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Calixarenes as aryloxides: oligonuclear europium(III) derivatives

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Synthetic and structural studies of europium complexes of calix[8]arene, *p*-t-Bu-calix[7]arene and *p*-t-Bu-calix[9]arene are reported. The complex $[Eu_2(\text{calix[8]arene-6H})(\text{dmso})_5]$ was found to have a similar structure to previously reported *p*-t-Bu- and p-nitro-calix[8]arene complexes of the lanthanides. Despite being prepared under similar conditions, the complex of *p*-t-Bu-calix[7]arene was found to be a tetranuclear assembly, formulated as $[(HO)_2(OCO_2)Eu_4(p\text{-t-Bu-calix[7]arene-4H})_2(\text{dmso})_6]$. Expanding the ligand to *p*-t-Bu-calix[9]arene resulted in the isolation of a larger oligonuclear assembly, $[(HO)_9(H_2O)_2Eu_7(p\text{-t-Bu-calix[9]arene-6H})_2(\text{dmso})_6]$. In contrast to the consistent structural type found with the calix[8]arene system, however, use of a different solvent (acetone) gave rise to a much simpler species, $[Eu_2(p\text{-t-Bu-calix[9]arene-3H})_2(\text{dmso})_4]$.

Introduction

Considerable interest has recently been focussed on the synthesis of hydroxo/oxo-bridged oligonuclear lanthanide complexes,[1,2] the obvious matters of significance in relation to these compounds being their electronic, magnetic and possible catalytic properties. As alkoxide ligand coordination chemistry is characterised by oligomer formation,[3–5] often resulting from partial hydrolysis, this would seem an area of lanthanide chemistry open to further exploitation, especially through the use of constrained multidentate ligands, and indeed there is literature indicative of the promise of this approach.[6,7] For the actinide element uranium (as U(VI)), for which only recently have thorough structural studies of simple aryloxide (as distinct from alkoxide) complexes been reported,[8] structural studies of the complexes of various macrocyclic polyphenols, calixarenes and homo-oxacalixarenes have established the formation of a series of polyuranates, of forms depending on the specific nature of the macrocycle.[9] Thus, the obvious question arises as to whether such behaviour might be mirrored for the lanthanides.

The remarkable variety of functionalisation wrought upon calixarenes in developing their use in all forms of complex formation, not solely with metals,[10] has somewhat obscured the potential of the "parent" species as aryloxide (phenoxide) donors, though this has not been entirely neglected.[11–13] It is very true, nonetheless, that much remains possible for the larger calix[n]arenes ($n > 4$).[14,15] As a preliminary step in further developing this chemistry, we have studied europium(III) complexes of the ligands n = 7–9, and report herein structural and synthetic studies which expose some of the significant properties of these systems.

Experimental

Synthesis

p-t-Bu-calix[7]arene,[16] *p*-t-Bu-calix[9]arene,[16] and calix[8]arene[17] were synthesised following literature procedures.

1. $[Eu_2(\text{calix[8]arene-6H})(\text{dmso})_5]$. Calix[8]arene (0.10 g, 0.12 mmol) was slurried in dmso (4 mL), and triethylamine added dropwise until a clear solution was formed. $Eu(ClO_4)_3\cdot 8\text{dmso}$ (0.26 g, 0.24 mmol) was then added and the solution heated until all the solid dissolved. The solution was filtered and left to stand for a prolonged period (approx. 12 months) until yellow crystals appropriate for structure determination were deposited.

2. $[(HO)_2(OCO_2)Eu_4(p\text{-t-Bu-calix[7]arene-4H})_2(\text{dmso})_6]$. *p*-t-Bu-calix[7]arene (16 mg, 0.014 mmol) was slurried in dmso (0.5 mL), and triethylamine (~0.1 mL) added dropwise until a clear solution was formed. To this solution was added $Eu(ClO_4)_3\cdot 8\text{dmso}$ (31 mg, 0.029 mmol) in acetonitrile (1 mL). On standing a crystalline yellow product was deposited, along with a white powder.

3. $[(HO)_9(H_2O)_2Eu_7(p\text{-t-Bu-calix[9]arene-6H})_2(\text{dmso})_6]$. *p*-t-Bu-Calix[9]arene (41 mg, 0.028 mmol) was slurried in acetonitrile (2 mL), and triethylamine added dropwise until a clear solution was formed. $Eu(ClO_4)_3\cdot 8\text{dmso}$ (60 mg, 0.056 mmol) was then added and the solution heated until all the solid dissolved. The solution was filtered and left to stand until yellow crystals appropriate for structure determination were deposited, along with a microcrystalline white powder.

4. $[Eu_2(p\text{-t-Bu-calix[9]arene-3H})_2(\text{dmso})_4]$. Procedure as for **3**, with acetone used in place of acetonitrile as solvent. Orange crystals deposited in very low yield on standing.

Structure determinations

General procedure. (Individual variations, difficulties, (*etc.*) are mentioned for each structure below). For **2** and **3**, unique data sets were measured at *ca.* 295 K, using a single counter instrument in $2\theta/\theta$ scan mode, gaussian absorption corrections being applied; for the remainder, full spheres of CCD area detector data were measured at *ca.* 153 K (Bruker AXS instrument, ω-scans) yielding $N_{t(otal)}$ data, merging after 'empirical'/multiscan absorption correction (proprietary software) to N unique (R_{int} cited), N_o with $F > 4\sigma(F)$ ($I > 3\sigma(I)$, single counter data) being considered 'observed' and used in the large block least squares refinements, refining anisotropic displacement parameter forms for the non-hydrogen atoms, $(x, y, z, U_{iso})_H$ constrained at estimates where possible. Monochromatic Mo Kα radiation sources (λ = 0.7107$_3$ Å) were employed. Conventional residuals R ($\Sigma\Delta|F|/\Sigma|F_o|$), R_w $((\Sigma w\Delta^2/\Sigma wF_o^2)^{1/2})$ (weights: $(\sigma^2(F) + 0.0004\ F^2)^{-1}$) are quoted at convergence. Neutral atom complex scattering factors were employed within the context of the Xtal 3.7 program system.[18] Pertinent results are given below and in the tables and figures, the latter showing

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Table 1 Selected crystal/refinement data

Compound	**1**·≈41/3dmso	**2**·≈5H$_2$O·4MeCN	**3**·≈10MeCN·2H$_2$O	**4**·≈14Me$_2$CO·H$_2$O
Formula	$C_{74.66}H_{98}Eu_2O_{17.33}S_{9.33}$	$C_{175}H_{248}Eu_4N_4O_{30}S_6$	$C_{230}H_{323}Eu_7N_{10}O_{37}S_6$	$C_{248}H_{356}Eu_2O_{37}S_4$
M_r	1876.1	3688.1	5076.3	4361.7
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$ (#14)	$P2_1/n$ (#14)	Cc (#9)	$P2_1/n$ (#14)
a/Å	21.507(2)	21.152(4)	35.97(2)	19.062(4)
b/Å	18.007(2)	33.453(7)	24.21(1)	18.531(4)
c/Å	21.564(2)	30.524(5)	36.61(4)	35.801(7)
β/°	101.227(2)	92.54(2)	104.67(1)	92.080(5)
V/Å^3	8191	21578	30842	12637
D_c/g cm^{-3} (Z)	1.52_1 (4)	1.13_5 (4)	1.09_3 (4)	1.14_6 (2)
μ/cm^{-1}	18.2	12.6	15.0	5.9
'T'$_{min,max}$	0.72, 0.86	0.79, 0.85	0.66, 0.81	0.72, 0.93
N_t ($2\theta_{max}$/°)	79697 (58)	n/a (50)	n/a (50)	105461 (58)
N (R_{int})	20612 (0.028)	37850 (n/a)	26871 (n/a)	31130 (0.052)
N_o	15787	12379	17257	21488
R, R_w	0.042, 0.052	0.093, 0.11	0.069, 0.085	0.053, 0.065

20% (room temperature), 50% (low temperature) probability amplitude displacement envelopes for the non-hydrogen atoms, hydrogen atoms having arbitrary radii of 0.1 Å. A common difficulty is rotational disorder within some of the t-butyl groups, such being modelled in terms of a pair of equal or major and minor components summing to unit occupancy. A further common difficulty concerns assignment of the degree of protonation in the presence of very heavy atoms, phenolic hydrogens being estimated as present or otherwise (in the absence of other evidence) as indicated by the magnitude of the relevant O · · · O spacings. Difference map residues were modelled in terms of solvent, often disordered, as indicated. See Table 1 for selected crystal/refinement data.

CCDC reference numbers 209933–209936.

See http://www.rsc.org/suppdata/dt/b3/b305041f/ for crystallographic data in CIF or other electronic format.

Variata 1. [Eu$_2$(calix[8]arene-6H)(dmso)$_5$]. Phenyl ring and phenolic (11,51) hydrogen atoms were refinable in (x, y, z, U_{iso})$_H$. Sulfur atoms of dmso(3,5,7) were modelled as disordered over pairs of sites of equal occupancy in the usual way. Me(802) on dmso(8) was modelled as disordered over a pair of equally populated sites. dmso(9) was modelled as disordered about an inversion centre, population set at 1/3 after trial refinement.

*2. [(HO)$_2$(OCO$_2$)Eu$_4$(*p*-t-Bu-calix[7]arene-4H)$_2$(dmso)$_6$].* ^{t}Butyl groups 114, 144, 174, 214, 224, 234, 244, 274 were modelled as rotationally disordered over pairs of sites of equal occupancy, with constrained geometries and isotropic displacement parameter forms. dmso sulfur atoms were all modelled as disordered over pairs of sites in the usual way, occupancies x (S(#1–6)) 0.49(3), 0.54(2), 0.75(2), 0.69(1), 0.69(1), 0.5(−) and complements $1 - x$. Entities assigned as MeCN were modelled with constrained geometries.

*3. [(HO)$_9$(H$_2$O)$_2$Eu$_7$(*p*-t-Bu-calix[9]arene-6H)$_2$(dmso)$_6$].* ^{t}Butyl groups 114, 154, 164, 174, 184, 214, 264 were modelled as rotationally disordered over pairs of locations, occupancies set at 0.5, with non-hydrogen atom displacement parameter forms isotropic, the latter also true for MeCN(1–10) where geometries were constrained. Sulfur atoms of dmso 11,13 were disordered, also methyl 110 of dmso 11, occupancies 0.5.

*4. [Eu$_2$(*p*-t-Bu-calix[9]arene-3H)$_2$(dmso)$_4$].* The sulfur atoms of the coordinated dmso were modelled as disordered over sites of occupancy x, $1 - x$, $x = 0.863(2)$ (#1), 0.598(2) (#2). Acetone #9 was modelled as disordered over a pair of sites, occupancies $x = 0.671(7)$, $1 - x$. Phenolic hydrogen atoms were refined in (x, y, z, U_{iso})$_H$.

Figure generation. In an effort to pictorially simplify the more complex structures, stylised figures, where the calixarene phenyl moieties are replaced by a fitted ribbon, were generated in the GDis program.[19] The ribbons were fitted by analysing the connectivity in the underlying structure. Lists, or chains, of bonded carbon atoms were constructed and classified as either open or closed (cyclic). Subsequently, ribbon segments were created for every pair of closed chains that were connected *via* a single open chain. The centroid of each closed chain was required to lie on the surface of the ribbon, with the surface normal taken to be that of the approximately flat cyclic group. Control points, generated from the relative spatial orientation of the closed chains, were employed to manipulate the curvature of the ribbon segment. Fig. 1(b) shows a ribbon fitted to **1**, and Fig. 1(c) shows the ribbon and the calixarene, giving an indication of the fit.

Results and discussion

To begin in the middle of the ligand series studied here, it has in fact been long known that *p*-t-Bu-calix[8]arene provides a structurally similar series of chiral, binuclear complexes, [Ln$_2$-(*p*-t-Bu-calix[8]arene-6H)(S)$_5$] (solvent S = dmf or dmso) for all lanthanides.[20] This form, in which two phenoxide moieties and a solvent oxygen bridge the two lanthanide ions, otherwise bound to phenol, phenoxide and solvent oxygen donors, appears remarkably robust[21] and we have now found that the Eu(III) complex of calix[8]arene, [Eu$_2$(calix[8]arene-6H)-(dmso)$_5$], **1**, adopts the same form, solvated with *ca.* 4.33 dmso (Fig. 1). Unlike the dmso solvates of the *p*-t-Bu-calix[8]arene complexes, which were found to have an intramolecular crystallographic *2*-axis, the binuclear unit in **1** is devoid of crystallographic symmetry. Nonetheless, in the present structure the molecular form has an intramolecular symmetry close to *2*, with similar dimensions (Table 2) and a similar conformation, as evidenced (*e.g.*) by interplanar dihedral angles and ring torsion angles. Thus, for this particular calixarene ring size, it would appear that the form of at least the Eu(III) complexes is insensitive to solvent or to alkyl group substitution on the calixarene "upper rim" (provided the metal : ligand stoichiometry is 2 : 1). It is noteworthy that the phenolic protons, found on O(11,51), have been located and refined in **1**, confirming previous suppositions concerning the location of phenol groups in the related calix[8]arene structures, which were made largely on the basis of Ln · · · O distances.

Given the formation of a 1 : 1 complex (of Eu(III)) in which the ligand is bound simply as a unidentate species for *p*-t-Bu-calix[6]arene,[22] it appeared likely that *p*-t-Bu-calix[7]arene might define a point of significant structural change and indeed this appears to be the case. Its crystalline Eu(III) complex **2**, prepared under similar conditions to those used for the calix[8]arene complexes, is tetranuclear in the solid state, with carbonate and adventitious hydroxide bridging what might be regarded as a pair of binuclear units, each incompletely enveloped by a calix[7]arene. The formula deduced from the

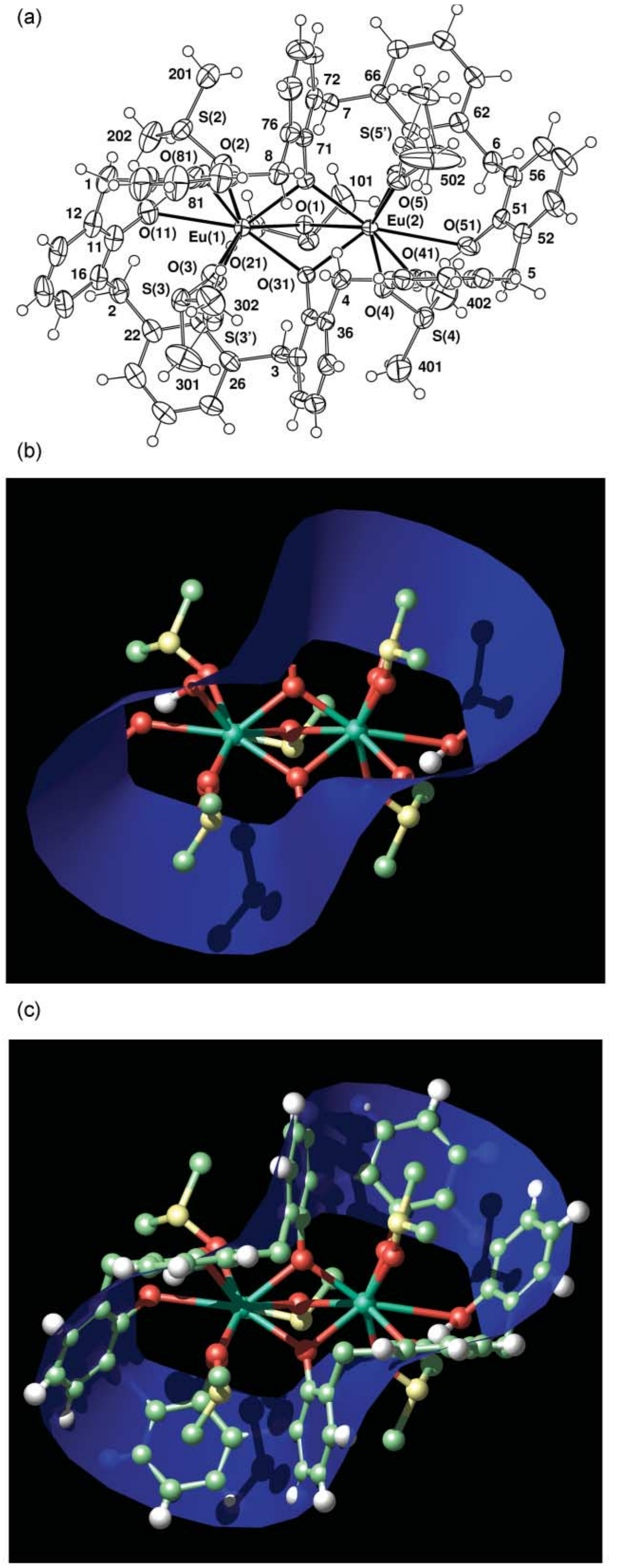

Fig. 1 (a) Projection of the [Eu)(calix[8]arene-6H)(dmso)$_5$] aggregate of **1**, *quasi*-normal to the Eu{μ-O(phenoxide)$_2$}Eu 'plane'; (b) a stylised representation in the same projection, generated by the program GDis,[19] (see Experimental for details); and (c) as for (b) with both calixarene phenyl groups and ribbon.

structure determination is [(HO)$_2$(OCO$_2$)Eu$_4$(calix[7]arene-4H)$_2$(dmso)$_6$], solvated by residues modelled as water oxygen and acetonitrile, the entity plausibly modelled as carbonate presumably originating in atmospheric exposure. The overall symmetry of the aggregate is *quasi-2* but that of the core approaches *2m* (Fig. 2). In respect of the latter, the carbonate and one pair of europium atoms, Eu(1,3), lie in one putative plane, the other europiums Eu(2,4), to either side, lying in the other; the *quasi-2*-axis passes through the central bond of the carbonate. The carbonate is found in the not-unusual 'bis-chelate' mode, also found for nitrate, wherein one 'central' oxygen bridges a pair of metal atoms, the other two oxygen atoms to either side completing a pair of 'chelates', the europium atoms closely coplanar (δ_{Eu}(1,3) 0.11(3), −0.27(3) Å), as also are a pair of μ$_3$-O entities assigned as hydroxyl groups (Table 3). The 'in-plane' europiums each carry a pair of dmso ligands, disposed to either side of the plane [quite unsymmetrically so in the case of Eu(1)], with calix[7] phenoxy oxygen atoms occupying the last of the eight coordination sites about each metal atom, the two 'terminal' and two bridging to the other pair of europium atoms being disposed to either side of the plane in each case. The latter europium atoms are also eight-coordinated, each by a pair of μ$_3$-hydroxy oxygen atoms, the central carbonate oxygen atom (which interacts with four metal atoms), one terminal dmso oxygen atom, and four phenoxy oxygen atoms, two of which bridge to Eu(1,3). Eu ··· Eu lie between 3.757(2)–3.777(2) Å, *i.e.* closely tetrahedral, *except* for the edge Eu(1) ··· Eu(3) which carries the inserted carbonate central oxygen. Each of the ligands is coiled with four sequential oxygens quadridentate about one of the 'out-of-plane' europiums, with a further sequential oxygen reaching to one of the 'in-plane' metal atoms, with close oxygen contacts between two further sequential oxygen atoms beyond, followed by a weaker one as likely locations for phenolic hydrogen atoms, with further possibilities for the latter in respect of neighbouring hydroxy oxygens. As in the calix[8]arene complexes, the dmso ligands are distributed over included and non-included environments, the included species providing further examples of inclusion associated with coordination. The achiral calixarene conformation is similar to that found in other calix[7]arene derivatives of different degrees of deprotonation.[23,24] It is notable that this conformation differs from that found in the hexanuclear uranyl complex of *p*-benzylcalix[7]arene.[25] The conformations of the ligands in the present complex are essentially those of 'extended' calixes embracing the larger cluster; in the centrosymmetric hexanuclear uranyl complex, the pair of UO$_2$ entities are accommodated within two halves of an everted structure.

Perhaps unsurprisingly, preparation of an Eu(III) complex of *p*-t-Bu-calix[9]arene under conditions similar to those used for the calix[7]arene compound produced a crystalline complex in which an even larger oligonuclear species is trapped between two calixarene units. The array of compound **3**, like the other complexes, is assigned a neutral stoichiometry, [(HO)$_9$(H$_2$O)$_2$-Eu$_7$(*p*-t-Bu-calix[9]arene-6H)$_2$(dmso)$_6$], solvated by residues modelled as water and acetonitrile, with similar sources of uncertainty in regard to protonation. The array comprises a pair of Eu$_4$O$_4$ cubanoid entities, fused at a common europium, Eu(4), OEu$_3$O$_3$EuO$_3$Eu$_3$O, with additional oxygen atoms O(9,10) buttressing/linking the central europium on either side to one of the Eu$_3$ triad atoms, Eu(1,5). The array conforms quite reasonably in detail to overall *2*-symmetry about the central europium, with a further oxygen coordinated to it lying on the putative *2*-axis (Fig. 3). The Eu$_3$ triangles each lie within a calix[9] ligand, successive triads of phenoxy oxygen atoms coordinating the europium atoms of the triangle. The protonation patterns of the calix[9] ligands are presumed similar, each ligand exhibiting three short O ··· O distances between adjacent phenoxy oxygens at the junctures between the triads of successive europium atoms (Table 4, footnote) which may be presumed to be the location of hydrogen atoms. Assignment of association of the resulting three unrefinable phenolic hydrogen atoms with specific phenoxy oxygen atoms by correlation with variation of the associated Eu–O distances is fraught with difficulty, the Eu–O distances varying rather widely and without a consistent pattern: within each triad the central member has a markedly shorter Eu–O distance, but the peripheral

Table 2 The dimensions of the europium environments of **1**. In this and subsequent tables, *r* (Å) are the Eu–O distances, other entries in the matrices being the angles subtended by the relevant atoms at the head of the row and column[a]

(a) Eu(1)	*r*/Å	O(21)	O(31)	O(71)	O(81)	O(1)	O(2)	O(3)
O(11)	2.774(3)	77.4(1)	150.0(1)	132.72(9)	55.42(9)	133.73(8)	67.9(1)	74.7(1)
O(21)	2.218(3)		90.2(1)	144.3(1)	131.9(1)	79.1(1)	94.0(1)	84.5(1)
O(31)	2.383(3)			70.8(1)	125.62(9)	68.14(9)	141.1(1)	77.0(1)
O(71)	2.363(3)				82.6(1)	65.95(9)	84.0(1)	118.2(1)
O(81)	2.446(3)					139.7(1)	77.7(1)	75.4(1)
O(1)	2.545(7)						74.73(9)	141.1(1)
O(2)	2.416(3)							141.9(1)
O(3)	2.331(3)							

(b) Eu(2)	*r*/Å	O(61)	O(71)	O(31)	O(41)	O(1)	O(4)	O(5)
O(51)	2.947(8)	73.0(1)	153.8(9)	132.8(1)	54.8(1)	129.18(8)	67.41(9)	81.18(9)
O(61)	2.194(3)		90.9(1)	146.5(1)	126.1(1)	79.6(1)	92.8(1)	84.6(1)
O(71)	2.371(3)			71.0(1)	130.57(9)	64.87(8)	135.48(9)	76.8(1)
O(31)	2.367(3)				85.9(1)	67.37(9)	82.3(1)	116.5(1)
O(41)	2.399(3)					143.4(1)	80.1(1)	75.7(1)
O(1)	2.604(3)						72.25(9)	137.9(1)
O(4)	2.391(3)							147.7(1)
O(5)	2.342(3)							

[a] Eu(1) ··· Eu(2) 3.6991(4); O(1) ··· O(31,71) 2.764(4), 2.676(4); O(31) ··· O(71) 2.750(4) Å; Eu(1)–O(1,31,71)–Eu(2) 91.83(8), 102.3(1), 102.8(1)°. O(41) ··· .O(51) 2.507(5); O(81) ··· O(11) 2.445(5) Å. Eu(1) deviates from phenoxide C_6 planes 7,8,1,2,3 by 1.799(9), 1.696(10), 2.124(10), 1.352(2), 1.752(8) Å, and Eu(2) from planes 3,4,5,6,7 by 1.732(8), 1.554(9), 2.607(9), 1.188(9), 1.761(9) Å.

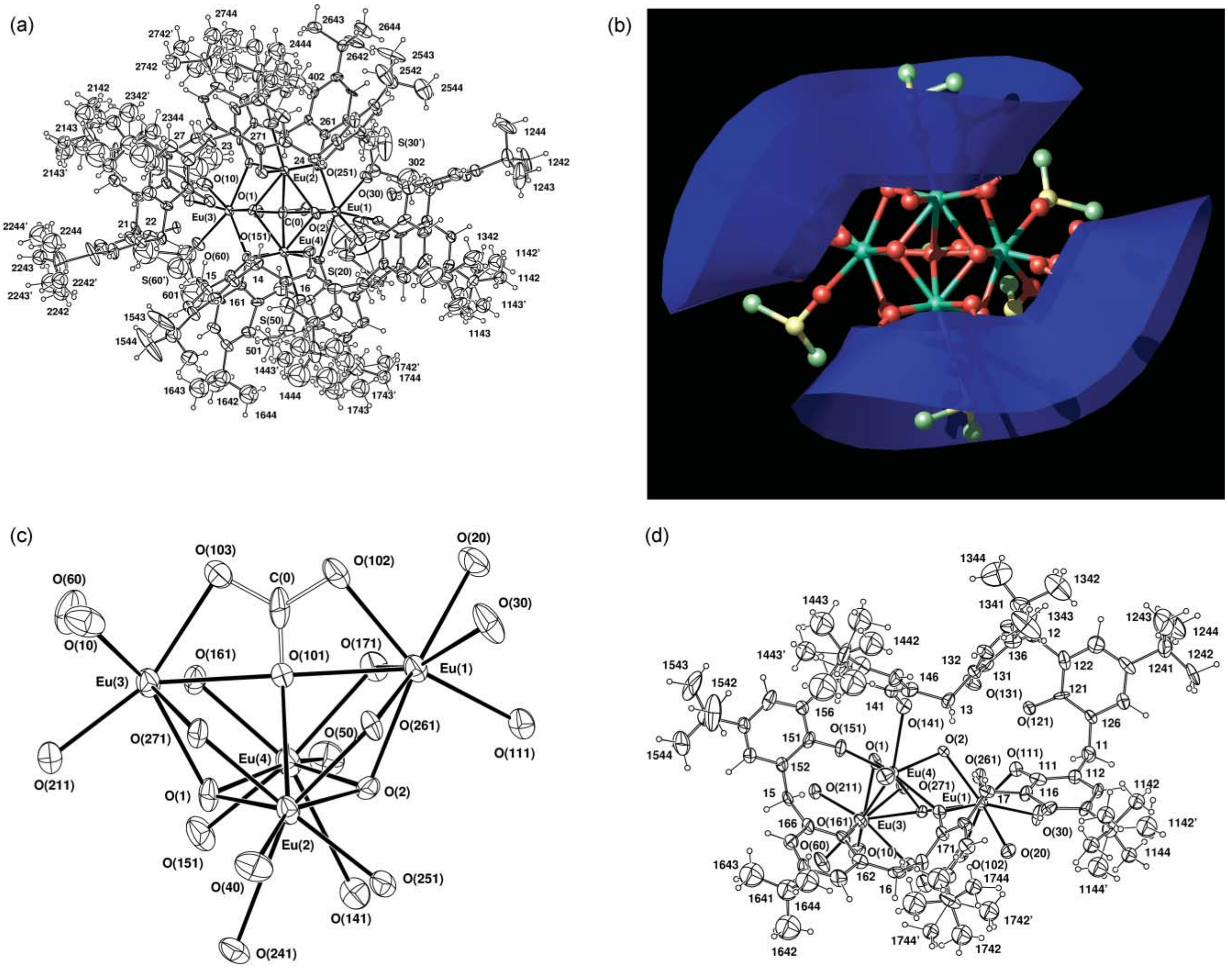

Fig. 2 (a) Projection of the $[(HO)_2(OCO_2)Eu_4(calix[7]arene\text{-}4H)_2(dmso)_6]$ aggregate of **2**, normal to the Eu_4 plane, (b) stylised representation with calixarenes represented as ribbons, (c) the molecular core, and (d) ligand 1 with its associated core atoms (the counterpart projection for ligand 2 is similar).

Table 3 The dimensions of the europium environments of **2**[a]

(a) (ii) Eu(1)	*r*/Å	O(101)	O(102)	O(111)	O(171)	O(261)	O(20)	O(30)
O(2)	2.46(1)	65.4(5)	120.3(5)	80.6(5)	70.5(5)	72.0(5)	144.7(5)	134.0(5)
O(101)	2.48(1)		55.0(5)	144.3(5)	69.2(5)	71.4(5)	118.6(5)	127.4(6)
O(102)	2.36(2)			157.8(5)	90.2(5)	86.2(5)	75.2(6)	85.6(2)
O(111)	2.31(2)				90.2(5)	109.1(5)	83.2(6)	83.9(6)
O(171)	2.43(1)					133.9(5)	78.5(5)	152.6(5)
O(261)	2.43(2)						143.2(6)	72.9(5)
O(20)	2.40(2)							74.3(6)
O(30)	2.43(2)							
(ii) Eu(3)	*r*/Å	O(101)	O(103)	O(211)	O(271)	O(161)	O(10)	O(60)
O(1)	2.40(1)	65.0(5)	119.8(5)	81.9(5)	69.3(5)	71.4(5)	144.3(6)	132.2(6)
O(101)	2.49(1)		54.7(5)	145.8(5)	70.3(5)	67.4(5)	120.9(6)	124.9(6)
O(103)	2.43(1)			156.1(6)	88.4(5)	86.7(5)	75.3(6)	87.7(6)
O(211)	2.30(1)				90.8(5)	111.4(5)	81.1(6)	83.6(6)
O(271)	2.44(1)					131.1(5)	79.8(6)	156.0(6)
O(161)	2.36(2)						144.3(6)	72.3(6)
O(10)	2.22(2)							76.3(6)
O(60)	2.34(2)							
(b) (i) Eu(2)	*r*/Å	O(2)	O(101)	O(241)	O(251)	O(261)	O(271)	O(40)
O(1)	2.35(1)	75.7(5)	59.3(4)	72.9(4)	125.4(5)	125.0(5)	72.5(5)	122.8(5)
O(2)	2.46(1)		59.3(4)	99.7(5)	69.0(5)	74.0(5)	124.4(5)	154.7(5)
O(101)	2.88(1)			130.7(4)	124.8(5)	65.8(5)	65.3(5)	143.2(5)
O(241)	2.88(1)				73.7(5)	156.8(5)	112.4(5)	73.0(5)
O(251)	2.23(1)					83.2(5)	161.7(5)	85.7(6)
O(261)	2.31(1)						88.8(5)	102.9(6)
O(271)	2.30(1)							80.0(5)
O(40)	2.34(2)							
(ii) Eu(4)	*r*/Å	O(1)	O(101)	O(141)	O(151)	O(161)	O(171)	O(50)
O(2)	2.33(1)	76.2(5)	62.4(5)	71.8(5)	125.2(5)	125.3(5)	73.5(6)	122.1(6)
O(1)	2.45(1)		60.2(4)	101.6(5)	69.4(6)	71.4(5)	124.8(5)	155.6(5)
O(101)	2.76(1)			133.3(4)	125.1(6)	63.3(5)	65.0(5)	140.4(5)
O(141)	2.78(2)				75.0(6)	156.8(5)	111.0(5)	72.9(5)
O(151)	2.21(2)					81.9(6)	160.7(5)	86.3(6)
O(161)	2.31(2)						90.4(5)	104.1(6)
O(171)	2.38(1)							78.4(6)
O(50)	2.39(2)							

[a] Eu(1) ··· Eu(2–4) 3.768(2), 4.961(2), 3.757(2) Å; Eu(2) ··· Eu(3,4) 3.765(2), 3.777(2) Å, and Eu(3) ··· Eu(4) 3.763(2) Å. O(111) ··· O(121) 2.41(2), O(121) ··· O(131) 2.55(2), O(131) ··· O(141) 2.75(2), O(151) ··· O(161) 2.96(2), O(211) ··· O(221) 2.48(2), O(221) ··· O(231) 2.54(2), O(231) ··· (O241) 2.78(2), O(251) ··· O(261) 3.01(2) Å; O(1) ··· O(101,151,161,271) 2.63(2), 2.66(2), 2.78(2), 2.75(2) Å; O(2) ··· O(101,171,251,261) 2.67(2), 2.82(2), 2.66(2), 2.87(2) Å.

counterparts vary widely and seemingly unsystematically. The coordination environment of each of the peripheral europium atoms is made up of three phenoxy oxygen atoms (non-bridging), one dmso oxygen atom (terminal) at the extreme periphery of the cluster, one peripheral (μ_3-)oxygen, (the pair of these (O(1,3)) together with O(11) being assigned as hydroxide) and two inner (μ_3-) oxygens, also assigned as hydroxide; the environments of Eu(1,5), in addition, are augmented by O(9,10), considered to be water molecule oxygen atoms. Eu(1,5) are thus eight-coordinate and Eu(2,3,6,7) seven-coordinate. The environment of the central europium comprises O(11) terminal and O(9,10) (bridging to Eu(1,5)) (weakly coordinated), together with the pair of (μ_3-O)$_3$ triads.

In detail, a number of other features may be noted, incorporating degradation of local symmetry consequent upon the overriding putative *2*- and *3*-axes overall and through Eu(4) and O(1,3). It should be noted that Eu(4) ··· O(1)/Eu(4) ··· O(3) are not collinear, intersecting at an angle of 20.2° and making angles of 15.1(3), 13.1(3)° with the Eu(4)O(9–11) plane; the two Eu$_3$ planes similarly lie at 15.3(3), 14.7(3)° to the central plane. A number of the 'inner' bridging and ligand oxygen atoms lie in proximity to those of the central plane, providing further possible hydrogen-bonding sites for water or phenolic hydrogen atoms. The 'inward' inclination of the ligand ring planes is such that deviations of the central Eu(4) from these planes do not exceed 1.1 Å, many being much less, with the exception of planes 2 whose perversities are presumably consequent on the proximity of bridging water molecules 9 and 10 (Table 5). These deviations are less than those of the more closely associated individual other europium atoms with each phenoxide plane, these typically 1.7 ± 0.3 Å (exception: the anomalous planes 2 where the deviations are much less). The triads of planes about each outer europium are inclined within the triad at *ca.* 50–75° to each other. We finally note that the two pairs of Eu$_4$ aggregates associated with each cube make quite reasonable tetrahedra, Eu ··· Eu overall lying between 3.876(3)–3.939(3), perturbations generally corresponding to the diminutions in symmetry occasioned by the interactions noted above.

In striking contrast to the calix[8]arene species, however, those obtained with Eu(III) and *p*-t-Bu-calix[9]arene are very dependent on the solvent used for synthesis. Thus, from acetone, a much simpler species, though still one with the lanthanide ions sandwiched between two calixarenes, can be crystallised, its formulation being [{Eu(*p*-t-Bu-calix[9]arene-3H)(dmso)$_2$}$_2$]·14Me$_2$CO·H$_2$O (**4**). The binuclear unit is some-

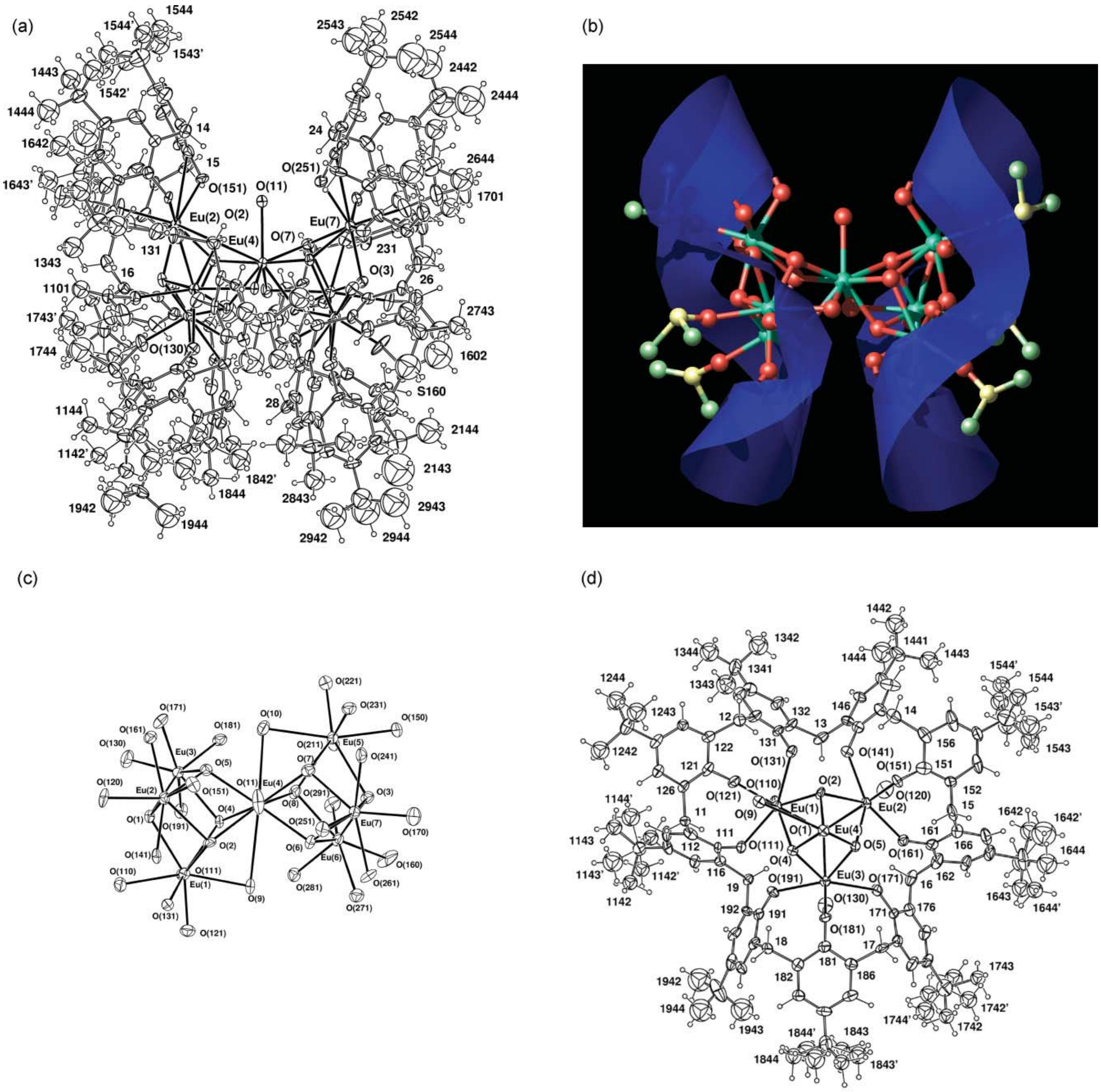

Fig. 3 (a) Projection of the $[(HO)_9(H_2O)Eu_7(calix[9]arene\text{-}6H)_2(dmso)_6]$ aggregate of **3**, normal to the central Eu(4)–O(11) line, (b) stylised representation in the same projection, (c) the molecular core, and (d) ligand 1 and its associated cubanoid cluster (the counterpart projection for ligand 2 is similar).

what like that found in the calix[8]arene complexes, though with the bridging being exclusively by two phenoxide oxygen atoms from separate calixarene entities and all the coordinated dmso molecules being in an inclusion environment and unidentate (Table 6, Fig. 4). The number of coordinated ligand oxygens (three adjacent) is fewer about each metal and from each ligand, perhaps concomitant with the (presumedly) greater degree of protonation of each ligand. The metal environment is thus six-coordinate, the two coordinated dmso solvents making up the totality of the array, which is well-removed from any ideal (*e.g.* octahedral or trigonal prismatic) symmetry. One half of the dimer, now centrosymmetric, comprises the asymmetric unit of the structure. Pairing of the phenoxide oxygens, as given in Table 7, is suggestive of the location of five phenolic hydrogen atoms, confirmed by refinement, on O(41,51,61,81,91), the only other short O(ligand) ··· O contact O(71) ··· O(90) (x, y + 1, z) 2.753(5) Å having a refinable hydrogen in association with O(71). Eu ··· Eu in **4** is longer than in **1**, in keeping with the absence of a third bridging oxygen.

Obviously, the prospects for the use of larger calixarenes as 'cluster keepers'[26] appear intriguing though it is clearly still difficult to define factors which would allow any certain prediction of the species likely to be obtained. For the lanthanides, phenoxide bridging is a common but not universal feature of calixarene complexes,[13] and oligomerisation *via* hydroxide bridging, whether arising from the presence of adventitious water or by its deliberate addition, is not a dominant factor, since it does not occur with all calixarenes and can be avoided by a simple change of solvent without particular effort to avoid traces of water in that solvent.

Table 4 The dimensions of the europium environments of **3**[a]

(a) Eu(4)	*r*/Å	O(2)	O(7)	O(4)	O(8)	O(5)	O(6)	O(9)	O(10)
O(11)	2.52(2)	71.4(5)	69.9(5)	139.7(5)	141.8(5)	85.5(6)	88.7(6)	111.5(6)	108.2(6)
O(2)	2.44(1)		141.2(5)	70.3(5)	144.9(5)	71.3(5)	105.2(5)	60.0(4)	133.7(4)
O(7)	2.38(1)			148.0(5)	72.6(5)	109.0(5)	70.5(5)	133.9(4)	64.4(5)
O(4)	2.43(1)				78.3(5)	70.7(4)	113.0(5)	57.5(4)	89.8(4)
O(8)	2.37(1)					113.0(5)	72.8(5)	90.1(4)	59.2(4)
O(5)	2.36(1)						174.0(5)	117.1(4)	62.7(4)
O(6)	2.36(1)							63.5(4)	121.0(4)
O(9)	3.20(2)								140.3(4)
O(10)	3.07(2)								

(b) (i) Eu(1)	*r*/Å	O(1)	O(2)	O(4)	O(9)	O(111)	O(121)	O(131)
O(110)	2.45(1)	70.2(5)	125.4(4)	126.9(5)	158.1(5)	80.6(5)	82.2(5)	78.9(5)
O(1)	2.52(1)		71.3(4)	69.8(4)	131.5(5)	98.1(5)	152.3(5)	98.0(4)
O(2)	2.41(2)			70.2(4)	72.4(4)	142.2(5)	127.7(6)	69.8(5)
O(4)	2.47(1)				68.3(5)	72.1(5)	132.2(5)	140.0(5)
O(9)	2.50(1)					91.4(5)	76.2(5)	98.6(5)
O(111)	2.43(2)						77.9(6)	147.8(5)
O(121)	2.17(2)							74.8(5)
O(131)	2.51(2)							

(b) (ii) Eu(5)	*r*/Å	O(3)	O(7)	O(8)	O(10)	O(211)	O(221)	O(231)
O(150)	2.44(2)	68.9(5)	122.7(6)	126.6(5)	163.4(6)	81.5(6)	88.1(6)	80.2(6)
O(3)	2.60(1)		68.8(4)	69.1(4)	127.4(5)	94.8(5)	157.0(5)	96.7(5)
O(7)	2.46(2)			68.0(5)	71.4(5)	138.6(5)	127.2(5)	68.4(5)
O(8)	2.55(2)				64.7(5)	70.6(5)	129.6(5)	136.3(5)
O(10)	2.61(1)					92.8(5)	75.6(5)	99.3(5)
O(211)	2.45(1)						82.0(5)	153.1(5)
O(221)	2.11(2)							77.9(5)
O(231)	2.48(2)							

(c) (i) Eu(2)	*r*/Å	O(1)	O(2)	O(5)	O(141)	O(151)	O(161)
O(120)	2.34(2)	92.1(6)	138.1(6)	142.2(6)	76.7(6)	104.2(6)	78.9(6)
O(1)	2.44(1)		71.5(5)	71.9(5)	98.1(5)	163.6(5)	97.6(5)
O(2)	2.48(1)			69.9(5)	68.3(4)	94.4(5)	140.0(5)
O(5)	2.41(1)				138.0(4)	95.8(5)	70.1(5)
O(141)	2.42(2)					83.8(6)	151.3(4)
O(151)	2.19(1)						87.9(6)
O(161)	2.34(2)						

(c) (ii) Eu(7)	*r*/Å	O(3)	O(7)	O(6)	O(241)	O(251)	O(261)
O(170)	2.32(2)	97.2(6)	144.4(7)	142.4(6)	79.4(6)	103.2(7)	75.8(6)
O(3)	2.39(1)		72.9(4)	72.4(5)	102.3(5)	159.0(5)	95.9(5)
O(7)	2.44(1)			68.4(5)	70.0(5)	92.8(5)	138.0(5)
O(6)	2.42(1)				137.7(5)	88.1(5)	69.6(5)
O(241)	2.39(2)					86.5(6)	150.8(5)
O(251)	2.27(1)						84.4(6)
O(261)	2.44(1)						

(d) (i) Eu(3)	*r*/Å	O(1)	O(4)	O(5)	O(171)	O(181)	O(191)
O(130)	2.25(2)	94.2(6)	140.3(6)	142.2(5)	79.7(6)	105.5(7)	77.5(6)
O(1)	2.44(2)		72.2(4)	70.7(5)	97.7(5)	160.3(5)	95.3(5)
O(4)	2.41(1)			69.2(4)	137.8(5)	91.3(5)	67.4(5)
O(5)	2.47(1)				68.8(5)	93.7(5)	136.6(5)
O(171)	2.32(1)					87.3(6)	154.5(5)
O(181)	2.18(1)						87.9(5)
O(191)	2.36(1)						

Table 4 (*Contd.*)

(d) (ii) Eu(6)	r/Å	O(3)	O(8)	O(6)	O(271)	O(281)	O(291)
O(160)	2.29(2)	97.2(7)	146.5(6)	140.0(6)	74.9(6)	102.2(7)	80.5(6)
O(3)	2.39(1)		75.1(5)	70.1(5)	97.8(5)	160.3(4)	99.7(6)
O(8)	2.41(1)			68.8(5)	137.9(5)	90.2(5)	69.1(5)
O(6)	2.55(1)				69.8(4)	92.6(5)	137.9(5)
O(271)	2.49(2)					84.2(5)	151.3(5)
O(281)	2.26(1)						86.7(6)

[a] Eu(4) ··· Eu(1,2,3,5,7,6) 3.909(2), 3.876(3), 3.882(3), 3.904(3), 3.889(2), 3.890(3) Å; Eu(1) ··· Eu(2,3) 3.927(3), 3.929(4) Å; Eu(2) ··· Eu(3) 3.888(2) Å; Eu(5) ··· Eu(7,6) 3.939(3), 3.925(4) Å; Eu(6) ··· Eu(7) 3.901(2) Å; O(111) ··· O(121) 2.90(2), O(121) ··· O(131) 2.87(2), O(131) ··· O(141) 2.44(2), O(161) ··· O(171) 2.47(2), O(191) ··· O(111) 2.42(2); O(211) ··· O(221) 3.00(2), O(291) ··· O(211) 2.34(2), O(261) ··· O(271) 2.51(2), O(231) ··· O(241) 2.44(2) Å; O(11) ··· O(151,251) 2.67(2), 2.73(2), O(9) ··· O(121,281) 2.89(2), 2.66(2); O(10) ··· O(221,181) 2.93(2), 2.58(2); O(2) ··· O(131,141) 2.81(2), 2.75(2); O(7) ··· O(231,241) 2.78(2), 2.77(2); O(4) ··· O(111,191) 2.88(2), 2.64(2); O(8) ··· O(211,291) 2.89(2), 2.69(2); O(5) ··· O(161,171) 2.71(2), 2.73(2); O(6) ··· O(261,271) 2.78(2), 2.89(2) Å. Eu(1)–O(1)–Eu(2) 104.8(5), Eu(1)–O(1)–Eu(3) 104.8(5), Eu(2)–O(1)–Eu(3) 105.8(6), Eu(1)–O(2)–Eu(2) 107.0(5), Eu(1)–O(2)–Eu(4) 107.5(6), Eu(2)–O(2)–Eu(4) 104.0(5), Eu(5)–O(3)–Eu(6) 103.6(5), Eu(5)–O(3)–Eu(7) 104.1(0), Eu(6)–O(3)–Eu(7) 109.4(6), Eu(1)–O(4)–Eu(3) 107.4(4), Eu(1)–O(4)–Eu(4) 106.0(5), Eu(3)–O(4)–Eu(4) 106.9(5), Eu(2)–O(5)–Eu(3) 105.7(5), Eu(2)–O(5)–Eu(4) 108.7(6), Eu(3)–O(5)–Eu(4) 106.9(5), Eu(4)–O(6)–Eu(6) 104.6(5), Eu(4)–O(6)–Eu(7) 108.8(6), Eu(6)–O(6)–Eu(7) 103.2(5), Eu(4)–O(7)–Eu(5) 107.5(6), Eu(4)–O(7)–Eu(7) 107.8(6), Eu(5)–O(7)–Eu(7) 107.0(5), Eu(4)–O(8)–Eu(5) 105.1(5), Eu(4)–O(8)–Eu(6) 109.2(6), Eu(5)–O(8)–Eu(6) 104.7(5), Eu(1)–O(9)–Eu(4) 85.7(4), Eu(4)–O(10)–Eu(5) 86.3(4), Eu(1)–O(111)–C(111) 129(1), Eu(1)–O(121)–C(121) 153(1), Eu(1)–O(131)–C(131) 129(1), Eu(2)–O(141)–C(141) 133(1), Eu(2)–O(151)–C(151) 125(1), Eu(2)–O(161)–C(161) 141(1), Eu(3)–O(171)–C(171) 134(1), Eu(3)–O(181)–C(181) 126(1), Eu(3)–O(191)–C(191) 132(1), Eu(5)–O(211)–C(211) 126(1), Eu(5)–O(221)–C(221) 158(1), Eu(5)–O(231)–C(231) 125(1), Eu(7)–O(241)–C(241) 138(1), Eu(7)–O(251)–C(251) 122(1), Eu(7)–O(261)–C(261) 141(1), Eu(6)–O(271)–C(271) 133(1), Eu(6)–O(281)–C(281) 122(1), Eu(6)–O(291)–C(291) 135(1)°.

Table 5 Ligand plane parameters for **3**

(a) Interplanar dihedral angles/°

	Ligand 1				Ligand 2			
Plane	1	2	3	4	1	2	3	4
9	78.9(8)	90.0(9)	80.2(10)	22.6(9)	80.4(9)	87.3(10)	88.8(9)	13.9(9)
1		64.5(9)	48.7(9)	81.3(9)		63.2(1)	51.8(9)	89.4(9)
2			66.8(9)	88.8(9)			65.9(9)	83.4(9)
3				78.6(10)				75.0(9)
Plane	4	5	6	7	4	5	6	7
3	78.6(10)	53.1(10)	68.6(10)	30.2(9)	75.0(9)	54.0(9)	69.5(9)	33.4(8)
4		72.4(10)	66.9(9)	76.9(9)		67.3(9)	71.6(9)	78.4(9)
5			66.5(10)	47.5(9)			64.0(10)	49.5(9)
6				85.5(10)				83.3(9)
Plane	7	8	9	1	7	8	9	1
6	85.5(10)	48.5(9)	82.0(9)	25.6(9)	83.3(9)	48.4(10)	77.9(10)	28.4(9)
7		67.1(9)	59.8(9)	70.3(9)		61.0(9)	66.2(9)	71.3(9)
8			71.6(9)	56.7(9)			74.5(10)	57.3(9)
9				78.9(8)				80.4(9)

(b) Out-of-plane deviations of the europium atoms, δ_{Eu}/Å

	Ligand 1				Ligand 2			
Plane	Eu(1)	Eu(2)	Eu(3)	Eu(4)		Eu(5)	Eu(7)	Eu(6)
1	1.85(4)			0.30(8),	0.30(8)	2.00(4)		
2	0.87(5)			4.64(6),	4.48(7)	0.74(5)		
3	2.07(5)			0.53(9),	0.65(9)	2.02(5)		
4		1.89(5)		0.12(9),	−0.58(9)		1.78(9)	
5		1.84(5)		−0.61(9),	−0.94(8)		2.33(9)	
6		1.40(5)		−1.08(9),	−0.40(8)		0.66(6)	
7			1.75(4)	−0.34(7),	0.91(9)			1.24(7)
8			1.70(4)	−1.04(7),	−0.98(8)			2.33(9)
9			1.92(5)	0.13(8),	−0.35(8)			1.73(5)

Table 6 The dimensions of the europium environments of **4**[a]

Atom	r/Å	O(21)	O(31)	O(10)	O(20)	O(21′)
O(11)	2.277(3)	90.91(9)	161.26(9)	96.34(9)	81.3(1)	99.28(9)
O(21)	2.307(3)		87.71(9)	155.59(9)	103.4(1)	68.32(9)
O(31)	2.27(3)			92.54(9)	80.8(1)	97.56(9)
O(10)	2.302(3)				100.8(1)	87.48(9)
O(20)	2.321(3)					171.6(1)
O(21′)	2.313(3)					

[a] Primed atoms are inversion related. Eu ··· Eu′ 3.8223(7), O(21) ··· O(21′) 2.594(3) Eu–O(21)–Eu′ 111.7(1)°. O(31) ··· O(41′) 2.591(4), O(41) ··· O(51) 2.823(4), O(61) ··· O(71) 2.799(4), O(81) ··· O(91) 2.804(4), O(91) ··· O(11) 2.638(4) Å. Eu deviates from C_6 phenoxide planes 1,2,3,2′ by 1.918(4), 1.826(6), 1.692(7), −1.990(6) Å.

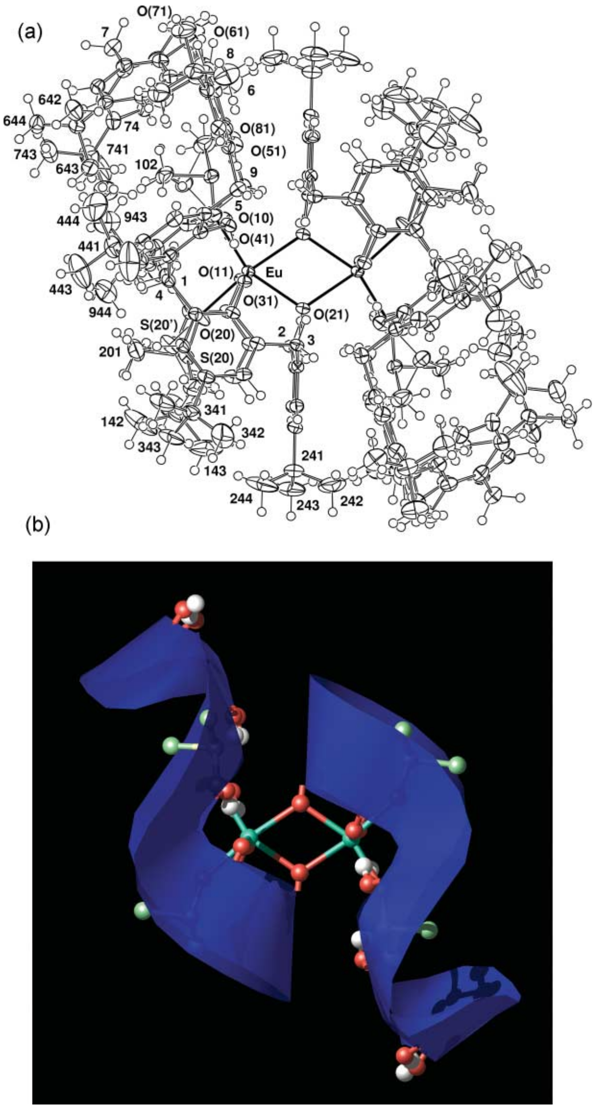

Fig. 4 Projection of the $[(Eu_2)(calix[9]arene\text{-}3H)(dmso)_4]$ aggregate of **4**, normal to the Eu{μ-O(phenoxide)$_2$}Eu 'plane', and stylised representation in the same projection.

References

1 R. Y. Wang, D. T. Song and S. M. Wang, *Chem. Commun.*, 2002, 368.
2 R. Y. Wang, H. D. Selby, H. Liu, M. D. Carducci, T. Z. Jin, Z. P. Zheng, J. W. Anthis and R. J. Staples, *Inorg. Chem.*, 2002, **41**, 278.
3 G. Westin, M. Moustiakimov and M. Kritikos, *Inorg. Chem.*, 2002, **41**, 3249.
4 R. C. Mehrotra and A. Singh, *Prog. Inorg. Chem.*, 1997, **46**, 239.
5 W. van der Sluys and A. P. Sattelberger, *Chem. Rev.*, 1990, **90**, 1027.
6 S. Daniele, L. G. Hubert-Pfalzgraf, P. B. Hitchcock and M. F. Lappert, *Inorg. Chem. Commun.*, 2000, **3**, 218.
7 A. Bilyk, A. K. Hall, J. M. Harrowfield, M. W. Hosseini, B. W. Skelton and A. H. White, *Aust. J. Chem.*, 2000, **53**, 895.
8 M. P. Wilkerson, C. J. Burns, D. E. Morris, R. T. Paine and B. L. Scott, *Inorg. Chem.*, 2002, **41**, 3110.
9 P. Thuery, M. Nierlich, J. Vicens and B. Masci, *J. Chem. Soc., Dalton Trans.*, 2001, 3410.
10 C. D. Gutsche, in *Calixarenes 2001*, ed. Z. Asfari, V. Böhmer, J. M. Harrowfield and J. Vicens, Kluwer Academic, Dordrecht, 2001, p. 1.
11 S. Steyer, C. Jeunesse, D. Armspach, D. Matt and J. M. Harrowfield, in *Calixarenes 2001*, ed. Z. Asfari, V. Böhmer, J. M. Harrowfield and J. Vicens, Kluwer Academic, Dordrecht, 2001, p. 536.
12 C. Floriani and R. Floriani-Moro, in *Calixarenes 2001*, ed. Z. Asfari, V. Böhmer, J. M. Harrowfield and J. Vicens, Kluwer Academic, Dordrecht, 2001, p. 536.
13 P. Thuéry, M. Nierlich, J. M. Harrowfield and M. I. Ogden, in *Calixarenes 2001*, ed. Z. Asfari, V. Böhmer, J. M. Harrowfield and J. Vicens, Kluwer Academic, Dordrecht, 2001, p. 561.
14 V. C. Gibson, C. Redshaw and M. R. J. Elsegood, *J. Chem. Soc., Dalton Trans.*, 2001, 767.
15 V. C. Gibson, C. Redshaw and M. R. J. Elsegood, *Chem. Commun.*, 2002, 1200.
16 D. R. Stewart and C. D. Gutsche, *J. Am. Chem. Soc.*, 1999, **121**, 4136.
17 C. D. Gutsche and L.-G. Lin, *Tetrahedron*, 1986, **42**, 1633.
18 S. R. Hall, D. J. du Boulay and R. Olthof-Hazekamp, The Xtal 3.7 System, University of Western Australia, 2001.
19 S. Fleming, *GDis*, 2003; http://gdis.seul.org.
20 J. M. Harrowfield, M. I. Ogden and A. H. White, *Aust. J. Chem.*, 1991, **44**, 1237.
21 J. C. G. Bunzli, F. Ihringer, P. Dumy, C. Sager and R. D. Rogers, *J. Chem. Soc., Dalton Trans.*, 1998, 497.
22 L. M. Engelhardt, B. M. Furphy, J. M. Harrowfield, D. L. Kepert, A. H. White and F. R. Wilner, *Aust. J. Chem.*, 1988, **41**, 1465.
23 G. D. Andreetti, F. Ugozzoli, Y. Nakamoto and S. I. Ishida, *J. Inclusion Phenom. Mol. Recognit. Chem.*, 1991, **10**, 241.
24 M. Perrin, S. Lecocq and Z. Asfari, *C. R. Acad. Sci. Paris*, 1990, **310**, 515.
25 P. Thuéry, M. Nierlich, B. Souley, Z. Asfari and J. Vicens, *J. Chem. Soc., Dalton Trans.*, 1999, 2589.
26 J. M. Harrowfield, *Gazz. Chim. Ital.*, 1997, **127**, 663.