Synthesis, characterisation and extraction behaviour of calix[4]arene-based phosphonic acids †

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Three new bis(phosphonic) acids were prepared by derivatization of *p-tert*-butylcalix[4]arene on the lower rim by $-(CH_2)_xPO_3H_2$ groups and were fully characterized by NMR spectroscopy; some of them were further investigated by X-ray analysis. The compounds obtained were tested as extractants for La^{3+}, Eu^{3+}, Yb^{3+} and Th^{4+} in 0.1–1 M HNO_3. Structural details of the complex $HLn(H_2L^1)_2$ where Ln = Y, La, Eu were elucidated by NMR techniques in solution. The extraction efficiencies decrease with increasing length of the CH_2 spacer; the dependence is not monotonic, and an extraordinary selectivity was observed for Yb. The extraction efficiency of Ln^{3+} for all of the ligands studied increased significantly with decreasing ionic radius.

Introduction

The reprocessing of nuclear waste is based on the separation of its components. The elements present differ remarkably in their toxicity, the type and energy of the emitted radiation, life-times and, of course, in the reprocessing methods required.

The industrially used PUREX[1] process effectively removes plutonium and uranium from nuclear fuel. Lanthanides and actinides are removed in the next step using the TRUEX[2] process, which is a liquid–liquid extraction utilising [(*N*,*N*-diisobutylcarbamoyl)methyl]octyl(phenyl)phosphine oxide (CMPO, Fig. 1) to transfer cations into the organic phase.

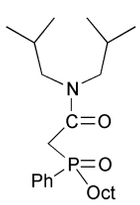

Fig. 1

The disadvantage of using CMPO is that it discriminates only slightly between lanthanides and actinides: both lanthanide and actinide ions bind three CMPO molecules which are not preorganised to form a coordination site. For this reason, a variety of compounds and technologies are now being explored in attempts to achieve better selectivity and efficiency of the extracting agent.

Suitably substituted calixarenes are now widely studied[3] as extracting agents as they can act as ligands that (i) are capable of saturating the relatively high coordination numbers of f-block elements (8 or higher), (ii) have the advantage of a preorganised coordination environment in the cone conformation and (iii) are sufficiently lipophilic to transfer a metal into the organic phase as a complex. Calix[4]arenes substituted at either the lower or the upper rim with CMPO moieties seem to be the most promising.[4,5] These compounds are more efficient extractants for lanthanides or actinides than CMPO itself and also show far better actinide/lanthanide selectivity. Calix[4]arenes substituted with phosphine oxides,[6] carboxylates,[7] aminocarboxylates,[8] amides[9] and hydroxamate[10] have also been studied, but they were found to be remarkably weaker extractants in highly acidic solutions than the CMPO-substituted calixarenes.

So far, there have been no attempts to use lower-rim phosphonate-bearing calix[4]arene derivatives as extracting agents. Upper rim phosphonate derivatives of calixarenes have until now been little studied.[11] In this report we describe the synthesis and extraction properties of a series of calix[4]arenes substituted with two phosphonic acid groups (compounds **1b**–**3b**, Fig. 2). Being a relatively strong and hard acid (in terms of the HSAB theory) with an affinity for lanthanides, the phosphonic acid group is thought to form stable complexes with f-elements even in highly acidic solution.

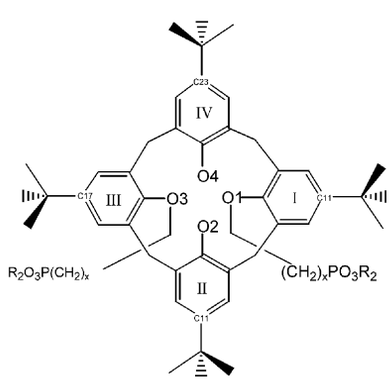

Fig. 2 General formula of the synthesized compounds and atom numbering scheme.

Experimental

The starting *p-tert*-butylcalix[4]arene[12] and the starting phosphonate esters[13] were prepared by established literature procedures. All solvents used in syntheses were dried by standard methods.[14] The syntheses were carried out under an Ar atmosphere. Column chromatography was performed using

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Merck silica gel 60 (230–400 mesh) and TLC of the tetraesters using Merck silica 60 F_{254} plates. In the extraction experiments, Th^{4+} and Ln^{3+} were used as their nitrates $Th(NO_3)_4 \cdot 5H_2O$, $La(NO_3)_3 \cdot 6H_2O$, $Eu(NO_3)_3 \cdot 5H_2O$ and $Yb(NO_3)_3 \cdot 5H_2O$; the metal contents were determined gravimetrically. Metal concentrations in the phases were determined using a Jobin Ivon JY 170 Ultrace ICP/AES instrument. All compounds were characterised by ^1H, ^{13}C, COSY, NOESY, HSQC and HMBC NMR spectra (recorded on a 400 MHz Unity Varian spectrometer) and by X-ray diffraction. Their purity was confirmed by TLC, elemental analysis and NMR. The NMR data are given in the form: solvent, reference, other conditions. The calix[4]arene compounds were thoroughly dried for several hours *in vacuo* before characterisation, as they show a tendency to occlude organic solvents and water.

Syntheses

Compound 1a. A suspension of 5 g of *p-tert*-butylcalix[4]-arene (1 : 1 complex with toluene, 6.7 mmol) and 4.7 g of K_2CO_3 (freshly calcined, 34 mmol) in 50 ml of dry acetonitrile was stirred and refluxed for 30 min. A solution of 4 g of $(C_2H_5O)_2P(O)CH_2OSO_2CF_3$ (16 mmol) in 30 ml of dry acetonitrile was added, and the mixture was stirred and refluxed until the reaction was complete (as monitored by TLC, mobile phase chloroform–ethyl acetate 1 : 1, UV detection, $R_F = 0.5$). After removal of the solvent, 200 ml of dichloromethane were added, the suspension was extracted twice with the same amounts of 2 M HCl and water, and dried over anhydrous Na_2SO_4. Solvent removal and recrystallisation from methanol of the yellow oil obtained yielded 4.2 g (67%) of a colourless crystalline solid.

^1H NMR ($CDCl_3$, TMS) δ (ppm): 0.86 (18H, s, $(CH_3)_3C$ subst. rings), 1.32 (18H, s, $(CH_3)_3C$ unsubst. rings), 1.41 (12H, t, $^3J_{(H,H)} = 7.0$ Hz, CH_2CH_3), 3.32 (4H, AB d, $^2J_{(H,H)} = 13.6$ Hz, Ar-CH_2-Ar eq), 4.27 (4H, AB d, $^2J_{(H,H)} = 13.6$ Hz, Ar-CH_2-Ar ax), 4.29–4.38 (12H, m, P-O-CH_2 + Ar-O-CH_2), 6.67 (4H, s, Ar-*H* subst. rings), 7.09 (4H, s, Ar-*H* unsubst. rings), ^{13}C NMR ($CDCl_3$, TMS) δ (ppm): 16.6 (d, $^3J_{(C,P)} = 5.7$ Hz, CH_2CH_3), 30.9 [$(CH_3)_3C$ subst. rings], 31.7 [$(CH_3)_3C$ unsubst. rings], 31.7 (Ar-CH_2-Ar), 33.8 and 33.9 [$(CH_3)_3C$], 63.1 (d, $^2J_{(C,P)} = 6.1$ Hz, O-CH_2-CH_3), 69.4 (d, $^1J_{(C,P)} = 162$ Hz, Ar-O-CH_2), 125.1 (*Ar*-H, unsubst. ring), 125.7 (*Ar*-H, subst. ring), 127.7 (*Ar*-CH_2 unsubst. ring), 131.5 (*Ar*-CH_2 subst. ring), 141.6 (*Ar*-*t*Bu unsubst. ring), 147.3 (*Ar*-*t*Bu subst. ring), 150.5 (*Ar*-OH), 150.7 (*Ar*-O-CH_2), ^{31}P NMR ($CDCl_3$, ref. ext. 85% H_3PO_4) δ (ppm): 16.9. Elem. anal.: calcd. 68.3 C, 8.28 H for $C_{54}H_{78}O_{10}P_2$, found 67.1 C, 8.00% H.

Compound 1b. A solution of 3.8 g of **1a** (4 mmol) and 6.2 ml of trimethylsilyl bromide (7.35 g, 48 mmol) in dry acetonitrile (20 ml) was stirred and refluxed for 6 h. 5 ml of methanol were added, the reaction mixture was refluxed for 2 h and then cooled to room temperature. The solvent was removed, the residue was co-evaporated three times with 20 ml of dry toluene, dissolved in 10 ml of chloroform and filtered. After solvent removal, the product was purified by recrystallisation from methanol. Yield 2.6 g (79%), mp 300 °C (decomp.).

^1H NMR (CD_3OD, $CHD_2OD = 3.3$ ppm) δ (ppm): 1.10 [18H, s, $(CH_3)_3C$ subst. rings], 1.22 [18H, s, $(CH_3)_3C$ unsubst. rings], 3.40 (4H, d, $^2J_{(H,H)} = 12.8$ Hz, Ar-CH_2-Ar eq), 4.28 (4H, d, $^2J_{(P,H)} = 8.8$ Hz, Ar-O-CH_2), 4.39 (4H, d, $^2J_{(H,H)} = 12.8$ Hz, Ar-CH_2-Ar ax), 7.11 and 7.12 (4H, s, Ar-*H*), ^{13}C NMR (CD_3OD, $CD_3OD = 49$ ppm) δ (ppm): 31.6 [$(CH_3)_3C$ subst. rings], 32.1 [$(CH_3)_3C$ unsubst. rings], 32.2 (Ar-CH_2-Ar), 34.7 and 35.1 [$(CH_3)_3C$], 71.6 (d, $^1J_{(C,P)} = 166$ Hz, Ar-O-CH_2), 126.1 (*Ar*-H, unsubst. ring), 127.2 (*Ar*-H, subst. ring), 129.4 (*Ar*-CH_2 unsubst. ring), 134.7 (*Ar*-CH_2 subst. ring), 143.4 (*Ar*-*t*Bu unsubst. ring), 149.5 (*Ar*-*t*Bu subst. ring), 150.9 (*Ar*-OH), 151.8 (*Ar*-O-CH_2), ^{31}P NMR (CD_3OD, ref. ext. 85% H_3PO_4) δ (ppm): 18.5. Elem. anal: calcd. 66.0 C, 7.46 H for $C_{46}H_{62}O_{10}P_2$, found 66.1 C, 7.63% H.

Compound 2a. Bis(2-bromoethyl)calix[4]arene: a mixture of 8.9 g of *p-tert*-butylcalix[4]arene (1 : 1 complex with toluene, 12 mmol), 6.6 g of K_2CO_3 (freshly calcined, 48 mmol), 36 g of 1,2-dibromoethane (192 mmol) and 160 ml of dry acetonitrile was stirred and refluxed for 16 h. Acetonitrile was removed, the residue was dissolved in 100 ml of dichloromethane and extracted subsequently with 100 ml of 3 M and 0.5 M HCl. After removal of the dichloromethane, the product was evaporated twice with 20 ml of dry ethanol, dissolved in 40 ml of dichloromethane, filtered and concentrated to a volume of 20 ml. Then 60 ml of dry ethanol were added and the solution was slowly evaporated on a rotary evaporator to about half the volume. The precipitate was filtered off, washed with dry ethanol, dried *in vacuo* and used in the next step without purification. Yield 7.4 g, 64%.

^1H NMR ($CDCl_3$, TMS) δ (ppm): 0.95 [18H, s, $(CH_3)_3C$ subst. rings], 1.29 [18H, s, $(CH_3)_3C$ unsubst. rings], 3.33 (4H, AB d, $^2J_{(H,H)} = 13.0$ Hz, Ar-CH_2-Ar eq), 3.83 (4H, t, $^3J_{(H,H)} = 6.4$ Hz, Br-CH_2), 4.30 (4H, t, $^3J_{(H,H)} = 6.5$ Hz, Ar-O-CH_2), 4.31 (4H, AB d, $^2J_{(H,H)} = 13.0$ Hz, Ar-CH_2-Ar ax), 6.79 (4H, s, Ar-*H* subst. rings), 7.06 (4H, s, Ar-*H* unsubst. rings), ^{13}C NMR ($CDCl_3$, TMS) δ (ppm): 29.3 (Br-CH_2), 30.9 [$(CH_3)_3C$ subst. rings], 31.6 [$(CH_3)_3C$ unsubst. rings], 31.7 (Ar-CH_2-Ar), 33.8 and 33.9 [$(CH_3)_3C$], 75.4 (Ar-O-CH_2), 125.1 (*Ar*-H, unsubst. ring), 125.6 (*Ar*-H, subst. ring), 127.7 (*Ar*-CH_2 unsubst. ring), 132.3 (*Ar*-CH_2 subst. ring), 141.6 (*Ar*-*t*Bu unsubst. ring), 147.2 (*Ar*-*t*Bu subst. ring), 149.3 (*Ar*-O-CH_2), 150.5 (*Ar*-OH).

The intermediate bis(2-bromoethyl)calix[4]arene (7.4 g, purity about 90% according to ^1H NMR, 7.7 mmol) and 25.6 g of triethyl phosphite (154 mmol) were stirred and heated to 165 °C (bath temperature) for 16 h. The volatile components were removed by distillation *in vacuo* (0.1 Torr), with the temperature rising from ambient to 160 °C, to give a practically quantitative yield of **2a** in about 90% purity (^1H NMR analysis); the product was converted to **2b** without purification. Compound **2a** can be further purified to give a white solid by column chromatography with chloroform–ethyl acetate 1 : 1.

^1H NMR ($CDCl_3$, TMS) δ (ppm): 0.91 [18H, s, $(CH_3)_3C$ subst. rings], 1.30 [18H, s, $(CH_3)_3C$ unsubst. rings], 1.34 (12H, t, $^3J_{(H,H)} = 7.0$ Hz, CH_2CH_3), 2.54 (4H, m, CH_2P), 3.32 (4H, AB d, $^2J_{(H,H)} = 13.2$ Hz, Ar-CH_2-Ar eq), 4.08–4.24 (12H, m, P-O-CH_2 + Ar-O-CH_2), 4.24 (4H, AB d, $^2J_{(H,H)} = 13.2$ Hz, Ar-CH_2-Ar ax), 6.73 (4H, s, Ar-*H* subst. rings), 7.06 (4H, s, Ar-*H* unsubst. rings), ^{13}C NMR ($CDCl_3$, TMS) δ (ppm): 16.4 (d, $^3J_{(C,P)} = 5.7$ Hz, CH_2CH_3), 27.0 (d, $^1J_{(C,P)} = 138$ Hz, P-CH_2), 30.9 [$(CH_3)_3C$ subst. rings], 31.6 [$(CH_3)_3C$ unsubst. rings], 31.6 (Ar-CH_2-Ar), 2 × 33.8 [$(CH_3)_3C$], 61.9 (d, $^2J_{(C,P)} = 6.5$ Hz, P-O-CH_2), 70.0 (d, $^2J_{(C,P)} = 1.5$ Hz, Ar-O-CH_2), 125.0 (*Ar*-H, unsubst. ring), 125.5 (*Ar*-H, subst. ring), 127.8 (*Ar*-CH_2 unsubst. ring), 132.1 (*Ar*-CH_2 subst. ring), 141.6 (*Ar*-*t*Bu unsubst. ring), 147.0 (*Ar*-*t*Bu subst. ring), 149.5 (*Ar*-O-CH_2), 150.3 (*Ar*-OH), ^{31}P NMR ($CDCl_3$, ref. ext. 85% H_3PO_4) δ (ppm): 25.3.

Compound 2b. Compound **2b** was prepared from **2a** (2 mmol), using the same procedure as for **1b**, and a fourfold excess of trimethylsilyl bromide with respect to **2b**. The product **2b** was isolated by filtration of its toluene solution, solvent removal, dissolution in 10 ml of methanol and reprecipitation with 20 ml of water, giving 1.55 g (90%) of product, mp 230 °C (decomp.).

^1H NMR (CD_3OD, $CHD_2OD = 3.3$ ppm) δ (ppm): 1.07 [18H, s, $(CH_3)_3C$ subst. rings], 1.24 [18H, s, $(CH_3)_3C$ unsubst. rings], 2.65 (4H, dt, $^2J_{(P,H)} = 13.2$ Hz, $^3J_{(H,H)} = 8.1$ Hz, CH_2P), 3.40 (4H, d, $^2J_{(H,H)} = 13.2$ Hz, Ar-CH_2-Ar eq), 4.24–4.30 (8H, t + d, Ar-O-CH_2 + Ar-CH_2-Ar), 7.06 (4H, s, Ar-*H* subst. rings), 7.13 (4H, s,

Ar-*H* unsubst. rings), ^{13}C NMR (CD_3OD, CD_3OD = 49 ppm) δ (ppm): 29.6 (d, $^1J_{(C,P)}$ = 136 Hz, P-CH_2), 31.6 [$(CH_3)_3C$ subst. rings], 32.1 [$(CH_3)_3C$ unsubst. rings], 32.4 (Ar-CH_2-Ar), 34.7 [$(CH_3)_3C$ unsubst. rings], 35.0 [$(CH_3)_3C$ subst. rings], 72.1 (d, $^2J_{(C,P)}$ = 4.5 Hz, Ar-O-CH_2), 126.3 (*Ar*-H, unsubst. ring), 127.0 (*Ar*-H, subst. ring), 129.6 (*Ar*-CH_2 unsubst. ring), 134.5 (*Ar*-CH_2 subst. ring), 143.8 (*Ar*-*t*Bu unsubst. ring), 149.3 (*Ar*-*t*Bu subst. ring), 150.5 (*Ar*-O-CH_2), 150.8 (*Ar*-OH), ^{31}P NMR (CD_3OD, ref. ext. 85% H_3PO_4) δ (ppm): 26.0. Elem. anal.: calcd 66.7 C, 7.70 H for $C_{48}H_{66}O_{10}P_2$, found 65.4 C, 7.58% H.

Compound 3a. A suspension of 2.96 g of *p*-*tert*-butylcalix[4]-arene (1 : 1 complex with toluene, 4 mmol) and 2.76 g of K_2CO_3 (freshly calcined, 20 mmol) in 30 ml of dry acetonitrile was stirred and refluxed for 30 min. 2.8 g of diethyl (3-bromopropyl)phosphonate (9.6 mmol, prepared according to ref. 13) dissolved in 10 ml of dry acetonitrile were then added and the reaction mixture was stirred and refluxed until practically complete conversion into **3a** was achieved (monitored by TLC on silica gel 60 F_{254}, mobile phase chloroform–ethyl acetate 1 : 1, UV detection, R_F = 0.25). The solvent was then removed, the residue was suspended in 50 ml of dichloromethane, extracted twice with the same amounts of 2 M HCl and water, and dried over anhydrous Na_2SO_4. Evaporation of dichloromethane gave a yellow oil which was dissolved in methanol. The desired product crystallised giving a yield of 3.3 g (82%), mp 297–300 °C (decomp.).

^{1}H NMR ($CDCl_3$, $CHCl_3$ = 7.26 ppm) δ (ppm): 0.97 [18H, s, $(CH_3)_3C$ subst. rings], 1.28 [18H, s, $(CH_3)_3C$ unsubst. rings], 1.35 (12H, t, $^3J_{(H,H)}$ = 6.8 Hz, CH_2CH_3), 2.14–2.35 (8H, m, CH_2P + CH_2CH_2P), 3.32 (4H, AB d, $^2J_{(H,H)}$ = 12.8 Hz, Ar-CH_2-Ar eq), 4.06 (4H, t, $^3J_{(H,H)}$ = 6.0 Hz, Ar-O-CH_2), 4.15 (8H, m, P-O-CH_2), 4.25 (4H, AB d, $^2J_{(H,H)}$ = 12.8 Hz, Ar-CH_2-Ar ax), 6.81 (4H, s, Ar-*H* subst. rings), 7.26 (4H, s, Ar-*H* unsubst. rings), ^{13}C NMR ($CDCl_3$, $CDCl_3$ = 77.0 ppm) δ (ppm): 16.5 (d, $^3J_{(C,P)}$ = 6.1 Hz, CH_2CH_3), 22.1 (d, $^1J_{(C,P)}$ = 142 Hz, P-CH_2), 23.2 (d, $^2J_{(C,P)}$ = 5.3 Hz, P-CH_2CH_2), 31.0 [$(CH_3)_3C$ subst. rings], 31.6 [$(CH_3)_3C$ unsubst. rings], 31.7 (Ar-CH_2-Ar), 33.8 and 33.9 [$(CH_3)_3C$], 61.5 (d, $^2J_{(C,P)}$ = 6.5 Hz, P-O-CH_2), 75.8 (d, $^3J_{(C,P)}$ = 15 Hz, Ar-O-CH_2), 125.0 (*Ar*-H, unsubst. ring), 125.5 (*Ar*-H, subst. ring), 127.7 (*Ar*-CH_2 unsubst. ring), 132.8 (*Ar*-CH_2 subst. ring), 141.9 (*Ar*-*t*Bu unsubst. ring), 147.4 (*Ar*-*t*Bu subst. ring), 149.5 and 150.3 (*Ar*-O), ^{31}P NMR ($CDCl_3$, ref. ext. 85% H_3PO_4) δ (ppm): 30.3. Elem. anal.: calcd 69.3 C, 8.62 H for $C_{58}H_{86}O_{10}P_2$, found 67.7 C, 8.54% H.

Compound 3b. Compound **3b** was prepared in an analogous manner to compound **2b**, yield 88%.

^{1}H NMR (CD_3OD, CHD_2OD = 3.3 ppm) δ (ppm): 1.10 [18H, s, $(CH_3)_3C$ subst. rings], 1.22 [18H, s, $(CH_3)_3C$ unsubst. rings], 2.21 (4H, m, CH_2P), 2.40 (4H, m, P-CH_2CH_2), 3.38 (4H, AB d, $^2J_{(H,H)}$ = 12.6 Hz, Ar-CH_2-Ar eq), 4.05 (4H, t, $^3J_{(H,H)}$ = 6.4 Hz, Ar-O-CH_2), 4.30 (4H, AB d, $^2J_{(H,H)}$ = 12.6 Hz, Ar-CH_2-Ar ax), 7.10 and 7.11 (8H, s, Ar-*H*), ^{13}C NMR (CD_3OD, CD_3OD = 49 ppm) δ (ppm): 25.0 (d, $^2J_{(C,P)}$ = 4.6 Hz, P-CH_2CH_2), 25.1 (d, $^1J_{(C,P)}$ = 141 Hz, P-CH_2), 31.6 [$(CH_3)_3C$ subst. rings], 32.1 [$(CH_3)_3C$ unsubst. rings], 32.4 (Ar-CH_2-Ar), 34.7 and 35.1 [$(CH_3)_3C$], 77.9 (d, $^3J_{(C,P)}$ = 19.8 Hz, Ar-O-CH_2), 126.2 (*Ar*-H, unsubst. ring), 126.90 (*Ar*-H, subst. ring), 129.5 (*Ar*-CH_2 unsubst. ring), 134.8 (*Ar*-CH_2 subst. ring), 143.4 (*Ar*-*t*Bu unsubst. ring), 149.1 (*Ar*-*t*Bu subst. ring), 150.8 and 151.3 (*Ar*-O), ^{31}P NMR (CD_3OD, ref. ext. 85% H_3PO_4) δ (ppm): 32.8. Elem. anal.: calcd 67.3 C, 7.90 H for $C_{50}H_{70}O_{10}P_2$, found 63.8 C, 7.75% H.

General procedure for extraction experiments

Equal volumes (1.5 ml) of an aqueous solution of metal nitrate [$c_M = 1 \times 10^{-4}$ in dil. HNO_3, the exact $c(HNO_3)$ is given in the text] and a solution of the ligand (concentrations adapted to give an appropriate concentration of the metal in the aqueous phase after extraction) in chloroform were mixed and shaken for 30 min at room temperature. Preliminary experiments showed that extraction equilibrium was reached after 20 min at 20 °C. A volume of 1 ml of the aqueous phase was taken after the time given and after separation of the phases. The concentration of metal in this solution was measured using a Jobin Ivon JY 170 Ultrace ICP/AES instrument.

Typical procedure for preparation of complexes

25 μmol of $Eu(NO_3)_3 \cdot 5H_2O$ and a stoichiometric amount of **1b** (either 25 or 50 μmol of $C_{46}H_{62}O_{10}P_2$) were dissolved in 2 ml of MeOH acidified with 150 μl of 0.1 M aqueous HNO_3. The complex $H_2Eu(C_{46}H_{58}O_{10}P_2)(NO_3) \cdot 3H_2O$ separated in several hours, while the complex $H_5Eu(C_{46}H_{58}O_{10}P_2)_2 \cdot 4H_2O$ precipitated from solution almost immediately. The solid complexes were filtered and air-dried before elemental analysis. Elem. anal.: calcd 50.1 C, 6.03 H, 1.26 N for $H_2Eu(C_{46}H_{58}O_{10}P_2)(NO_3) \cdot 3H_2O$, found 49.4 C, 5.81 H, 1.27% N. Calcd 58.3 C, 6.80 H for $H_5Eu(C_{46}H_{58}O_{10}P_2)_2 \cdot 4H_2O$, found 56.6 C, 6.4% H.

X-Ray investigation

The single crystals needed for X-ray study were prepared by crystallisation at room temperature from methanol solution (**1a**), by the hanging drop method (27% methanol, 73% polyethylene glycol) (**3a**) and from methanol solution (**3b**). The crystals obtained were crystallosolvates that liberated the solvent upon exposure to air. Hence, the X-ray measurements were performed at 180 K in a nitrogen stream (Table 1). The needle-like crystals of **1a** and **3b** were protected by covering them with Apiezon N (also used as a glue), while the crystal of **3a** was quickly mounted on a glass fiber using a silicone grease. Diffraction data were collected on an Enraf Nonius CAD 4 diffractometer for **3a** (Mo-Kα radiation) and on a KUMA kappa-axis four-circle diffractometer equipped with a CCD area detector (resolution 16.7 pixels mm^{-1}) for **1a** and **3b** using standard measuring procedures and software.‡ The structures were solved and refined with SHELXS86 (ref. 15) and SHELXL97 (ref. 16). A list of the relevant crystallographic parameters is given in Table 1. The common numbering scheme is shown in Fig. 2.

Discussion

Syntheses

The general protocol for synthesising lower-rim calix[4]arene derivatives is based on the alkylation of the phenolic groups with an appropriate alkylating agent.[3] This strategy was used to prepare phosphonate esters **1a**–**3a**, which were converted into the target phosphonic acids **1b**–**3b** (Fig. 3).

Compound **1a** was prepared by starting with the alkylation of *p*-*tert*-butylcalix[4]arene with CF_3SO_2–O–$CH_2P(O)(OCH_2CH_3)_2$. Our attempts to use less reactive alkylating agents did not afford the disubstituted product under the conditions employed. Compound **2a** was prepared using a different synthetical protocol. First, a bis(2-bromoethyl) intermediate was prepared using classical conditions for distal dialkylation of *p*-*tert*-butylcalix[4]arene in 64% yield and 90% purity (^{1}H NMR). Diethoxyphosphoryl groups were introduced in the next step by Arbuzov reaction. Our attempts to alkylate *p*-*tert*-butylcalix[4]arene with diethyl (2-bromoethyl)phosphonate in acetonitrile–K_2CO_3 failed and resulted in complete decomposition of the reagent and formation of

‡ CCDC reference numbers 179147–179149. See http://www.rsc.org/suppdata/p2/b1/b105489a/ for crystallographic files in .cif or other electronic format.

Table 1 Experimental data for the X-ray diffraction studies of compounds **1a**, **3a** and **3b**

	1a	**3a**	**3b**
Formula	$C_{54}H_{78}O_{10}P_2 \cdot CH_3OH \cdot 0.33H_2O$	$C_{58}H_{86}O_{10}P_2$	$C_{50}H_{70}O_{10}P_2 \cdot 2.5H_2O \cdot 4.5CH_3OH$
M	981.48	1005.21	1052.56
T/K	180(1)	180(1)	180(1)
Crystal dimensions/mm	0.05 × 0.1 × 0.4	0.3 × 0.4 × 0.4	0.05 × 0.05 × 0.55
Shape and colour	Pale yellow needle	Colorless, irregular	Colorless needle
Crystal system	Triclinic	Triclinic	Monoclinic
Space group	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no. 2)	$C2/c$ (no. 15)
A/Å	18.856(1)	11.994(2)	39.454(10)
B/Å	20.962(1)	12.123(2)	17.486(3)
C/Å	23.912(1)	21.235(5)	21.540(3)
α/°	71.093(4)	102.46(2)	90
β/°	75.343(4)	93.04(2)	123.03(2)
γ/°	88.723(4)	93.85(2)	90
U/Å^3	8632(1)	3001.0(6)	12459(4)
Z	2	2	8
d_c/g cm^{-3}	1.133	1.112	1.122
λ/Å	0.71069	0.71069	0.71069
μ/mm^{-1}	0.129	0.12	0.130
F(000)	3178	1088	4484
θ range of data collection/°	3.35–29.41	0.98–22.98	3.33–29.34
Index ranges	−24,25;−15,28;−31,31	−13,13;−13,13;0,23	−53,43;−23,22;−10,28
Number of reflections measured	75 773	8 325	34 044
R_σ	0.0730	0.0447	0.1177
Number of reflections observed [$I > 2\sigma(I)$]	19038	5692	6230
Number of independent reflections	40373	8323	14684
R_{int}	0.0333	—	0.0910
Data, restraints, parameters	40373/0/1873	8323/0/622	14684/0/727
Goodness-of-fit on F^2	1.270	1.565	1.070
Final R, R' [$I \geq 2\sigma(I)$][a,b]	0.1305; 0.3750	0.1241; 0.3681	0.1175; 0.3381
Shift (esd)	0.046 (0.836)	0.00 (0.00)	0.003 (0.035)
Largest difference peak and hole/e Å^3	1.002; −2.467	1.445; −0.611	0.774; −0.522

[a] $w = 1/[\sigma^2(F_o^2) + (A \times P)^2 + B \times P]$ where $P = (F_o^2 + 2F_c^2)/3$, $A = 0.2$; $B = 0.0$ in all of the structures (SHELXL97, ref. 17). [b] $R = gS|F_o - F_c|/\Sigma|F_c|$, $R' = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$ (SHELXL97, ref. 17).

diethyl vinylphosphonate. Compound **3a** was prepared by alkylation of *p-tert*-butylcalix[4]arene with diethyl (3-bromopropyl)phosphonate under mild conditions in refluxing acetonitrile. Ligands **1b**–**3b** were obtained in high yields by a general method using transesterification with trimethylsilyl bromide in acetonitrile and subsequent hydrolysis of the trimethylsilyl ester.

The identity and purity of ligands **1b**–**3b** were checked by NMR and organic analysis. The NMR spectra were in complete agreement with the structures given and did not indicate the presence of any impurities. The results of organic combustion analysis were less satisfactory (the found values for %C and %H were smaller than the calculated values). We were not able to obtain better analytical results despite extensive purification and drying of the analytical samples. We ascribe the deviations in analysis to problems with the combustion of the highly thermally stable phosphorylated calix[4]arenes. The structure of the ligands was further confirmed in the solid state by X-ray diffraction analysis (see below). According to the NMR spectra, compounds **1a**–**3a** and **1b**–**3b** exist exclusively in the cone conformation, without undergoing equilibration to other conformers.

Complexes of 1b–3b in solution

As models for the investigation of the complexing and extraction properties of ligands **1b**–**3b** we selected three lanthanides, namely La^{3+}, Eu^{3+} and Yb^{3+}. This group was extended to Th^{4+} for the extraction experiments. We chose the lanthanide cations given as they vary widely in their ionic radii and, thus, can be considered as representatives of the whole lanthanide series. This choice was also governed by the magnetic properties of Y^{3+}, Eu^{3+} and Yb^{3+} that are favourable for NMR investigations of the solution structures of their calixarene complexes. The La^{3+} cation is diamagnetic, while Eu^{3+} and Yb^{3+} are paramagnetic and are known for their ability to induce large NMR shifts.

We studied the types of complexes formed by ^{1}H and ^{31}P NMR in solutions containing **1b** and $La(NO_3)_3$. Throughout the NMR experiments $CDCl_3$–CD_3OD (8 : 2) was used as the solvent in which narrow linewidths could be obtained. We also performed ^{1}P NMR following titration of $La(NO_3)_3$ with **1b** using ratios φ = La : **1b** from 2 : 1 to 1 : 5.

These experiments revealed the formation of a new compound in solution for $\varphi \leq 1 : 2$, characterized by four lines of equal intensity in the ^{31}P NMR spectrum [the spectrum is given in the electronic supplementary information (ESI), Fig. S2]. When $\varphi < 1 : 2$, a signal was found at 15.21 ppm due to an excess of the free ligand **1b**. This complex undergoes slow exchange on the NMR timescale with the free ligand at 25 °C. The four line pattern can be explained by the formation of a kinetically stable complex with a metal to ligand ratio equal to two and four non-equivalent phosphonate groups. The signals observed at 3.5 and 4.9 ppm belong to the deprotonated phosphonate groups directly bonded to La^{3+}, while the signals at 10.4 and 13.3 ppm can be ascribed to the weakly interacting phosphonate groups. The ^{1}H NMR spectrum of a solution of 1 equiv. of $La(NO_3)_3$ and 2 equiv. of **1b** in the same solvent revealed that the characteristic AB pattern of the Ar-CH_2-Ar hydrogens remains intact after complex formation, providing evidence that **1b** retains the cone conformation in the complex.

The formation of a complex with a ratio Ln : **1b** = 1 : 2 was also demonstrated for Ln = Eu, using $Eu(NO_3)_3$ instead of $La(NO_3)_3$ in the same experiments. Four paramagnetically shifted lines of equal intensity were found in the ^{31}P NMR spectrum. Two of these lines, with chemical shifts of −92 and −140 ppm, belong to the coordinated phosphonate group. The high paramagnetic shift is caused by the close proximity of the ^{31}P nuclei to the lanthanide centre. The remaining phosphonate groups, with signals at −8 and −24 ppm, are more distant from

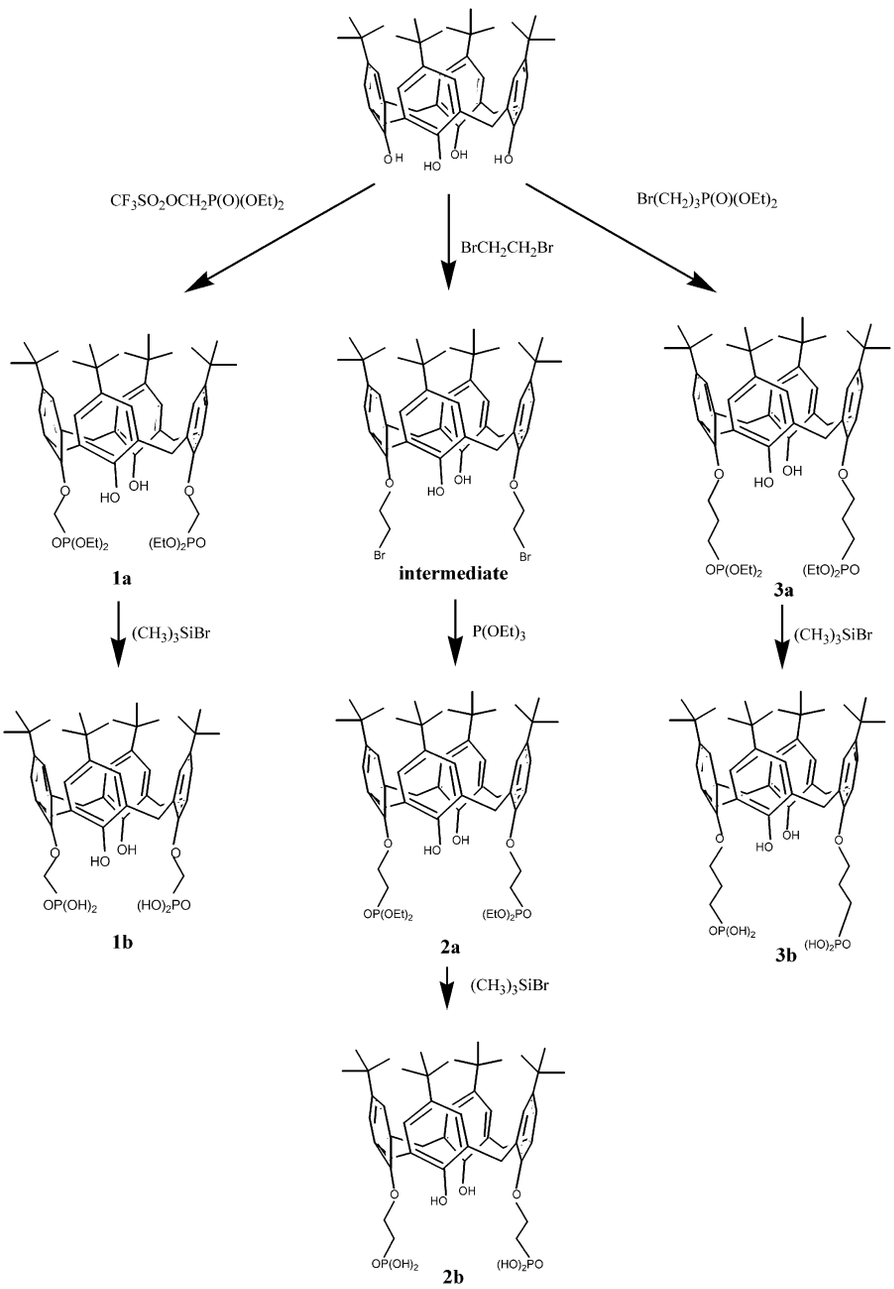

Fig. 3 Scheme of the synthesis of compounds **1b**–**3b**.

the Ln centre. On the basis of the above-mentioned experiments it is not possible to exclude the presence of coordinated nitrate group(s) in the complex that occurs in solution.

Extraction experiments

Extraction experiments were designed to compare the results obtained for **1b**–**3b** with the data published in the literature and to investigate the potential industrial applicability of the ligands studied (low concentration of Ln, cheap organic solvent, highly acidic nitrate solutions).[17] The activity of all three ligands in the extraction of lanthanides and Th^{4+} from 1 M nitric acid solution with their chloroform solutions (c_L = 1×10^{-3}) is illustrated in Fig. 4, with the measured data collected in Table S1 (ESI).

The extraction efficiencies (%E) of **1b**–**3b** under these conditions are comparable with those of the ligands based on calixarene–CMPO[4] and are far better than that of CMPO itself.[4] The most efficient extractant for all of the lanthanides and even Th^{4+} is **1b**; **2b** and **3b** are remarkably less efficient. Their extraction efficiencies decrease with increasing length of the spacer between the calixarene lower rim and the phosphonic group. This may be caused either by the increasing acidity of the phosphonic groups in this direction, and consequently, the

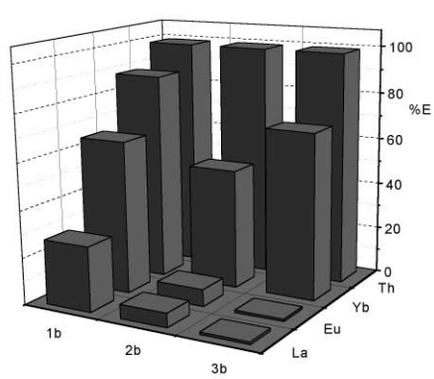

Fig. 4 Extraction efficiencies E for the extraction of Th^{4+} and selected Ln^{3+} ions with ligands **1b**–**3b**. Aqueous phase: $c_M = 1 \times 10^{-4}$ M in 1 M HNO_3, organic phase: $c_L = 1 \times 10^{-3}$ M in chloroform. E = $([M]_{organic\ phase}/[M]_{total})100\%$.

higher negative charge (assuming that the primary interaction of the metal ion with the ligand is of electrostatic origin) or, more probably, by the spatial proximity of the lower-rim oxygen donor atoms of the $–PO_3^{2-}$ and Ar–*O*–CH_2– groups in the **1b** molecule.

The proximity of two negatively charged, strongly electron-donating PO_3^{2-} and four phenolic oxygen groups at the lower rim of ligand **1b** can lead to stronger interaction with the metal cation owing to the formation of a cavity that is spatially defined by the phenolic oxygen atoms and the oxygen atoms of the pendant arm phosphonate groups. This cavity, which is already present in free ligand **1b**, appears to be advantageous for Ln complexation. Thus, ligand **1b** can satisfy the requirements of high coordination numbers. This explanation is supported by an NMR study of La and Eu complexes in $CDCl_3$–MeOH solution. Moreover, the preorganisation of the donor site can even be demonstrated in the solid state X-ray structures (see below).

The dependence of the extraction efficiency E on the chain length in ligands **1b**–**3b** was monotonic for La and Eu, but not for Yb. The extraction efficiency of **3b** is higher than that of **2b** for Yb^{3+}, which makes ligand **3b** the most selective of all the three tested under these conditions. Compound **3b** exhibits surprising selectivity in the extraction of Yb^{3+} in comparison with the lighter lanthanides, the difference in E being about an order of magnitude higher relative to La^{3+}. This behaviour, which we are not able to explain theoretically, could be interesting for the separation of heavy and light lanthanides by extraction methods.

The extraction efficiency of Ln^{3+} for all of the ligands studied depends on the ionic radii of the lanthanide cations. The value of E (Fig. 4) and the distribution coefficients D [Table S1, ESI, $D = E/(100 - E)$] increase significantly with decreasing ionic radius. This is a unique feature of ligands **1b**–**3b** that stands in contrast to the other known selective lanthanide extractants that are based on calixarenes.[4] In a competitive experiment [0.1 M HNO_3, $c_{\text{ligand 3b}} = 4 \times 10^{-4}$ M, $c(La^{3+}) = c(Eu^{3+}) = c(Yb^{3+}) = 1 \times 10^{-4}$ M in the aqueous phase, ligand **3b** in chloroform], the separation factor (ratio of distribution coefficients) was $D_{Yb}/D_{La} = 690$ and $D_{Yb}/D_{Eu} = 410$, which demonstrates the extraordinary selectivity of extractant **3b** for the heavier lanthanides.

In agreement with the presence of phosphonic acid groups as binding sites, the extraction efficiency is strongly dependent on the concentration of nitric acid in solution (Fig. 5).

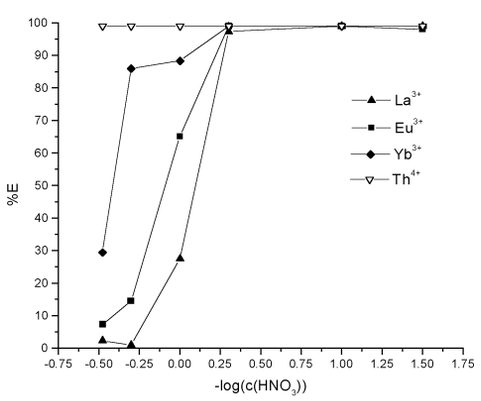

Fig. 5 Dependence of %E on $c(HNO_3)$ for ligand **1b** in the Th^{4+} and Ln^{3+} systems. Aqueous phase: $c_M = 1 \times 10^{-4}$ M, HNO_3. Organic phase: $c_L = 1 \times 10^{-3}$ M in chloroform.

In contrast to most CMPO-based calixarenes,[4,5,9,18] the extraction efficiency of ligands **1b**–**3b** is highest at low concentrations of HNO_3 [formation of extraordinarily stable emulsions (several days) precluded studies below pH 1.5] and strongly decreases as the acidity rises. This trend is close to the behaviour of CMPO[4] itself. Nevertheless, the lower acidity constants of alkylphosphonic acids[19] indicate that the decrease is not as rapid as in the case of carboxylates[7] or hydroxamates.[10] A comparison of the extraction efficiencies of ligands **1b**–**3b** with those of selected extractants from the literature is given in Table S3 of the ESI.

The ability to selectively separate lanthanide and actinide ions is an important requirement for extraction agents in waste reprocessing. We focused on Th^{4+}, which is known to be a good model of Pu^{4+} (ref. 17). The ligands studied, **1b**–**3b**, are efficient extractants for Th^{4+} under the experimental conditions described, particularly **1b**. The distribution coefficients are higher by more than two orders of magnitude for Th^{4+} than for the lanthanides. In all cases the Th ions were extracted much more efficiently than the lanthanides. This behaviour could be explained by possible formation of stable electroneutral complexes between Th^{4+} and the potentially four based ligands **1b**–**3b**. A similar difference in the stability of Th and Ln complexes has been observed by potentiometric studies of carboxylate complexes. On the basis of the data given, the extractants **1b**–**3b** could be useful for the selective separation of Th^{4+} from Ln^{3+}–Th^{4+} mixtures.

We have studied the performance of compound **1a** in an extraction experiment to compare the extraction efficiencies of **1a** and **1b**. Compound **1a** was expected to be more lipophilic than **1a** owing to the non-ionic form of **1a** and its greater similarity to CMPO than **1b**. On the other hand, the interaction of **1a** with Ln ions is expected to be weaker than that of **1b**. In the case of **1a**, an extraction efficiency of $E = 42$ was found for the extraction of Eu^{3+} ions from the aqueous phase to chloroform ($c_{\text{ligand 1a}} = c_{Eu(NO_3)_3} = 1 \times 10^{-3}$ M, pH of aqueous phase = 5.8). Comparison of this result with those shown in Fig. 4 (extraction from 1 M nitric acid) leads to the conclusion that **1a** is a worse extractant of Eu than **1b**, even at such low pH. This is in accordance with the proposed model in which the electrostatic interaction between the extractant molecule **1b** and Ln ion leads to stable complexes. Nevertheless, the extraction performance of **1a** is comparable with that of phosphine oxide derivatives of the CMPO-type based on calix[4]arenes. This corresponds with the known dependence on pH of the stability of lanthanide complexes of calixarene derivatives, bearing carboxylatomethyl groups at the lower rim, in methanol.

In order to get insight into the composition of the lanthanide complexes extracted from aqueous solutions of $Ln(NO_3)_3$, acidified by HNO_3, into the organic phase, we studied the extraction of the lanthanides (expressed as log D) with ligands **1b**–**3b** as a function of the logarithm of the free ligand concentration in the organic phase (Fig. 6).

The slopes of the linear dependences were measured in 1 M HNO_3 for Yb^{3+} and in 0.1 M HNO_3 for Eu^{3+} and La^{3+}; only Eu^{3+} was studied at both concentrations of nitric acid. The values of the slopes, n, range from 1.6 to 3, which indicates that the extracted species differ in their metal : ligand ratio, depending on the concentration of nitric acid employed (Eu^{3+}: ligand **1b**) and ligand (Eu^{3+}, La^{3+}: ligands **1b**, **2b**). In some cases an equilibrium probably exists between the different species under the conditions given (Yb^{3+}: **1b**, **2b**, **3b**; Eu^{3+}, La^{3+}: **1b**). Lower metal : ligand ratios at higher nitric acid concentrations might lead to more successful competition of the NO_3^- anion with, under these conditions, the more protonated (and, consequently, less charged) phosphonic groups of ligand. A higher concentration of the ligand, as well as a lower acidity of the aqueous phase leads to the formation of complexes with a Ln : ligand ratio equal to two, similar to those studied in the NMR titrations.

Solid state study

Several unsuccessful attempts were made to isolate a complex of La^{3+} and **1b**–**3b** from methanolic solutions containing $La(NO_3)_3$ and the ligand neutralized by LiOH, NaOH or KOH.

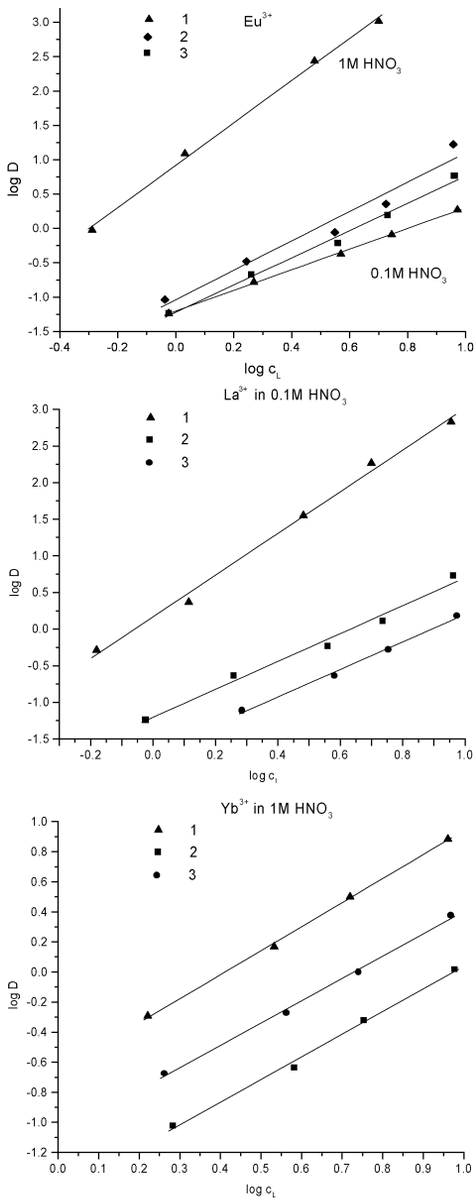

Fig. 6 log D as a function of c_L for the extraction of the nitrates of La^{3+}, Eu^{3+}, Yb^{3+} ($c_M = 1 \times 10^{-4}$, 1 or 0.1 M HNO_3) into chloroform. $D = E/(100 - E)$.

In contrast, in the acidic region, by using HNO_3 for pH adjustment and varying the Ln : ligand **1b** ratio, two types of complexes were isolated, $H_2Ln(C_{46}H_{58}O_{10}P_2)(NO_3)\cdot xH_2O$ and $H_5Ln(C_{46}H_{58}O_{10}P_2)_2\cdot xH_2O$. The complexes of the first type separated in the form of microcrystals from solutions with an excess of Ln, while the complexes of the second type were obtained from solutions containing an excess of ligand. The types of complexes isolated in the solid state correspond to the types of complexes proposed in the extraction experiments, despite the known differences between the solid and solution state. In the solid state the complexes were obtained only in microcrystalline form, thus precluding any X-ray studies.

We performed X-ray diffraction experiments on single crystals of extractants **1a**, **3a** and **3b** to gain more information about their conformation and shape and the steric requirements of the title compounds. The solid state structures of **1a**, **3a**, and **3b** consist of discrete calix[4]arene molecules in the cone conformation (Fig. 7). There was one crystallographically independent molecule in the cell of **3a**, two in the cell of **3b** and three in the cell of **1a**. In the cases of **3b** and **1a**, the independent molecules differ only slightly in their geometrical parameters. The molecules of all three compounds have preorganised

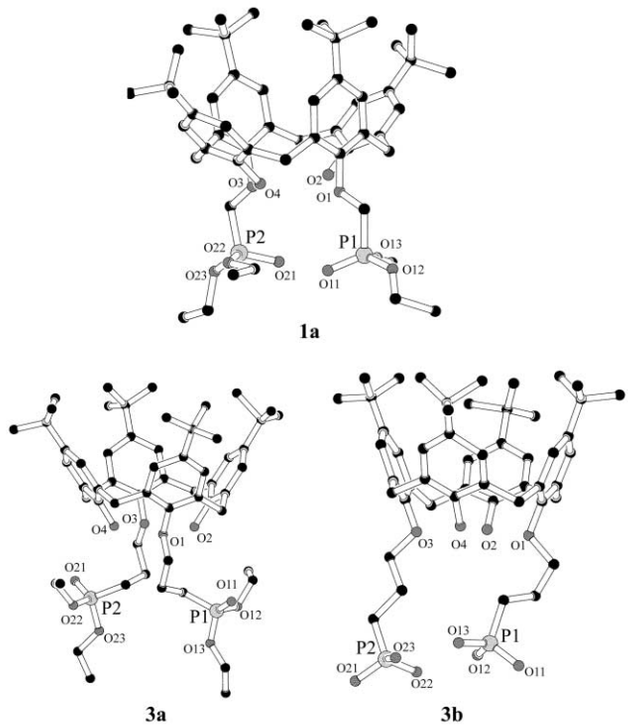

Fig. 7 X-Ray structures of compounds **1a**, **3a** and **3b**. Black circles denote carbon atoms, hydrogen atoms are omitted for clarity.

donor sites Ar–*O*–CH_2 and PO_3 advantageous for coordination of ions with high coordination numbers. The aliphatic 4-*tert*-butyl groups in **1a** and **3b** and the ethyl chains in **1a** are remarkably disordered and the cone conformations of the calix[4]arene rings are distorted: the benzene rings I/III and II/IV (for numbering scheme see Fig. 2) are tilted with the average angles being 7.2 and 83.4° (**1a**), 53.4 and 65.7° (**3a**) and 43.9 and 68.3° (**3b**). Some of the unusual bonding lengths calculated for the structure of **1a** are caused by difficulties in obtaining an appropriate description of the disorder in this structure.

The X-ray investigation of **1a**, **3a** and **3b** points to a contribution of the hydrogen bonding system between the substituted and unsubstituted phenolic oxygen atoms at the lower rims to the stabilization of the cone conformation of the calix[4]arene moiety. The hydrogen bonding system causes a small distortion of the cavity from C_{2v} symmetry: in the case of **3a** the appropriate hydrogens H2*x* and H4*x* were localized [*d*(O3–O4) = 2.69, *d*(O1–O2) = 2.70 Å)], but in the case of **1a**, the presence of these bonds was deduced from the interatomic distances. The distances between the lower-rim oxygen atoms of **1a** range from 2.86 to 3.37 Å, differing in each independent molecule and showing no trends. Although the hydrogens between the oxygen atoms of the phenolic groups in **3b** were not unequivocally localized, the interatomic distances of 2.72 and 2.77 Å agree with the presence of hydrogen bonds O1–O2 and O3–O4. Values for selected angles and lengths are summarized in Table S2 (ESI).

Conclusion

Three new calixarene extractants for lanthanides and actinides were prepared by alkylation of *p-tert*-butylcalix[4]arene. Extraction studies showed the ligands to be efficient extractants for thorium over lanthanides, and much more efficient than CMPO. The most efficient extractant is **1b** owing to an appropriate pendant arm length and the location of donor groups in the molecule. An unexpected selectivity in the extractions of heavy lanthanides was found for **3b**. The separation factor for Yb^{3+} over La^{3+} differs by nearly three orders of magnitude. Owing to the presence of groups that can be

deprotonated, the extraction power of all the ligands decreases as the acidity rises, but no as fast as in the case of carboxylates,[19] which allows the efficient extraction of lanthanide and thorium from 1 M nitric acid by compounds **1b**–**3b**. Ethyl ester **1a** was found to be comparable with CMPO with respect to extraction behaviour, but less efficient than compound **1b**.

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