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Partially reduced calix[4]arenes: structures and co-ordination chemistry

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Reduction of the carbonyl group of tetrahydrocalix[4]arene by $NaBH_4$ occurred readily to provide a mixture of two diastereomeric cyclohexanol derivatives in which the predominant (95%) species H_4L has the alcohol-carbon hydrogen atom directed towards the 'upper rim' but the hydrogen atoms of the adjacent carbon atoms directed away, while the minor species H_4L' has all three of these hydrogen atoms directed towards the upper rim, as shown by crystal structure determinations. Compound H_4L is isomorphous with its fully aromatic parent, like it being disposed about a crystallographic mirror plane with non-included solvent. In both H_4L and H_4L', concerted intramolecular hydrogen bonding between the hydroxyl groups, phenolic and aliphatic, appears to be an important aspect of their structure. While in both fusion of the aliphatic ring into the macrocycle takes place through equatorial sites, with the hydroxyl substituent on the intervening carbon atom axial with respect to the macrocycle, the dispositions of the ring axes lie normal and parallel, respectively, to the macrocycle axes. Reaction between H_4L and anhydrous europium(III) trifluoromethanesulfonate in dimethylformamide (dmf) in the presence of triethylamine provided yellow crystals of the neutral, binuclear complex $[Eu_2(HL)_2(dmf)_4]\cdot 4dmf$.

The remarkable utility of calixarenes as co-ordinating agents[1–3] continues to be developed[4] and we have recently shown[5] that rhodium-catalysed partial hydrogenation of calix[4]arene defines a mode of ligand synthesis which has the potential to create an extensive range of new systems. An obvious extension of the hydrogenation, which converts a calixarene phenolic ring into a cyclohexanone, is completion of the reduction of this ring to its cyclohexanol form. A feature of interest emerging from this is that the macrocycles generated not only have subtly different donor sites but also have different barriers to conformational interconversions. Concomitant with the reduction of one ring, with consequent diminution of the ability of the macrocycle to act as a π-donor species, potential emerges for new patterns of metal-ion selectivity to be observed with these calixarene derivatives. We report herein our first efforts to assess these possibilities, tetrahydroborate reduction of the monoketone derived by addition of four hydrogen atoms to calix[4]arene providing two diastereomeric tetrols, both of which adopt cone-like conformations. The major diastereomer has been shown to form a binuclear complex with europium(III), in which preferential deprotonation of the phenolic sites appears to occur.

Experimental

Syntheses

Hexahydrocalix[4]arene diastereoisomers, H_4L and H_4L'. Sodium tetrahydroborate (600 mg, 15.9 mmol) was added portionwise over 1 h to a suspension of tetrahydrocalix[4]arene (600 mg, 1.40 mol) in methanol (20 cm^3) cooled at −5 °C. The tetrahydrocalixarene slowly dissolved in this time. More $NaBH_4$ (600 mg) was then added and the mixture stirred at −5 °C for 3 h. Finally, hydrochloric acid (2 mol l^{-1}, 30 cm^3) was added cautiously, with cooling. The mixture was filtered to collect the precipitate, which was washed with water and cold methanol. The crude product was recrystallised three times from dichloromethane–ethanol to give the diastereomer H_4L (520 mg, 86%). ^1H NMR ($CDCl_3$; atom numbering follows the crystallographic scheme): δ 0.93 (dddd, $J = 3.9$, 12.7, 12.7, 12.7, H^{13}_{ax}, H^{15}_{ax}), 1.37 (dtt, $J = 3.3$, 12.7, 12.7, H^{14}_{ax}), 1.58–1.63 (m, H^{13}_{eq}, H^{14}_{eq}, H^{15}_{eq}), 1.90–1.83 (m, H^{12}, H^{16}), 2.38 (dd, $J = 3.3$, 14.3, H^1_{eq}, H^4_{eq}), 2.51 (t, $J = 10.2$, H^{11}), 3.39 (dd, $J = 4.2$, 14.3, H^1_{ax}, H^4_{ax}), 3.56 (d, $J = 13.9$, H^2_{eq}, H^3_{eq}), 4.29 (d, $J = 13.9$, H^2_{ax}, H^3_{ax}), 6.73 (t, $J = 7.5$, H^{24}, H^{44}), 6.82 (dd, $J = 1.6$, 7.5, H^{25}, H^{43}), 6.83 (t, $J = 7.5$, H^{34}), 7.10 (dd, $J = 1.6$, 7.5, H^{23}, H^{45}), 7.17 (d, $J = 7.5$ Hz, H^{33}, H^{35}) and 10.06 (br s, OH). ^{13}C NMR ($CDCl_3$): δ 25.54 (C^{14}), 29.87 (C^{13}, C^{15}), 31.35 (C^2, C^3), 31.87 (C^1, C^4), 44.61 (C^{12}, C^{16}), 72.59 (C^{11}), 120.80 (C^{26}, C^{42}), 122.20 (C^{34}), 124.43, 127.87, 128.69 (aromatic C), 128.57 (C^{33}, C^{35}), 128.94 (C^{23}, C^{45}), 131.07 (C^{25}, C^{43}) and 149.04, 150.59 (C^{21}, C^{31}, C^{41}). FAB mass spectrum: *m*/*z* 430 (M^+, calc. 430) [Found: C, 73.5; H, 7.0. $(C_{28}H_{30}O_4)_3\cdot CH_2Cl_2$ requires C, 74.17; H, 6.74%].

The mother-liquors from the three recrystallisations of H_4L were combined and evaporated to dryness. The residue (40 mg) was subjected to chromatography (preparative TLC) on silica using CH_2Cl_2–hexane (1 : 1) as eluent. Two poorly-separated bands were observed and the material in the leading band (H_4L' contaminated with ≈15% of H_4L) was twice more subjected to the same chromatographic treatment to finally provide pure H_4L' (11 mg, 2.2%) as colourless, rhombic crystals after recrystallisation from CH_2Cl_2–ethanol. ^1H NMR ($CDCl_3$; atom numbering follows the crystallographic scheme): δ 1.31–1.40 (m, H^{14}_{ax}), 1.43–1.52 (m, H^{12}, H^{16}), 1.53–1.62 (m, H^{13}_{ax}, H^{13}_{eq}, H^{15}_{ax}, H^{15}_{eq}), 1.81 (dtt, $J = 3.2$, 3.2, 13.0, H^{14}_{eq}), 2.42 (dd, $J = 3.9$, 14.2 Hz, H^1_{eq}, H^4_{eq}), 2.86 (dd, $J = 12.0$, 14.2, H^1_{ax}, H^4_{ax}), 3.30 (t, $J = 2.4$, H^{11}), 3.52 (d, $J = 13.9$, H^2_{eq}, H^3_{eq}), 4.26 (d, $J = 13.9$, H^2_{ax}, H^3_{ax}), 6.73 (t, $J = 7.5$, H^{24}, H^{44}), 6.81 (t, $J = 7.5$, H^{34}), 6.87 (dd, $J = 1.6$, 7.5, H^{25}, H^{43}), 7.02 (dd, $J = 1.6$, 7.5, H^{23}, H^{45}), 7.14 (d, $J = 7.5$ Hz, H^{33}, H^{35}) and 9.86 (br s, OH). ^{13}C NMR ($CDCl_3$): δ 25.60, 28.79, 31.69, 33.70 (CH_2), 43.95 (C^{12}, C^{16}), 66.45 (C^{11}), 121.56 (C^{24}, C^{44}), 121.95 (C^{34}), 126.67, 127.78, 128.48 (aromatic C), 128.31, 128.93, 129.60 (aromatic CH), 149.39 (C^{31}) and 150.48 (C^{21}, C^{41}).

$[Eu_2(HL)_2(dmf)_4]\cdot 4dmf$ (dmf = dimethylformamide). Triethylamine (1 drop) was added to a solution of H_4L (40 mg, 93 μmol) and anhydrous $Eu(O_3SCF_3)_3$ (36 mg, 97 μmol) in dry dimethylformamide (5 cm^3). The resulting yellow solution was allowed to stand overnight for the neutral europium complex to precipitate as yellow plates (45 mg, 56%).

Crystallography

Unique room-temperature four-circle diffractometer data sets were measured (2θ–θ scan mode, $2\theta_{max}$ 50°; monochromatic Mo-Kα radiation, $\lambda = 0.7107_3$ Å, $T \approx 295$ K) on capillary-mounted specimens, yielding N independent reflections, N_o of which with $I > 3\sigma(I)$ were considered 'observed' and used in the full-matrix (large block, europium adduct) least-squares refinements after Gaussian absorption correction. Anisotropic thermal parameters were refined for the non-hydrogen atoms; $(x, y, z, U_{iso})_H$ were included constrained at estimated values. Conventional residuals R, R' on $|F|$ are quoted at convergence, statistical weights derivative of $\sigma^2(I) = \sigma^2(I_{diff}) + 0.0004\sigma^4(I_{diff})$ being employed. Neutral atom complex scattering factors were employed, computation using the XTAL 3.4 program system.[6] Pertinent results are given in the figures (20% thermal ellipsoids shown for non-hydrogen atoms, H with arbitrary radii of 0.1 Å) and tables.

Crystal/refinement data. $H_4L \cdot 0.33CH_2Cl_2$. $C_{28}H_{30}O_4 \cdot 0.33CH_2Cl_2$, $M = 458.5$, hexagonal, space group $P6_3/m$ (C^2_{6h}, no. 176), $a = 15.121(7)$, $c = 17.890(5)$ Å, $U = 3543$ Å^3, D_c (Z = 6) = 1.29 g cm^{-3}, $F(000) = 1462.8$, $\mu_{Mo} = 1.6$ cm^{-1}, specimen 0.40 × 0.60 × 0.45 mm, $A^*_{min,max} = 1.05, 1.07$, $N = 2103$, $N_o = 741$, $R = 0.069$, $R' = 0.066$.

The co-ordinate setting and numbering conforms to that of the recently recorded acetonitrile solvate[7] (the numbering as transferred to the europium adduct described below unfortunately is not congruent with that of the similar, previously recorded[8] binuclear complex formed by *p-tert*-butylcalix[4]arene). Difference-map residues were modelled as dichloromethane solvent, following consideration of the history and analysis of the sample, fully weighted after trial refinement but disordered about the 3 axis. Hydroxyl hydrogen atoms were observed in difference maps. The crystals were of poor quality, diffracting weakly, and a symmetry-related data set was measured ($N_{total} = 4509$) for which R_{int} was 0.27; examination of the data suggested deficient crystal quality rather than lower symmetry to be responsible for this high value.

H_4L'. $C_{28}H_{30}O_4$, $M = 430.6$, monoclinic, space group $C2/c$ (C^6_{2h}, no. 15), $a = 20.251(4)$, $b = 12.191(2)$, $c = 18.682(3)$ Å, $\beta = 103.73(1)°$, $U = 4480$ Å^3, D_c ($Z = 8$) = 1.28 g cm^{-3}, $F(000) = 1840$, $\mu_{Mo} = 0.8$ cm^{-1}, specimen 0.60 × 0.52 × 0.15 mm (no correction), $N = 3925$, $N_o = 2367$, $R = 0.054$, $R' = 0.063$.

$(x, y, z, U_{iso})_H$ were refined.

$[Eu_2(HL)_2(dmf)_4] \cdot 4dmf$. $C_{80}H_{108}Eu_2N_8O_{16}$, $M = 1741.7$, triclinic, space group $P\bar{1}$ (C^1_i, no. 2), $a = 18.864(4)$, $b = 17.188(7)$, $c = 16.737(7)$ Å, $\alpha = 62.98(3)$, $\beta = 67.82(3)$, $\gamma = 81.55(2)°$, $U = 4475$ Å^3, $D_c = 1.29$ g cm^{-3}, $F(000) = 1796$, $\mu_{Mo} = 14.6$ cm^{-1}, specimen 0.40 × 0.45 × 0.22 mm, $A^*_{min,max} = 1.25, 1.32$, $N = 15\,723$, $N_o = 8393$, $R = 0.056$, $R' = 0.069$.

Specimens were very fragile and were mounted by floating into capillaries, draining and sealing, one specimen eventually surviving and permitting data acquisition. Even so, it deteriorated by 75% during measurement, data being scaled from the standards in compensation. Not surprisingly, high thermal motion, real or apparent, was found amongst the solvent molecules; populations of the lattice solvent molecules 103 and 203 were set at unity after trial refinement, those of 104, 204, 105 and 205 being set at 0.5, in keeping with their apparent close proximity. Associated geometries of the latter were constrained during refinement. One half of each of a pair of independent centrosymmetric dimers makes up the asymmetric unit of the structure.

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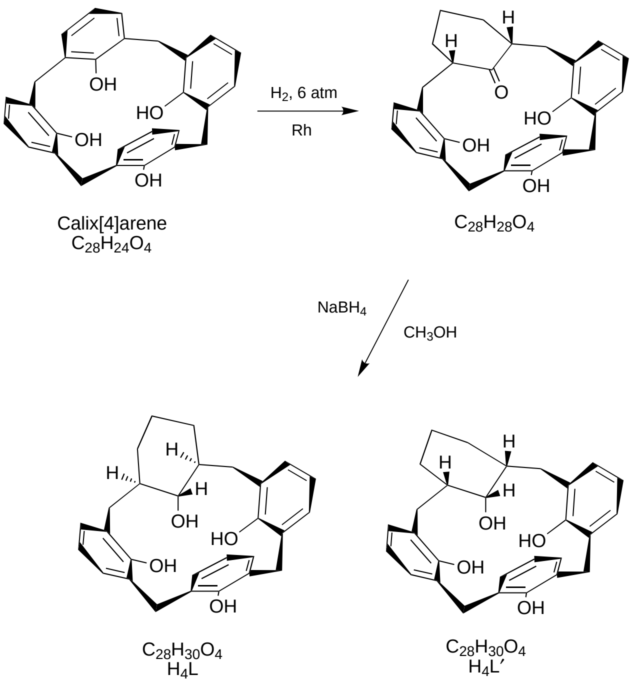

Scheme 1 Stepwise processes leading to the full reduction of one phenyl ring of calix[4]arene; atm = 101 325 Pa

Results and Discussion

The results of the room-temperature, single-crystal structure studies are consistent with the formulations given (see also Scheme 1) in terms of stoichiometry and connectivity. Surprisingly, H_4L is isomorphous with its fully aromatic parent in its (variously solvated) $P6_3/m$ hexagonal forms,[7,9] the molecules in each case conforming to crystallographic m symmetry and possessing conformations which may be described as 'cone'[1] in the sense that all hydroxyl groups lie to one side of the macrocycle. The three-fold crystallographic axes define macrocycle triplets in which one molecule may be considered partly included by the next, apparently through aromatic edge-to-face interactions in the parent and CH_2-π interactions in H_4L. In the parent the pitch of the C_6 ring planes *vis-à-vis* the O_4 plane is not uniform, those rings (1,3) bisected by the mirror plane being more steeply inclined than the mirror-related pair of ring planes 2. In H_4L, as in H_4L' below, the aliphatic ring fusion into the macrocycle takes place by way of equatorial sites, the aliphatic ring being one of those bisected by the mirror plane (necessarily so in the absence of disorder), with its hydroxyl substituent being in the plane and, in H_4L, equatorially disposed in relation to the saturated ring, though axially in relation to the macrocycle. The remainder of the ring in H_4L is disposed so that its axis lies normal to that of the macrocycle, *i.e.* directed towards (approximately) the centre of gravity of the system, so that, overall, the constituent atoms of the ring lie disposed about the putative aromatic ring it replaces. The variation in pitch of the ring 'planes' *vis-à-vis* the macrocycle is thus preserved as in the parent. Also as in the parent, the solvent molecules, disposed about symmetry axes between the macrocyclic molecules, are not included within the macrocycle cavities. Hydrogen atoms, located in difference maps but not refined, form a similar $(OH)_4$ concerted array as in the parent solvates, with the four hydrogen atoms lying in the O_4 'plane', approximately midway between the oxygen atoms, unsymmetrical dispositions predicating disorder not resolved or resolvable in the present experiment.

In unsolvated H_4L', we find a complete 'cone' molecule devoid of crystallographic symmetry comprising the asymmetric unit of the structure, although, apart from the hydroxyl hydrogen atoms, resolved and refined here with concerted but unsymmetrical associations O–H · · · O with their related O · · · O

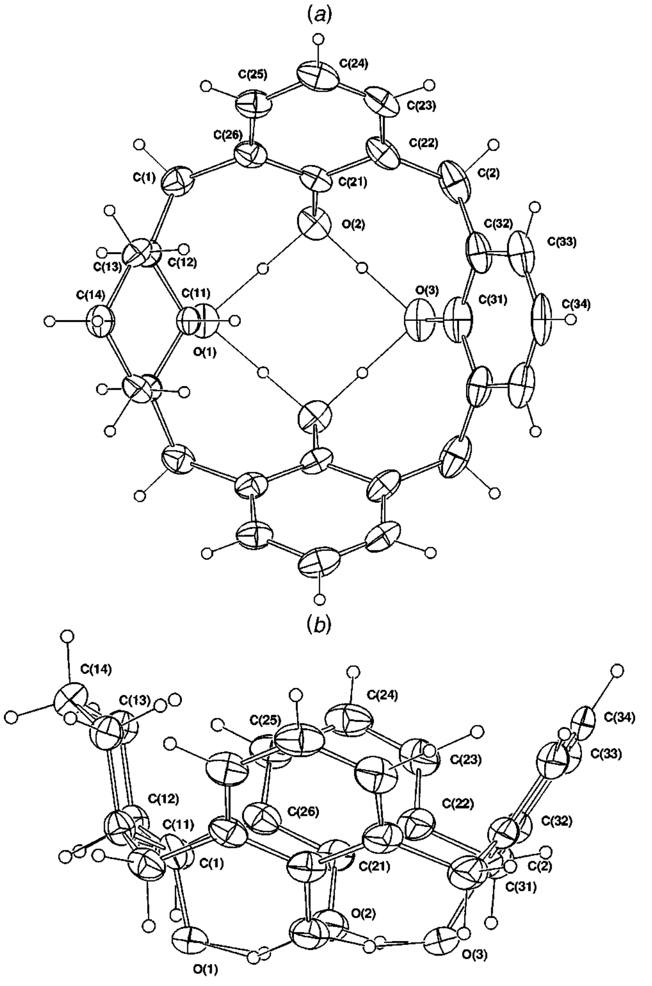

Fig. 1 Molecular projections of H_4L (*a*) normal to, and (*b*) through, the $(CH_2)_4$ plane

pairs, the quasi-*m* symmetry of H_4L and the fully aromatic parent is retained. Here, however, the six-membered ring conformation, again a chair, is such that the ring axis is quasi-parallel to the macrocycle axis, so that the hydroxyl substituent, still oriented axially with respect to the macrocycle, now also forms an axial substituent on the six-membered ring. Asymmetry in '(mirror-) equivalent' molecular parameters (angles, torsions, *etc.*) is minor (Table 1); the aliphatic C–O distance is longer than its aromatic counterparts by approximately 0.05 Å (consistent with the less precise result for H_4L). In terms of the lattice structure, H_4L' is unlike H_4L in that pairs of macrocyclic molecules related by the crystallographic 2 axis of space group *C*2/*c* may be discerned as 'self-included' units, similar to those seen in tetra- and octa-hydrocalix[4]arenes.[5]

Although the tetrahydrocalix[4]arene, obtained by Rh-catalysed hydrogenation of calix[4]arene,[5] is essentially insoluble in methanol, in the presence of $NaBH_4$ dissolution occurs readily before reduction is apparent. This we interpret as indicative of deprotonation and the formation of a sodium complex (or ion pair). In the solid state the sodium complex of *p-tert*-butylcalix[4]arene monoanion contains the sodium bound to two oxygen atoms of the cone-form calixarene.[10] If the monoanion of tetrahydrocalix[4]arene retains the conformation of the neutral compound itself[5] and forms a complex in methanol of similar structure to that of *p-tert*-butylcalix[4]arene monoanion, and BH_4^- attack at the carbonyl centre is an intramolecular process due to initial binding to sodium, then the stereochemistry of H_4L, the major product of reduction (Scheme 1), is readily understood, since the hydride addition would occur on the face of the carbonyl carbon remote from the 'C(2)' and 'C(6)' hydrogen atoms (of the cyclohexanone moiety). The structure of crystalline H_4L (Fig. 1) shows that, if

Table 1 Selected features of the molecular geometry (distances in Å, angles in °) for H_4L'

O(1)–C(11)–C(12)	108.8(2)	O(1)–C(11)–C(16)	110.1(3)
C(11)–C(12)–C(1)	114.9(3)	C(11)–C(16)–C(4)	113.7(3)
C(12)–C(1)–C(26)	118.1(3)	C(16)–C(4)–C(42)	117.4(3)
C(1)–C(26)–C(21)	121.7(3)	C(4)–C(42)–C(41)	121.1(3)
C(26)–C(21)–O(2)	119.8(3)	C(42)–C(41)–O(4)	118.8(3)
C(22)–C(21)–O(2)	117.4(3)	C(46)–C(41)–O(4)	119.2(3)
C(21)–C(22)–C(2)	122.3(3)	C(41)–C(46)–C(3)	122.4(3)
C(22)–C(2)–C(36)	113.6(3)	C(46)–C(3)–C(32)	112.4(3)
C(2)–C(36)–C(31)	122.3(3)	C(3)–C(32)–C(31)	121.0(3)
C(36)–C(31)–O(31)	119.0(3)	C(32)–C(31)–O(3)	118.2(3)

Torsions (atoms denoted by number only, oxygen italicised)

12–11–16–4	176.4(3)	16–11–12–1	−174.5(3)
1–11–16–4	55.1(4)	*1*–11–12–1	−52.4(4)
11–16–4–42	59.0(4)	11–12–1–26	−59.5(4)
16–4–42–41	−98.8(4)	12–1–26–21	93.1(4)
4–42–41–*4*	1.1(5)	1–26–21–*2*	−0.3(4)
4–42–41–46	−176.2(3)	1–26–21–22	175.8(3)
42–41–46–3	−179.9(3)	26–21–22–2	−179.6(3)
4–41–46–3	2.9(5)	*2*–21–22–2	−3.4(4)
41–46–3–32	95.5(4)	21–22–2–36	−92.5(4)
46–3–32–31	−79.8(4)	22–2–36–31	83.8(4)
3–32–31–*3*	−8.7(5)	2–36–31–*3*	5.7(5)
3–32–31–36	172.4(3)	2–36–31–32	−175.5(3)

O(1)–H(1)	0.82(5)	O(3)–H(3)	1.08(7)
O(4)–H(4)	1.11(5)	O(2)–H(2)	1.25(5)
O(4)···H,O(1)	2.02(5), 2.839(3)	O(1)···H,O(2)	1.49(5), 2.733(3)
O(3)···H,O(4)	1.58(5), 2.672(3)	O(2)···H,O(3)	1.61(7), 2.671(3)
O(1)–C(11)	1.439(4)	O(3)–C(31)	1.384(4)
O(2)–C(21)	1.391(4)	O(4)–C(41)	1.385(4)

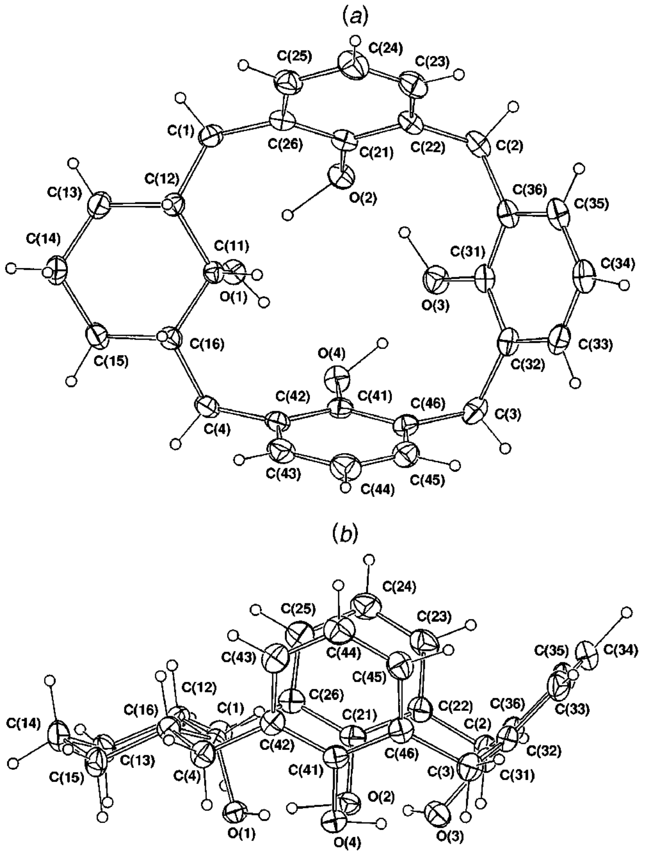

Fig. 2 Molecular projections of H_4L' (*a*) normal to, and (*b*) through, the $(CH_2)_4$ plane

this is so, ring inversion follows the reduction. Of course, the isolation of the diastereoisomer H_4L' (Fig. 2) shows that not all aspects of the reaction can be explained in this way but it may be noted that the yield of H_4L' relative to H_4L increases with

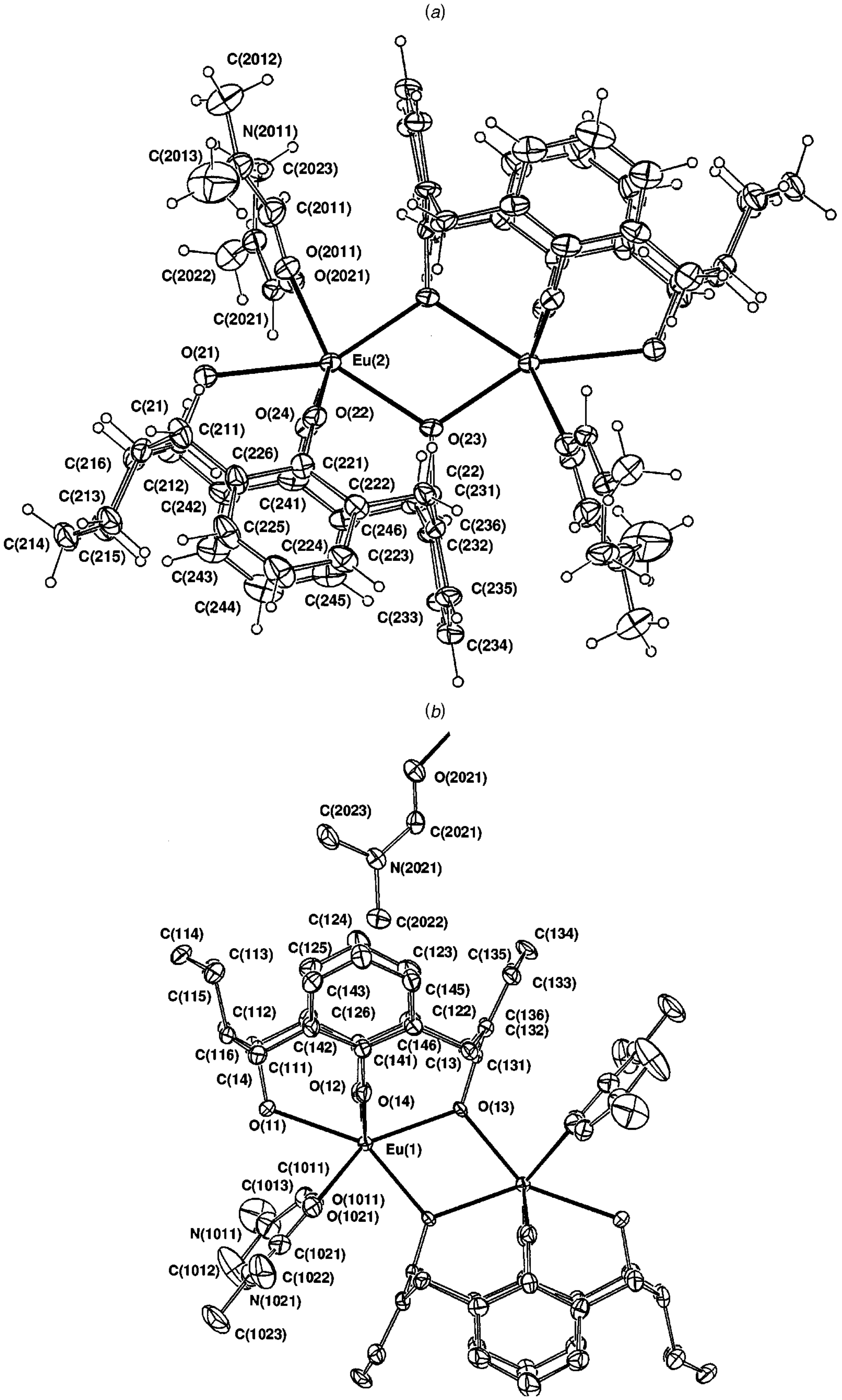

Fig. 3 Projections of (*a*) molecule 2, and (*b*) molecule 1, of $[Eu_2(HL)_2(dmf)_4]\cdot 4dmf$ normal to their Eu(μ-O)$_2$Eu planes

temperature, consistent with thermally induced dissociation of the O-co-ordinated complex to give an ion pair of different structure or even to give an inclusion complex like the caesium complex of *p*-*tert*-butylcalix[4]arene monoanion,[11] where the sodium also binds the BH_4^- anion so as to cause it to attack the face of the carbonyl group nearer to the 'C(2), C(6)' hydrogen atoms. (There are other obvious alternatives, such as O-bound sodium and included BH_4^-, which would also explain how H_4L might be derived from tetrahydrocalix[4]arene without conformational change.) In the three related structures of H_4L, H_4L' and tetrahydrocalix[4]arene there is a striking similarity to the structure of calix[4]arene in regard to the orientations of each

Table 2 Europium atom environments in $[Eu_2(HL)_2(dmf)_4]\cdot4dmf$. Counterpart values given in italics below those for molecules 1, 2 of the present array are the equivalent values for the *p-tert*-butylcalixarene adduct (data from ref. 9; incongruent numbering); *r*/Å is the metal–donor atom distance, the other entries being the angles subtended at Eu by the atoms at the head of the relevant row and column; φ/° is the associated Eu–O–C angle; primed atoms are related by inversion

Atom	*r*/Å	φ/°	O(2)	O(3)	O(4)	O(3′)	O(011)	O(012)
O(1)	2.489(7)	119.2(6)	76.9(3)	140.3(2)	77.1(3)	149.4(2)	74.8(3)	73.6(3)
	2.512(8)	117.8(6)	76.7(3)	140.8(3)	75.4(3)	152.3(7)	73.2(3)	77.7(3)
	2.558(6)	*124.3(5)*	*75.7(2)*	*142.1(2)*	*77.2(2)*	*149.3(2)*	*71.9(2)*	*73.4(2)*
O(2)	2.200(9)	153.1(9)		82.5(3)	111.5(3)	117.4(3)	76.7(3)	143.6(3)
	2.167(9)	162(1)		81.0(3)	108.6(4)	113.9(3)	85.4(3)	150.8(2)
	2.143(6)	*172.3(6)*		*81.0(2)*	*108.0(2)*	*119.6(2)*	*81.8(2)*	*145.1(3)*
O(3)	2.406(7)	126.5(6)			79.6(3)	70.2(2)	132.4(3)	133.9(2)
	2.422(6)	124.0(6)			81.7(3)	66.9(3)	136.7(3)	128.1(2)
	2.395(6)	*123.2(5)*			*82.3(2)*	*68.5(2)*	*133.6(3)*	*133.9(2)*
O(4)	2.16(1)	163.3(8)				116.9(3)	147.9(3)	82.1(3)
	2.16(1)	163.8(9)				120.8(3)	141.5(3)	78.1(3)
	2.150(7)	*162.8(5)*				*117.4(2)*	*144.1(3)*	*80.3(2)*
O(3′)	2.360(7)	123.7(6)	Eu···Eu′	3.898(1)			82.2(2)	81.3(3)
	2.353(9)	122.8(5)		3.985(2)			81.9(3)	83.8(3)
	2.332(5)	*125.2(6)*		*3.9067(7)*			*83.6(2)*	*82.4(2)*
O(011)	2.463(8)	130.1(9)	O(3)···O(3′)	2.742(9)				75.4(3)
	2.42(1)	133.3(9)		2.63(1)				73.9(3)
	2.466(7)	*150(1)*		*2.661(6)*				*73.7(3)*
O(012)	2.46(1)	130(1)	Eu–O(3)–Eu′	109.8(3)				
	2.508(9)	130(1)		113.1(4)				
	2.465(7)	*140(1)*		*111.5(2)*				

set of four oxygen atoms and the hydrogen bonding between them. It would appear that, as with calix[4]arene,[7,8] this hydrogen-bonding array is the prime determinant of the solid-state, cone conformation. Although the solution ^1H nuclear magnetic resonance spectra of these three compounds are all consistent with the maintenance of the solid-state structure in solution, the conformational isomerism in these systems is more complex than for calix[4]arene[1] and the various species not so distinctly different in symmetry, so that details of the solution conformations cannot be considered established with certainty. There are many calix[4]arene systems, *e.g.* refs. 12 and 13, where marked differences between solid-state and solution conformations are clearly established. Nonetheless, it is observed for H_4L that the methine proton H^{11} resonance (δ 2.51 in $CDCl_3$) is split into a triplet by coupling to H^{12} and H^{16} and the coupling constant ($J = 10.2$ Hz) is consistent with the axial–axial orientations seen in the solid. In contrast, the H^{11}/H^{12}, H^{16} coupling constant for H_4L' is only 2.4 Hz, consistent with the axial–equatorial relationship of the solid. Close adherence to the solid-state conformations was also indicated by nuclear Overhauser effect spectroscopy (NOESY) experiments, which showed, for example, that the Overhauser effects between the aromatic protons H^{25} and H^{43} and the cyclohexyl protons were very different for H_4L and H_4L'. In the NOESY spectrum of H_4L negative cross-peaks were observed for H^{25} with both $H^{13}{}_{ax}$ and $H^{13}{}_{eq}$ (as well as for H^{43} with $H^{15}{}_{ax}$ and $H^{15}{}_{eq}$) while no Overhauser effect was observed between H^{12} and H^{25} (or H^{11} and H^{43}), indicative of the same upright orientation of the cyclohexyl ring as in the solid, where H^{12} and H^{16} point away from the macrocycle cavity. For H_4L' no effects were observed between H^{25} and $H^{13}{}_{ax}$ or $H^{13}{}_{eq}$ (nor between H^{43} and $H^{15}{}_{ax}$ or $H^{15}{}_{eq}$), whilst an effect was observed between H^{12} and H^{25} (and H^{16} and H^{43}), again consistent with proximity of these protons as seen in the solid.

The structure (Fig. 3) of the binuclear complex of europium(III) with the trianion derived from H_4L is very similar to that of the complex of the trianion of *p-tert*-butylcalix[4]arene.[8] In both structures the complex is a neutral molecule of stoichiometry $Eu(HL)(dmf)_2$, with additional molecules of dmf of solvation (modelled as 3.5 in the *tert*-butylcalixarene complex and 2 in the present, incorporated in the lattice). The complex molecules are binuclear, the dimer being centrosymmetric, with the seven-co-ordinate europium(III) environment comprising an O_4-quadridentate calixarene, with one of the oxygen atoms bridging to the symmetry-related europium atom (and thus a fifth phenoxide oxygen atom entering the co-ordination sphere as a result of reciprocal bridging by the calixarene of this second europium), plus the two co-ordinated dmf molecules. The *tert*-butyl ligand substituents aside, the conformations of the dimers in both complexes are very similar; in the *tert*-butylcalixarene adduct one half of the dimer comprises the asymmetric unit of the structure in space group *C*2/*c*, while in the present adduct the asymmetric unit comprises a pair of similar half-dimers (independent) in space group $P\bar{1}$. The geometries about the metals, of approximate *m* symmetry, are compared for the two systems in Table 2, showing few notable differences. There is, however, a striking difference between the two {and between the present complex and the less closely related europium(III) complex of *p-tert*-butyldihomooxacalix[4]arene[14]} in that although the included solvent found within the macrocyclic cavities of the present molecule 2 can be considered dmf of solvation, that included by molecule 1 is co-ordinated dmf, bound to europium ions of adjacent molecules 2 [Fig. 3(*b*)]. This might in some way be a consequence of the conversion of one calixarene phenyl ring into its saturated form, though it seems more plausible that it may simply reflect greater accessibility of the cavity due to the absence of *tert*-butyl substituents. It appears to be commonly true that inclusion by calix[4]arene is less effective than that of its *p*-alkyl derivatives,[15] but the fact that most examples of inclusion apply to solids, where the extended lattice must be a factor to be considered, makes it uncertain as to what factors are controlling such behaviour. There is clear evidence that CH_3-π interactions within the cavity of calix[4]arene (neutral or as its monoanion) can give rise to inclusion[16] and since it is conventionally assumed[15] that such interactions are the cause of inclusion of molecules such as dimethylformamide by calixarenes, it is difficult to see that substitution with *tert*-butyl groups should do other than inhibit inclusion by enhancing repulsive interactions with a guest. Thus, it is reasonable that a guest with very large substituents attached remote from its interaction site with the host might be more readily accommodated in the cone cavity of calix[4]arene than of *p-tert*-butylcalix[4]arene, so that complexed dmf might attach to the former but only 'free' dmf to the latter. The mode of polymerisation identified in the europium complex has some similarity to the formation of 'koilates' derived from binuclear calixarene complexes of Si^{IV} and Ti^{IV}, though there the link between monomer units involves inclusion for both ends of a bridging species.[17]

Since both H_4L and H_4L', like calix[4]arene, can be regarded as tetraprotic acids, there must be one residual hydroxylic proton per metal(III) in complexes such as the present one. In the complexes of europium(III) with both *p-tert*-butylcalix[4]arene and *p-tert*-butyldihomo-oxacalix[4]arene there is structural evidence that the phenolic group opposite that which acts as a bridge to form the dimer is the one to retain its proton. This assignment of an effectively enhanced basicity to the phenoxide of ring 1 (= ring 3 in refs. 8 and 14) is consistent with the occupancy of this site by the cyclohexanol moiety in the present complex, since deprotonation of H_4L to give an alkoxide anion would be expected to be considerably more difficult (thermodynamically) than its deprotonation to give an aryloxide species. As in the related structures, the bond between Eu and the O of ring 1 is the longest of all the metal–calixarene interactions. Thus, the presence of the reduced ring may be considered as enhancing the natural asymmetry of the bound macrocycle, and therefore its potential selectivity in guest binding, in this way as well as by its removal of one possible site for alkane hydrogen/π system interactions. The latter factor, which eliminates the formal degeneracy of interaction of a four-fold-symmetric host with a three-fold-symmetric guest such as a methyl group, is not clearly of importance in the present case, since the included dmf is certainly not symmetrically juxtaposed with respect to the three aromatic rings.

Acknowledgements

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