

Two triethylammonium ion complexes of monoanionic calix[4]arene

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Two complexes between mono-deprotonated calix[4]arene and Et_3HN^+ are reported. The first, triethylammonium 26,27,28-trihydropentacyclo[19.3.1.1^{3,7}.1^{9,13}.1^{15,19}]octacos-1(25),3,5,7(28),9,11,13(27),15,17,19(26),21,23-dodecaen-25-olate, $\text{C}_6\text{H}_{16}\text{N}^+\cdot\text{C}_{28}\text{H}_{23}\text{O}_4^-$, comprises only the cationic and anionic species, whereas the second, tris(triethylammonium) tris[26,27,28-trihydropentacyclo[19.3.1.1^{3,7}.1^{9,13}.1^{15,19}]octacos-1(25),3,5,7(28),9,11,13(27),15,17,19(26),21,23-dodecaen-25-olate] acetonitrile solvate, $3\text{C}_6\text{H}_{16}\text{N}^+\cdot 3\text{C}_{28}\text{H}_{23}\text{O}_4^- \cdot \text{C}_2\text{H}_3\text{N}$, comprises one acetonitrile solvent molecule for three such units. In both cases, the units are stacked in columns so that the ammonium cation is hydrogen bonded to a phenolic or phenolate O atom of one molecule and included in the hydrophobic cavity of another neighbouring calixarene. The short contacts present indicate that cation $\cdots\pi$ and C—H $\cdots\pi$ interactions are likely to be involved in the inclusion phenomena.

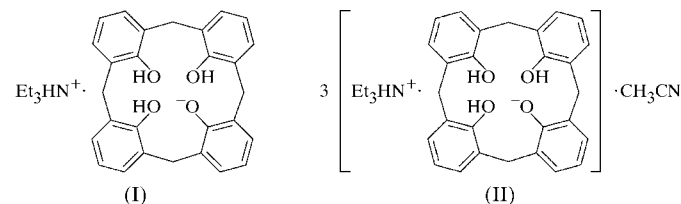
Comment

The complexation of organic cations by anionic calixarenes or homoaxalixarenes is a topic of current interest which has been widely covered from a crystallographic point of view, particularly in the case of quaternary ammonium ions (Shinkai *et al.*, 1990; Harrowfield *et al.*, 1993; Harrowfield, Richmond, Sobolev & White, 1994; Atwood *et al.*, 1995; Abidi *et al.*, 1996; Casnati *et al.*, 2001), in conjunction with the biologically relevant cation acetylcholine (Harrowfield, Richmond & Sobolev, 1994; Lehn *et al.*, 1995). The interactions involved have been shown to be both electrostatic and hydrophobic in origin. The existence of cation $\cdots\pi$ and C—H $\cdots\pi$ interactions has also been discussed.

Tertiary ammonium cations differ from the quaternary species by their ability to act as hydrogen-bond donors, but other interaction modes can also be discerned in some instances. Some examples of calixarene or homoaxalixarene complexes with triethylammonium have been obtained as side products, or in order to aid comparison in the course of

investigations of metal ion complexation with triethylamine as a deprotonating agent (see Thuéry *et al.*, 1995, 2001).

Apart from these examples, a search of the Cambridge Structural Database (Version 5.22; Allen & Kennard, 1993) for tertiary or secondary alkylamine or ammonium complexes of calixarenes gives only three other structures, involving either triethylamine (Bavoux & Perrin, 1992) or secondary ammonium ions, such as morpholinium (Barbour *et al.*, 1996) or piperidinium (Nachtigall *et al.*, 1998). We report herein the structures of two species of the triethylammonium complex of calix[4]arene, *i.e.* (I) and (II) below.



Since compound (II) includes an acetonitrile solvent molecule, the two compounds can be described as pseudo-poly-morphs. The structures of (I) and (II) share numerous common features and will be discussed together.

The asymmetric unit of (I) contains one each of the monoanionic calix[4]arene and the triethylammonium ion, whereas that of (II) contains three calixarene molecules, hereinafter denoted *A*, *B* and *C*, and three cations, as well as one acetonitrile solvent molecule located in a lattice void.

In both compounds, the calix[4]arenes are in the usual slightly distorted cone conformation, with dihedral angles between the mean planes defined by the four C atoms of the methylene bridges and the four aromatic rings in the range 47.42 (8)–60.97 (11)° in (I) and 45.0 (1)–69.1 (1)° in (II). These ranges are similar in (I) and larger in (II) than the values observed in the piperidinium ion complex of calix[4]arene (46.3–61.0°; Nachtigall *et al.*, 1998).

Only three hydroxy H atoms remain in each molecule and these are involved in intramolecular hydrogen bonding, the

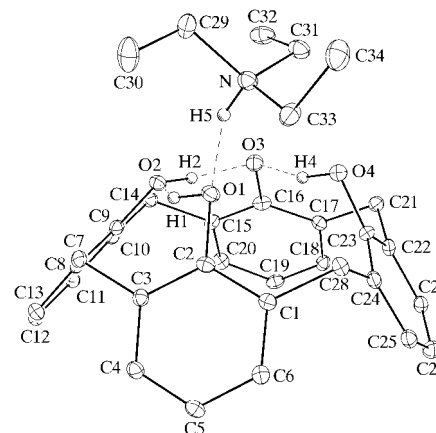


Figure 1

A view of the molecule of (I) with the atom-numbering scheme. H atoms have been omitted for clarity, except for those involved in hydrogen bonding, which are drawn as small spheres of arbitrary radii. The hydrogen bonds are shown as dashed lines and displacement ellipsoids are drawn at the 20% probability level.

deprotonated O atom being hydrogen bonded to its two neighbours, as in the previously reported piperidinium complex (Nachtigall *et al.*, 1998). The O...O intramolecular distances between adjacent phenolic groups reflect the absence of one hydrogen bond in the usual cyclic pattern, with values in the range 2.479 (4)–2.683 (4) Å in (I) and 2.523 (5)–2.846 (5) Å in (II) for hydrogen-bonded O atoms, and 3.017 (4) Å in (I) and 2.876 (6)–3.027 (5) Å in (II) for atoms not directly linked to each other.

Each calixarene molecule is associated *via* hydrogen bonding to its triethylammonium cation, the bonded O atom being protonated in (I) or anionic in (II). In both (I) and (II), the calixarene–ammonium assemblages are stacked into columns. In (I), neighbouring molecules along the column are related by the glide plane perpendicular to the *a* axis. In (II), molecule *A* is stacked with its symmetry-related equivalent through the glide plane perpendicular to the *b* axis, whereas molecules *B* and *C* are stacked alternately along the *c* axis. The dihedral angles between the mean planes of neighbouring molecules along the columns are 41.66 (5)° in (I), and 54.56 (7) (molecule *A*) and 56.62 (8)° (molecules *B* and *C*) in (II). In this way, the cations are located near the cavity of the neighbouring calixarene along the column.

The shortest H...centroid distances, involving the H atoms of the cation alkyl chains and the centroids of the aromatic rings, are nearly equal in both compounds, being 2.720 Å in (I), and 2.719 (molecule *A*) and 2.723 Å (molecules *B* and *C*) in (II). In all cases, the H atoms involved in the shortest contacts are those of the C atoms bonded to N atoms. These values correspond to C...centroid separations of 3.503, 3.616 and 3.466 Å, respectively. Such distances suggest that, apart from cation... π interactions, C–H... π interactions (Takahashi *et al.*, 2000; Suezawa *et al.*, 2001) are likely to play some role in ammonium ion inclusion in these molecules.

The present results, in which the triethylammonium cation displays both *exo* and *endo* bindings with respect to one or other of the two closest calixarenes, are at variance with the piperidinium complex, which has been described as an *exo* complex held together by hydrogen-bonding interactions (Nachtigall *et al.*, 1998).

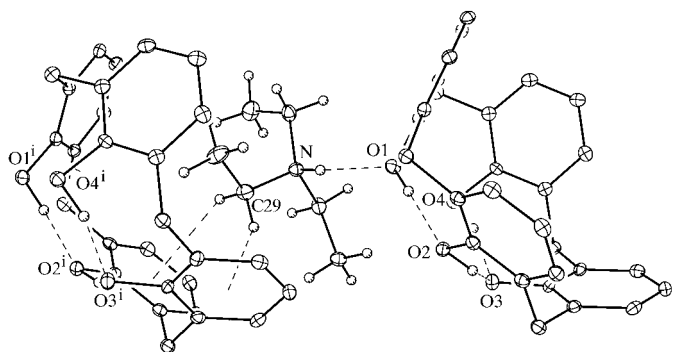


Figure 2

A view of the packing in (I). The H atoms of the calixarene framework have been omitted for clarity, and the remaining H atoms are drawn as small spheres of arbitrary radii. The hydrogen bonds and C–H... π interactions are shown as dashed lines [symmetry code: (i) $\frac{1}{2} - x, y - \frac{1}{2}, z - \frac{1}{2}$]. Displacement ellipsoids are plotted at the 20% probability level.

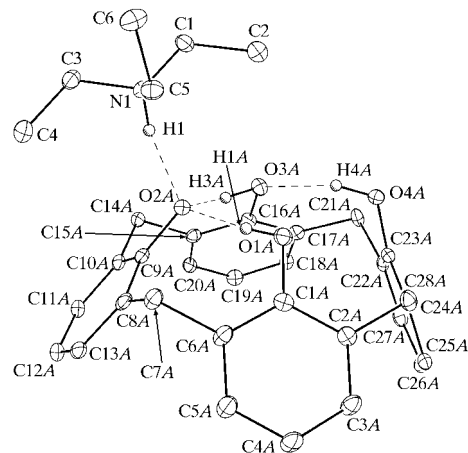


Figure 3

A view of molecule *A* in (II) with the atom-numbering scheme. H atoms have been omitted for clarity, except for those involved in hydrogen-bonding, which are drawn as small spheres of arbitrary radii. The hydrogen bonds are shown as dashed lines and displacement ellipsoids are drawn at the 20% probability level.

A columnar arrangement analogous to that found here in (I) and (II) (but in which the mean planes of the macrocycles are parallel), and involving the same ammonium cation, has been observed in the uranyl complex of *p*-phenyl-tetrahomodioxacalix[4]arene, with two hydrogen-bonded triethylammonium counter-ions (Masci *et al.*, 2001).

Calix[4]arene is notoriously less liable to include organic molecules than its *para*-substituted counterparts (particularly the widely used *p-tert*-butylcalix[4]arene; Harrowfield *et al.*, 1993). However, it appears that, in the present cases, it can be involved in the building of columnar supramolecular assemblies based on both directed hydrogen bonding and inclusion of ammonium ions *via* feeble interactions.

Experimental

Calix[4]arene was synthesized according to the method of Ungaro & Pochini (1984). Colourless crystals of (I) and (II) were obtained by recrystallization from chloroform and acetonitrile, respectively, in the presence of triethylamine.

Compound (I)

Crystal data

$C_6H_{16}N^+ \cdot C_{28}H_{23}O_4^-$
 $M_r = 525.66$
 Orthorhombic, $Pna2_1$
 $a = 18.3531$ (18) Å
 $b = 10.8710$ (12) Å
 $c = 13.8210$ (12) Å
 $V = 2757.5$ (5) Å³
 $Z = 4$
 $D_x = 1.266$ Mg m⁻³

Mo $K\alpha$ radiation
 Cell parameters from 15 424 reflections
 $\theta = 2.7$ – 25.7°
 $\mu = 0.08$ mm⁻¹
 $T = 100$ (2) K
 Platelet, colourless
 $0.25 \times 0.25 \times 0.10$ mm

Data collection

Nonius KappaCCD area-detector diffractometer
 φ scans
 15 424 measured reflections
 2702 independent reflections
 1909 reflections with $I > 2\sigma(I)$

$R_{int} = 0.089$
 $\theta_{max} = 25.7^\circ$
 $h = 0 \rightarrow 22$
 $k = 0 \rightarrow 13$
 $l = 0 \rightarrow 16$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.057$
 $wR(F^2) = 0.124$
 $S = 1.08$
 2702 reflections
 353 parameters

H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0470P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.23 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.25 \text{ e } \text{\AA}^{-3}$

Table 1

Hydrogen-bonding geometry (\AA , $^\circ$) for (I).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$N-H5\cdots O1$	0.89	1.95	2.790 (6)	158
$O1-H1\cdots O2$	0.83	1.75	2.544 (5)	162
$O2-H2\cdots O3$	0.82	1.67	2.478 (5)	169
$O4-H4\cdots O3$	0.82	1.87	2.689 (5)	177

Compound (II)

Crystal data

$3C_6H_{16}N^+ \cdot 3C_{28}H_{23}O_4^- \cdot C_2H_3N$
 $M_r = 1618.04$
 Monoclinic, Cc
 $a = 20.1364 (14) \text{ \AA}$
 $b = 30.9080 (14) \text{ \AA}$
 $c = 16.0088 (10) \text{ \AA}$
 $\beta = 118.587 (3)^\circ$
 $V = 8748.9 (9) \text{ \AA}^3$
 $Z = 4$

$D_x = 1.228 \text{ Mg m}^{-3}$
 Mo $K\alpha$ radiation
 Cell parameters from 15 261 reflections
 $\theta = 2.6\text{--}25.7^\circ$
 $\mu = 0.08 \text{ mm}^{-1}$
 $T = 100 (2) \text{ K}$
 Parallelepiped, colourless
 $0.6 \times 0.3 \times 0.2 \text{ mm}$

Data collection

Nonius KappaCCD area-detector diffractometer
 φ scans
 15 261 measured reflections
 8240 independent reflections
 5760 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.066$
 $\theta_{\text{max}} = 25.7^\circ$
 $h = -21 \rightarrow 24$
 $k = -37 \rightarrow 37$
 $l = -18 \rightarrow 0$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.056$
 $wR(F^2) = 0.140$
 $S = 1.03$
 8240 reflections
 1082 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0624P)^2 + 4.0660P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.52 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.28 \text{ e } \text{\AA}^{-3}$

Table 2

Hydrogen-bonding geometry (\AA , $^\circ$) for (II).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$O1A-H1A\cdots O2A$	0.82	1.75	2.551 (5)	165
$O3A-H3A\cdots O2A$	0.93	1.68	2.552 (5)	155
$O4A-H4A\cdots O3A$	0.89	2.05	2.846 (5)	148
$N1-H1\cdots O2A$	0.93	1.78	2.667 (5)	160
$O1B-H1B\cdots O2B$	0.81	1.73	2.539 (5)	176
$O3B-H3B\cdots O2B$	0.96	1.64	2.585 (5)	168
$O4B-H4B\cdots O1B$	0.92	1.79	2.703 (5)	169
$N2-H2\cdots O2B$	0.99	1.74	2.699 (5)	161
$O1C-H1C\cdots O2C$	0.82	1.72	2.523 (5)	170
$O3C-H3C\cdots O2C$	0.86	1.80	2.625 (5)	158
$O4C-H4C\cdots O1C$	0.87	1.83	2.683 (5)	164
$N3-H3\cdots O2C$	0.96	1.83	2.729 (5)	155

Some O—H bond lengths in (I), being somewhat longer than usual, were restrained to the standard value of 0.82 \AA ; otherwise the N—H distances were 0.89–0.99 \AA and the O—H distances were 0.81–0.96 \AA . Some constraints were applied to the displacement parameters of the acetonitrile solvent molecule in (II). Because of the lack of any significant anomalous dispersion effect, the absolute structure could not be determined from the diffraction experiment for either (I) or (II), so the Friedel pairs were merged prior to refinement.

For both compounds, data collection: *KappaCCD Server Software* (Nonius, 1997); cell refinement: *DENZO-SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO-SMN*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1999); software used to prepare material for publication: *SHELXTL* and *PARST97* (Nardelli, 1995).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: DN1006). Services for accessing these data are described at the back of the journal.

References

- Abidi, R., Baker, M. V., Harrowfield, J. M., Ho, D. S. C., Richmond, W. R., Skelton, B. W., White, A. H., Varnek, A. & Wipff, G. (1996). *Inorg. Chim. Acta*, **246**, 275–286.
- Allen, F. H. & Kennard, O. (1993). *Chem. Des. Autom. News*, **8**, 1, 31–37.
- Atwood, J. L., Barbour, L. J., Junk, P. C. & Orr, G. W. (1995). *Supramol. Chem.* **5**, 105–108.
- Barbour, L. J., Damon, A. K., Orr, G. W. & Atwood, J. L. (1996). *Supramol. Chem.* **7**, 209–213.
- Bavoux, C. & Perrin, M. (1992). *J. Inclusion Phenom. Mol. Recognit. Chem.* **14**, 247–256.
- Bruker (1999). *SHELXTL*. Version 5.1. Bruker AXS Inc., Madison, Wisconsin, USA.
- Casnati, A., Sciotto, D. & Arena, G. (2001). *Calixarenes 2001*, edited by Z. Asfari, V. Böhmer, J. M. Harrowfield & J. Vicens, pp. 440–456. Dordrecht: Kluwer Academic Publishers.
- Harrowfield, J. M., Ogden, M. I., Richmond, W. R., Skelton, B. W. & White, A. H. (1993). *J. Chem. Soc. Perkin Trans. 2*, pp. 2183–2190.
- Harrowfield, J. M., Richmond, W. R. & Sobolev, A. N. (1994). *J. Inclusion Phenom. Mol. Recognit. Chem.* **19**, 257–276.
- Harrowfield, J. M., Richmond, W. R., Sobolev, A. N. & White, A. H. (1994). *J. Chem. Soc. Perkin Trans. 2*, pp. 5–9.
- Lehn, J. M., Méric, R., Vigneron, J. P., Cesario, M., Guilhem, J., Pascard, C., Asfari, Z. & Vicens, J. (1995). *Supramol. Chem.* **5**, 97–103.
- Masci, B., Gabrielli, M., Levi Mortera, S., Nierlich, M. & Thuéry, P. (2001). *Polyhedron*. In the press.
- Nachtigall, F. F., Vencato, I., Lazzarotto, M. & Nome, F. (1998). *Acta Cryst.* **C54**, 1007–1010.
- Nardelli, M. (1995). *J. Appl. Cryst.* **28**, 659.
- Nonius (1997). *KappaCCD Server Software*. Windows 3.11 Version. Nonius BV, Delft, The Netherlands.
- Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.
- Sheldrick, G. M. (1997). *SHELXL97* and *SHELXS97*. University of Göttingen, Germany.
- Shinkai, S., Araki, K., Matsuda, T., Nishiyama, N., Ikeda, H., Takasu, I. & Iwamoto, M. (1990). *J. Am. Chem. Soc.* **112**, 9053–9058.
- Suezawa, H., Yoshida, T., Hirota, M., Takahashi, H., Umezawa, Y., Honda, K., Tsuboyama, S. & Nishio, M. (2001). *J. Chem. Soc. Perkin Trans. 2*, pp. 2053–2058.
- Takahashi, H., Tsuboyama, S., Umezawa, Y., Honda, K. & Nishio, M. (2000). *Tetrahedron*, **56**, 6185–6191.
- Thuéry, P., Keller, N., Lance, M., Vigner, J. D. & Nierlich, M. (1995). *J. Inclusion Phenom. Mol. Recognit. Chem.* **20**, 89–96.
- Thuéry, P., Nierlich, M., Vicens, J. & Masci, B. (2001). *J. Chem. Soc. Dalton Trans.* pp. 867–874.
- Ungaro, R. & Pochini, A. (1984). *J. Chem. Soc. Perkin Trans. 2*, pp. 1979–1985.