Supporting Information

1. Details and idiosyncrasies ('Variata') of individual structure determinations:

1. LH_4 = $C_{40}H_{48}O_4S_4$

Variata.- The parent ligand, as is also the case with many of its relatives and derivatives, exhibits disorder in one or more t-butyl groups, here at C(44), rotationally about the pendent C-C bond, site occupancies of the two components here refining as not significantly different from 0.5 and constrained at that value. Phenolic hydrogen atoms were also modelled as disordered over two sets of sites of equal occupancy between the oxygen atoms.

2. [$LH_4.CHCl_3$] = $C_{41}H_{49}Cl_3O_4S_4$

Variata.- Data were measured at room temperature (*ca* 295 K) on a capillary-mounted specimen using a four-circle instrument, $2\theta_{max} = 50$ °. A gaussian absorption correction was applied. (x, y, z, $U_{iso})_H$ were constrained at estimated values, the phenolic hydrogen being observed in difference maps. The included chloroform solvent was modelled as disordered about the crystallographic *4*-axis. Reflections with $I > 3\sigma(I)$ were considered 'observed' in the refinement.

3. [LH_4.pyridine] = $C_{45}H_{53}NO_4S_4$

Variata.- The t-butyl group was modelled as rotationally disordered over two sets of sites, occupancies refining to 0.816(9) and complement, (x, y, z, $U_{iso})_H$ for the minor component being constrained at calculated estimates. The included pyridine was modelled as rotationally disordered over two orientations about the *4*-axis as its principal axis, with N innermost in the cone, associated (x, y, z, $U_{iso})_H$ also constrained as estimates.

4. [$HN(C_2H_5)_3$][LH_3] (unsolvated) = $C_{46}H_{63}NO_4S_4$

Variata.- The *t*-butyl substituent at C(24) was modelled as rotationally disordered over two sets of sites, occupancies refining to 0.72(1) and complement. (x, y, z, $U_{iso})_H$ were generally not meaningfully refinable, being refined only for two of the phenolic hydrogens ultimately, the remainder constrained at estimated values. This low temperature determination was carried out

after an initial determination at *ca* 300 K in an effort to improve the precision. Although the resultant change was not dramatic, data from the room temperature result is included since it shows small but significant changes in the cone conformation parameters. The specimen was obtained from a separate crystallisation, t-butyl disordered component occupancies being modelled as 0.5; the variations may be consequent as much on variations in crystallisation conditions as the change in temperature and any associated variation in resolution. For the *ca* 300 K determination, a = 12.100(3), b = 13.347(3), c = 16.335(4) Å, α = 106.357(4), β = 100.626(5), γ = 111.118(5) °, V = 2238 Å^3. D_c = 1.22$_0$ g cm^{-3}. μ_{Mo} = 2.5 cm^{-1} specimen: 0.42x0.25x0.20 mm (no correction). N_t = 24975, N = 7675 (R_{int} = 0.102), N_o = 4845; R = 0.089, R_w = 0.10; n_v = 524, $|\Delta\rho_{max}|$ = 0.67(3) e Å^{-3}.

5. [HN(C$_2$H$_5$)$_3$][LH$_3$.dmf] = $C_{49}H_{70}N_2O_5S_4$

Variata.- The *t*-butyl substituents at C(14, 44) were modelled as rotationally disordered over two sets of sites, occupancies set at 0.5 after trial refinement. $(x, y, z, U_{iso})_H$ were meaningfully refinable except for the hydrogens associated with disordered components, which were constrained at estimates.

6. [HN(C$_2$H$_5$)$_3$][LH$_3$.dmso] = $C_{48}H_{69}NO_5S_5$

Variata.- $(x, y, z, Uiso)_H$ were refined throughout, excepting those associated with the minor components of the disordered t-butyl group at C(44) (populations: 0.629(5) and complement), and the included dmso solvent for which S was disordered in the usual way over sites with occupancies = 0.912(2) and complement.

7. [{(thf)(LH$_2$)}Li$_2$(thf)(OH$_2$)$_2$].2thf = $C_{56}H_{82}Li_2O_{10}S_4$

Variata.- The included thf was modelled as disordered over two sets of sites, occupancies refining to, and constrained at 0.7 and complement. The *t*-butyl substituent at C(14) was modelled as rotationally disordered over two sets of sites, occupancies set at 0.5 after trial refinement. $(x, y, z, U_{iso})_H$ were refined for all hydrogen atoms except those associated with the disorder, which were constrained at estimates.

8. $[\{(thf)(LH_3)\}Na(thf)(OH_2)].2thf = C_{56}H_{81}NaO_9S_4$

Variata.- The included thf(1) was modelled as disordered over two sets of sites; the *t*-butyl substituents at C(12, 13, 22, 23) were modelled as rotationally disordered over two sets of sites. Coordinated water and thf(2) were both modelled as disordered over two sets of sites, as was lattice thf(3). Occupancies of all disordered sites were set at 0.5 after trial refinement. (x, y, z, $U_{iso})_H$ were refined for phenolic hydrogens only, the remainder being constrained at estimated values, those for the water fragments not being located. There was some suggestion of a cell with doubled c axis in the initial data; if true, however, it is so weak as to render modelling of the structure unsustainable, and better material was not available to usefully pursue the matter further.

9. $[(LH_3)_2K_2(OH_2)(O(C_2H_5)_2)_2].2CH_3OH = C_{90}H_{124}K_2O_{13}S_8$

Variata.- The *t*-butyl substituents at C(24, 34, 44) were modelled as rotationally disordered, site occupancies refining to 0.5 (constrained after trial), 0.771(5) and 0.561(6) and complements. 'Solvent' residues were modelled as indicated, associated hydrogen atoms not being resolvable for the water and methanol moieties (the latter disordered over sites refining to occupancies of 0.697(6) and complement). Other hydrogens were included in the refinement constrained at estimated values (exception (x, y, z, $U_{iso})_H$ refined for the phenolic hydrogen atoms). Again, this result was obtained subsequent to an initial study carried out at *ca* 300 K, the specimen being obtained from a separate crystallisation. Here, the *t*-butyl groups at C(14, 34, 44) were modelled as rotationally disordered, site occupancies refining to 0.651(7), 0.620(6), 0.743(8) and complements. (x, y, z, $U_{iso})_H$ were refined for the phenolic groups. For this determination ($2\theta_{max} = 50$ °), $a = 17.388(1)$, $b = 17.974(1)$, $c = 32.319(2)$ Å, $V = 10100$ Å^3. $D_c = 1.15_0$ g cm^{-3}. $\mu_{Mo} = 3.1$ cm^{-1}; specimen: 0.18x0.18x0.05 mm; '$T'_{min,max}$ 0.76, 0.93. $N_t = 110141$, $N = 8878$ ($R_{int} = 0.028$), $N_o = 6597$; $R = 0.059$, $R_w = 0.067$; $n_v = 593$, $|\Delta\rho_{max}| = 0.78(2)$ e Å^{-3}.

10. $[\{(LH_3)_2(dmf)_2\}(LH_3)_2Rb_4(OH_2)(dmf)_9] = C_{193}H_{267}N_{11}O_{28}Rb_4S_{16}$

Variata.- The molecular aggregate, as modelled in space group $P\bar{1}$, is disposed about a

crystallographic inversion centre. Modelling of the non-hydrogen atoms of the two independent calixarene moieties is essentially unproblematical, the *t*-butyl substituents of ligand 2 at C(214, 224, 234) being modelled as rotationally disordered, each over two sets of sites, occupancies set at 0.5 after trial refinement. The core of the aggregate is modelled with substantial components of disorder (attempts to model the structure in space group *P*1 being inherently unfruitful), Rb(2,3), dmf molecules (2-6, 2'-6') being refined with site occupancies 0.5. (Note that a number of these are mutually incompatible with full occupancy in a centrosymmetric model.) $(x, y, z, U_{iso})_H$ were constrained at estimated values throughout the refinement, phenolic hydrogen atoms not being located.

11. [{(dmf)(LH$_3$)$_3$}{(dmf)(LH$_4$)}Cs$_3$(dmf)$_3$(OH$_2$)$_4$] = $C_{181}H_{246}Cs_3N_7O_{27}S_{16}$

Variata.- As in the rubidium structure, the molecular aggregate, as modelled in space group *Pccn*, uniquely determined, is again disposed about a crystallographic symmetry element, this time a twofold axis. Again there are two crystallographically independent calixarene moieties, the non-hydrogen atoms again modelled unproblematically, only one *t*-butyl substituent that at C(124) requiring modelling as rotationally disordered over two sets of sites, population set at 0.5 after trial refinement. The core of the aggregate is again modelled with substantial components of disorder, Cs(2), dmf molecules 3-5, $(H_2)O$ (01-04) being modelled with site occupancies 0.5, as also were the two disordered oxygen components of dmf 1. $(x, y, z, U_{iso})_H$ were constrained at estimated values throughout the refinement, phenolic hydrogen atoms not being located.