Lanthanide Ion Complexes of the Calixarenes. Part 4. Double Inclusion by *p*-t-Butylcalix[4]arene (H_4L). Crystal Structures of $[Eu_2(HL)_2(dmf)_4]\cdot7dmf$ (dmf = dimethylformamide) and $H_4L\cdot dmso$ (dmso = dimethyl sulphoxide) *

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Reaction of europium(III) with *p*-t-butylcalix[4]arene (H_4L) under the same conditions as used for reactions with larger calixarenes yields a yellow crystalline complex structurally characterised as $[Eu_2(HL)_2(dmf)_4]\cdot7dmf$, where dmf = *N*,*N*-dimethylformamide. The crystals are monoclinic, space group *C*2/*c* with a = 35.03(2), b = 16.12(2), c = 23.38(2) Å, β = 98.40(4)°, and Z = 4 dimers; the structure was refined to R = 0.096 for 9 248 'observed' reflections. The complex is binuclear and centrosymmetric with the europium atoms bridged by one phenoxide group from each calixarene ligand and each europium being bound to two unidentate dmf ligands as well as the three other phenolic oxygens of a calixarene ligand. The calixarene ligands adopt a distorted 'cone' conformation in which a dmf molecule is included but in such a manner that there is clearly no co-ordinate interaction with europium. The same type of inclusion is found in the dimethyl sulphoxide (dmso) adduct of *p*-t-butylcalix[4]arene, $H_4L\cdot dmso$, this compound having been used in ligand purification. It forms large tetragonal crystals, space group *P*4/*n*, a = 12.811(4), c = 13.082(4) Å; R = 0.11 for 895 'observed' reflections.

The group of molecules termed 'cyclophanes' are an important group of receptor species capable of forming stable inclusion complexes with both charged and neutral molecules.[1] The particular subgroup of cyclophanes termed the 'calixarenes' has been widely studied since the recent clarification of the phenol/formaldehyde condensation reaction involved in calixarene syntheses.[2] The name 'calixarene' derives from the perceived resemblance of the preferred structure of the smallest calix[4]arene to that of a calyx, though in fact *X*-ray crystallographic investigations have shown that this is the only calixarene which commonly adopts a truly 'cup-like' form.[2] The largest calixarenes, whether free or complexed, appear preferentially to adopt a conformation closer to a 'ruffled disc', though we have shown that *p*-t-butylcalix[6]arene can take the form of a somewhat flattened cup.[3] Such conformational variations are expected to influence the metal-ion co-ordinating abilities of the calixarenes and the properties of their complexes, a large flat ring allowing the calixarene to envelop a metal ion in the manner usually observed for polyamine macrocyclic ligand complexes,[4] while a rigid cup-like ligand with donor groups directed out of the macrocyclic cavity could well be expected to endow its complexes with a diminished lability as has been well established for complexes of 1,3,5-triaminocyclohexane.[5]

p-t-Butylcalix[4]arene (H_4L) is known to form complexes with transition-metal ions in which its cup shape is preserved and, in some cases, include a solvent molecule within the cup.[6] The generation of a base to the cup by metal-ion co-ordination is analogous to the building of a 'floor' into cyclodextrins[7] and might similarly be expected to modify the inclusion tendencies of the receptor. Indeed, if co-ordination to the metal ion through the cup were to be possible, considerable selectivity in inclusion complex formation might arise. As part of our investigations of co-ordination of calixarenes to the lanthanides, we have found that the europium(III) complex of *p*-t-butylcalix[4]arene does contain the ligand in its 'cup' conformation and indeed does form an inclusion complex with dimethylformamide (dmf). We report herein the crystallographic characterisation of this compound, $[Eu_2(HL)_2(dmf)_4]\cdot7dmf$, which may be regarded as a 'double' inclusion complex in the sense that both europium(III) and dimethylformamide are associated with the ligand. To provide an indication of the influence of the europium(III) ion we include comparison with the structure of the simple inclusion complex formed between dimethyl sulphoxide (dmso) and unionised *p*-t-butycalix[4]arene, $H_4L\cdot dmso$.

Experimental

Synthesis of $[Eu_2(HL)_2(dmf)_4]\cdot7dmf$.—A slurry of *p*-t-butylcalix[4]arene[8] (0.65 g) in dimethylformamide (12 cm^3) was heated to 80 °C, under an inert atmosphere, and triethylamine (0.40 g) added dropwise until a clear colourless solution formed. The complex $[Eu(NO_3)_3(dmso)_4]$ (0.65 g) was quickly dissolved in this mixture, to give a clear orange solution, which on slow cooling to room temperature deposited yellow-orange crystals (0.35 g). For *X*-ray diffraction studies, crystals were sealed in capillaries wet with the supernatant solution. Crystals collected in the laboratory atmosphere, washed with dmf, and dried by vacuum desiccation slowly effloresced and became opaque. Microanalyses were consistent with some loss of dmf, and introduction of water, relative to the stoicheiometry implied by the structure determination {Found: C, 61.0; H, 7.5; N, 2.7 $[Eu_2(HL)_2(dmf)_4]\cdot7dmf$ requires C, 60.5; H, 7.7; N, 6.4 $[Eu_2(HL)_2(dmf)_4]\cdot5H_2O$ requires C, 60.7; H, 7.3; N, 2.8%}.

Structure Determinations.—(1) *The europium complex.* The diffraction data, although relatively extensive for a compound of this type, were weak, presumably largely in consequence of the large cell, and with the high backgrounds typical of use of a capillary; a hemisphere was measured to $2\theta_{max.}$ 50° and merged to give a unique set [R (all data) 0.11], 11 478 (= N)

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* *p*-t-Butylcalix[4]arene = 4,8,11,25-tetra-t-butyl[1.1.1.1]metacyclophane-7,14,21,28-tetraol.

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1989, Issue 1, pp. xvii—xx.

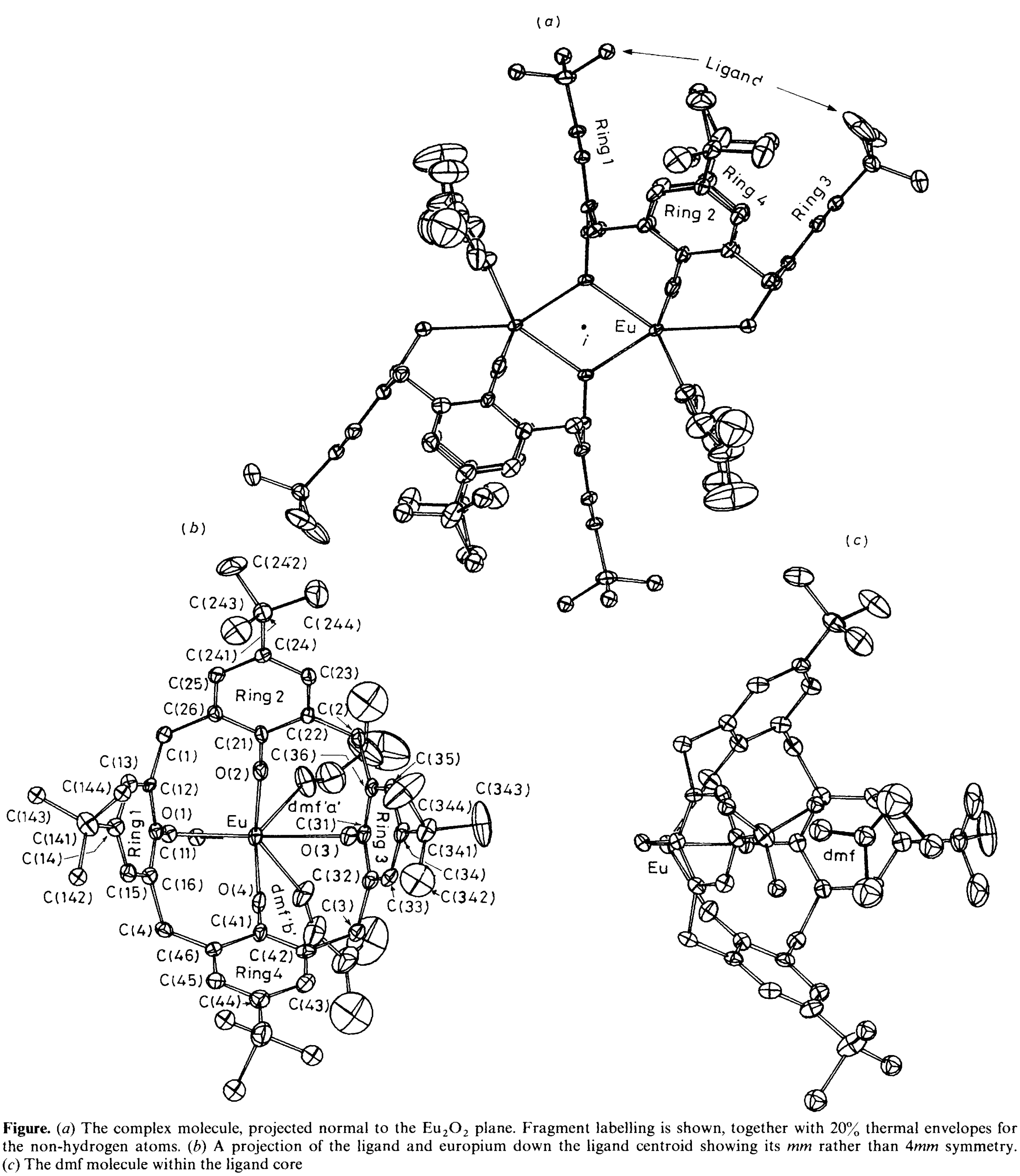

Figure. (*a*) The complex molecule, projected normal to the Eu_2O_2 plane. Fragment labelling is shown, together with 20% thermal envelopes for the non-hydrogen atoms. (*b*) A projection of the ligand and europium down the ligand centroid showing its *mm* rather than 4*mm* symmetry. (*c*) The dmf molecule within the ligand core

independent reflections, N_o = 9 248 'observed' at the $I > 2\sigma(I)$ level being used in the 9 × 9 block-diagonal least-squares refinement without absorption correction. Anisotropic thermal parameters were refined for all non-hydrogen atoms (except those of the disordered t-butyl and dmf groups); hydrogen atoms were included located at estimated values. Conventional R, R' at convergence were 0.096, 0.101 [statistical weights derived from $\sigma^2(I) = \sigma^2(I_{diff}) + 0.000n_w\sigma^4(I_{diff})(n_w = 8)$]. Neutral atom complex scattering factors were employed;[9] computation used the XTAL 2.4 program system[10] implemented by S. R. Hall.

Crystal data. $C_{100}H_{134}Eu_2N_2O_{12}\cdot 7C_3H_7NO$, M = 2 399.8, monoclinic, space group $C2/c$ (C_{2h}^6, no. 15), a = 35.03(2), b = 16.12(2), c = 23.38(2) Å, β = 98.40(4)°, U = 13 060 Å^3, D_c (Z = 4 dimers) = 1.22 g cm^{-3}, $F(000)$ = 5 056, monochromatic Mo-K_α radiation, λ = 0.710 69 Å, μ_{Mo} = 9.4 cm^{-1}; specimen, cuboid, *ca.* 0.5 mm (capillary). Enraf-Nonius CAD-4 diffractometer.

Table 1. Non-hydrogen atom co-ordinates of the europium complex

Atom	*x*	*y*	*z*
Eu	0.262 31(1)	0.318 91(3)	0.436 43(2)
O(1)	0.287 0(1)	0.244 6(3)	0.522 6(3)
C(11)	0.325 4(2)	0.241 5(5)	0.544 5(4)
C(12)	0.342 1(2)	0.299 8(4)	0.584 6(4)
C(13)	0.379 5(2)	0.287 4(5)	0.613 0(4)
C(14)	0.401 8(2)	0.220 1(5)	0.602 3(4)
C(141)	0.441 7(2)	0.203 6(6)	0.639 5(5)
C(142)*	0.461 5(5)	0.127(1)	0.618 7(9)
C(143)*	0.434 3(5)	0.193(1)	0.702 9(9)
C(144)*	0.468 1(5)	0.281(1)	0.634 2(8)
C(145)*	0.472 6(9)	0.178(2)	0.595(2)
C(146)*	0.442(1)	0.121(2)	0.661(2)
C(147)*	0.458 4(9)	0.279(2)	0.665(2)
C(15)	0.386 2(2)	0.168 7(5)	0.557 5(4)
C(16)	0.349 2(2)	0.179 2(5)	0.527 2(4)
C(1)	0.320 8(2)	0.378 0(5)	0.599 0(4)
C(2)	0.295 3(2)	0.416 3(4)	0.482 5(3)
C(21)	0.319 5(2)	0.469 0(5)	0.511 2(4)
C(22)	0.331 2(2)	0.539 8(5)	0.483 8(4)
C(23)	0.356 6(3)	0.595 5(5)	0.515 1(4)
C(24)	0.371 1(2)	0.583 5(5)	0.573 8(4)
C(241)	0.399 0(3)	0.644 6(6)	0.608 5(5)
C(242)	0.381 1(5)	0.674 3(9)	0.662 3(7)
C(243)	0.437 1(4)	0.601(1)	0.629 6(7)
C(244)	0.406 2(5)	0.720 4(9)	0.573 8(7)
C(25)	0.358 1(3)	0.512 1(5)	0.599 8(4)
C(26)	0.333 5(2)	0.455 4(5)	0.570 3(4)
C(2)	0.316 3(2)	0.554 3(5)	0.420 3(4)
O(3)	0.283 4(1)	0.409 8(4)	0.357 0(3)
C(31)	0.322 1(2)	0.431 6(5)	0.353 7(4)
C(32)	0.343 8(2)	0.379 7(5)	0.322 9(4)
C(33)	0.380 4(2)	0.406 4(6)	0.316 3(4)
C(34)	0.396 9(2)	0.480 2(6)	0.338 1(4)
C(341)	0.435 3(3)	0.512 2(7)	0.325 9(5)
C(342)	0.460 3(3)	0.441(1)	0.308 0(9)
C(343)	0.430 6(4)	0.571(1)	0.279 1(8)
C(344)	0.459 3(4)	0.547(1)	0.378 2(8)
C(35)	0.374 2(2)	0.525 5(5)	0.370 8(4)
C(36)	0.337 2(2)	0.503 3(5)	0.380 5(4)
C(3)	0.330 0(2)	0.295 2(6)	0.298 3(4)
O(4)	0.301 5(2)	0.239 6(4)	0.399 3(3)
C(41)	0.333 0(2)	0.204 9(5)	0.386 4(4)
C(42)	0.351 7(2)	0.141 8(5)	0.422 4(4)
C(43)	0.385 2(3)	0.106 2(6)	0.407 9(5)
C(44)	0.399 9(3)	0.125 0(6)	0.359 5(5)
C(441)	0.437 8(4)	0.849(8)	0.344 0(6)
C(442)*	0.422 1(6)	−0.018(1)	0.328(1)
C(443)*	0.470 0(6)	−0.075(1)	0.394(1)
C(444)*	0.447 4(6)	0.105(1)	0.287(1)
C(445)*	0.467(1)	0.151(2)	0.323(2)
C(446)*	0.435(1)	0.034(2)	0.309(2)
C(447)*	0.450 6(—)	0.479(—)	0.400 6(—)
C(45)	0.381 3(3)	0.186 5(6)	0.323 8(5)
C(46)	0.348 1(2)	0.225 4(5)	0.336 5(4)
C(4)	0.336 0(2)	0.119 4(5)	0.476 0(4)
dmf(a)			
O	0.214 9(2)	0.432 0(5)	0.415 4(4)
Cl	0.191 7(5)	0.458(1)	0.389 3(9)
N	0.173 6(3)	0.524 6(7)	0.371 6(7)
C2	0.139 8(7)	0.536(2)	0.347(2)
C3	0.190 6(8)	0.593(2)	0.405(1)
dmf(b)			
O	0.221 1(2)	0.280 9(5)	0.345 6(3)
Cl	0.221 1(5)	0.241(1)	0.310 9(6)
N	0.196 8(4)	0.228 8(8)	0.258 9(5)
C2	0.162 3(6)	0.270(2)	0.243(1)
C3*	0.212 1(9)	0.165(2)	0.222(2)
dmf(c)			
O(A)*	0.073(7)	0.793(1)	0.031(1)
O(B)*	−0.050(5)	0.853(1)	0.024(8)
C1(A)*	0.273(8)	0.837(2)	0.023(1)
C1(B)*	0.037(1)	0.917(3)	−0.007(2)
N*	0.592(2)	0.861 5(5)	0.170(4)
C2(A)*	0.623(6)	0.941(1)	−0.019(1)
C2(B)*	0.050(1)	0.781(2)	0.045(2)
C3(A)*	0.933(7)	0.823(1)	0.041(1)
C3(B)*	0.100 4(6)	0.863(1)	0.024(1)
dmf(d)			
O(A)*	0.152(2)	0.306(3)	0.086(3)
O(B)*	0.118 2(9)	0.412(2)	−0.004(2)
C1(A)*	0.111 5(—)	0.352 4(—)	0.541(—)
C1(B)*	0.135 2(—)	0.365 6(—)	0.462(—)
N*	0.823(4)	0.347 7(8)	0.412(7)
C2(A)*	0.792(—)	0.410 7(—)	−0.063(—)
C2(B)*	0.797(8)	0.273(2)	0.085(1)
C3(A)*	0.483(—)	0.311 2(—)	0.474(—)
C3(B)*	0.479(7)	0.376(2)	0.008(1)
dmf(e)			
O(A)*	0.245 8(5)	0.414(1)	0.243(1)
O(B)*	0.230 1(8)	0.514(2)	0.287(1)
C1(A)*	0.263 6(8)	0.426(2)	0.203(1)
C1(B)*	0.236(1)	0.460(2)	0.258(2)
N*	0.234 9(5)	0.472(1)	0.179 3(9)
C2*	0.234 5(9)	0.491(2)	0.119(1)
C3*	0.202(1)	0.498(3)	0.181(2)
dmf(f)			
O*	0.284(1)	0.772(3)	0.412(2)
C1*	0.275(1)	0.746(4)	0.466(3)
N*	0.256(2)	0.826(3)	0.477(3)
C2*	0.250 0(—)	0.750 0(—)	0.500 0(—)
C3*	0.230(1)	0.812(3)	0.421(2)

* Thermal parameter refinement isotropic on account of disorder [or high thermal motion: dmf(a,b)]

Table 2. Europium environment in $[Eu_2(HL)_2(dmf)_4]\cdot7dmf$: *r* is the europium–oxygen distance (Å); other entries in the matrix are the angles (°) subtended at the europium by the relevant atoms at the head of the row and column; φ is the associated Eu–O–C angle; O(1′) is related by inversion

Atom	*r*	φ	O(1′)	O(2)	O(3)	O(4)	O(a)	O(b)
O(1)	2.395(6)	123.2(5)	68.5(2)	81.0(2)	142.1(2)	82.3(2)	133.6(3)	133.9(2)
O(1′)	2.332(5)	125.2(6)		119.6(2)	149.3(2)	117.4(2)	83.6(2)	82.4(2)
O(2)	2.143(6)	172.3(6)			75.7(2)	108.0(2)	81.8(2)	145.1(3)
O(3)	2.558(6)	124.3(5)				77.2(2)	71.9(2)	73.4(2)
O(4)	2.150(7)	162.8(6)					144.1(3)	80.3(2)
O(a)	2.466(7)	150(1)						73.7(3)
O(b)	2.465(7)	140(1)						

Eu–O(1)–Eu′ is 111.5(2); Eu · · · Eu′ 3.906 7(7), O(1) · · · O(1′) 2.661(6) Å.

Atomic co-ordinates are given in Table 1, selected bond lengths and angles in Table 2.

(2) *The ligand dmso solvate*, H_4L·dmso. Data for this compound, crystallising in the familiar $P4/n$ array,[11] were perhaps more extensive than usual and provided a smaller proportion of 'observed' reflections in spite of the use of a very substantial specimen; the results suggest the core of the calixarene component of the structure to be firmly located in the crystal, but the dmso was disordered, and, further, may not be fully occupied. Refinement of site occupancies suggested a value of *ca.* 0.75 for the molecule. Thermal parameters of S and O were high and suggest an off-axis disposition, however.

Crystal data. $C_{46}H_{62}O_5S$, $M = 727.1$, tetragonal, space group $P4/n$ (C^3_{4h}, no. 85), $a = 12.811(4)$, $c = 13.082(4)$ Å, $U = 2\,147(1)$ Å^3, $D_c (Z = 2) = 1.12$ g cm^{-3}, $F(000) = 788$, $\mu_{Mo} = 1.2$ cm^{-1}; specimen 0.48 × 0.30 × 0.18 mm (capillary, no absorption correction), $2\theta_{max.} = 55°$, $N = 2\,372$, $N_o[I > 3\sigma(I)] = 895$, $R = 0.11$, $R' = 0.10$ ($n_w = 1$). Syntex $P2_1$ diffractometer. Atomic co-ordinates are given in Table 3.

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

Discussion

Despite the experimental problems described above, the results of the structure determination of the europium(III) derivative are well defined in respect of the metal complex component of the structure; the present determination is the first recorded for a lanthanide ion complex of a calix[4]arene ligand. The complex molecule has the stoicheiometry Eu(HL)(dmf)$_2$, with four additional dmf molecules of solvation with associated disorder, high thermal motion, and possibly partial occupancy. The form of the ligand is that of a cone, as recorded elsewhere[2,6,11] and herein for the free ligand, variously solvated. The structure of the complex, however, is a dimer (Figure), with an Eu_2O_2 four-membered ring core; the asymmetric unit of the structure is the monomer unit Eu(HL)(dmf)$_2$, which lies close to a crystallographic inversion centre generating a dimer conforming to $\bar{1}$ symmetry, and associated lattice solvent molecules. The Eu_2O_2 core is necessarily an exact plane; this plane may be further extended in describing the rest of the molecule which conforms surprisingly well to (non-crystallographic) *m* symmetry (Figure). The bridging oxygen atoms are derived from the calix[4]arene ligands rather than dmf units {*cf.* the binuclear complex of europium(III) with the calix[8]arene analogue, also obtained from dmf and in which the pair of europium atoms are bridged by both calix[8]arene and dmf oxygen atoms[12]}. Oxygen O(3) of the calix[4]arene is also quasi-coplanar with the Eu_2O_2 plane, with oxygens O(2,3) lying astride that plane, as are the dmf a,b oxygen atoms, so that the europium atoms are seven-co-ordinate, with quasi-*m* symmetry. Although the calix[4]arene conformation is essentially 'conical', the idealized 4*mm* symmetry of the free ligand is perturbed and the core 'squashed', with an 'elliptical' rather than 'circular' cross-section, idealised to *mm* rather than 4*mm* (Figure). For oxygens O(2,4), Eu–O are very short, *ca.* 2.15 Å, with very obtuse Eu–O–C angles [172.3(6) and 162.8(6)°]. The distances Eu–O(1,1′;3) are longer and with more acute Eu–O–C angles, suggesting that the remaining phenolic hydrogen associated with the ligand is carried by O(3); Eu–O(3) [2.558(6) Å], in fact, is outstandingly long. These features are reflected in the ligand torsion angles, symmetrical to either side of each C(*n*) and largest for C(1,3), and in the deviations of the europium atoms from the phenyl ring planes (Table 4). Remarkably, one of the solvent dmf molecules (c) is located (disordered) within the calyx as is the case with many solvates (*e.g.* the present dmso adduct) of this ligand.[2] Because of the large volume of the co-ordination sphere occupied by the calix[4]arene ligand, the system does not lend itself to easy description in terms of those common seven-co-ordinate environments which contain a mirror plane.

Table 3. Non-hydrogen atom co-ordinates of H_4L·dmso

Atom	*x*	*y*	*z*
C(1)	0.069 0(7)	0.341 5(7)	0.039 8(7)
O(1)	0.119 4(5)	0.314 0(5)	−0.049 6(4)
C(2)	0.082 9(7)	0.440 5(7)	0.083 7(7)
C(21)	0.162 1(7)	0.517 1(6)	0.040 2(6)
C(3)	0.027 0(7)	0.467 7(7)	0.171 5(7)
C(4)	−0.045 0(7)	0.400 4(7)	0.215 9(7)
C(41)	−0.108 9(9)	0.431 3(9)	0.310 3(9)
C(42)	−0.082 8(14)	0.534 1(11)	0.351 1(12)
C(43)	−0.098 1(13)	0.349 5(12)	0.391 5(10)
C(44)	−0.222 7(11)	0.432 8(13)	0.279 9(11)
C(5)	−0.056 8(9)	0.301 5(7)	0.171 5(7)
C(6)	−0.001 4(6)	0.272 2(7)	0.085 2(7)
Solvent (populations: O, S, 0.75; C, 0.375)			
O	$\frac{1}{4}$	$\frac{1}{4}$	0.248(2)
S	$\frac{1}{4}$	$\frac{1}{4}$	0.362(2)
C	0.156(4)	0.227(4)	0.443(3)

In the europium(III)–calix[8]arene dimer an EuO_2Eu core derived from the containment of a pair of Eu atoms within the macrocycle and bridged by an opposed pair of oxygen atoms is found; unlike the present array, that core is bent at the O ··· O line, with a further dmf oxygen atom also bridging the two europium atoms (so that the core is EuO_3Eu effectively) and lifting the europium co-ordination number to eight. In that complex, Eu ··· Eu is 3.692(1) Å; in the present complex it is 3.906 7(7) Å.

Both the dimethyl sulphoxide adduct of the free ligand and the dimethylformamide adduct of the europium(III) complex of *p*-t-butylcalix[4]arene contain solvent bound within the ligand cavity in the manner classified as 'type 1' inclusion by Andreetti and co-workers.[11] In the complex ion adduct the orientation of the solvent is such as to preclude any weak ligation by the europium as the cause of the binding, and in both systems orientational disorder of the included solvent molecules renders, as for other systems,[11] analysis of the nature of their interactions with the calixarene periphery highly speculative. Nonetheless,

Table 4. Macrocycle torsion angles (°) (Eu complex): θ is the dihedral angle of the phenyl ring plane *n* to the (exact) Eu_2O_2 plane, δ the deviation of Eu from plane *n*

n	C(*n*1)–C(*n*2)–C(*n*)–C(*n* + 16)	C(*n*1)–C(*n*6)–C(*n* − 1)–C(*n* − 12)	θ	δ
1	−102(1)	103(1)	89.4(2)	1.51
2	−79(1)	78(1)	45.8(3)	0.23
3	−102(1)	102(1)	90.0(3)	1.83
4	−82(1)	80(1)	39.7(3)	0.59

For the dmso solvated ligand the C–C–C–C torsion angles are ±87(1)°.

comparison with the structures of europium(III) complexes of both *p*-t-butylcalix-[6]- and -[8]-arene[3,12] (where unco-ordinated solvent inclusion is not observed) confirms the obvious assumption that the close proximity of calixarene substituents induced by the cone conformation of calix[4]arene is important for solvent inclusion and hence suggests that subtle control of inclusion may well be possible by modification of the cone conformation through metal co-ordination.

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