1.00 (3 H, t, $POCH_2CH_2CH_2CH_3$, $^3J_{HH}$ = 7.4), 1.09–1.14 [36 H, br s, $C(CH_3)_3$], 1.42–1.48 (2 H, m, $POCH_2CH_2CH_2CH_3$), 1.50–1.58 (2 H, m, $POCH_2CH_2CH_2CH_3$), 1.63 (2 H, br s, $POCH_2CH_2CH_2CH_3$), 1.90–1.95 (2 H, m, $POCH_2CH_2CH_2CH_3$), 3.36, 4.69 (2 H, AB q, RCH_2R, $^2J_{HH}$ = 15.3), 3.37, 4.71, (4 H, AB q, RCH_2R, $^2J_{HH}$ = 14.3), 3.45, 5.10 (2 H, AB q, RCH_2R, $^2J_{HH}$ = 15.5), 4.14–4.18 (2 H, m, $POCH_2CH_2CH_2CH_3$), 4.54–4.58 (2 H, m, $POCH_2CH_2CH_2CH_3$) and 6.76, (8 H, br s, H of R), ^{13}C (125.76 MHz), δ 13.49, 13.89 (2 s, $POCH_2CH_2CH_2CH_3$), 18.57, 18.74 (2 s, $POCH_2CH_2CH_2CH_3$), 29.54, 36.83, 37.33 (3 s, RCH_2R), 31.30 [s, $(CH_3)_3$], 32.20, 32.58 (2 d, $POCH_2CH_2CH_2CH_3$, $^3J_{CP}$ = 5.7, 6.4), 33.91, 33.97 (2 s, quaternary C), 69.20, 69.62 (2 d, $POCH_2CH_2CH_2CH_3$, $^2J_{CP}$ = 5.9, 5.2), 124.75, 124.92 (2 br s, *m*-C of R), 127.15, 127.31 (2 s, *m*-C of R), 129.56, 129.74 (2 vbr s, *o*-C of R), 130.90, 131.78 (2 br s, *o*-C of R), 146.29, 146.77 (2 s, *p*-C of R), 146.56, 146.74 (2 d, RO, $^2J_{CP}$ = 9.9, 7.3 Hz); ^{31}P (202.46 MHz), δ −5.82 and −11.83 (2 s).

1,2-μ-3,4-μ′-Di(*n*-butoxyphosphoryl)-*p*-(1,1,3,3-tetramethylbutyl)calix[4]arene, '*exo-exo*' A and '*exo-endo*' B isomers. Using a procedure based on the GB method, a solution of 50% NaOH (50 cm^3) was added dropwise to a stirred solution of *p*-(1,1,3,3-tetramethylbutyl)calix[4]arene (1.42 g, 1.54 mmol), butyl dichlorophosphate (5 cm^3) and NBu_4Br (0.11 g, 0.34 mmol) in dichloromethane (100 cm^3). After 6 h of heating at reflux the solution was cooled to room temperature, the organic phase separated, washed (NaCl), dried (Na_2SO_4) and the solvent evaporated, leaving a white, waxy solid. Thin-layer chromatography of the solid (toluene–ethyl acetate, 19:1) showed it to be a mixture of two compounds. Flash chromatography (toluene–ethyl acetate, 19:1) gave 0.63 g (37%) of the '*exo-exo*' calixarene **A** and 0.22 g (13%) of the '*exo-endo*' calixarene **B**.

Isomer **A**: m.p. 232–233 °C (Found: C, 73.4; H, 9.8; P, 5.4. $C_{68}H_{102}O_8P_2$ requires C, 73.6; H, 9.25; P, 5.6%). NMR ($CDCl_3$, 298 K): ^1H (500.14 MHz), δ 0.67 [36 H, s, $C(CH_3)_3$], 1.02 (6 H, t, $POCH_2CH_2CH_2CH_3$, $^3J_{HH}$ = 7.4), 1.07 [12 H, s, $C(CH_3)_2$], 1.22 [12 H, s, $C(CH_3)_2$], 1.48–1.57 (12 H, m, CH_2, $POCH_2CH_2CH_2CH_3$), 1.94–2.00 (4 H, m, $POCH_2CH_2CH_2CH_3$), 3.35, 4.56 (4 H, AB q, RCH_2R, $^2J_{HH}$ = 14.0), 3.46, 5.28 (4 H, AB q, RCH_2R, $^2J_{HH}$ = 15.7), 4.43–4.49 (4 H, m, $POCH_2CH_2CH_2CH_3$), 6.77 (4 H, br s, H of R) and 6.84 (4 H, br s, H of R); ^{13}C (125.76 MHz), δ 13.82 (s, $POCH_2CH_2CH_2CH_3$), 18.78 (s, $POCH_2CH_2CH_2CH_3$), 29.05, 38.04 (2 s, RCH_2R), 29.94, 31.79, 32.27 (3 s, CH_3), 32.33, 37.97 (2 s, quaternary C), 32.85 (d, $POCH_2CH_2CH_2CH_3$, $^3J_{CP}$ = 2.0), 57.22 (s, CH_2), 69.73 (d, $POCH_2CH_2CH_2CH_3$, $^2J_{CP}$ = 5.0), 126.34, 127.69 (2 s, *m*-C of R), 129.36 (br s, *o*-C of R), 130.51 (d, *o*-C of R, $^3J_{CP}$ = 7.7), 145.97 (s, *p*-C of R) and 146.33 (d, RO, $^2J_{CP}$ = 6.8 Hz); ^{31}P (202.46 MHz), δ −4.81 (s).

Isomer **B**: m.p. 232–234 °C (Found: C, 73.5; H, 9.4; P, 5.5). NMR ($CDCl_3$, 298 K): δ 0.67 [18 H, s, $C(CH_3)_3$], 0.70 [18 H, s, $C(CH_3)_3$], 0.85 (3 H, t, $POCH_2CH_2CH_2CH_3$, $^3J_{HH}$ = 7.4), 1.00 (3 H, t, $POCH_2CH_2CH_2CH_3$, $^3J_{HH}$ = 7.4), 1.05–1.85 [32 H, br m, $C(CH_3)_2$, CH_2], 1.20–1.28 (2 H, m, $POCH_2CH_2CH_2CH_3$), 1.45–1.50 (2 H, m, $POCH_2CH_2CH_2CH_3$), 1.50–1.58 (2 H, m, $POCH_2CH_2CH_2CH_3$), 1.90–1.95 (2 H, m, $POCH_2CH_2CH_2CH_3$), 3.36, 4.74 (2 H, AB q, RCH_2R, $^2J_{HH}$ = 15.5), 3.37, 4.70 (4 H, AB q, RCH_2R, $^2J_{HH}$ = 14.2), 3.45, 5.15 (2 H, AB q, RCH_2R, $^2J_{HH}$ = 15.5), 4.09–4.14 (2 H, br m, $POCH_2CH_2CH_2CH_3$), 4.54–4.58 (2 H, br m, $POCH_2CH_2CH_2CH_3$) and 6.77 (8 H, br s, H of R); ^{13}C (125.76 MHz), δ 13.52, 13.88 (2 s, $POCH_2CH_2CH_2CH_3$), 18.63, 18.73, (2 s, $POCH_2CH_2CH_2CH_3$), 29.42, 37.21, 37.59 (3 s, RCH_2R), 29.42, 29.74, 31.73, 31.78, 31.83 [5 s, $(CH_3)_2$, $(CH_3)_3$]; 32.27, 32.37, 32.95, 37.92, 37.98 (5 s, quaternary C), 32.11, 32.61 (2 d, $POCH_2CH_2CH_2CH_3$, $^3J_{CP}$ = 6.4, 5.9), 57.12, 57.25 (2 s, CH_2), 68.98, 69.53 (2 d, $POCH_2CH_2CH_2CH_3$, $^2J_{CP}$ = 5.9, 5.1), 125.81 (vbr s, *m*-C of R), 127.54, 127.96 (2 s, *o*-C of R), 128.53, 128.56, 128.93 (3 s, *m*-C of R), 130.54, 131.31 (2 vbr s, *o*-C of R), 145.88, 145.96 (2 s, *p*-C of R), 146.45, 146.62 (2 d, RO, $^2J_{CP}$ = 9.9, 6.9 Hz), ^{31}P (202.46 MHz), δ −6.13 and −12.34 (2 s).

***O*^{1},*O*^{3}-Dibenzyl-2,4-bis(diethoxyphosphoryl)-*p*-*tert*-butylcalix[4]arene.** At 0 °C in an atmosphere of dry nitrogen, diethyl chlorophosphate (3.34 g, 2.00 mmol) was added to a stirred solution of 0.72 mol dm^{-3} $LiBu^n$ (1.68 cm^3, 1.21 mmol) and 1,3-dibenzyl ether-*p*-*tert*-butylcalix[4]arene (1.00 g, 1.21 mmol) in dry tetrahydrofuran (thf) (100 cm^3). The reaction mixture was stirred at 0 °C for 30 min, raised to room temperature and stirring continued for 18 h. The solvent was removed from the reaction mixture and water (10 cm^3) added to the orange residue. The yellow, waxy solid that precipitated was collected, dried (silica gel, 24 h) to remove water and recrystallized from light petroleum to give 0.59 g (44%) of large, white crystals. R_f (TLC, light petroleum–ethyl acetate, 1:1) = 0.37. M.p. 217–219 °C (Found: C, 72.0; H, 7.8; P, 5.5. $C_{66}H_{86}O_{10}P_2$ requires C, 72.0; H, 7.85; P, 5.6%). NMR ($CDCl_3$, 298 K): δ 0.83, ^1H (500.14 MHz), [18 H, s, $C(CH_3)_3$], 1.23 (12 H, td, $POCH_2CH_3$, $^3J_{HH}$ = 7.1, $^4J_{HP}$ = 1.0), 1.35 [18 H, s, $C(CH_3)_3$], 3.07, 4.32 (8 H, AB q, RCH_2R, $^2J_{HH}$ = 13.3), 3.99–4.02 (4 H, m, $POCH_2CH_3$), 4.06–4.11 (4 H, m, $POCH_2CH_3$), 5.29 (4 H, s, $ROCH_2Ph$), 6.46 (4 H, s, H of R), 7.07 (4 H, s, H of R) and 7.29–7.59 (10 H, m, CH_2Ph); ^{13}C (125.76 MHz), δ 16.16 (d, $POCH_2CH_3$, $^3J_{CP}$ = 6.7), 30.99, 31.68 [2 s, $(CH_3)_3$], 32.25 (s, RCH_2R), 33.61, 34.01 (2 s, quaternary C), 64.03 (d, $POCH_2CH_3$, $^2J_{CP}$ = 5.5), 75.37 (s, CH_2Ph), 124.83, 125.65, 127.43, 127.87, 130.52 (5 s, *m*-C of R, *o*-, *m*- and *p*-C of CH_2Ph), 131.70 (d, *o*-C of R, $^3J_{CP}$ = 3.1), 135.83, 137.78 (2 s, *o*-C of CH_2Ph), 142.64 (d, RO, $^2J_{CP}$ = 8.2 Hz), 145.15 (s, RO), 145.62, 152.33 (2 s, *p*-C of R); ^{31}P (202.46 MHz), δ −3.81 (s).

Partial phosphorylation of *p*-*tert*-butylcalix[6]arene. Following the procedure described by Markovskii *et al.*[36] for the purported 1,3,5-triphosphorylation of *p*-*tert*-butylcalix[6]arene, triethylamine (3.74 g, 37.0 mmol) was added to a solution of *p*-*tert*-butylcalix[6]arene (1.00 g, 1.03 mmol) in anhydrous chloroform under an atmosphere of dry nitrogen. Diethyl chlorophosphate (0.89 g, 5.16 mmol) was added and the reaction mixture heated at reflux for 5 h. After cooling to room temperature the solvent was removed under reduced pressure and water (100 cm^3) added to the residue to give a brown solid (1.23 g). Flash chromatography of the solid (cyclohexane–ethyl acetate, 5:1, 3:1) gave 0.54 g (47%) of monosubstituted calixarene, 0.09 g (7%) of 1,4-disubstituted calixarene and 0.12 g (9%) of 1,3-disubstituted calixarene.

Diethoxyphosphoryl-*p*-*tert*-butylcalix[6]arene: R_f(TLC, cyclohexane–ethyl acetate, 5:1) = 0.29, m.p. 186–189 °C (Found: C, 75.8; H, 8.2; P, 3.0. $C_{70}H_{93}O_9P$ requires C, 75.8; H, 8.45; P, 2.8%). NMR ($CDCl_3$, 298 K): ^1H (500.14 MHz), δ 0.98

[9 H, s, $C(CH_3)_3$], 1.27 [9 H, s, $C(CH_3)_3$], 1.31 [18 H, s, $C(CH_3)_3$], 1.35 [18 H, s, $C(CH_3)_3$], 1.50 (6 H, td, $POCH_2CH_3$, $^3J_{HH}$ = 7.1, $^4J_{HP}$ = 0.8), 3.59 (2 H, d, RCH_2R, $^2J_{HH}$ = 14.6), 3.61 (2 H, d, RCH_2R, $^2J_{HH}$ = 13.5), 3.72 (2 H, br s, RCH_2R), 3.92 (4 H, br s, RCH_2R), 4.43–4.49 (4 H, m, $POCH_2CH_3$), 4.74 (2 H, d, RCH_2R, $^2J_{HH}$ = 15.3), 6.82 (2 H, s, H of R), 7.12, 7.20 (4 H, AB q, H of R, $^4J_{HH}$ = 2.3), 7.13 (2 H, s, H of R), 7.19 (4 H, s, H of R), 8.38 (1 H, br s, ROH) and 9.22, (2 H, br s, ROH); ^{13}C (125.76 MHz), δ 16.28 (d, $POCH_2CH_3$, $^3J_{CP}$ = 6.8), 31.17, 31.52, 31.60, 31.62 [4 s, $(CH_3)_3$]; 32.21, 32.31, 32.85 (3 s, RCH_2R), 34.00, 34.04, 34.12 (3 s, quaternary C), 65.42 (d, $POCH_2CH_3$, $^2J_{CP}$ = 6.3), 125.66, 125.88, 126.17 (3 s, *m*-C of R), 126.70, 127.28, 127.42 (3 s, *o*-C of R), 131.56 (d, *o*-C of R, $^3J_{CP}$ = 2.7), 143.34, 143.62, 144.21 (3 s, *p*-C of R), 147.95, 149.03 (2 s, RO) and 148.22 (d, *p*-C of R, $^2J_{CP}$ = 1.6 Hz); ^{31}P (202.46 MHz), δ −4.50 (s).

O^1,O^4-Bis(diethoxyphosphoryl)-*p*-*tert*-butylcalix[6]arene: R_f(TLC, cyclohexane–ethyl acetate, 5:1) = 0.09, m.p. 154–157 °C (Found: C, 71.7; H, 8.1; P, 5.0. $C_{74}H_{102}O_{12}P_2$ requires C, 71.35; H, 8.25; P, 4.95%). NMR ($CDCl_3$, 298 K): ^1H (500.14 MHz), δ 0.67 [18 H, br s, $C(CH_3)_3$], 1.05 (12 H, t, $POCH_2CH_3$, $^3J_{HH}$ = 7.0, $^4J_{HP}$ = unresolved), 1.28 [36 H, s, $C(CH_3)_3$], 3.5, 4.2, 4.5 (20 H, 3 vbr s, RCH_2R, $POCH_2CH_3$), 6.58 (4 H, br s, H of R), 7.05, 7.23 (8 H, AB q, H of R, $^4J_{HH}$ = 2.4), 8.37 (4 H, vbr s, ROH); (325 K) δ 0.74 [18 H, s, $C(CH_3)_3$], 1.09 (12 H, t, $POCH_2CH_3$, $^3J_{HH}$ = 7.0, $^4J_{HP}$ = unresolved), 1.29 [36 H, s, $C(CH_3)_3$], 3.4–4.7 (12 H, br hump, RCH_2R), 4.17–4.21 (8 H, m, $POCH_2CH_3$), 6.65 (4 H, s, H of R), 7.05, 7.22 (8 H, AB q, H of R, $^4J_{HH}$ = 2.3) and 8.00, (4 H, br s, ROH); ^{13}C (125.76 MHz), δ 15.70 (d, $POCH_2CH_3$, $^3J_{CP}$ = 6.5), 30.48, 32.06 (2 s, RCH_2R), 30.78, 31.57 [2 s, $(CH_3)_3$], 33.88, 33.92 (2 s, quaternary C), 65.70 (d, $POCH_2CH_3$, $^2J_{CP}$ = 5.4), 124.29 (s, *o*-C of R), 124.65, 125.95, 127.29 (3 s, *m*-C of R), 131.31 (d, *o*-C of R, $^3J_{CP}$ = 3.3 Hz), 142.32, 144.10, 147.46, 149.50 (4 s, *p*-C of R, RO); ^{31}P (202.46 MHz), δ −4.41 (s).

O^1,O^3-Bis(diethoxyphosphoryl)-*p*-*tert*-butylcalix[6]arene: R_f(TLC) (cyclohexane–ethyl acetate, 3:1) = 0.15, (cyclohexane–ethyl acetate, 1:1) = 0.47; m.p. 172–174 °C (Found: C, 71.5; H, 8.2; P, 5.1. $C_{74}H_{102}O_{12}P_2$ requires C, 71.35; H, 8.25; P, 4.95%). NMR ($CDCl_3$, 298 K): ^1H (500.14 MHz), δ 0.86, [18 H, s, $C(CH_3)_3$], 1.26 [18 H, s, $C(CH_3)_3$], 1.34 [9 H, s, $C(CH_3)_3$], 1.39 [9 H, s, $C(CH_3)_3$], 1.40 (12 H, t, $POCH_2CH_3$, $^3J_{HH}$ = 6.8, $^4J_{HP}$ = unresolved), 3.49, 4.68 (4 H, AB q, RCH_2R, $^2J_{HH}$ = 15.2), 3.63, 3.75 (4 H, AB q, RCH_2R, $^2J_{HH}$ = 14.4), 3.72, 4.47 (4 H, AB q, RCH_2R, $^2J_{HH}$ = 16.2), 4.28–4.36 (8 H, m, $POCH_2CH_3$), 6.40 [2 H, br s, H of R (2 or 5)], 6.73 [2 H, br s, H of R (5 or 2)], 7.05, 7.12 [4 H, AB q, H of R, $^4J_{HH}$ = 2.0 Hz (4 and 6)], 7.24 (4 H, s, H of R (1 and 3)]; ^{13}C (125.76 MHz), δ 16.10 (d, $POCH_2CH_3$, $^3J_{CP}$ = 6.6), 29.66, 33.93, 33.98 (3 s, quaternary C), 30.95, 31.50, 31.62, 31.67 [4 s, $(CH_3)_3$], 31.37, 32.49, 32.54 (3 s, RCH_2R), 65.09 (d, $POCH_2CH_3$, $^2J_{CP}$ = 6.3 Hz), 123.52, 124.54, 125.99, 126.09, 126.92, 127.49 (6 s, *m*-C of R), 125.19, 126.42, 126.73, 131.33, 131.73 (5 s, *o*-C of R), 142.68, 142.80, 143.12, 143.52, 147.70, 149.03, 150.05 (7 s, *p*-C of R, RO); ^{31}P (202.46 MHz), δ −4.30 (s).

Partial phosphorylation of *p*-*tert*-butylcalix[8]arene. Based on the above procedure, triethylamine (4.55 g, 45.0 mmol) was added to a solution of *p*-*tert*-butylcalix[8]arene (1.50 g, 1.16 mmol) in dry chloroform (150 cm^3) under an atmosphere of dry nitrogen. Diethyl chlorophosphate (1.56 g, 9.04 mmol) was added and the reaction mixture heated at reflux for 5 h. After cooling to room temperature the solvent was removed under reduced pressure and water (100 cm^3) added to the residue to give a brown solid (1.97 g), which was triturated in boiling ethanol (40 cm^3) and the insoluble residual *p*-*tert*-butylcalix[8]arene (0.37 g, 0.29 mmol) filtered off. The filtrate was taken to dryness and flash chromatographed (light petroleum–ethyl acetate, 5:1) to give 0.57 g (31%) of monosubstituted calixarene, 0.27 g (15%) of 1,3-disubstituted calixarene and 0.22 g (12%) of 1,5-disubstituted calixarene.

Diethoxyphosphoryl-*p*-*tert*-butylcalix[8]arene: m.p. 175–178 °C (Found: C, 76.9; H, 8.5; P, 2.3. $C_{92}H_{121}O_{11}P$ requires C, 77.05; H, 8.50; P, 2.15%). NMR ($CDCl_3$, 298 K): ^1H (500 MHz), δ 1.04 [9 H, s, $C(CH_3)_3$], 1.25 [18 H, s, $C(CH_3)_3$], 1.26 [9 H, s, $C(CH_3)_3$], 1.31 [18 H, s, $C(CH_3)_3$], 1.33 [18 H, s, $C(CH_3)_3$], 1.47 (6 H, t, $POCH_2CH_3$, $^3J_{HH}$ = 7.1, $^4J_{HP}$ = unresolved), 3.86 (4 H, br s, RCH_2R), 3.90 (8 H, br s, RCH_2R), 4.19 (4 H, br s, RCH_2R), 4.42 (4 H, qd, $POCH_2CH_3$, $^3J_{HH}$ = 7.1, $^3J_{HP}$ = 8.5), 6.80 (2 H, s, H of R), 7.10, 7.25 (4 H, AB q, H of R, $^4J_{HH}$ = 2.4), 7.13, 7.14 (4 H, AB q, H of R, $^4J_{HH}$ = 2.4), 7.14 (2 H, s, H of R), 7.18, 7.22 (4 H, AB q, H of R, $^4J_{HH}$ = 2.3); 8.70 (2 H, br s, ROH), 8.87 (3 H, br s, ROH) and 9.03 (2 H, br s, ROH), (323 K) δ 1.03 [9 H, s, $C(CH_3)_3$] 1.26 [18 H, s, $C(CH_3)_3$], 1.27 [9 H, s, $C(CH_3)_3$, 1.31 [18 H, s, $C(CH_3)_3$], 1.33 [18 H, s, $C(CH_3)_3$], 1.46 (6 H, td, $POCH_2CH_3$, $^3J_{HH}$ = 7.1, $^4J_{HP}$ = 0.5), 3.87 (4 H, s, RCH_2R), 3.90 (4 H, s, RCH_2R), 3.91 (4 H, s, RCH_2R), 4.19 (4 H, s, RCH_2R), 4.40 (4 H, qd, $POCH_2CH_3$, $^3J_{HH}$ = 7.1, $^3J_{HP}$ = 8.6), 6.80 (2 H, s, H of R), 7.10, 7.25 (4 H, AB q, H of R, $^4J_{HH}$ = 2.4), 7.13, 7.15 (4 H, AB q, H of R, $^4J_{HH}$ = 2.5), 7.14 (2 H, s, H of R), 7.17, 7.21 (4 H, AB q, H of R, $^4J_{HH}$ = 2.4), 8.67 (3 H, br s, ROH), 8.80 (2 H, br s, ROH) and 8.89, (2 H, br s, ROH); ^{13}C (125.76 MHz), δ 16.12 (d, $POCH_2CH_3$, $^3J_{CP}$ = 6.3), 31.07, 31.40, 31.43, 31.52, 31.56 [5 s, $(CH_3)_3$], 31.64, 31.90, 32.13, 32.38 (4 s, RCH_2R), 33.93, 33.96, 34.29 (3 s, quaternary C), 65.63 (d, $POCH_2CH_3$, $^2J_{CP}$ = 6.3), 124.43, 125.52, 125.56, 125.61, 125.65, 125.81, 125.89, 127.52 (8 s, *m*-C of R), 126.87, 127.43, 127.62, 127.69, 127.72, 127.97, 129.46, 131.50 (8 s, *o*-C of R), 142.90, 143.88, 143.95, 144.26, 144.31, 146.68, 146.92, 147.60, 148.07, 149.33 (10 s, *p*-C of R, RO); ^{31}P (202.46 MHz), δ −4.16 (s).

O^1,O^3-Bis(diethoxyphosphoryl)-*p*-*tert*-butylcalix[8]arene: m.p. 192–196 °C (Found: C, 73.4; H, 8.4; P, 3.8. $C_{96}H_{130}O_{14}P_2$ requires C, 73.45; H, 8.35; P, 3.95%). NMR ($CDCl_3$, 298 K): ^1H (500.14 MHz), δ 1.01 [18 H, s, $C(CH_3)_3$], 1.22 [18 H, s, $C(CH_3)_3$], 1.24 [9 H, s, $C(CH_3)_3$], 1.25 [9 H, s, $C(CH_3)_3$], 1.32 [18 H, s, $C(CH_3)_3$], 1.65 (12 H, vbr m, $POCH_2CH_3$), 3.81 (8 H, br s, RCH_2R), 1.06 (8 H, br s, RCH_2R), 4.28–4.37 (8 H, m, $POCH_2CH_3$), 6.61 (2 H, s, H of R), 6.97 (2 H, d, H of R, $^4J_{HH}$ = 1.7), 7.08, 7.24 (4 H, AB q, H of R, $^4J_{HH}$ = 2.4), 7.10 (2 H, s, H of R), 7.12 (6 H, br s, H of R), 8.67 (2 H, br s, ROH), 9.15 (1 H, br s, ROH) and 9.24 (2 H, br s, ROH); ^{13}C (125.76 MHz), δ 15.93 (d, $POCH_2CH_3$, $^3J_{CP}$ = 6.8), 31.03, 31.40, 31.44, 31.51, 31.53 [5 s, $(CH_3)_3$], 31.60, 32.13 (2 s, RCH_2R), 32.87, 33.88, 34.13 (3 s, quaternary C), 65.19 (d, $POCH_2CH_3$, $^2J_{CP}$ = 6.3 Hz), 124.40, 127.62, 128.23, 131.27, 131.45, 131.93 (6 s, *o*-C of R), 124.66, 125.35, 125.45, 125.59, 127.78 (5 s, *m*-C of R), 141.83, 143.81, 144.00, 144.14, 144.20, 146.93, 147.74, 149.16, 149.80 (9 s, *p*-C of R, RO); ^{31}P (202.46 MHz), δ −4.45 (s).

O^1,O^5-Bis(diethoxyphosphoryl)-*p*-*tert*-butylcalix[8]arene: m.p. 229–232 °C (Found: C, 73.8; H, 8.7; P, 3.9. $C_{96}H_{130}O_{14}P_2$: C, 73.45; H, 8.35; P, 3.95%). NMR ($CDCl_3$, 298 K): ^1H (500.14 MHz), δ 0.94 [18 H, s, $C(CH_3)_3$], 1.27 [36 H, s, $C(CH_3)_3$], 1.32 [18 H, s, $C(CH_3)_3$], 1.41 (12 H, td, $POCH_2CH_3$, $^3J_{HH}$ = 7.1, $^4J_{HP}$ = 0.8), 3.83 (8 H, br s, RCH_2R), 4.11 (8 H, br s, RCH_2R), 4.30–4.35 (8 H, m, $POCH_2CH_3$), 6.60 (4 H, s, H of R), 6.99 (2 H, s, H of R), 7.00 (2 H, s, H of R), 7.18 (8 H, s, H of R), 8.48 (2 H, vbr s, ROH) and 8.59 (4 H, vbr s, ROH); ^{13}C (125.76 MHz), δ 15.93 (d, $POCH_2CH_3$, $^3J_{CP}$ = 6.8), 31.00, 31.54, 31.57 [3 s, $(CH_3)_3$], 31.99, 32.13 (2 s, RCH_2R), 33.87, 33.93, 34.21 (3 s, quaternary C), 65.63 (d, $POCH_2CH_3$, $^2J_{CP}$ = 5.6), 124.65, 126.84, 127.11, 131.46 (4 s, *o*-C of R), 124.06, 125.75, 125.89, 127.48 (4 s, *m*-C of R), 142.70, 143.26 (2 s, RO), 144.03 (d, RO, $^2J_{CP}$ = 7.8 Hz), 147.88, 148.07, 149.38 (3 s, *p*-C of R); ^{31}P (202.46 MHz), δ −4.41 (s).

Hexa-*O*-methyl-*p*-(diethoxyphosphorylmethyl)calix[6]arene. The procedure described in the literature [37] for the preparation of the hexaphosphonic acid was followed only to the point of

isolating the intermediate phosphonate ester. Thus, *p-tert*-butylcalix[6]arene was chloromethylated with chloromethyl octyl ether–$SnCl_4$, and the resultant hexa-*O*-methyl-*p*-(chloromethyl)calix[6]arene (0.95 g, 0.939 mmol) heated at reflux for 5 h in the presence of triethyl phosphite (20 cm^3). Almost all of the excess of triethyl phosphite was removed under vacuum and the residue was dissolved in hot methanol (20 cm^3). Water (3 cm^3) was added and the solution allowed to cool. After 48 h the solution was filtered, the precipitate collected, the addition of water (2 cm^3) to the filtrate causing no further precipitation. The precipitate was dried (silica gel, 24 h) to give 1.17 g (77%) of a white powder, m.p. 131–133 °C (Found: C, 58.0; H, 7.3; P, 11.6. $C_{78}H_{114}O_{24}P_6$ requires C, 57.75; H, 7.1; P, 11.45%.) NMR ($CDCl_3$, 298 K): ^1H (500.14 MHz), δ 1.18 (36 H, t, $POCH_2CH_3$, $^3J_{HH}$ = 7.1, $^4J_{HP}$ = unresolved) 2.71 (12 H, d, RCH_2P, $^2J_{HP}$ = 20.5); 3.42 (18 H, s, $ROCH_3$); 3.86 (12 H, br s, RCH_2R); 3.89–3.95 (24 H, m, $POCH_2CH_3$) and 6.76 (12 H, s, H of R); ^{13}C (125.76 MHz), δ 16.38 (d, $POCH_2CH_3$, $^3J_{CP}$ = 5.4), 30.28 (s, RCH_2R), 32.71 (d, RCH_2P, $^1J_{CP}$ = 137.3), 60.48 (s, $ROCH_3$), 61.91 (d, $POCH_2CH_3$, $^2J_{CP}$ = 6.5), 126.58 (d, *p*-C of R, $^2J_{CP}$ = 8.7), 130.28 (d, *m*-C of R, $^2J_{CP}$ = 6.5 Hz), 134.16 (s, *o*-C of R) and 155.30 (s, RO); ^{31}P (202.46 MHz), δ 27.53 (s).

Bis{tetrakis-*O*-(diethyoxyphosphoryl)-*p-tert*-butylcalix[4]arene}lanthanum(III) picrate. Lanthanum(III) picrate dodecahydrate (0.1045 g, 0.100 mmol) was added to a solution of tetrakis-*O*-(diethoxyphosphoryl)-*p-tert*-butylcalix[4]arene (0.1194 g, 0.100 mmol) in dichloromethane (20 cm^3), causing an immediate change to yellow. Dichloromethane (80 cm^3) was added and the solution heated to dissolve most of the lanthanum picrate. The solution was filtered to remove undissolved lanthanum picrate and the solvent removed. The residue was dissolved in dichloromethane (4 cm^3) and ethanol (1 cm^3) added. Slow evaporation of the solvents resulted in deposition of bright yellow crystals (Found: C, 51.3; H, 5.9; N, 3.4. $C_{138}H_{190}LaN_9O_{53}P_8$ requires C, 51.65; H, 5.95; N, 3.95%.). NMR ($CDCl_3$, 298 K): ^1H (500.14 MHz), δ 1.08 [18 H, s, $C(CH_3)_3$], 1.10 [18 H, s, $C(CH_3)_3$], 1.25 (12 H, t, $POCH_2CH_3$, $^3J_{HH}$ = 7.0), 1.30 (12 H, td, $POCH_2CH_3$, $^3J_{HH}$ = 7.0, $^4J_{HP}$ = 1.0), 3.28, 4.64 (4 H, AB q, RCH_2R, $^2J_{HH}$ = 13.6), 3.28, 4.80 (4 H, AB q, RCH_2R, $^2J_{HH}$ = 13.6), 4.17–4.27 (8 H, m, $POCH_2CH_3$), 4.24–4.34 (8 H, m, $POCH_2CH_3$), 6.88, (4 H, s, H of R), 6.90, (4 H, s, H of R) and 8.84 (6 H, s, pic), ^{13}C (125.76 MHz), δ 15.94, 16.17 (2 d, $POCH_2CH_3$, $^3J_{CP}$ = 7.0, 6.8), 30.99, 31.18 (2 s, RCH_2R), 31.18, 31.30 [2 s, $(CH_3)_3$], 33.91, 34.03 (2 s, quaternary C), 64.54, 66.18 (2 d, $POCH_2CH_3$, $^2J_{CP}$ = 5.3, 6.4), 125.54, 125.86, 126.47, 130.72 (4 s, *m*-C of R 2 *m*, p-C of pic), 132.74, 133.46 (2 d, *o*-C of R, $^3J_{CP}$ = 2.9, 1.6), 140.63 (s, *o*-C of pic), 142.60, 142.77 (2 d, RO, $^2J_{CP}$ = 9.4, 9.2 Hz), 146.44, 147.85 (2 s, *p*-C of R) and 160.85 (s, pic), ^{31}P (202.46 MHz), δ −3.70 (s) and −9.51 (s).

Solvent extraction

Solvent-extraction experiments were carried out by shaking equal volumes of lanthanide picrate (2×10^{-5} mol l^{-1}) in pure water with an organic solution of calixarene (2×10^{-5} mol l^{-1}) for 30 min, this period of shaking being taken as long enough to establish equilibrium, since shaking periods of 10, 20 and 30 min gave essentially identical results. All extractions were conducted at 25.0 ± 0.5 °C. As the organic phase, dichloromethane, ethyl acetate and a 50% solution of tri-*n*-butyl phosphate in hexane were used. The picrate concentrations in both aqueous and organic phases were monitored by absorbance measurements at the lowest-energy picrate maximum. Values of the picrate concentration in the organic phase, measured directly and by difference from the aqueous-phase values, agreed well and were averaged.

Conformity to Beer's law was demonstrated for aqueous solutions of all the lanthanide picrates over the concentration range 1.25×10^{-6}–4×10^{-5} mol l^{-1}, with a common absorption maximum at 356 nm and a mean molar absorption coefficient of 14 600 ± 600 l mol^{-1} cm^{-1}. The literature value[38] for the picrate ion in dichloromethane (18 000 l mol^{-1} cm^{-1} at 378 nm) was used after confirmation for the present systems by difference measurements. For ethyl acetate and tributyl phosphate–hexane (1:1), maximum molar absorption coefficients of 14 300 ± 1300 and 14 200 ± 1100 l mol^{-1} cm^{-1} (at 366 and 354 nm, respectively) were estimated from organic-phase absorbances after calculating the picrate concentration in the organic phase by difference from the aqueous phase.

Crystallography

General procedure (variations as noted). Unique diffractometer data sets ($T \approx 295$ K; 2θ–θ scan mode, $2\theta_{max}$ 50°; monochromatic Mo-Kα radiation, $\lambda = 0.7107_3$ Å) were measured, yielding N independent reflections, N_o of these with $I > 3\sigma(I)$ being considered 'observed' and used in the full-matrix/large block least-squares refinements after Gaussian absorption correction. Anisotropic thermal parameters were refined for the non-hydrogen atoms (x, y, z, $U_{iso})_H$ being included constrained at estimated values. Neutral atom complex scattering factors[39] were employed; computation used the XTAL 3.2 program system[40] implemented by S. R. Hall. Conventional residuals R,R' on $|F|$ are cited, statistical weights being derivative of $\sigma^2(I) = \sigma^2(I_{diff}) + 0.0004\sigma^4(I_{diff})$.

1,2-μ-3,4-μ′-di(*n*-butoxyphosphoryl)-*p-tert*-butylcalix[4]arene, '*exo-exo*' isomer. *Crystal data.* $C_{52}H_{70}O_8P_2$, M = 855.1, orthorhombic, space group *Ibca* (D_{2h}^{27}, no. 73), a = 27.400(3), b = 21.48(1), c = 17.95(7) Å, U = 10 563 $Å^3$, D_c (Z = 8) = 1.11 g cm^{-3}, $F(000)$ = 3808, μ_{Mo} = 1.3 cm^{-1}, specimen 0.12 × 0.52 × 0.95 mm, $A^*_{min,max}$ = 1.02, 1.06, N = 4646, N_o = 2165, R = 0.068, R' = 0.067, n_v = 281.

Abnormal features/variations. The high residuals appear to be consequent on high thermal motion of the butyl substituents (both types), no disorder being resolvable.

1,2-μ-3,4-μ′-di(*n*-butoxyphosphoryl)-*p*-(2,2,3,3-tetramethylbutyl)calix[4]arene, '*exo-endo*' isomer. *Crystal data.* $C_{68}H_{102}O_8P_2$, M = 1109.5, monoclinic, space group $C2/c$ (C_{2h}^6, no. 15), a = 20.29(1), b = 25.222(8), c = 15.20(2) Å, β = 108.36(7)°, U = 7385 $Å^3$, D_c (Z = 4) = 1.00 g cm^3, $F(000)$ = 2352, μ_{Mo} = 1.0 cm^{-1}, specimen 0.50 × 0.32 × 0.70 mm (no correction), N = 6511, N_o = 3240, R = 0.085, R' = 0.101, n_v = 380.

Variations. The *n*-butyl substituent was disordered over the two oxygen sites offered by the phosphate, occupancies being set at 0.5 after trial refinement; with concomitant high thermal motion and limited high-angle data, not all substituent atom anisotropic thermal parameters would refine meaningfully and the isotropic form was adopted for C(113), C(123).

Bis{tetrakis-*O*-(diethoxyphosphoryl)-*p-tert*-butylcalix[4]arene}lanthanum(III) picrate. *Crystal data.* $C_{138}H_{190}LaN_9O_{53}P_8 \cdot \approx 12H_2O$, $M \approx$ 3419, triclinic, space group $P\bar{1}$ (C_i^1, no. 2), a = 31.943(7), b = 28.487(4), c = 20.563(7) Å, α = 86.91(2), β = 89.05(2), γ = 88.46(1)°, U = 18 675 $Å^3$. D_c (Z = 4) = 1.22 g cm^{-3}, $F(000) \approx$ 7192, μ_{Mo} = 3.8 cm^{-1}, specimen 0.52 × 0.40 × 0.30 mm, $A^*_{min,max}$ = 1.11, 1.16, $2\theta_{max}$ 45°, N = 39 885, N_o = 16 918, R = 0.13, R' = 0.17, n_v = 1734.

Variations. The crystals disintegrated into fine flakes at the slightest physical provocation; eventually one was successfully captured by flotation into a capillary and draining briefly. Data collection was terminated when well advanced by an extended diffractometer failure during which the crystal deteriorated; a further successfully mounted specimen not being achieved,

solution and refinement proceeded on the basis of the existing data which, although somewhat weak, presented a useful aggregate, albeit supportive of meaningful thermal parameter refinement for C, N, O only in the isotropic form for the ligand atoms (block-diagonal refinement). The cations were well defined and without disorder in the Bu^t groups. The picrate anions, not closely associated with the cations, were resolved only with some difficulty, picrates 1 and 2 being refined with geometrical constraints and 3–6 being treated as rigid bodies; the anions were also disposed amongst a considerable aggregate of 'water molecules', modelled by their oxygen atoms only, associated hydrogen atoms not being located, and far exceeding in total stoichiometry the degree of hydration of the readily dehydrated sample implied by the elemental analysis. Some of the water oxygen atoms were well defined, with associated anisotropic thermal parameters being refinable, but most were dispersed and diffuse, being modelled in terms of half-weighted components with isotropic thermal parameters.

Complete atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1.

Results and Discussion

Synthesis and characterization of phosphorylated calixarene extractants

Many of the compounds used in the present study were previously known, though in some instances our attempts to reproduce literature procedures did not provide the expected materials. In particular, in the partial phosphorylation of both *p-tert*-butyl-calix[6]arene and -calix[8]arene, we (and others before us[41]) have obtained mixtures of mono- and di-phosphorylated species under conditions claimed, in the case of *p-tert*-butylcalix[6]arene, to provide the triphosphorylated.[36] Establishment of the isomeric forms of the diphosphorylated compounds is not trivial and, given that the compounds were not useful extractants, we have based our assignments only upon NMR spectra and plausible reaction mechanisms. We assume that the calix[6]arene derivatives adopt either the 'pinched' cone or 1,2,3-alternate ('three up, three down') conformations[42–45] and that conformational inversion is very rapid relative to phosphorylation rates, though it is worthy of note that the monophosphorylated derivatives of both *p-tert*-butyl-calix[6]arene and -calix[8]arene show some broad resonances at room temperature, indicating that they are appreciably less flexible than the unsubstituted calixarenes,[42] and for all compounds heating to ≈ 50 °C was necessary to obtain sharp signals for all CH groups. For the compounds we have identified as O^1,O^3- and O^1,O^4-bis(diethoxyphosphoryl)-*p-tert*-butylcalix[6]arene, the simplest evidence for their isomeric form is the presence of four and two, respectively, *tert*-butyl methyl resonances in their ^{1}H NMR spectra. In other, more detailed studies of partial substitution on larger calixarenes by electrophilic attack on phenoxide centres[46,47] it has been shown that the product distribution can be rationalized by assuming that deprotonation is preferred at the site(s) with the greater number of adjacent phenolic groups (capable of hydrogen bonding). Thus, in a monophosphorylated calix[6]-arene, generation of a phenoxide ion adjacent to the substituted centre [*i.e.* at position 2 (=6)] would be less favourable than at either of the other two [3 (=5) and 4] because it would have only one, rather than two phenolic neighbours. Statistically, 1,3 would be favoured over 1,4, substitution, as appears to be the case. In the case of the *p-tert*-butylcalix[8]arene derivatives, the number of *tert*-butyl methyl resonances and their relative intensities are again clearly consistent with the assigned isomeric forms (assuming, say, an averaged 'pleated loop' conformation[42,43]). That the 1,2 isomer is not observed is consistent with the preferred deprotonation-site arguments given above but reasons for the absence of the 1,4 isomer are not apparent.

The phosphoryl oxygen is the donor site for co-ordination of phosphorus(v) esters to metal ions and thus the orientation of such donors in calixarene phosphates is one important factor related to their possible use in metal-ion extraction. Where the calixarene acts as a unidentate ligand towards P^V we assume that rotation about the calixarene O–P bond is sufficiently free to allow essentially all possible orientations of the phosphoryl oxygen with respect to the macrocyclic cavity. Where the calixarene acts as a bidentate ligand, however, the phosphorus atom becomes part of an eight-membered chelate ring with rather limited flexibility[48] and it is anticipated that compounds such as 1,2-μ-3,4-μ′-di(alkoxyphosphoryl) calix[4]arene should exist in three separable isomeric forms (Fig. 1), which we have termed '*exo-exo*', '*exo-endo*' and '*endo-endo*' in relation to a focus on the orientations of the two phosphoryl oxygen atoms. Only the *endo-endo* form has a convergent array of the atoms and can act as a chelate ligand towards a metal ion. Our syntheses resulted in the isolation of but two compounds in each of the reactions investigated [of *n*-butyl dichlorophosphate with *p-tert*-butyl- and *p*-(1,1,3,3-tetramethylbutyl)calix[4]arene, and crystal structure determinations (see below) were carried out on one member of each pair to establish their isomeric forms. For each of the pairs NMR spectroscopy revealed one member to be asymmetric, and therefore to be the *exo-endo* isomer, and the other to have two-fold symmetry and therefore to be the *exo-exo* or *endo-endo* form. Thus, it remains possible that the derivative of *p*-(1,1,3,3-tetramethyl)calix[4]arene not crystallographically characterized could be the *endo-endo* isomer but on the bases of its very close spectroscopic similarities to the *exo-exo* derivative of *p-tert*-butylcalix[4]arene and the observations of an apparent preference for the *exo-exo* form in a closely related species[48] and an *exo* orientation in a singly bridged compound[25] we assume it is not. Bridged calixarene phosphates may therefore be limited to action as unidentate (or possibly bridging) ligands, though there is evidence that *endo*-oriented phosphoryl groups can be obtained by esterification of an appropriate calixarene phosphoric acid.[49]

Fortunately, any barriers to reorientation of possibly divergent donor groups to bind in a multidentate array towards a metal ion do not appear to be insurmountable for cone tetrakis-*O*-(diethoxyphosphoryl)-*p-tert*-butylcalix[4]-arene, as is shown in the crystal structure of its lanthanum(III) complex described below. A reorientational barrier of a similar kind is known to be overcome in formation of complexes of tetrakis-*O*-(dialkylcarboxamidomethyl)-*p-tert*-butylcalix-[4]arene.[50]

Crystal structures

The results of the room-temperature single crystal studies of the calixarene phosphate esters *exo-exo*-1,2-μ-3,4-μ′-di(*n*-butyloxyphosphoryl)-*p-tert*-butylcalix[4]arene **A** and *exo-endo*-1,2-μ-3,4-μ′-di(*n*-butyloxyphosphoryl)-*p*-(2,2,3,3-tetramethylbutyl)calix[4]arene **B** are consistent with the stoichiometries and connectivities described above. Views of the solid-state conformations of the molecules are shown in Fig. 2. In each case, a crystallographic 2 axis passes through the cone of the molecule, so that only one half is crystallographically independent. The pitches of the phenyl ring planes to the plane of the O_4 array are similar in each case, the dihedral angles being 41.4(1), 83.4(2)° for rings 1 and 2 in **A** and 36.8(2), 91.3(2)° in **B**. The phosphate eight-membered rings likewise are similar in conformation in both complexes (Table 1) and seemingly not markedly different to those in pyrophosphate and chlorophosphite calixarene derivatives,[48] though, unsurprisingly, the *exo*-directed oxygen atoms are more divergent than in the pyrophosphate (and more akin in direction to those in the

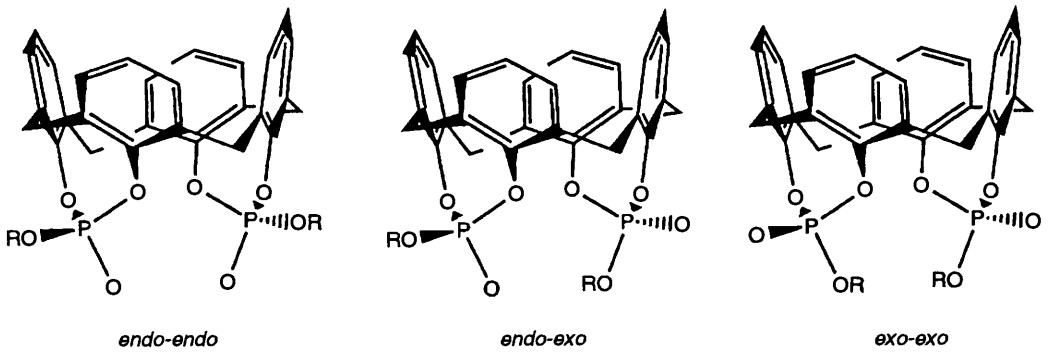

Fig. 1 Possible stereoisomeric forms of a calix[4]arene doubly bridged by alkoxyphosphoryl substituents

Table 1 Phosphate-ring conformations in compounds **A** and **B**: torsion angles/°

Atoms	A	B
O(2)–P–O(1)–C(11)	−103.7(4)	−95.6(5)
P–O(1)–C(11)–C(16)	39.4(7)	45.8(5)
O(1)–C(11)–C(16)–C(2)	7.9(8)	6.9(9)
C(11)–C(16)–C(2)–C(12)	53.4(7)	51.9(9)
C(16)–C(2)–C(22)–C(21)	−86.0(6)	−88.7(8)
C(2)–C(22)–C(21)–O(2)	−11.5(8)	−9.6(9)
C(22)–C(21)–O(2)–P	53.4(6)	69.4(7)
C(21)–O(2)–P–O(1)	26.0(4)	5.1(4)

phosphite). The near perpendicularity to the O_4 plane of rings 2 and 4 in both compounds means that the calixarene cavity is significantly obstructed by the *para* substituents on both but there is no evidence that 'self-inclusion'[51] of the 1,1,3,3-tetramethylbutyl group is more extensive than that of the *tert*-butyl group. The similar degree of cavity obstruction may explain why neither compound contains included solvent. In **A** the *n*-butyl ester substituent is found attached to one of the phosphate oxygen atoms only (*endo*) but in **B** it is disordered over the two available sites. Whether the dispositions of the pair within any given molecule are concerted or random is not clear from the study. In both arrays the molecules pack side by side in sheets normal to the cone/crystallographic 2 axis.

For the complex of lanthanum(III) picrate with tetrakis-*O*-(diethoxyphosphoryl)-*p*-*tert*-butylcalix[4]arene the results of the room-temperature single-crystal X-ray study are consistent with its formulation as an ionic species, $[La(calixarene)_2]^{3+}$ 3 pic^-, with two such entities comprising the asymmetric unit of a very large pseudo-symmetric structure. It is a unique example of a calixarene complex in that the 1 : 2 metal : ligand stoichiometry in the solid state is associated with direct co-ordination of both ligand molecules and not, for example, simply the incorporation of a molecule of ligand within the lattice of a 1 : 1 complex.[8] The cations are usefully defined and without disorder; the anions are poorly resolved, very high apparent thermal motion possibly being a foil for disorder, and were modelled as rigid bodies. The cations and anions are loosely held in sheets interspersed by a substantial body of lattice water molecules, some well defined and ordered, others much less so. As noted above, the crystals are remarkably fragile, disintegrating into micaceous leaves upon the slightest physical contact, perhaps in accord with the above packing mode, while the ready loss of solvent is apparently evidenced in respect of the substantial discrepancy between the degree of hydration as determined by the X-ray work and the elemental analysis.

The cations, perhaps because of very loose lattice restraints in keeping with the above, are remarkably similar and symmetrical and free from obvious irregularities normally associated with lattice perturbations (Tables 2, 3). The two quadridentate ligands are disposed to either pole of a quasi-$\bar{8}$ axis through their cones and their lanthanum atoms [Fig. 3(*a*)], the oxygen atoms defining very acceptable square-antiprismatic arrays (less usual among the early rare-earth metals) about the metal, the quasi-$\bar{8}$ axes of the two independent cations being almost parallel. The spread of La–O distances is quite tight [2.42(2)–2.55(2), mean 2.49 Å], while that among similar angles is also close. The La–O–P angles are in a narrow range [149(1)–155(1), mean 152°], as are the pitch angles of the associated phenyl rings [61.8(8)–66.6(8), mean 63.5°]. One of the ligands, typical of the four, is shown in projection down its quasi-4 axis in Fig. 3(*b*) with similar La–O–P–O–C dispositions. The latter, in association with ring locations, define a slight twist of each cone about its axis, causing well defined deviations from ideal 4*mm* symmetry. The *tert*-butyl group orientations are similar and not disordered, with one outer methyl directed away from the cone and the other pair outwards in alignment with the phenyl-ring plane, while a certain similarity may be discerned among the ethyl appendages of the phosphate moieties. The cone appears to be devoid of the otherwise abundantly distributed solvent.

Solvent extraction

The choice of a solvent for extraction studies is somewhat arbitrary, especially in an initial survey, and hence dichloromethane, ethyl acetate and tri-*n*-butylphosphate were examined largely because they are relatively cheap materials of quite different solvating powers. The rare-earth-metal picrates have high solubilities in $PO(OBu^n)_3$ and ultimately a choice was made of this solvent diluted with an equal volume of hexane to obtain a suitable medium. The background extraction by $PO(OBu^n)_3$–hexane (1 : 1) was observed to be rather similar to that for ethyl acetate and, as is apparent from Fig. 4(*a*), neither solvent displayed any significant selectivity across the complete rare-earth-metal series. Extraction of the rare-earth-metal picrates by pure dichloromethane was negligible.

The effect of addition of a calixarene to the extraction solvent was strongly dependent on the nature of the calixarene. Under the experimental conditions applied, however, enhancement of the degree of extraction was negligible for all species examined other than those containing four or more diethoxyphosphoryl substituents and even within this group the tetrakis(diethoxyphosphoryl)-*p*-*tert*-butyldihomooxacalix[4]arene was not useful. This last result was somewhat surprising, especially given that both *p*-*tert*-butyldihomooxacalix[4]arene and *p*-*tert*-butylcalix[4]arene readily form rare-earth-metal complexes,[10,14] though the introduction of bulky diethoxyphosphoryl substituents may well lead to considerably greater conformational differences than those that exist between the 'parent' calixarenes, and of course differences in complexion lipophilicity are as important as differences in stability for solvent extraction. Another surprising result was the ineffectiveness of the 'upper rim' substituted calix[6]arene, hexa-*O*-methyl-*p*-(diethoxyphosphorylmethyl)calix[6]arene, as related species[52–54] have been demonstrated to be effective

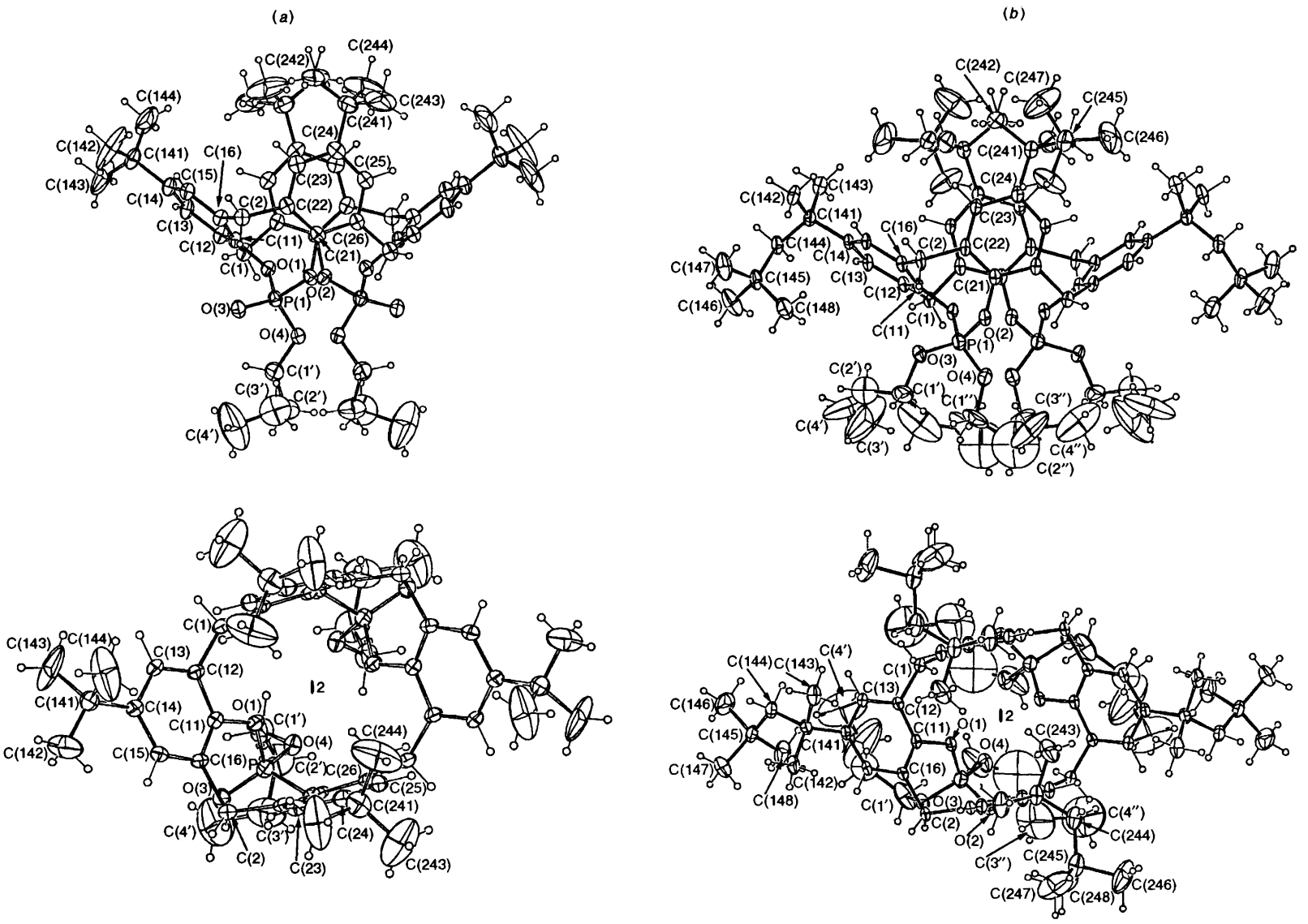

Fig. 2 Views of the solid-state structures of the bis(bridging phosphate)calix[4]arene ligands **A** (*a*) and **B** (*b*) down and normal to the two-fold axis; 20% thermal ellipsoids are shown for the non-hydrogen atoms and the hydrogen atoms are shown with arbitrary radii of 0.1 Å

Table 2 Lanthanum environments. Atoms O(1–4, 1′–4′) are derivative of ligands 1,2 in cation 1 and 3,4 in cation 2, the value for the latter being below that for the former; *r* is the La–O distance in Å; other entries in the matrix are the angles/° subtended at the lanthanum by the respective atoms at the head of the row and column. The final column, θ/°, is the angle La–O–P

Atom	*r*	O(2)	O(3)	O(4)	O(1′)	O(2′)	O(3′)	O(4′)	θ
O(1)	2.42(2)	72.3(6)	114.3(6)	74.2(6)	139.5(6)	76.0(6)	78.8(6)	145.1(6)	154(1)
	2.55(2)	73.5(6)	114.1(6)	71.6(6)	141.7(6)	77.4(6)	80.3(6)	143.8(5)	153(1)
O(2)	2.51(2)		70.5(6)	113.5(6)	76.5(6)	79.6(6)	145.0(6)	139.9(6)	153(1)
	2.50(2)		72.6(6)	115.1(6)	75.0(6)	78.8(6)	144.5(6)	140.7(6)	149(1)
O(3)	2.49(2)			73.9(6)	77.6(6)	142.3(6)	141.6(6)	77.3(6)	155(1)
	2.48(2)			74.4(6)	75.8(6)	143.7(5)	141.5(6)	77.8(6)	154(1)
O(4)	2.47(2)				143.6(6)	141.2(6)	75.8(6)	78.4(6)	151(1)
	2.53(2)				143.3(6)	139.6(6)	77.3(6)	80.0(6)	150(1)
O(1′)	2.48(2)					73.5(6)	116.9(6)	73.7(6)	152(1)
	2.50(2)					75.5(6)	116.0(6)	73.2(6)	151(1)
O(2′)	2.44(2)						74.5(6)	115.9(6)	150(1)
	2.50(2)						72.4(5)	114.1(6)	153(1)
O(3′)	2.48(2)							73.8(6)	152(1)
	2.50(2)							71.9(5)	156(1)
O(4′)	2.48(2)								153(1)
	2.51(2)								154(1)

Table 3 Ligand cone conformations in the lanthanum La complex. For the four O_4 arrays from each ligand, χ^2 (plane) are given, together with lanthanum deviations, δ_{La}/Å, and the dihedral angles (θ/°) of the C_6 planes of the associated phenyl rings

	Cation, ligand			
	1,1	1,2	2,3	2,4
χ^2	2.0	0.2	0.4	2.9
δ_{La}	1.348(2)	1.303(2)	1.359(2)	1.344(2)
θ_1	64.5(9)	64.3(9)	62.8(8)	66.2(8)
θ_2	63.2(8)	62.7(9)	63.8(8)	61.8(8)
θ_3	62.3(8)	66.6(8)	61.9(8)	66.2(8)
θ_4	64.7(8)	61.0(9)	62.0(8)	61.9(8)

Angles between the four O_4 planes, read as the rows of a matrix, are: 1.2(4), 5.0(5), 2.2(5); 3.8(5), 1.0(4); 2.9(5)°, *i.e.* the four O_4 planes are quite closely parallel, so that the axes of all cations in the lattice are closely parallel.

metal-binding agents, though molecular modelling (using the version of MM2[55] contained within the software package CHEM3D + [56]) indicates that on a calix[6]arene framework it is difficult to pose more than two oxygen atoms of different phosphoryl groups close enough to bind to one metal ion, and the ineffectiveness of O^1,O^3-bis(diethoxyphosphoryl)-*p-tert*-butylcalix[4]arene as an extractant suggests that mere bidentate co-ordination cannot be sufficient to result in extraction (again given the proviso of lipophilicity differences).

In absolute terms, addition of cone form tetrakis-*O*-(diethoxyphosphoryl)-*p-tert*-butylcalix[4]arene at a concentration of 2×10^{-5} mol l^{-1} to any of the three solvents had a similar effect on the percentage extraction of rare-earth-metal picrates [Fig. 4(*b*)], though the relative effect is by far the greatest for dichloromethane. Unfortunately, this is not associated with any apparent selectivity under the particular conditions used and only for $PO(OBu^n)_3$–hexane is there some evidence for a small preference, in this case for Pr/Nd. The extraction enhancement does not seem to depend significantly on whether the *para* substituent is Bu^t or $Bu^tCH_2CMe_2$ [Fig. 4(*c*) and 4(*d*)], though in ethyl acetate the differences, which are just outside experimental error in some cases, do consistently favour the $Bu^tCH_2CMe_2$ species. Rather more limited data for calix[8]arene analogues [Fig. 4(*e*)] do not indicate any significant differences, though they do show that extraction by calix[8]arene phosphates is considerably less efficient than that by the calix[4]arene compounds, as is also illustrated by the data directly compared in Fig. 4(*f*) and 4(*g*). The difference is of course less marked for ethyl acetate than for dichloromethane due to the greater background extraction. We assume that the poorer extraction ability of calix[8]arene phosphates may be associated with their greater conformational freedom, which would allow the bulky diethoxyphosphoryl groups to be oriented away from the centre of the macrocyclic ring and be well separated, thus inhibiting chelation to a metal ion (as suggested above to explain the poor extraction ability of calix[6]arene phosphonates). Certainly, it is not possible for a calix[8]arene octaphosphate to provide an externally lipophilic sheath for a metal ion by wrapping around it in the 'propeller' conformation structurally established for $[Ln_2L](H_6L$ = *p-tert*-butylcalix[8]arene) compounds.[7,9,11,13]

Most interesting of the present results were those obtained in comparing the cone and partial cone forms of tetrakis-(diethoxyphosphoryl)-*p-tert*-butylcalix[4]arene as extractants. It was initially surprising to discover that the partial cone form, with fewer metal-binding sites in close proximity, was actually the better extractant in all three solvents [Fig. 4(*h*)–4(*j*)]. For dichloromethane, however, the differences are only just outside experimental error, whereas for ethyl acetate and $PO(OBu^n)_3$–hexane they are very much more marked. These results we interpret in terms of the assumption that the most efficiently extracted species in all solvents would be the truly neutral complex formed by co-ordination of all three picrate ions as well as the calixarene to the metal (rather than, say, ion-pair species). Then, only for the partial cone calixarene, it is possible for picrate co-ordination to be assisted by π–π stacking with a calixarene phenyl ring as shown in Fig. 5. Assistance of binding by aromatic unit stacking has been demonstrated in a variety of systems [57] and stacking specifically of the type suggested here has recently been characterized in a crystal structure determination of a complex formed between europium picrate and a calix[4]arene tetramide derivative.[58] In dichloromethane, it is unlikely that solvent binding would inhibit picrate co-ordination but in both ethyl acetate and $PO(OBu^n)_3$–hexane the solvent molecules could act as much more effectively competing ligands and hence preserve the Ln(calixarene) moiety in a cationic, and therefore presumably less lipophilic form. A factor such as stacking which also facilitated anion binding could therefore have its most apparent influence in co-ordinating solvents. Whatever the case, it must still be noted that no significant selectivity was detected across the rare-earth-metal series. This is somewhat surprising in that appreciable selectivity in the binding of both cone and partial cone isomers of a different neutral calix[4]arene derivative to the alkali-metal cations (as picrates) has been observed [59] and the change in ionic radius between Na^+ and Cs^+, for example, is quite similar to that across the rare-earth metals. Presumably, differences in donor atoms, ligand denticity and complex-ion stereochemistry complicate such a comparison.

The stoichiometry of the extraction process was investigated

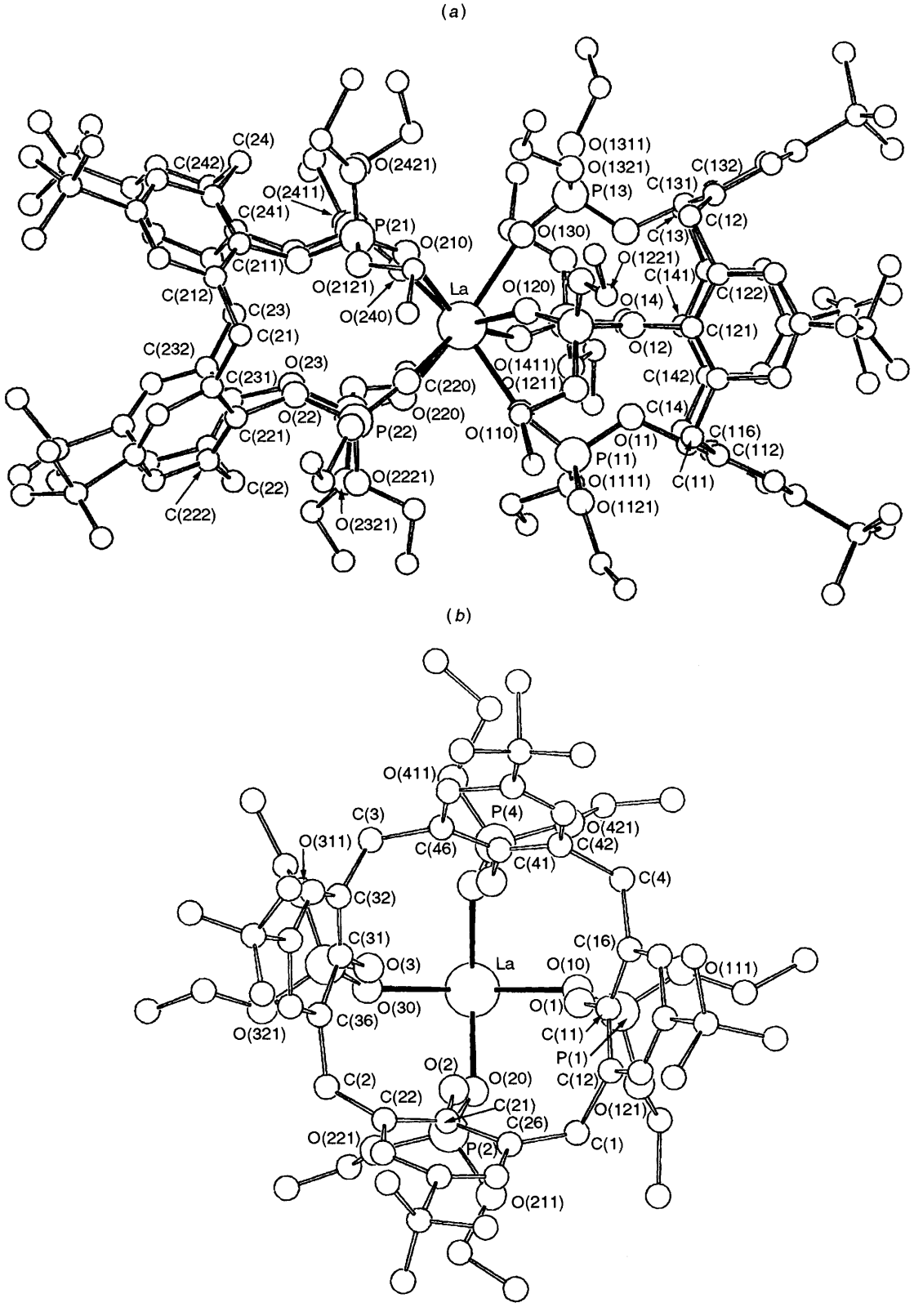

Fig. 3 (*a*) Cation 1 of the lanthanum complex. Projected normal to its principal axis. Cation 2 (not shown) is similar. (*b*) A typical ligand (ligand 2) of the complex, viewed down its pseudo-four-fold axis

in detail only in the case of cone form tetrakis-*O*-(diethoxyphosphoryl)-*p*-*tert*-butylcalix[4]arene. For concentrations of this extractant near 2×10^{-5} mol l^{-1} in dichloromethane, saturation of extraction of lanthanum picrate (using concentrations of this salt in the aqueous phase up to 100 times higher) gave a maximum picrate-ion concentration in the dichloromethane phase of 6×10^{-5} mol l^{-1}, indicating that a 1:1 complex was the extracted species. In contrast, at much higher metal and ligand concentrations a 2:1 (ligand:metal) complex crystallized from solution (see Experimental section) and this species has been characterized crystallographically in the present work. The ^{1}H NMR spectrum of this material in deuteriochloroform showed, however, two sets of calixarene proton resonances of equal intensity which could be assigned to free and coordinated calixarene, indicating that the 2:1 complex must dissociate fully into a 1:1 complex and free calixarene even

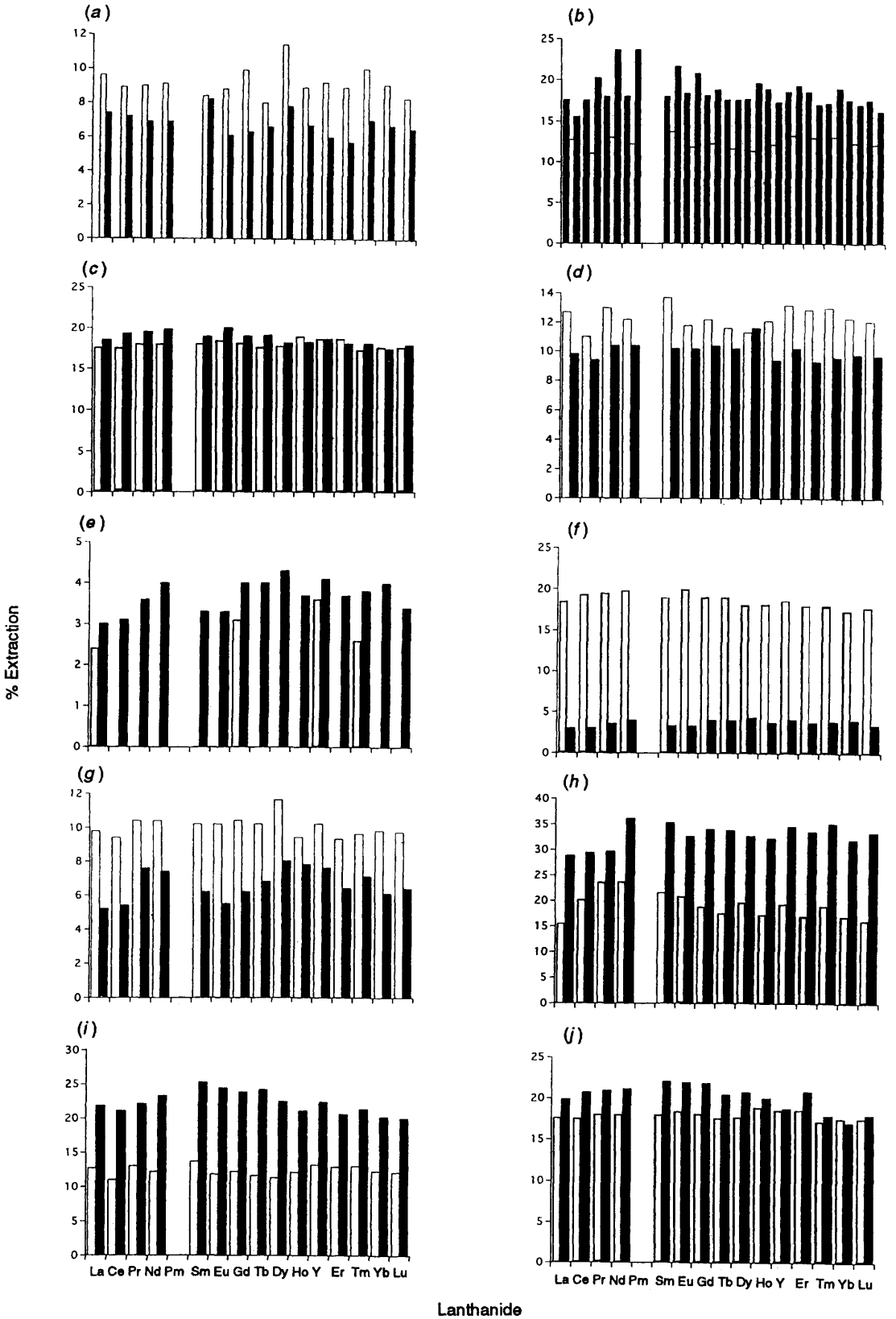

Fig. 4 Solvent extraction of the rare-earth-metal picrates into: (*a*) the simple solvents dichloromethane (black bars left, values are zero), ethyl acetate (white bars) and $PO(OBu^n)_3$–hexane (black bars, right); (*b*) the same solvents containing the cone form of tetrakis-*O*-(diethoxyphosphoryl)-*p*-*tert*-butylcalix[4]arene; (*c*) dichloromethane containing the cone form of tetrakis-*O*-(diethoxyphosphoryl)-*p*-*tert*-butylcalix[4]arene (white bars) or tetrakis-*O*-(diethoxyphosphoryl)-*p*-(1,1,3,3-tetramethylbutyl)calix[4]arene (black bars); (*d*) ethyl acetate containing the cone form of tetrakis-*O*-(diethoxyphosphoryl)-*p*-*tert*-butylcalix[4]arene (white bars) or tetrakis-*O*-(diethoxyphosphoryl)-*p*-(1,1,3,3-tetramethylbutyl)calix[4]arene (black bars); (*e*) dichloromethane containing octakis-*O*-(diethoxyphosphoryl)-*p*-*tert*-butylcalix[8]arene (white bars) or octakis-*O*-(diethoxyphosphoryl)-*p*-(1,1,3,3-tetramethylbutyl)calix[8]arene (black bars); (*f*) dichloromethane containing the cone form of tetrakis-*O*-(diethoxyphosphoryl)-*p*-(1,1,3,3-tetramethylbutyl)calix[4]arene (white bars) or octakis-*O*-(diethylphosphoryl)-*p*-(1,1,3,3-tetramethylbutyl)calix[8]arene (black bars); (*g*) ethyl acetate containing the cone form of tetrakis-*O*-(diethoxyphosphoryl)-*p*-(1,1,3,3-tetramethylbutyl)calix[4]arene (white bars) or octakis-*O*-(diethoxyphosphoryl)-*p*-(1,1,3,3-tetramethylbutyl)calix[8]arene (black bars); (*h*) dichloromethane containing the cone (white bars) or partial cone (black bars) forms of tetrakis-*O*-(diethoxyphosphoryl)-*p*-*tert*-butylcalix[4]arene; (*i*) ethyl acetate containing the cone (white bars) or partial cone (black bars) forms of tetrakis-*O*-(diethoxyphosphoryl)-*p*-*tert*-butylcalix[4]arene; (*j*) $PO(OBu^n)_3$–hexane (1 : 1) containing the cone (white bars) or partial cone (black bars) forms of tetrakis-*O*-(diethoxyphosphoryl)-*p*-*tert*-butylcalix[4]arene

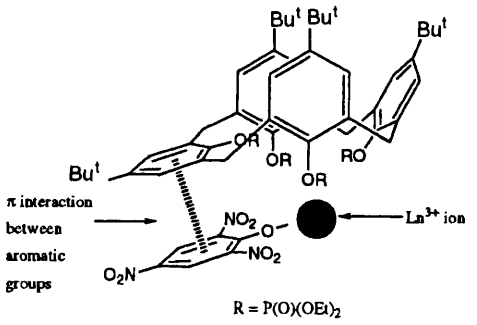

Fig. 5 Possible mode for π stacking of a picrate ligand with a phenyl group of a co-ordinated partial cone form calixarene

at the relatively high concentration used for the spectral measurement ($\approx 10^{-2}$ mol l^{-1}). That only the 1:1 complex needed to be considered as significant in the extraction process as conducted was also indicated by the fact that the variation of extraction into dichloromethane as a function of the concentration of lanthanum picrate could be adequately described in terms of an extraction equilibrium (1). Thus, a plot

$$La^{3+}(aq) + 3pic^{-}(aq) + calixarene(org) \rightleftharpoons [La(calixarene)(pic)_3](org) \quad (1)$$

of $\log(D/[pic^-]^3)$ *vs.* $\log c_f$ (where D is the distribution constant, *i.e.* the ratio of $[La^{3+}]$ in the dichloromethane phase to $[La^{3+}]$ in the aqueous phase, and c_f is the concentration of unco-ordinated calixarene in the organic phase) was linear with a slope of 0.8 ± 0.2.

Conclusion

Though all the present solvent-extraction experiments were conducted under only one set of conditions and there is evidence that at higher concentrations, ones that might well apply in any practical solvent-extraction process, new species may become important, there is little to encourage optimism that the simple calixarene phosphate esters could prove more useful than simple phosphates in rare-earth-metal separations. In this regard, they are clearly inferior to carboxymethyl calixarene ethers,[60] though these materials are obviously unsuitable for use in strongly acidic media such as might be encountered in the extraction of rare-earth metals present in radioactive wastes.[19] Under these conditions, carbamoylmethylphosphine oxide-substituted calixarenes[61] are known to be superior rare-earth-metal extractants to the carbamoylmethylphosphine oxides[62] upon which their synthesis was based, though their selectivity is yet to be fully characterized. If our proposed rationalization of the more efficient extraction of rare-earth-metal picrates by the partial cone rather than the cone conformer of tetrakis-*O*-(diethoxyphosphoryl)-*p*-*tert*-butylcalix[4]arene is correct, then facilitation of co-anion binding in extraction of a cation may be a factor to be considered in the design of improved neutral extractants. Calixarene analogues which bind simple anions such as chloride and nitrate are well known,[63] though these particular cationic macrocycles do not appear to be effective ligands for metal ions. Their structures show, however, that hydrogen bonding appears to contribute to nitrate inclusion, so that possibly a 2-hydroxyethoxyphosphoryl-substituted calixarene might prove to be an especially effective extractant for rare-earth-metal cations in nitrate media.

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