

## Alkylammonium Cation Interactions with Calixarene Anions. Part 2.<sup>1</sup> Structural Characterisation of a Salt of 2:3 Cation:Calixarene Stoichiometry

Jack M. Harrowfield,<sup>a</sup> William R. Richmond,<sup>a</sup> Alexander N. Sobolev<sup>a,b</sup> and Allan H. White<sup>a</sup>

<sup>a</sup> Chemistry Department and Research Centre for Advanced Minerals and Materials Processing, University of Western Australia, Nedlands, W.A. 6009

<sup>b</sup> L. Karpov Institute of Physical Chemistry, ul Obukha 10, Moscow 103064, Russia

A room temperature single crystal X-ray structure determination on the tetramethylammonium 'salt' of calix[4]arene ([1.1.1.1]metacyclophane-7,14,21,28-tetraol) has revealed an unusual stoichiometry and unusual structure for this compound. Crystals of salt are tetragonal, space group  $P4/nnc$ ,  $a = 18.230(4)$ ,  $c = 22.897(6)$  Å,  $Z = 4$  f.u.; the structure was refined to a residual of 0.087 for 1471 'observed' [ $I > 3\sigma(I)$ ] reflections. The solid has the composition  $\text{LH}_4 \cdot 2[\text{NMe}_4]^+ [\text{LH}_3]^- \cdot \text{H}_2\text{O}$  ( $\text{LH}_4 = \text{calix[4]arene}$ ) and contains the cation, 'C', in two distinct environments, both involving inclusion within the calixarene units but one involving simple inclusion by a single calixarene ('A') and the other encapsulation by a facing pair of symmetry-related calixarene entities ('B'). Interaggregate spacings by lattice water molecules, W, result in the 'A' moieties being stacked up the 4 axis  $\dots\text{WACCAW}\dots$ , while the 'B' moieties are stacked along the 2 axes in the  $ab$  diagonal,  $\dots\text{W'BCBW}'$ .

Solution <sup>1</sup>H nuclear magnetic resonance spectroscopy indicates that the tetramethylammonium cation interacts with the monoanion of calix[4]arene in a manner which involves inclusion of the cation within the (presumed) conical conformer of the calixarene.<sup>1</sup> Since in general the inclusion chemistry of calix[4]arene itself is far more restricted than that of its *p*-alkyl derivatives,<sup>2</sup> we sought to further characterise the system by determination of the crystal structure of what was considered to be the  $[\text{N}(\text{CH}_3)_4][\text{calix[4]arene} - \text{H}]$  'salt' in the belief that any interactions thereby exposed might well be those responsible for the solution characteristics. The structure has in fact proved to be quite unusual, revealing in addition to details of the cation-anion interaction that even a neutral calixarene can 'coordinate' a cation through inclusion, and it is the nature of this structure that is reported herein.

### Experimental

**Synthesis.**—The synthesis of  $[\text{N}(\text{CH}_3)_4]_2[\text{calix[4]arene} - \text{H}]_2[\text{calix[4]arene}] \cdot \text{H}_2\text{O}$  has been reported previously,<sup>1</sup> though at that time the compound was formulated, on the basis of its method of synthesis and elemental analyses, as the simple  $[\text{N}(\text{CH}_3)_4][\text{calix[4]arene} - \text{H}]$  species. Elemental analyses actually do not allow a ready distinction between the two formulations, especially since it appears, as observed in many other instances,<sup>1,3</sup> that drying of samples prior to microanalysis leads to significant desolvation of crystals used intact for structure determination. Hence, the particular formulation given herein is based upon the structure determination.

**Structure Determination.**—A room temperature diffractometer data set [ $T \sim 295$  K; monochromatic MoK $\alpha$  radiation ( $\lambda = 0.71073$  Å);  $2\theta/\theta$  scan mode;  $2\theta_{\text{max}} = 50^\circ$ ] was measured for an octant of reciprocal space yielding, after merging ( $R = 0.037$ ), 3387 unique data, 1471 of these with  $I > 3\sigma(I)$  being considered 'observed' and used in the full matrix least squares refinement without absorption correction. Anisotropic thermal parameters were refined for calixarene C, O, cation and solvent non-hydrogen atoms being refined with the isotropic form; ( $x, y, z, U_{\text{iso}}\text{H}$ ) were constrained at estimated values (CH) or difference

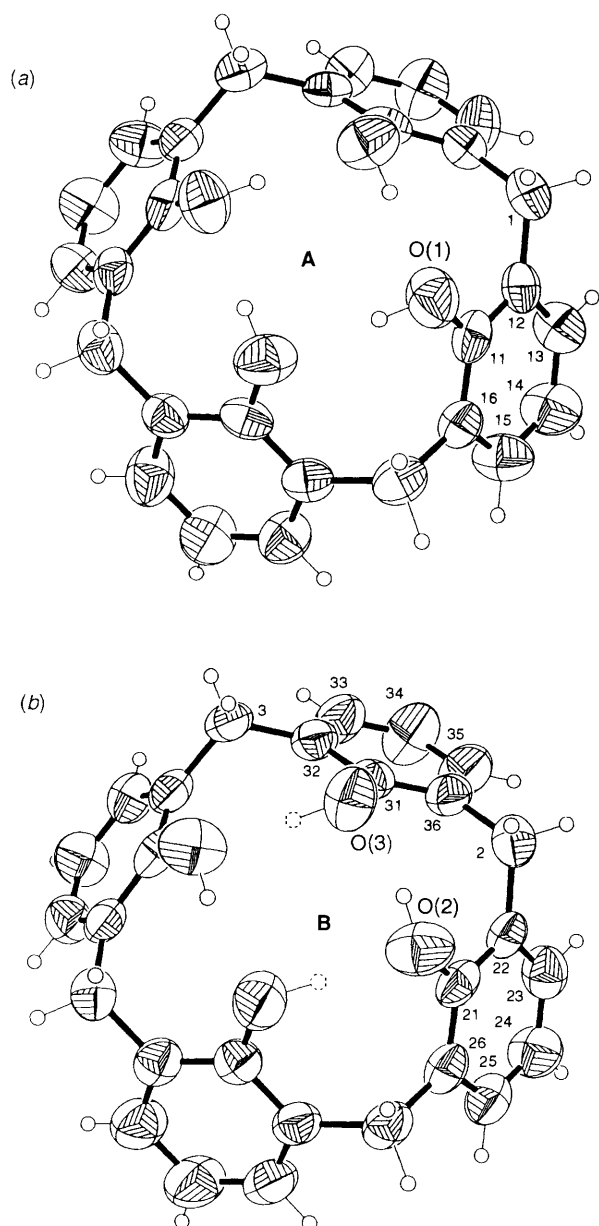
map estimates (OH) where these were considered to be of sufficient reliability. Conventional residuals  $R, R_w$  {reflection weights:  $[\sigma^2(F) + 0.005F^2]^{-1}$ } at convergence were 0.087, 0.113. Neutral atom complex scattering factors were employed, computation using the XTAL 3.2 program system<sup>4</sup> implemented by S. R. Hall. Pertinent results are given in the Figures and Tables; material deposited comprises thermal and hydrogen atom parameters, full molecular non-hydrogen geometries and macrocyclic torsion angles.

**Crystal Data.**— $2[\text{N}(\text{CH}_3)_4][\text{C}_{28}\text{H}_{23}\text{O}_4] \cdot [\text{C}_{28}\text{H}_{24}\text{O}_4] \cdot \text{H}_2\text{O} = \text{C}_{92}\text{H}_{96}\text{N}_2\text{O}_{13}$ ,  $M = 1437.7$ . Tetragonal, space group  $P4/nnc$  [ $D_{4h}^{12}$ , No. 126 (origin at  $\bar{1}$ )],  $a = 18.230(4)$ ,  $c = 22.897(6)$  Å,  $V = 7609(5)$  Å<sup>3</sup>.  $D_c$  ( $Z = 4$  f.u.) = 1.26 g cm<sup>-3</sup>;  $F(000) = 3064$ .  $\mu_{\text{Mo}}$  = 0.8 cm<sup>-1</sup> (no correction); specimen: cuboid  $\sim 0.5$  mm<sup>3</sup> (capillary).

**Abnormal features.** The high residual is considered to be a consequence of high thermal motion and disorder among the cations and solvent molecules. Two different cation types are found: in the final model, one is disordered about a special position of 222 symmetry, two independent associated carbon fragments being modelled with site occupancy 0.5, while the other is disordered about a site of 4 symmetry, with associated carbon components modelled as one fully ordered, located on that axis, and two independent associated fragments disordered about the axis and modelled with site occupancy 0.375; both cations were modelled with constrained geometries in the final cycle. Water molecule oxygen fragments are disposed on Wyckoff  $h$  and  $i$  two-fold axes with site occupancies 0.5; plausible associated hydrogen atoms were located in difference maps. Phenolic hydrogen atoms were also located in difference maps, their site occupancies being tentatively modelled on the basis of residues/refinement behaviour as unity for those associated with O(1,2) and 0.5 for that associated with O(3).

### Discussion

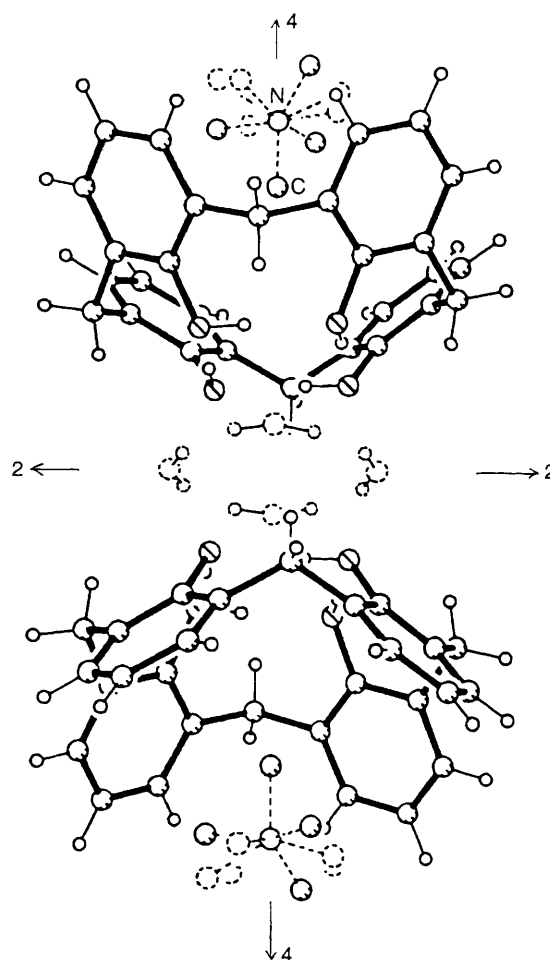
Assignment of the nature of the present substance as  $\text{LH}_4 \cdot 2[\text{NMe}_4]^+ [\text{LH}_3]^- \cdot \text{H}_2\text{O}$  ( $\text{LH}_4 = \text{calix[4]arene}$ ) is made primarily on the basis of a single crystal X-ray study, the results of which are consistent with this description in terms of



**Fig. 1** Calixarenes 'A', 'B' showing atom labelling and 50% thermal ellipsoids for the non-hydrogen atoms; hydrogen atoms have arbitrary radii of 0.1 Å

stoichiometry and connectivity despite the presence of high thermal motion and disorder. The structure is elegant, complex and interesting.

Two crystallographically independent calixarene units (Fig. 1) are found in the structure. In one, calixarene 'A', the calixarene is disposed about the unique crystallographic 4 axis (as cone axis), one methylene/phenolic component comprising the asymmetric unit; various evidence (see above) suggests that this species is a neutral molecule with the phenolic hydrogen atom sites fully occupied, *i.e.*, the molecule is tentatively identified as an undissociated calixarene. The (phenolic-O)<sub>4</sub> array is necessarily planar, with the plane normal to the 4 axis. The O<sub>4</sub>/C<sub>6</sub>(phenyl) dihedral angle is 53.2(2)°; the oxygen atom lies 0.09(1) Å out of the C<sub>6</sub> plane ( $\chi^2$  8.6), everted slightly outwards from the cone, and the methylene carbon deviation is -0.04(1) Å. As modelled, the hydrogen atoms lie along the O...O lines within the molecule, in fully occupied sites in a unidirectional manner (rather than being disordered over pairs of sites towards the two oxygen atoms to either side of the



**Fig. 2** The stack of 'A' calixarenes, O(1W) water molecules and cations '1' viewed down *a* (sequence ...WACCAW...)

datum oxygen). The phenolic O-C distance is 1.361(8) Å and the angle at the methylene carbon 114.6(6)°. Distances between the phenolic oxygen atoms are 2.673(3) Å. Each 'A' calixarene confronts a symmetry related counterpart of opposite polarity which approaches along the 4 axis; the *z*-coordinate of the phenolic oxygen array is 0.6443(2). (The table of final fractional atomic coordinates, the full list of bond lengths and angles and the list of thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.\*) The counterpart array at *z* = 0.8557(2) is generated by 2 axes disposed at *z* = 0.75. The distance between the pair of O(4) arrays is  $2 \times (0.75 - 0.6443) \times c$  [22.897(6) Å] = 4.84 Å. At *z* = 0.75 is a necessarily planar array of four water molecule residues, O(1W), each lying on a crystallographic 2 axis and 2.753(8) Å distant from phenolic oxygens to either side. Within the cone of each 'A' calixarene lies a tetramethylammonium cation, cation 1, one carbon of which lies on the fourfold axis with the *N*-methyl vector projecting into the cone, with the *N* and C(1) distances from the associated O<sub>4</sub> plane being 5.16(1), 3.70(1) Å, respectively. By implication, successive cationic ends of symmetry related arrays confront each other to either side of *z* = 0.25, the array being ...WACCAW... (W = water, C = cation), but the separation here  $\{N \dots N = 2 \times [0.4187(6) - 0.25] \times c = 7.7_3 \text{ Å}\}$  is large. Projections of the array down the

\* For full details of the CCDC deposition scheme, see the Journal's 'Instructions for Authors (1994)' *J. Chem. Soc., Perkin Trans. 2*, 1994, Issue 1.

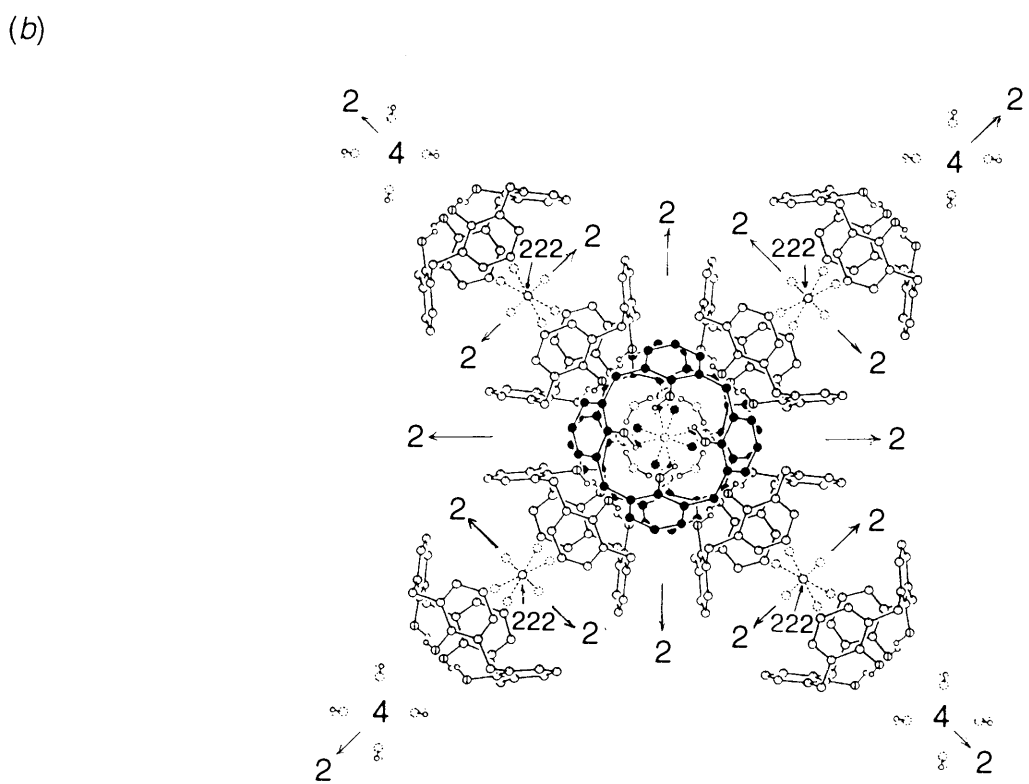
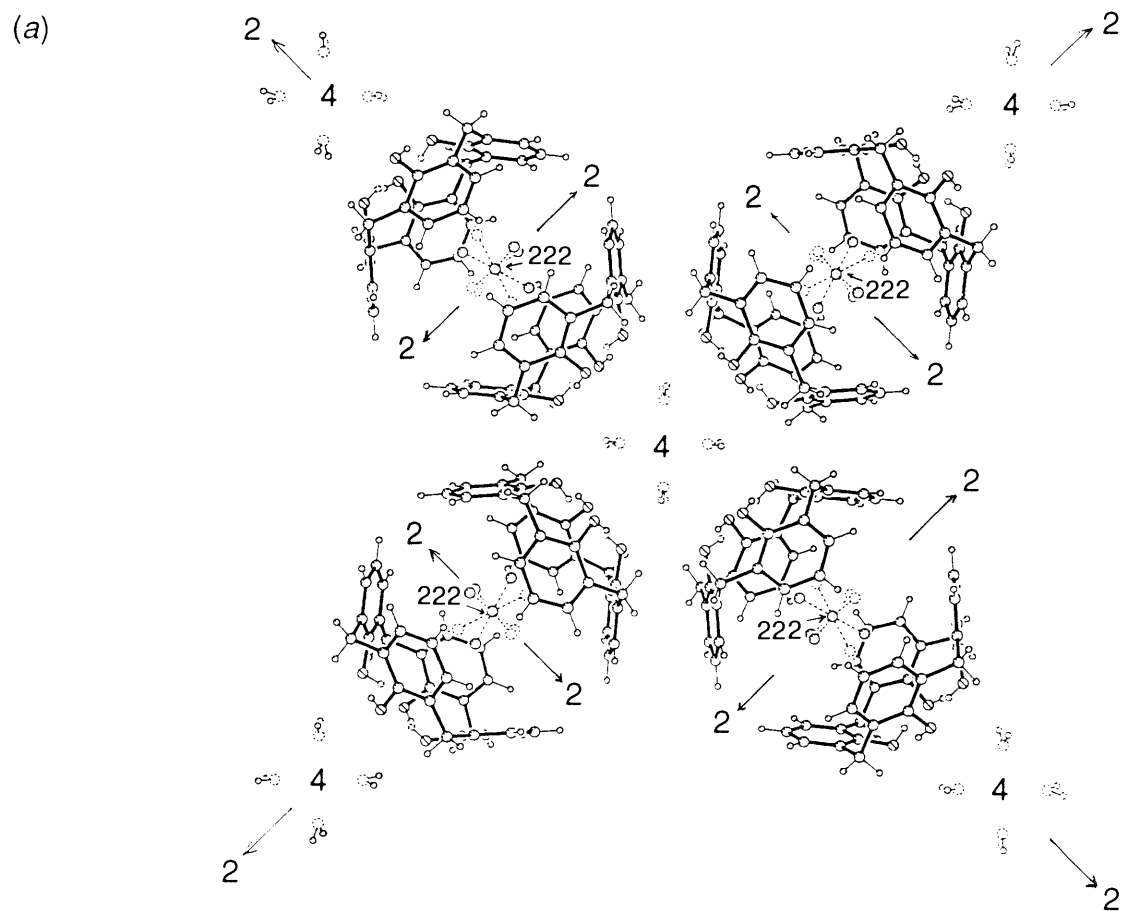
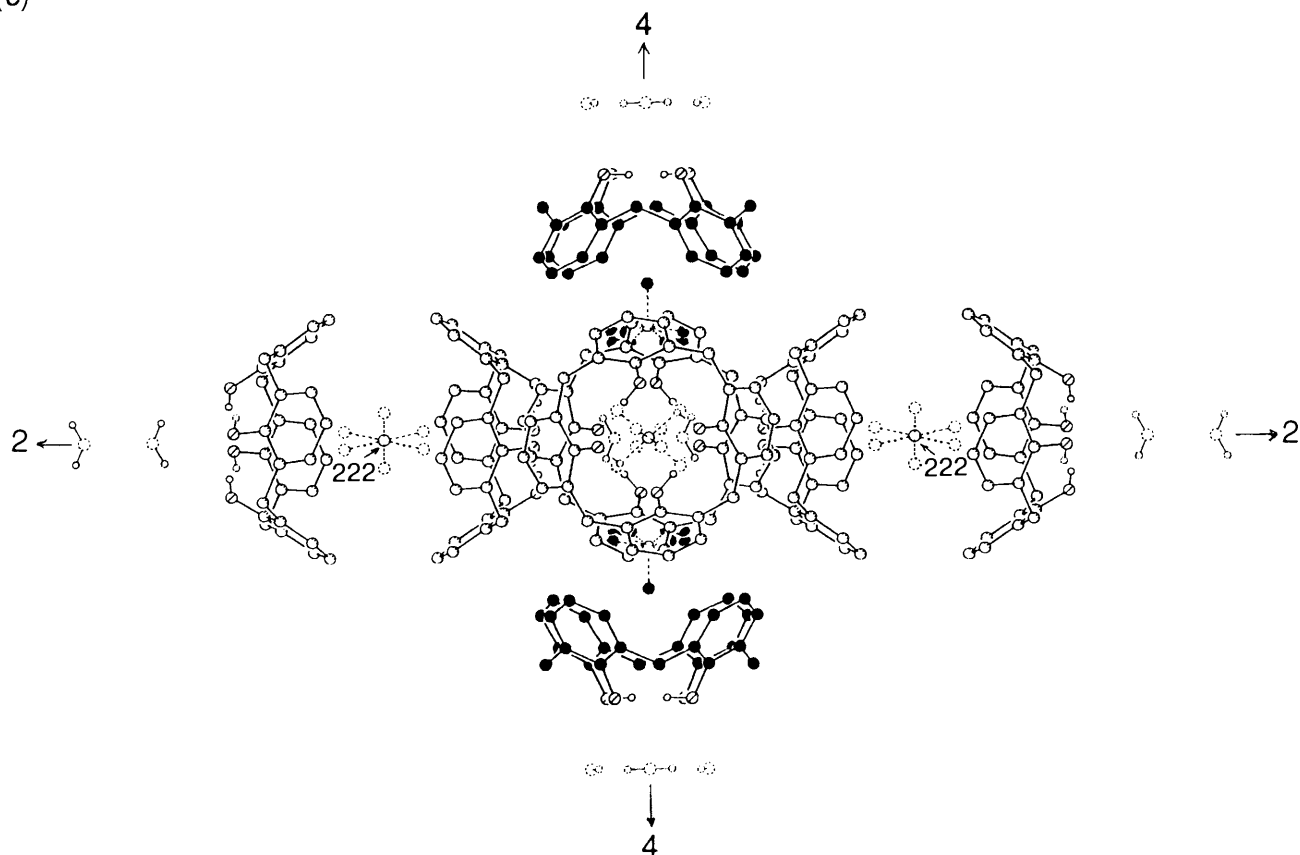


Fig. 3 (contd.)

(c)



**Fig. 3** The stack of 'B' calixarenes, O(2W) water molecules and cations '2' (sequence ...WBCBW...) viewed down *c*, (a) without, and (b) with the 'A' stack superimposed. (c) The interpenetrating array of 'A' and 'B' stacks viewed down one of the 'B' stack twofold axes. In (b) and (c), carbon atoms of the 'A' stack are shown as solids.

fourfold axis, and its disposition into the unit cell are shown in Fig. 2.

Calixarene 'B' is disposed about a Wyckoff '*h*' twofold axis (as cone axis); the  $O_4$  array is not rigorously planar [ $\chi^2$  119;  $\delta(O)$  0.03–0.06 Å], and the phenolic  $C_6$  planes have dihedral angles to it of, alternately, *ca.* 54.5 (rings 2) and 50° (rings 3), with phenolic O(2,3) lying 0.10(1) and 0.09(1) Å out of their respective  $C_6$  ring planes. C–O are 1.341(9) and 1.369(9) Å (rings 2,3) and the angles at the methylene carbon atoms C(2,3) are 114.3(6) and 115.5(6)°. O(2,3) have been assigned fully and half-weighted hydrogen atoms, respectively; within the asymmetric unit, O(2)···O(3), linked by the fully-weighted hydrogen, is 2.658(8) Å, while the other O(3)···O(2) distance, linked by the half-weighted hydrogen, is 2.588(8) Å. As with calixarene 'A', half-weighted water molecule fragments, O(2W), lie beyond the  $O_4$  apex of the cone, nearer O(3) [2.87(2) Å] than O(2) [3.43(2) Å] and close to the 4 axis; the distance between pairs of  $O_4$  planes opposed about the 4 axis is 7.83(2) Å. Within each 'B' cone, we find an associated cation, that associated with N(2); N(2) lies on a position of 222 symmetry with an environment suggestive of a pair of disordered, interpenetrating tetrahedral carbon arrays, and enclosed by a second 'B' cone generated by two of the rotational operations; the distance between the pair of  $O_4$  planes about the enclosed cation is 10.40(2) Å. We thus have, along the twofold axis across the *ab* diagonal, stacks of pairs of cones encapsulating cations, and separated by water molecule arrays ...WBCBW... [Fig. 3(a)]. The mode of interpenetration of 'A' and 'B' stacks is shown in Fig. 3(b,c).

The charges formally present on both the  $[N(CH_3)_4]^+$  cation

and  $[\text{calix}[4]\text{arene} - H]^-$  anion are presumably highly delocalised,<sup>5,6</sup> so that prediction of the structure which optimises attractive interactions between these ions is not immediately apparent from simple qualitative considerations. However, the interaction between an ion and a dipole would appear to be more readily predictable unless a factor other than simple electrostatics is operable. Thus, the fact that the present structure determination reveals what appears to be the interaction of the cation with the electropositive end of a neutral calixarene dipole (in the calixarene 'A' species) suggests that at least one other intermolecular force must play an important rôle in determining the overall structure. In the context of a large number of known structures of calixarene inclusion complexes, it would appear reasonable to once again postulate  $\text{CH}_3$ - $\pi$  attractions as this force.<sup>2,7</sup> In this sense, any neutral calixarene can therefore be regarded as a cation solvator, a situation which is yet to be observed with simple cations except where the calixarene contains ether-oxygen or more complicated donor groups.<sup>2,8</sup>

A remarkable feature of the model developed for the present structure is the fact that the encapsulated tetramethylammonium species involving calixarenes 'B' appears to be part of an ion-triplet containing two calixarene monoanions. The exact reasons why such a structure should be preferred to one involving one neutral and one anionic calixarene, with the other calixarene anion binding to the second cation, are obscure, though it seems that perhaps there must be a rather subtle balance between electrostatic and  $\text{CH}_3$ - $\pi$  attractions occurring within the solid. Within the encapsulated cation unit, it is possible for different cation methyl groups to be appropriately oriented to direct their hydrogen atoms towards the 'faces' of

groups of phenyl groups in different calixarene anions, and such bridging *via* CH<sub>3</sub>- $\pi$  attractions may well be associated with enhanced interactions between delocalised charges.

An interesting speculation concerning the encapsulated cation structure reported herein is that it might be considered a mimic of the intermediate presumably involved in the formation of 'carcerand' molecules,<sup>9</sup> especially those derived from calixarenes,<sup>10</sup> and hence that the use of tetramethylammonium bases could be a means of enhancing yields in carcerand syntheses, which are certainly known<sup>9</sup> to be subject to solvent template effects.

### Acknowledgements

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