Lanthanide Ions as Calcium Substitutes: A Structural Comparison of Europium and Calcium Complexes of a Ditopic Calixarene *

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Reaction of *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, H_8L) under carefully controlled conditions in dimethylformamide (dmf) solvent enables the isolation of 1:1 complexes with both europium(III) and calcium(II) ions. Crystal structure determinations have been performed at ≈295 K on $[Ca(H_6L)(dmf)_4]\cdot 3dmf$ [monoclinic, space group $P2_1/c$ (C_{2h}^5, no. 14), a = 22.24(2), b = 25.57(2), c = 22.07(2) Å, β = 115.91(5)°, Z = 4, R = 0.13 for 4915 'observed' reflections] and $[Eu(H_6L)(NO_3)(dmf)_4]\cdot 3dmf$ [monoclinic, space group $C2/c$ (C_{2h}^6, no. 15), a = 42.35(2), b = 18.48(2), c = 35.03(1) Å, β = 109.26(3)°, Z = 8, R = 0.086 for 7950 'observed' reflections]. Both complexes involve the calixarene in a hitherto unobserved bidentate co-ordination mode, with the metal-ion co-ordination spheres being filled by attachment of *O*-bound dmf molecules and (in the case of europium) one bidentate nitrate ion, the calcium thereby being six- and the europium eight-co-ordinate. The doubly deprotonated *p-tert*-butylcalix[8]arene ligand adopts a near-planar conformation which, in the case of the calcium complex, is very similar to the 'pleated loop' form known for the free calixarene. Proton NMR spectroscopy suggests that in solution the europium complex is both less flexible and more stable than the calcium species.

Luminescent rare-earth (lanthanide) metal ions have found useful applications as spectroscopically active substitutes for Ca^{2+} in many metalloproteins.[1] Such substitution is based upon the similar ionic radii of the ions and the close general similarities in chemical properties of the rare- and alkaline-earth metals. Nonetheless, the mere fact that the metal ions are different engenders some uncertainty in the detailed interpretation of any results,[1] especially since proteins may be regarded as polytopic metal-ion receptors with many different possible modes of metal-ion binding.[2] The large calixarene[3] *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) is a ligand which can act as a ditopic receptor for the lanthanide[4] and other[5,6] ions and hence in principle may bind in various ways to a single metal ion. There is some parallel, therefore, between the substitution of europium for calcium in a complex of this ligand and the same substitution in a metalloprotein system. We report herein the crystal structures of the monometallic europium(III) and calcium(II) derivatives of *p-tert*-butylcalix[8]arene, both to characterise further the co-ordination chemistry of this ligand and to refine our understanding of the consequences of such substitution.

Experimental

Syntheses.—*p-tert*-Butylcalix[8]arene (H_8L)[7] and $[Eu(NO_3)_3(dmso)_4]$[8],† (dmso = dimethyl sulphoxide) were prepared by literature methods.

$Ca(ClO_4)_2\cdot 6dmso$. An aqueous solution of $Ca(ClO_4)_2$ was prepared by adding $HClO_4$ (70%, 5.0 cm^3) to a slurry of $CaCO_3$ (3.0 g) in a little water (≈3 cm^3). Dimethyl sulphoxide (20 cm^3), ethanol (25 cm^3) and diethyl ether (25 cm^3) were added and the solution cooled to 0 °C for 2 h to give a white precipitate, which was recrystallised twice from dmso–ethanol–ether and dried by vacuum desiccation over silica gel. Yield: 9.7 g (46%) (Found: C, 20.1; H, 4.95; Cl, 10.2; S, 27.0. Calc. for $C_{12}H_{36}CaCl_2O_{14}S_6$: C, 20.4; H, 5.15; Cl, 10.0; S, 27.2%).

$[Ca(H_6L)(dmf)_4]\cdot 4dmf$ (dmf = *dimethylformamide*). Under a dry argon atmosphere, triethylamine (0.5 cm^3) was added to a warm (60 °C) slurry of *p-tert*-butylcalix[8]arene (0.5 g) in dimethylformamide (5 cm^3), to form a clear solution. The salt $Ca(ClO_4)_2\cdot 6dmso$ (0.5 g) was added and quickly dissolved, the solution becoming pale red. Cooling at 0 °C for 24 h produced a colourless precipitate, which was recrystallised from hot dmf to provide crystals suitable for X-ray structure determination. Yield: 0.22 g (30%) (Found: C, 70.0; H, 8.7; Ca, 1.9; N, 5.7. Calc. for $C_{112}H_{166}CaN_8O_{16}$: C, 70.0; H, 8.70; Ca, 2.10; N, 5.85%). ^{1}H NMR [$(CD_3)_2CO$]: δ 7.95 (s, 8, NCHO), 7.15 (s, 16, aryl H), 3.91 (s, 16, aryl–CH_2–aryl), 2.92 [s, 24, $N(CH_3)_2$], 2.77 [s, 24, $N(CH_3)_2$] and 1.22 [s, 72, $C(CH_3)_3$].

$[K_2(H_6L)]\cdot 3CH_3CN\cdot H_2O$. Under a dry argon atmosphere, K_2CO_3 (0.25 g) was added to a slurry of *p-tert*-butylcalix[8]arene (0.5 g) in acetonitrile (10 cm^3) and the ligand dissolved by warming to 60 °C. The hot solution was filtered, then cooled at 0 °C overnight to give a white powder which was collected by filtration, washed twice with acetonitrile and dried *in vacuo*. Yield: 0.28 g (48%) (Found: C, 74.8; H, 7.9; K, 4.7; N, 2.7. Calc. for $C_{94}H_{121}K_2N_3O_9$: C, 74.5; H, 8.05; K, 5.15; N, 2.75%). ^{1}H NMR [$(CD_3)_2CO$]: δ 7.06 (s, 16, aryl H), 3.84 (br s, 16, aryl–CH_2–aryl), 2.91 (br s, 2, H_2O), 2.02 (s, 9, CH_3CN) and 1.21 (s, 72, $C(CH_3)_3$].

$[Eu(H_6L)(NO_3)(dmf)_4]\cdot 3dmf$. In the normal laboratory atmosphere, a mixture of *p-tert*-butylcalix[8]arene (0.5 g) and K_2CO_3 (0.2 g) was heated (60 °C) and stirred until the

* *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii–xxii.

† Note that the general method given for the preparation of the dmso adducts of rare-earth-metal nitrates is not, in this paper, applied to europium in particular but it is, in fact, as satisfactory for Eu as for Sm and Gd, for example.

calixarene dissolved. The excess of K_2CO_3 was removed by filtration, giving a clear solution to which was added $[Eu(NO_3)_3(dmso)_4]$ (0.26 g), which dissolved to give a clear yellow solution. Large yellow crystals deposited on standing for 72 h. Yield: 0.30 g (39%) (Found: C, 65.0; H, 8.2; N, 5.5. Calc. for $C_{109}H_{159}EuN_8O_{18}$: C, 64.8; H, 7.95; N, 5.55%).

$[NH(C_2H_5)_3]_3[H_5L]\cdot CH_3CN\cdot 2H_2O$. Under a dry argon atmosphere, triethylamine (2 cm^3) was added to a slurry of *p-tert*-butylcalix[8]arene (1.0 g) in acetonitrile (15 cm^3) and the ligand dissolved by warming to 60 °C. The solution was filtered and a white precipitate deposited rapidly on cooling to room temperature. The product was collected by filtration, washed twice with acetonitrile and dried *in vacuo*. Yield: 0.96 g (71%) (Found: C, 77.1; H, 9.0; N, 2.8. Calc. for $C_{108}H_{164}N_4O_{10}$: C, 77.3; H, 9.85; N, 3.35%). ^1H NMR $[(CD_3)_2CO]$: δ 7.16 (s, 16, aryl H), 4.6–4.4 (br s, 4, H_2O), 3.92 (s, 16, aryl–CH_2–aryl), 2.75 [q, 18, $N(CH_2CH_3)_3$], 2.03 (s, 3, CH_3CN), 1.22 [s, 72, $C(CH_3)_3$] and 1.09 [t, 27, $N(CH_2CH_3)_3$].

Structure Determinations.—Unique data sets were measured at 295 K within the limit $2\theta_{max} = 45°$ on specimens mounted in capillaries, using diffractometers in 2θ–θ scan mode and fitted with monochromatic Mo-Kα radiation sources ($\lambda = 0.7106_9$ Å). N Independent reflections were obtained, N_o with $I > n\sigma(I)$ being considered 'observed' and used in the large-block least-squares refinements. Hydrogen atoms were included at estimated (x, y, z, U_{iso}); anisotropic thermal parameter refinement was as specified. As usual with complexes of this type, the available data were limited in extent and intensity in consequence of excessive thermal/disorder effects, and residuals, conventional R,R' on $|F|$, are high. Statistical weights, derivative of $\sigma^2(I) = \sigma^2(I_{diff}) + 0.0004\sigma^4(I_{diff})$, were used. Neutral-atom complex scattering factors were employed;[9] computation using the XTAL 3.0 program system.[10] Pertinent results are given in Figures 1 and 2, and Tables 1–3.

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

Crystal/refinement data. $[Ca(H_6L)(dmf)_4]\cdot 3dmf$, $C_{100}H_{138}CaN_4O_{12}\cdot 3C_3H_7NO$, $M = 1847.6$, monoclinic, space group $P2_1/c$ (C_{2h}^5, no. 14), $a = 22.24(2)$, $b = 25.57(2)$, $c = 22.07(2)$ Å, $\beta = 115.91(5)°$, $U = 11\,291$ Å^3, $D_c(Z = 4) = 1.09$ g cm^{-3}, $F(000) = 4008$, $\mu_{Mo} = 0.83$ cm^{-1}, specimen 0.5 × 0.4 × 0.4 mm (no absorption correction), $N = 13\,329$, N_o ($n = 2$) = 4915, $R = 0.13$, $R' = 0.11$, $n_v = 639$. Syntex $P2_1$ diffractometer.

Abnormal features/variations in procedure. Anisotropic thermal parameters were refined for Ca, O(1)–O(7) and the peripheral carbon atoms for Bu^t groups 1–5 only. *tert*-Butyl groups 6–8 are disordered and were refined in terms of two components, the major ones only being shown in the figures. Solvent dmf molecules (e–g) were refined as rigid groups, disorder about N in groups f and g being modelled in terms of two equally populated fragments.

$[Eu(H_6L)(NO_3)(dmf)_4]\cdot 3dmf$, $C_{100}H_{138}EuN_5O_{15}\cdot 3C_3H_7NO$, $M = 2021.5$, monoclinic, space group $C2/c$ (C_{2h}^6, no. 15), $a = 42.35(2)$, $b = 18.48(2)$, $c = 35.03(1)$ Å, $\beta = 109.26(3)°$, $U = 25\,885$ Å^3, $D_c(Z = 8) = 1.04$ g cm^{-3}, $F(000) = 8608$, $\mu_{Mo} = 4.9$ cm^{-1}, specimen 0.65 × 0.60 × 0.40 mm, $A^*_{min,max}$ (Gaussian correction) = 1.24, 1.36, $N = 16\,854$, N_o ($n = 3$) = 7950, $R = 0.086$, $R' = 0.11$, $n_v = 1092$. Enraf-Nonius CAD-4 diffractometer.

Abnormal features/variations in procedure. Anisotropic thermal parameters were refined throughout except for dmf molecules d–g. Solvent dmf molecules e–g were refined as rigid groups. The oxygen of dmf g (for which thermal motion was very high) was not located and hydrogen atoms were not assigned. Thermal motion was very high on the Bu^t groups, which could, nevertheless, be modelled without disorder.

Results and Discussion

Bimetallic complexes of *p-tert*-butylcalix[8]arene with the rare earths (including yttrium) as well as titanium(IV), zirconium(IV), tin(IV) and vanadium(V) all appear to contain the ligand in a chiral, 'propeller-like' conformation.[4–11] This is not the conformation found for the free ligand,[12] and hence it may be determined by the particular bound metals and mode of binding, though it might also be characteristic of the manifold-deprotonated calixarene. However, although the form seen for the seven-fold-deprotonated ligand in its titanium(IV) complex[5,6] is very similar to, if somewhat less twisted than, that of the six-fold-deprotonated ligand in bimetallic rare-earth-metal complexes, both are unlike the 'cone' form of the six-fold-deprotonated ligand found in its thorium(IV) complex.[11] Hence it is obvious that the conformational preferences of the ligand may be in delicate balance with the influence of specific bonding interactions with the metal. It is well known that the higher charge of the lanthanide ions can result in their ineffectual substitution for calcium,[1] and thus the present structures of monometallic derivatives of *p-tert*-butylcalix[8]arene require comparison not only with respect to stoichiometry but also with respect to the details of differences in ligand conformation. Although the co-ordination of a nitrate ligand to europium(III) formally creates a moiety of the same charge as that of Ca^{2+}, the electric fields of each may still differ significantly, of course.

In gross aspect, the structures of the mono-calcium and -europium derivatives of *p-tert*-butylcalix[8]arene (Fig. 1) are strikingly similar, the only obvious differences being the co-ordination numbers of the metal ions, six for the Ca^{2+} and eight for the Eu^{3+}. As is usual in room-temperature structure determinations of calixarenes and their complexes, the precision of either study is not high, chiefly in respect of the consequences of limited data resulting from high thermal motion, the presence of Bu^t substituents, and disorder of the latter and solvent molecules. Nevertheless, the features of interest to be expected in species such as the present, as in proteins, are principally in respect of the metal atom environments and the gross stereochemistry and conformation of the complexes, and we address these in our considerations of the structures.

Both structures have certain features in common. Unlike our previous reports of structure determinations of metal [europium(III)] complexes with *p-tert*-butylcalix[8]arene,[4] the present derivatives of both calcium(II) and europium(III) have 1:1 rather than 1:2 ligand:metal stoichiometry. The 1:2 europium complex has been structurally characterised as a dimethylformamide (dmf) solvate in two independent polymorphs, and the three independent complex molecules so defined all contain arrays with quasi-*2* symmetry and with *all* calixarene oxygen atoms, protonated or not, interacting with the pair of eight-co-ordinate europium atoms. About each europium atom, there are three 'unidentate' phenoxide donors and two bridging, with the remainder of the co-ordination sphere being made up by a pair of unidentate and one bridging dimethylformamide solvent species. In both of the present 1:1 complexes, the doubly deprotonated ligand is only bidentate, by way of a pair of adjacent phenoxide groups, with the remainder of the metal-ion co-ordination sphere being made up of solvent (and anion, in the case of europium) groups. The 'bidentate' O···O distances in the calcium and europium species are 3.39(1) and 3.27(1) Å, respectively, which represent a somewhat greater splaying than for many other adjacent O···O contacts. The latter may be shortened in some cases as a result of bonding through unresolved ligand hydrogen atoms which, presumably, are associated with the six non-co-ordinating phenoxide oxygen atoms. In the calcium complex, the eight distances O(1)···O(2), O(2)···O(3),···O(7)···O(8) and O(8)···O(1), respectively, are 2.42(1), 2.52(1), 2.73(2), 3.46(2), 2.72(1), 2.58(1), 2.43(1) and 3.39(1) Å, while in the europium complex, their counterparts are 2.46(2), 2.61(2), 2.85(1), 4.66(2), 2.70(2), 4.37(2), 2.67(1) and 3.27(1) Å.

The calcium atom is six-co-ordinate, the other four co-ordination sites being occupied by four dimethylformamide solvent molecules. The mean Ca–O(calix) distance is 2.29 Å,

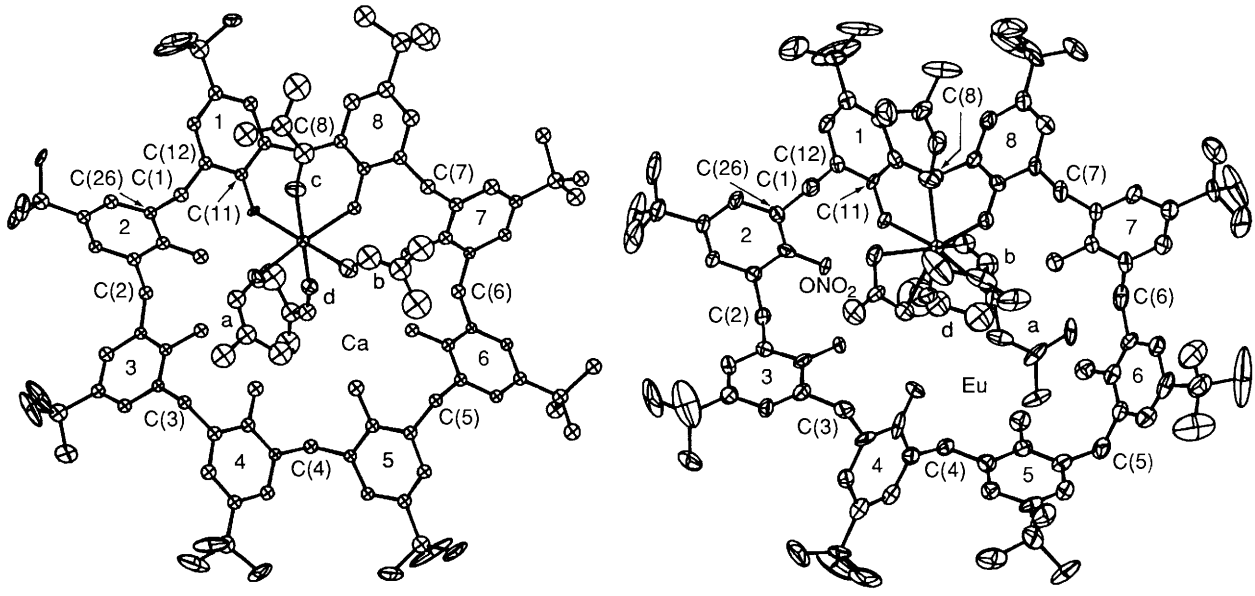

Fig. 1 Projections of the calcium and europium complexes normal to their planes; 20% thermal envelopes are shown for the non-hydrogen atoms

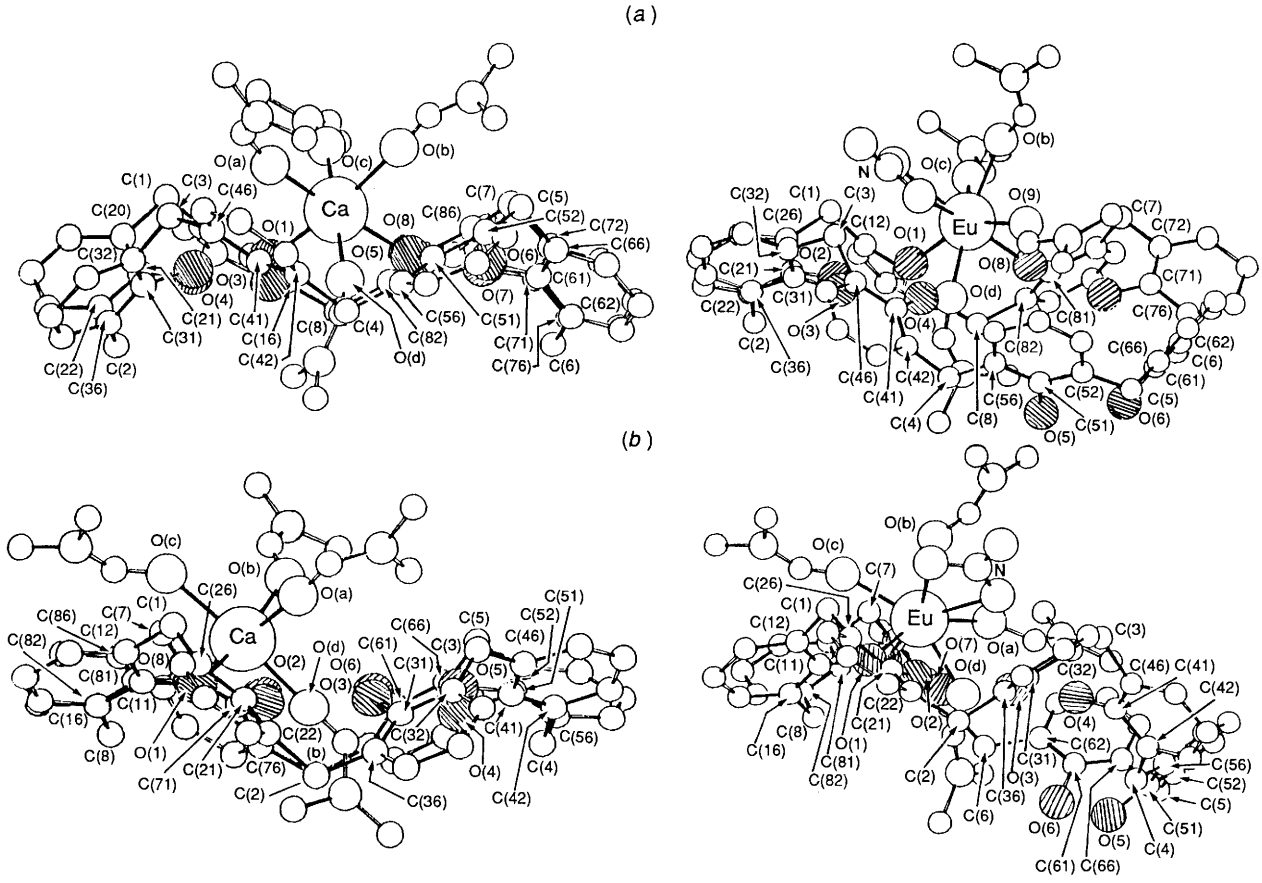

Fig. 2 (*a*) Views of the two complex species (approximately) down the line through C(4)–C(8). For clarity Bu^t groups have been omitted and atom types represented by envelopes of uniform size. The bonds of the continuous macrocycle component of the skeleton, together with the metal co-ordination, are shown as solid, with the relevant carbon atoms labelled. (*b*) As in (*a*) but down C(2)–C(6). Note, in both complexes, the approach of one of the dmf molecules through the macrocycle

while the mean Ca–O(dmf) distance is 2.31 Å, but in both cases the spread is large and the significance of the difference minimal. The O–Ca–O angles (*cis*) range between 83.6(4) and 95.5(3)°, while the *trans* angles are 170.9(4)–175.1(4)°. By comparison, Ca–O(H_2) in, for example, *trans*-[$CaCl_2(OH_2)_4$] are 2.334(3) and 2.325(2) Å.[13] The europium atom, by contrast, is eight-co-ordinate, with four of the remaining co-ordination sites occupied by dmf oxygen atoms and two by the more distant approach of oxygen atoms of a bidentate nitrate anion. Here there is a clear hierarchy of bonding strengths, with bonds to calixarene oxygen atoms being shortest and to those of the nitrate longest. The large and small 'bites' of these two bidentate ligands may well influence other associated bonding distances.

The conformations of the calixarene ligands themselves are of interest. As noted above, in the 1:2 ligand:Eu complexes they

Table 1 Non-hydrogen atom coordinates

	Calcium compound			Europium compound		
Atom	*x*	*y*	*z*	*x*	*y*	*z*
(*a*) Metal and calixarene						
M	0.259 2(2)	0.176 6(1)	0.247 3(2)	0.285 87(2)	0.259 95(5)	0.288 77(3)
O(1)	0.326 0(4)	0.126 9(3)	0.216 8(4)	0.267 6(3)	0.183 2(6)	0.233 4(3)
C(11)	0.392 0(6)	0.128 0(5)	0.239 2(6)	0.272 2(4)	0.180(1)	0.196 3(4)
C(12)	0.422 6(6)	0.152 1(5)	0.200 0(6)	0.245 7(4)	0.197(1)	0.161 9(5)
C(13)	0.490 9(7)	0.149 2(5)	0.224 3(6)	0.251 3(5)	0.191(1)	0.124 3(5)
C(14)	0.533 5(7)	0.127 9(6)	0.285 9(7)	0.280 2(5)	0.166(1)	0.118 1(6)
C(141)	0.610 5(8)	0.125 4(6)	0.308 8(8)	0.285 0(6)	0.163(2)	0.078 6(6)
C(142)	0.646 8(9)	0.127(2)	0.382 4(9)	0.304(1)	0.218(2)	0.073(1)
C(143)	0.633 9(8)	0.170 7(9)	0.282(1)	0.300(1)	0.097(2)	0.073 0(9)
C(144)	0.625(1)	0.074 7(9)	0.286(2)	0.256 0(9)	0.155(3)	0.046 0(9)
C(15)	0.504 5(7)	0.108 3(6)	0.324 5(7)	0.304 5(5)	0.151(1)	0.153 3(5)
C(16)	0.434 7(6)	0.105 9(5)	0.304 0(6)	0.302 1(4)	0.154(1)	0.191 9(5)
C(1)	0.378 5(7)	0.174 7(6)	0.131 9(7)	0.211 8(5)	0.222(1)	0.164 4(5)
O(2)	0.265 8(4)	0.105 0(3)	0.098 4(4)	0.216 0(3)	0.120 1(6)	0.231 2(3)
C(21)	0.301 4(6)	0.103 6(5)	0.062 0(6)	0.191 0(4)	0.113 1(9)	0.195 7(5)
C(22)	0.282 5(6)	0.067 5(5)	0.008 8(6)	0.166 4(4)	0.060 3(9)	0.191 7(5)
C(23)	0.316 8(6)	0.063 2(5)	−0.028 9(6)	0.139 5(4)	0.053(1)	0.155 2(5)
C(24)	0.371 9(6)	0.095 8(5)	−0.015 7(6)	0.136 1(4)	0.095(1)	0.123 0(5)
C(241)	0.412 8(8)	0.090 5(6)	−0.056 5(7)	0.105 6(5)	0.087(1)	0.085 0(6)
C(242)	0.485 4(8)	0.083(1)	−0.009 1(9)	0.101 9(8)	0.010(2)	0.071 4(9)
C(243)	0.391 4(9)	0.047 1(8)	−0.106 3(9)	0.108 0(7)	0.132(2)	0.051 3(8)
C(244)	0.409(1)	0.141 2(8)	−0.093 3(9)	0.074 4(5)	0.101(3)	0.090 8(8)
C(25)	0.389 5(7)	0.131 0(5)	0.034 0(7)	0.160 2(4)	0.150(1)	0.126 5(5)
C(26)	0.357 6(6)	0.136 2(5)	0.074 6(6)	0.186 9(4)	0.160 9(9)	0.162 7(5)
C(2)	0.221 9(7)	0.031 7(5)	−0.007 1(7)	0.168 9(4)	0.013 6(9)	0.228 3(5)
O(3)	0.142 7(4)	0.110 9(3)	0.021 9(4)	0.206 8(2)	0.091 8(6)	0.299 7(3)
C(31)	0.121 7(6)	0.092 4(5)	−0.044 5(6)	0.172 7(4)	0.087(1)	0.289 4(5)
C(32)	0.064 5(6)	0.115 1(5)	−0.093 5(6)	0.155 6(5)	0.117(1)	0.314 3(5)
C(33)	0.041 5(7)	0.094 9(5)	−0.158 1(6)	0.121 8(4)	0.114(1)	0.304 8(5)
C(34)	0.074 3(7)	0.055 4(5)	−0.174 5(7)	0.102 7(4)	0.080(1)	0.271 1(5)
C(341)	0.050 6(8)	0.035 0(6)	−0.249 1(8)	0.063 9(5)	0.080(2)	0.261 4(8)
C(342)	0.085(1)	−0.013 1(9)	−0.253 2(9)	0.048 8(6)	0.033(2)	0.226(1)
C(343)	−0.020(1)	0.027(1)	−0.280(1)	0.050 9(7)	0.155(2)	0.254(1)
C(344)	0.067(1)	0.077(1)	−0.286 3(9)	0.054 8(7)	0.050(2)	0.297 3(8)
C(35)	0.132 5(7)	0.036 1(6)	−0.123 9(7)	0.118 0(4)	0.050(1)	0.246 4(6)
C(36)	0.156 9(6)	0.053 4(5)	−0.057 8(6)	0.152 9(4)	0.050(1)	0.255 9(5)
C(3)	0.029 0(6)	0.157 9(5)	−0.078 8(6)	0.177 6(5)	0.152(1)	0.354 7(6)
O(4)	0.027 2(5)	0.104 2(4)	0.036 5(4)	0.250 1(3)	0.109 0(8)	0.381 0(4)
C(41)	−0.031 2(6)	0.123 0(5)	−0.013 7(7)	0.230 5(4)	0.077(1)	0.397 6(5)
C(42)	−0.088 9(6)	0.114 0(5)	−0.005 9(6)	0.240 7(4)	0.023(1)	0.426 9(5)
C(43)	−0.149 1(7)	0.131 7(5)	−0.057 5(7)	0.217 9(5)	−0.010(1)	0.443 3(5)
C(44)	−0.153 2(7)	0.158 2(5)	−0.113 5(7)	0.184 3(5)	0.006(1)	0.435 5(6)
C(441)	−0.219 6(8)	0.176 8(6)	−0.169 3(8)	0.161 4(5)	−0.032(1)	0.454 8(6)
C(442)	−0.240(1)	0.142(1)	−0.230(1)	0.126 6(6)	−0.029(2)	0.430 9(9)
C(443)	−0.213 9(9)	0.228 1(9)	−0.194(1)	0.166(1)	0.011(2)	0.490 8(9)
C(444)	−0.276 4(9)	0.175(1)	−0.152(1)	0.168 6(7)	−0.109(1)	0.460(1)
C(45)	−0.095 0(7)	0.165 3(6)	−0.118 8(7)	0.173 3(4)	0.060(1)	0.405 8(5)
C(46)	−0.033 6(7)	0.148 4(6)	−0.070 0(7)	0.196 1(5)	0.092 6(9)	0.388 2(5)
C(4)	−0.088 3(7)	0.082 9(5)	0.053 5(6)	0.276 1(4)	0.000(1)	0.440 5(5)
O(5)	−0.005 2(5)	0.140 8(4)	0.170 1(4)	0.346 0(3)	−0.004 0(7)	0.465 5(4)
C(51)	−0.073 9(6)	0.139 7(5)	0.153 0(6)	0.332 2(5)	0.033(1)	0.489 4(5)
C(52)	−0.097 5(6)	0.167 6(5)	0.194 7(6)	0.352 7(5)	0.065(1)	0.525 0(5)
C(53)	−0.165 6(6)	0.165 8(5)	0.174 3(6)	0.339 0(5)	0.102(1)	0.548 9(5)
C(54)	−0.208 1(7)	0.138 6(5)	0.119 8(6)	0.305 4(5)	0.109(1)	0.539 1(5)
C(541)	−0.284 4(8)	0.138 7(6)	0.098 2(8)	0.288 5(6)	0.149(1)	0.566 7(7)
C(542)	−0.306 8(8)	0.176 5(9)	0.134(1)	0.290 0(6)	0.227(1)	0.558 9(6)
C(543)	−0.302(1)	0.089 5(8)	0.108(2)	0.250 6(7)	0.135(1)	0.557 0(7)
C(544)	−0.322 5(9)	0.153(1)	0.026(1)	0.305 1(7)	0.138(2)	0.612 0(6)
C(55)	−0.184 5(6)	0.114 9(5)	0.079 4(6)	0.283 7(4)	0.076(1)	0.503 3(5)
C(56)	−0.116 4(6)	0.114 0(5)	0.094 9(6)	0.297 1(5)	0.038(1)	0.478 9(5)
C(5)	−0.051 3(6)	0.193 1(5)	0.260 4(6)	0.389 8(5)	0.065(1)	0.537 9(6)
O(6)	0.073 4(4)	0.140 8(3)	0.305 5(4)	0.404 2(3)	0.057 3(7)	0.466 6(4)
C(61)	0.036 4(6)	0.131 3(5)	0.340 1(6)	0.412 8(5)	0.121(1)	0.489 1(5)
C(62)	0.056 2(6)	0.095 0(5)	0.392 3(6)	0.427 9(4)	0.172(1)	0.475 3(5)
C(63)	0.017 0(6)	0.086 3(5)	0.424 5(6)	0.437 2(4)	0.233(1)	0.497 7(5)
C(64)	−0.044 2(6)	0.111 2(5)	0.405 1(6)	0.430 1(5)	0.238(1)	0.533 4(5)
C(641)	−0.088 8(7)	0.097 6(6)	0.441 6(7)	0.442 6(6)	0.316(2)	0.556 5(7)
C(642)	−0.049(1)	0.107(1)	0.517(1)	0.423(1)	0.322(2)	0.585(1)
C(643)	−0.110(1)	0.039(1)	0.427(1)	0.434 9(8)	0.382(2)	0.529 9(8)
C(644)	−0.151(1)	0.134(1)	0.418(1)	0.480 1(8)	0.316(2)	0.576(1)
C(65)	−0.065 3(6)	0.147 0(5)	0.351 4(6)	0.414 2(5)	0.182(1)	0.544 9(6)
C(66)	−0.025 3(6)	0.157 2(5)	0.319 1(6)	0.406 2(4)	0.124(1)	0.522 8(5)

Table 1 (*continued*)

	Calcium compound			Europium compound		
Atom	*x*	*y*	*z*	*x*	*y*	*z*
C(6)	0.120 9(7)	0.066 6(6)	0.414 5(7)	0.436 9(5)	0.165(1)	0.436 2(6)
O(7)	0.200 9(4)	0.135 2(3)	0.378 5(4)	0.384 4(3)	0.218 9(6)	0.370 5(3)
C(71)	0.216 3(7)	0.129 0(5)	0.448 0(6)	0.413 4(4)	0.258(1)	0.380 3(5)
C(72)	0.269 8(7)	0.159 9(5)	0.495 0(6)	0.416 0(4)	0.320(1)	0.359 5(5)
C(73)	0.287 4(7)	0.150 5(6)	0.562 5(7)	0.446 0(4)	0.356(1)	0.370 3(5)
C(74)	0.253 7(6)	0.114 9(5)	0.582 8(6)	0.474 3(5)	0.332(1)	0.403 5(6)
C(741)	0.275 0(7)	0.102 7(6)	0.660 0(7)	0.507 3(5)	0.379(1)	0.416 0(6)
C(742)	0.271(1)	0.152(1)	0.692(1)	0.513 6(9)	0.409(2)	0.458 7(9)
C(743)	0.240(1)	0.056(1)	0.674(1)	0.510 4(8)	0.433(2)	0.387(1)
C(744)	0.354(1)	0.085(1)	0.691(1)	0.536 3(6)	0.328(2)	0.425(1)
C(75)	0.200 6(6)	0.088 8(5)	0.535 5(6)	0.469 4(5)	0.268(1)	0.424 3(6)
C(76)	0.182 0(6)	0.093 9(5)	0.467 1(6)	0.440 0(4)	0.231(1)	0.414 1(5)
C(7)	0.309 9(7)	0.195 5(6)	0.472 2(7)	0.389 1(4)	0.345(1)	0.322 6(6)
C(8)	0.297 5(4)	0.142 1(3)	0.354 8(4)	0.339 9(2)	0.234 6(6)	0.296 4(3)
C(81)	0.360 4(6)	0.143 1(5)	0.409 3(6)	0.360 8(4)	0.241(1)	0.275 1(5)
C(82)	0.412 2(6)	0.114 5(5)	0.407 9(6)	0.358 1(4)	0.196(1)	0.241 2(5)
C(83)	0.473 4(7)	0.116 3(6)	0.463 0(7)	0.380 0(4)	0.209(1)	0.220 3(5)
C(84)	0.483 2(7)	0.144 6(6)	0.519 5(7)	0.403 9(4)	0.265(1)	0.228 6(5)
C(841)	0.554 9(8)	0.147 1(7)	0.586 6(8)	0.425 3(6)	0.270(2)	0.201 8(7)
C(842)	0.552(2)	0.107(1)	0.630(2)	0.404 3(8)	0.325(4)	0.166(1)
C(843)	0.610(1)	0.139(1)	0.564(1)	0.453 6(7)	0.312(2)	0.222 0(9)
C(844)	0.562(2)	0.203(1)	0.618(2)	0.425(1)	0.216(3)	0.180(2)
C(85)	0.428 3(7)	0.172 8(6)	0.521 2(7)	0.406 0(5)	0.307(1)	0.261 3(6)
C(86)	0.366 6(6)	0.170 0(5)	0.466 7(6)	0.386 0(4)	0.297(1)	0.286 1(5)
C(8)	0.406 9(7)	0.082 4(5)	0.348 3(7)	0.331 4(4)	0.136(1)	0.229 3(5)
(*b*) Solvent and anion						
dmf (a)						
O	0.212 8(5)	0.212 0(4)	0.141 3(5)	0.312 2(3)	0.273 7(6)	0.362 3(3)
C(1)	0.185 5(8)	0.239 6(7)	0.090 9(8)	0.310 8(5)	0.243(1)	0.395 9(6)
N	0.123 7(7)	0.255 9(6)	0.066 7(7)	0.330 4(4)	0.262 9(9)	0.431 1(4)
C(2)	0.097(1)	0.291 9(9)	0.011(1)	0.324 5(7)	0.221(1)	0.464 8(6)
C(3)	0.080(1)	0.239 2(8)	0.095(1)	0.355 4(5)	0.319(1)	0.436 5(6)
dmf (b)						
O	0.198 9(5)	0.238 4(4)	0.274 1(5)	0.285 9(3)	0.385 6(6)	0.306 5(4)
C(1)	0.211(1)	0.271 1(9)	0.311(1)	0.289 9(6)	0.426(1)	0.337 5(6)
N	0.181 5(8)	0.291 4(6)	0.339 0(8)	0.272 0(5)	0.468 6(8)	0.345 9(6)
C(2)	0.211(1)	0.332(1)	0.386(1)	0.238 5(7)	0.478(1)	0.311(1)
C(3)	0.117(1)	0.274(1)	0.326(1)	0.283 6(8)	0.508(1)	0.383 1(7)
dmf (c)						
O	0.351 1(5)	0.234 3(4)	0.287 1(5)	0.289 3(3)	0.331 5(7)	0.233 6(4)
C(1)	0.407 6(9)	0.238 2(7)	0.335 2(9)	0.304 3(5)	0.351(1)	0.210 8(6)
N	0.460 4(7)	0.256 2(6)	0.331 6(7)	0.296 7(4)	0.381 9(8)	0.177 9(4)
C(2)	0.459(1)	0.278 8(9)	0.272(1)	0.263 3(6)	0.401(2)	0.158 0(8)
C(3)	0.519(1)	0.257(1)	0.391(1)	0.322 0(8)	0.401(2)	0.158 7(9)
dmf (d)						
O	0.179 4(5)	0.113 0(4)	0.214 0(5)	0.285 5(3)	0.140 1(6)	0.316 6(3)
C(1)	0.137 4(8)	0.080 0(6)	0.187 2(7)	0.292 3(6)	0.079(1)	0.310 4(7)
N	0.141 4(6)	0.031 6(5)	0.169 3(6)	0.310 7(5)	0.036(1)	0.325 8(6)
C(2)	0.206(1)	0.015(1)	0.182(1)	0.336 7(7)	0.052(2)	0.361 7(9)
C(3)	0.090(1)	−0.004 9(8)	0.137(1)	0.310(1)	−0.041(3)	0.306(1)
dmf (e)						
O	0.453(2)	−0.102 6(7)	0.156 5(9)	0.124(2)	0.346(2)	0.131(1)
C(1)	0.443(1)	−0.082 0(5)	0.177 7(6)	0.138 2(7)	0.318(2)	0.173 6(9)
N	0.427 2(5)	−0.037 0(5)	0.177 1(5)	0.112 5(5)	0.287(1)	0.183 2(6)
C(2)	0.380(1)	−0.014(1)	0.180(1)	0.124(1)	0.229(1)	0.210 9(8)
C(3)	0.451(2)	0.008 3(7)	0.156(1)	0.085 8(5)	0.293(3)	0.171 3(9)
dmf (f)						
O	−0.092(1)	0.328 7(8)	0.205 4(8)	0.100(1)	0.340(2)	0.349(1)
C(1)	−0.089 1(9)	0.315 9(6)	0.169 8(7)	0.112 6(9)	0.340(1)	0.329 0(8)
N	−0.140 5(6)	0.294 5(4)	0.105 4(6)	0.112 4(4)	0.403(1)	0.314 1(6)
C(2)	−0.213 5(6)	0.308(1)	0.064(1)	0.139 1(9)	0.431(3)	0.287(1)
C(3)	−0.130(1)	0.259 9(6)	0.057 9(9)	0.106(1)	0.494(2)	0.330(1)

Table 1 (*continued*)

	Calcium compound			Europium compound		
Atom	*x*	*y*	*z*	*x*	*y*	*z*
dmf (g)						
O	0.357 2(7)	0.023 1(8)	0.501(1)			
C(1)	0.315 0(6)	0.005 5(5)	0.462 1(8)	0.471(1)	0.173(2)	0.335 1(9)
N	0.258 8(6)	−0.026 1(4)	0.450 4(6)	0.453 7(5)	0.120(1)	0.326 1(5)
C(2)	0.229(1)	−0.048 2(8)	0.493(1)	0.421 6(8)	0.081(3)	0.323(1)
C(3)	0.231 1(9)	−0.033 1(8)	0.359 5(6)	0.460(1)	0.065(2)	0.295(1)
Nitrate						
N				0.215 8(4)	0.288 7(9)	0.288 3(4)
O(1)				0.238 3(3)	0.260 9(7)	0.318 2(3)
O(2)				0.224 8(3)	0.302 4(7)	0.258 2(3)
O(3)				0.189 2(3)	0.304(1)	0.289 4(5)

(*c*) Disordered components (calcium compound only)

tert-Butyl components				dmf (f) (component populations: 0.5)			
C(645)	−0.161(2)	0.086(1)	0.385(2)	O(2)	−0.027 0(6)	0.292(1)	0.172(1)
C(646)	−0.069(2)	0.049(2)	0.485(2)	C(4)	−0.078 9(8)	0.281 7(6)	0.119 1(9)
C(647)	−0.097(2)	0.143(2)	0.477(2)	C(5)	−0.178(1)	0.327 0(7)	0.132(1)
C(745)	0.213(2)	0.119(2)	0.677(2)	C(6)	−0.178(1)	0.264 3(9)	0.042 8(8)
C(746)	0.334(2)	0.140(2)	0.708(2)				
C(747)	0.293(2)	0.051(2)	0.676(2)	dmf (g) (component populations: 0.5)			
C(845)	0.551(2)	0.162(2)	0.649(2)	O(2)	0.262(1)	0.010 0(8)	0.367 7(7)
C(846)	0.574(2)	0.090(2)	0.599(2)	C(4)	0.286 5(7)	−0.006 7(5)	0.412 1(7)
C(847)	0.599(2)	0.183(1)	0.567(2)	C(5)	0.306 6(8)	−0.007 1(7)	0.510 3(6)
				C(6)	0.205 7(9)	−0.062 0(7)	0.444(1)

Major component populations of the *tert*-butyl methyls are: C(642)–C(644), 0.58(1); C(742)–C(744), 0.59(1); C(842)–C(844), 0.61(1), with total component populations of unity.

Table 2 Metal atom environments: *r* is the metal–ligand atom distance (Å); other entries in the matrix are the angles (°) subtended by the relavant atoms at the head of the row and column

(*a*) Calcium complex

Atom	*r*	O(8)	O(a)	O(b)	O(c)	O(d)	
O(1)	2.27(1)	95.5(3)	88.9(4)	170.9(4)	83.6(4)	91.3(4)	
O(8)	2.32(1)		175.1(4)	89.6(4)	89.2(4)	86.8(3)	
O(a)	2.29(1)			86.4(4)	93.6(4)	90.7(4)	
O(b)	2.31(1)				88.9(4)	96.6(4)	
O(c)	2.36(1)					173.2(4)	
O(d)	2.28(1)						

(*b*) Europium complex; nitrate oxygens are italicised

Atom	*r*	O(8)	O(a)	O(b)	O(c)	O(d)	*O(1)*	*O(2)*
O(1)	2.32(1)	91.1(4)	148.2(4)	141.1(4)	75.8(4)	74.5(4)	104.6(4)	79.9(4)
O(8)	2.26(1)		78.8(4)	104.8(4)	83.2(4)	84.4(4)	149.0(4)	161.9(4)
O(a)	2.46(1)			70.6(4)	131.6(4)	74.6(4)	73.8(4)	116.8(4)
O(b)	2.40(1)				71.3(5)	141.2(4)	79.7(5)	74.2(4)
O(c)	2.39(1)					147.5(4)	126.3(4)	79.3(4)
O(d)	2.42(1)						74.5(4)	107.9(4)
O(1)	2.55(1)							49.2(4)
O(2)	2.57(1)							

Table 3 Macrocycle torsion angles (°): the two values in each entry are for the calcium and europium complexes respectively

C(82)–C(8)–C(16)–C(11)	−104(1), −100(2)	C(16)–C(8)–C(82)–C(81)	101(2), 106(2)
C(11)–C(12)–C(1)–C(26)	−88(2), −89(2)	C(81)–C(86)–C(7)–C(72)	86(2), 97(2)
C(12)–C(1)–C(26)–C(21)	84(2), 73(2)	C(86)–C(7)–C(72)–C(71)	−86(1), −72(2)
C(21)–C(22)–C(2)–C(36)	91(2), 85(2)	C(71)–C(76)–C(6)–C(62)	−86(2), −96(2)
C(22)–C(2)–C(36)–C(31)	−75(2), −98(2)	C(76)–C(6)–C(62)–C(61)	87(2), 154(2)
C(31)–C(32)–C(3)–C(46)	−101(2), −75(2)	C(61)–C(66)–C(5)–C(52)	94(2), −88(2)
C(32)–C(3)–C(46)–C(41)	71(2), 104(2)	C(66)–C(5)–C(52)–C(51)	−84(2), 86(2)
C(41)–C(42)–C(4)–C(56)	123(1), 96(2)	C(51)–C(56)–C(4)–C(42)	−97(1), −166(2)

adopt a quasi-*2* symmetry, while in the present instances the maximum potential symmetry is found for the calcium complex, where the ligand symmetry is quasi-*mm* (as in the 'pleated loop' conformation of the free species[12]), reduced to *m* by its interaction with the calcium. A somewhat similar array is found in the europium complex, but the potential symmetry of the

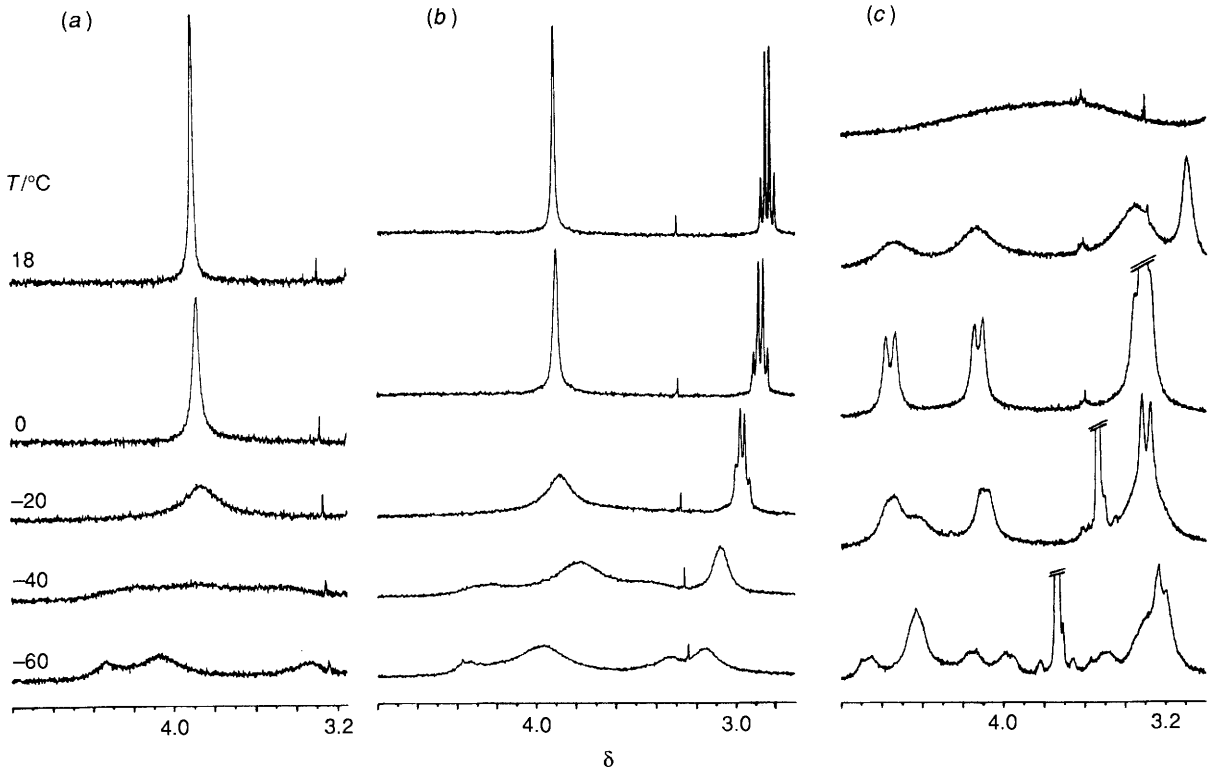

Fig. 3 300 MHz Proton NMR spectra, at various temperatures (same values in each case) in $(CD_3)_2CO$ solvent, showing the region of the calixarene methylene proton resonances: (*a*) $[Ca(H_6L)(dmf)_4]\cdot 4dmf$, (*b*) $[NH(C_2H_5)_3]_3[H_5L]\cdot CH_3CN\cdot H_2O$ and (*c*) $[K_2(H_6L)]\cdot 3CH_3CN\cdot H_2O$

ligand is further degraded by eversion of the bridging carbon C(5). Whereas in the calcium complex and the free calixarene the bridging carbons are alternately 'up' (U) and 'down' (D), C(5) disturbs this array in the europium complex, so that the sequence of bridging carbon atoms 1–8, UDUDUDUD in the calcium complex, becomes UDUDDDUD in the europium (Table 3).

The isolation of a europium(III)–*p*-*tert*-butylcalix[8]arene complex of 1:1 metal:ligand stoichiometry contrasts with our earlier observations[4] that only a 2:1 species could be readily isolated, no matter what the ratio made up in solution. The significant difference is that these earlier preparations involved the use of a large excess of triethylamine as a deprotonating agent, whereas in the present experiments K_2CO_3 was used to limit deprotonation to the formation of a dianion. Reaction of *p*-*tert*-butylcalix[8]arene alone with excess of triethylamine in fact enables a salt of the calixarene trianion to be isolated, and even this will react with an equimolar amount of europium(III) in dimethylformamide to disproportionate, giving a precipitate of the neutral calixarene and a solution of the dieuropium complex. It is possible, therefore, that the extent of deprotonation of the calixarene has a significant influence on the relative stability of the 1:1 and 1:2 ligand:europium complexes, though in solvents, as used in the present syntheses, which promote ion association, the nature of other cations present (K^+ or NEt_3H^+) may also have a marked effect on the course of reaction. The complexity and ease of isolation of products from the reaction between Ti^{IV} and *p*-*tert*-butylcalix[8]arene have also been observed to depend on the degree of deprotonation of the calixarene and associated counter cations.[6]

The methods of synthesis used for the present complexes do illustrate one of the significant differences between calcium(II) and europium(III) in that while it is easy to prepare a bimetallic derivative of *p*-*tert*-butylcalix[8]arene with europium,[4] there is no evidence for the formation of such a species with calcium. This is presumably indicative of a significantly stronger co-ordinate bonding interaction of phenoxide donors with europium than with calcium. Whether there is some formation of a 2:1 calcium:calixarene complex in solution in the presence of excess of base is difficult to establish because the lability of the system is such that the ^1H NMR spectrum reflects apparent eight-fold symmetry for the ligand even when the metal:ligand ratio is as high as 20:1. Shifts in the free (deprotonated) ligand resonances as a consequence of the addition of Ca^{2+} are small and give no reliable indication of the formation of other than the 1:1 species.

Variable-temperature ^1H NMR measurements in acetone solvent reveal that under all conditions the spectra of the ligand in its 1:1 calcium complex and in its tris(triethylammonium) salt are essentially identical (Fig. 3) and indicative of eight-fold rotational symmetry. This is true even when the temperature is low enough for ring inversion to be slow and the diastereotopicity of the calixarene methylene group protons to be apparent.[14] These observations may simply mean that the dissolved species are fully dissociated in both cases (and that proton exchange between the phenoxide sites is rapid), though for the calcium complex it may otherwise mean that there is rapid exchange of the calcium ion between all eight oxygen atoms of the macrocycle rather than substantial dissociation. In contrast, the spectrum of the dipotassium complex in acetone, though indicative of eight-fold symmetry at room temperature, changes at −20 °C to one displaying three singlet resonances of Bu^t (in the ratio 2:1:1). This spectrum is in fact very similar to that observed at elevated temperatures (≈60 °C) for the diyttrium complex,[11,15] which at room temperature gives a spectrum completely consistent with it having the same structure as has been established for the dieuropium complex in the solid state.[4] A simple interpretation[15] of the changes in the yttrium complex spectrum is that the high-temperature form reflects rapid racemisation of its chiral 'propeller' structure, and thus it may be that the dipotassium complex also adopts the structure found for rare-earth-metal complexes but is undergoing rapid inversion in solution at −20 °C. Unfortunately, the 1:1 europium(III)–*p*-*tert*-butylcalix[8]arene complex is too insoluble in acetone for a satisfactory spectrum to be obtained, but in toluene it provides a spectrum which is not only markedly temperature-dependent and strongly shifted but is also complicated by generally broad

signals. Although a full assignment of this spectrum has not been made, it is apparent that *four* resonances for Bu^t (δ 0.90, 0.99, 1.32 and 1.77) appear at room temperature. This observation is consistent with the continued association of the europium ion and the calixarene in toluene solvent (as is the yellow colour of the solution[4]), although the apparent *m* symmetry of the dissolved complex is not preserved in the solid-state structure. The broadness of the spectrum suggests that this change in apparent symmetry may be due to conformational flexibility of the complex in solution. Cooling of the solution results in increased broadening of the spectral resonances, while warming to the highest attainable temperature (60 °C) results in the coalescence of the four resonances of Bu^t to a broad singlet (δ ≈ 1.2), which may indicate either dissociation of the complex or exchange of the europium ion between the phenolic oxygens, as suggested for the calcium complex.

Acknowledgements

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