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Structure of the p-sulfonatocalix[4]arene complex with tetramethylammonium ions, $[NME_4]_5$[p-sulfonatocalix[4]arene]·$4H_2O$

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Structure of the p-sulfonatocalix[4]arene complex with tetramethylammonium ions, $[NMe_4]_5$[p-sulfonatocalix[4]arene]·$4H_2O$

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Treatment of p-calix[4]arene sulfonic acid with excess tetramethylammonium hydroxide yields $[NMe_4]_5$[p-sulfonatocalixarene]·$4H_2O$. The compound crystallizes from aqueous solution in the triclinic space group P1 with a = 13.125(3), b = 14.881(3), c = 16.320(4) Å, α = 77.19(1), β = 77.30(1), γ = 72.30(1)°, and D_c = 1.35 g cm^{-3} for Z = 2 ($C_{48}H_{87}O_{20}N_5S_4$). Refinement based on 5044 observed reflections yielded a final R value of 0.084. The overall structure consists of bilayers of calix[4]arenes separated by regions which contain the cations and water molecules. One of the tetramethylammonium ions is bound within the hydrophobic calix[4]arene cavity.

INTRODUCTION

The inclusion chemistry of calix[4]arenes is well documented[1] and studies of the water-soluble [p-sulfonatocalix[4]arene]$^{n-}$ (n = 4, 5) have generated interest owing to similarities to biological function,[2] enzyme mimicry[3] and clay structure.[4] The cavity of the anionic p-sulfonatocalix[4]arene has been found to house cationic,[5] neutral,[2,4b,4c,6] and anionic guests.[7] In the case of the latter, $(NH_4^+)_5$[p–sulfonatocalix[4]arene]$^{5-}$[NH_4^+][$MeSO_4^-$], the cavity selected the methyl sulfate anion over the NH_4^+ cations.[7] However, there are several reports of complexes formed between tetraalkylammonium ions and calix[n]arenes, where the tetraalkylammonium ion has been found to reside within the bowlic cavity of the calixarene,[8] including the results given in the preceeding article in this Journal.[9] In this contribution we report the synthesis and X-ray crystal structure of the title compound which contains a cavity-bound $[NMe_4]^+$ ion and an interesting bilayer packing arrangement.

RESULTS AND DISCUSSION

The [p-sulfonatocalix[4]arene]$^{5-}$ anion was produced at neutral pH which resulted in the ionization of one of the phenolic protons. This disrupts the tight intramolecular hydrogen bonding scheme, as evidenced by O...O distances of 2.50, 2.58, 2.61, and 2.80 Å. The latter, between O21 and O31 (Figure 1), shows the lack of a hydrogen atom for bonding. This observation is consistent with the literature.[4b,4c]

The cone conformation of the calix[4]arene is shown in Figure 2. The embedded tetramethylammonium ion displays one methyl group deep within the cavity and three at the upper rim. The carbon atom of the methyl

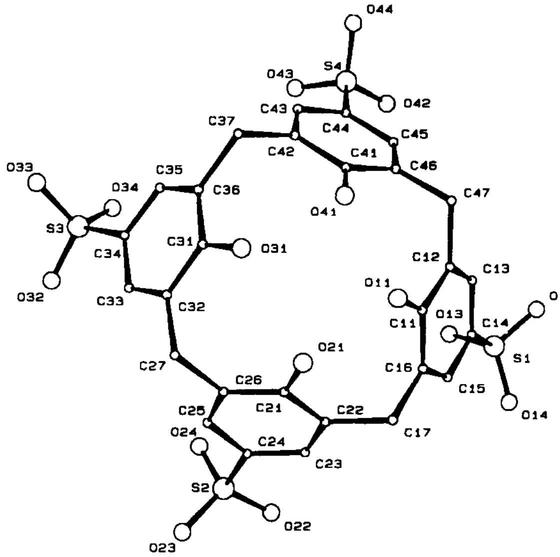

Figure 1 Perspective view of the p-sulfonatocalix[4]arene molecule showing the atomic labelling.

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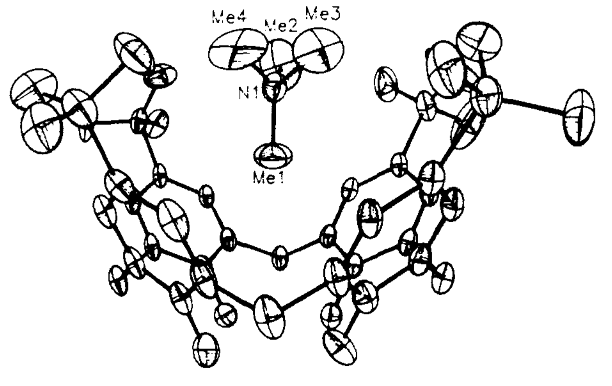

Figure 2 Structure of p-sulfonatocalix[4]arene showing the included NMe_4+ ion bound within the cone.

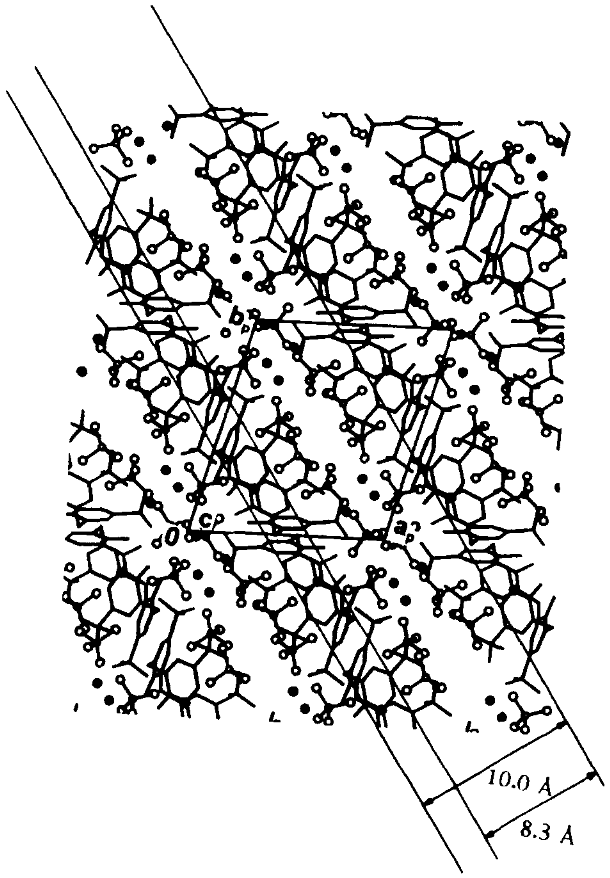

Figure 3 Bilayer packing arrangement in the [NMe_4]5[p-sulfonatocalix[4]arene]·$4H_2O$ structure. The lines are least-squares best planes of the aromatic carbon atoms of the -SO_3- groups.

group Me1 is situated at distances of 3.71 to 3.78 Å from the centroids of the four aromatic rings. These values are longer than those typically found for C-H...π aromatic hydrogen bonding.[10–13] It is suggested that the position of the cation is stabilized by strong electrostatic interactions with the electron-rich sulfonato groups. The shape of the cavity is regular with respect to the plane angles formed by the distal aromatic rings. This is in contrast to that observed in the structure of Na_4[p-sulfonatocalix[4]arene]·13.5 H_2O, where the calixarene is distorted from approximate C_{4v} symmetry to approximate C_{2v} symmetry.[14] In the latter structure, O-H...π hydrogen bonds between a water molecule and a pair of distal rings reduces the plane angle to 32°, while the angle between the remaining pair of rings is 66°.

Figure 3 shows that the remaining four tetramethylammonium ions and the H_2O molecules are situated in the region between the calixarene bilayers. In particular, the bilayer repeat distance of the structure of Na_5[p-sulfonatocalix[4]arene] · 12 H_2O was found to be 13.7 Å, with the hydrophilic layer 8.3 Å in thickness. In the present structure, the bilayer repeat distance is 10.0 Å, and the hydrophilic layer is 8.3 Å thick. Further scrutiny of Figure 3 shows that the cations pack among themselves and the water molecules reside in channels running through the crystal.

EXPERIMENTAL SECTION

Materials for the synthesis of calixarenes were purchased from Aldrich Chemical Co. and were not purified prior to use. p-Calix[4]arene sulfonic acid was prepared according to the literature method.[1b]

Preparation of [NMe_4]$_5$[p-sulfonatocalix[4]arene]·$4H_2O$

To a stirred sample of p-calix[4]arene sulfonic acid (0.50g, 0.67mmol) in water (10mL) at room temperature, was rapidly added NMe_4OH (0.61g, 6.7mmol). The reaction mixture was stirred for approx. 1h, whereupon the solvent was reduced and left to stand for crystallization to take place. Large, colorless crystals were formed from solution after several days.

X-ray structure determination of [NMe_4]$_5$[p-sulfonatocalix[4] arene]·$4H_2O$

The compound decomposes with loss of H_2O, so single crystals were sealed in thin-walled glass capillaries with a few drops of mother liquor and mounted on an Enraf Nonius diffractometer. Intensity data were collected at 298K using graphite monochromated Cu Kα radiation (λ = 1.5418 Å). Accurate cell parameters were obtained by least-squares analysis of the setting angles of 24 high angle reflections (2θ > 30°). The structure was solved using SHELXS-86[15] and refined using SHELX-76.[16] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed at calculated positions and their parameters were not refined. Refinement converged with R = 0.084 for 5044 observed reflections.

Details of data collection and structure refinement are given in Table 1 and final fractional atomic coordinates and thermal parameters are given in Table 2. The numbering scheme of the p-sulfonatocalix[4]arene is shown in Figure 1. Phenolic O···O and sulfonato S···S distances for all rings are given in Table 3 together with centroid···centroid distances and plane angles between distal rings.

Table 1 Crystal data and summary of data collection for [NMe$_4$]$_5$[p-sulfonatocalix[4]arene]· 4H$_2$O

Mol. Formula	$C_{48}H_{87}O_{20}N_5S_4$
Mol. Wt.	1182.5
Space group	$P\bar{1}$
cell constants	
a, Å	13.125(3)
b., Å	14.881(3)
c, Å	16.320(4)
α, deg	77.19(1)
β, deg	77.30(1)
γ, deg	72.30(1)
V, Å^3	2921
molecules/unit cell	2
D_c, g cm^{-3}	1.349
μ, cm^{-1}	20.9
radiation	Cu Kα
scan width, deg	0.80 + 0.20 tan θ
decay of stds	< 2%
2θ range, deg	4-100
no. of obsd reflcns	5044
no. of params varied	721
sigma cutoff	3σ
temp of data colln, deg	23°C
R	0.084
R_w	0.088

Table 2 Final fractional coordinates and thermal parameters for [NMe$_4$]$_5$[p-sulfonatocalix[4]arene]·4H$_2$O.

Atom	*x/a*	*y/b*	*z/c*	*U(eqv)*
S(1)	.2683(2)	.9252(2)	.4129(1)	0.059
O(11)	.7114(5)	.9512(4)	.2573(3)	0.061
O(12)	.2461(5)	.9462(5)	.4980(4)	0.091
O(13)	.2736(6)	.8262(5)	.4159(5)	0.114
O(14)	.1937(5)	.9892(6)	.3599(4)	0.104
C(11)	.6100(7)	.9459(5)	.2932(5)	0.049
C(12)	.5813(7)	.9213(5)	.3811(5)	0.044
C(13)	.4783(6)	.9169(5)	.4164(5)	0.044
C(14)	.3962(6)	.9396(5)	.3669(5)	0.045
C(15)	.4244(7)	.9666(5)	.2800(5)	0.051
C(16)	.5270(7)	.9711(5)	.2409(5)	0.049
C(17)	.5559(7)	1.0015(5)	.1442(5)	0.054
S(2)	.4901(3)	.7432(2)	.0015(2)	0.082
O(21)	.7853(5)	.9164(4)	.1018(4)	0.079
O(22)	.3808(7)	.7990(6)	.0236(6)	0.132
O(23)	.5252(7)	.7473(5)	-.0900(4)	0.112
O(24)	.5086(8)	.6474(5)	.0462(5)	0.128
C(21)	.7149(8)	.8749(6)	.0828(5)	0.056
C(22)	.6024(8)	.9148(5)	.0984(5)	0.052
C(23)	.5345(8)	.8757(5)	.0732(5)	0.056
C(24)	.5747(8)	.7959(6)	.0336(5)	0.062
C(25)	.6860(9)	.7549(7)	.0210(5)	0.068
C(26)	.7566(8)	.7925(6)	.0445(5)	0.059
C(27)	.8785(8)	.7417(7)	.0323(5)	0.072
S(3)	.9195(2)	.3802(2)	.1768(1)	0.063
O(31)	.9451(6)	.7702(4)	.1771(4)	0.083
O(32)	.8849(6)	.3791(5)	.0987(4)	0.100
O(33)	1.0298(5)	.3214(5)	.1809(5)	0.100
O(34)	.8457(6)	.3552(5)	.2521(4)	0.091
C(31)	.9340(7)	.6820(6)	.1781(5)	0.055
C(32)	.9050(7)	.6614(6)	.1064(5)	0.054
C(33)	.9001(6)	.5705(6)	.1068(5)	0.052
C(34)	.9203(6)	.4969(6)	.1760(5)	0.048
C(35)	.9459(6)	.5197(6)	.2466(5)	0.049
C(36)	.9533(6)	.6090(6)	.2489(5)	0.050
C(37)	.9818(6)	.6302(6)	.3280(5)	0.056
S(4)	.7036(2)	.5410(2)	.5960(2)	0.066
O(41)	.8595(4)	.8242(4)	.3224(3)	0.058
O(42)	.5981(6)	.5779(6)	.6288(6)	0.117
O(43)	.727(1)	.4582(6)	.5632(7)	0.209
O(44)	.7720(8)	.520(1)	.6577(7)	0.214
C(41)	.8229(6)	.7601(6)	.3850(5)	0.049
C(42)	.8806(6)	.6608(6)	.3932(5)	0.049
C(43)	.8440(6)	.5974(6)	.4571(5)	0.050
C(44)	.7496(6)	.6248(5)	.5149(5)	0.044
C(45)	.6945(6)	.7206(6)	.5074(5)	0.046
C(46)	.7298(6)	.7886(5)	.4446(5)	0.045
C(47)	.6687(6)	.8930(5)	.4388(5)	0.050
N(1)	.5680(6)	.6294(5)	.3106(5)	0.068
Me(1)	.641(1)	.6940(9)	.2774(8)	0.133
Me(2)A	.492(4)	.671(5)	.382(4)	0.123
Me(2)B	.507(4)	.630(3)	.403(2)	0.190
Me(3)A	.639(4)	.531(2)	.349(3)	0.146
Me(3)B	.614(4)	.534(3)	.296(6)	0.271
Me(4)A	.516(6)	.612(5)	.247(3)	0.252
Me(4)B	.469(4)	.672(4)	.268(3)	0.162
N(2)	.0030(6)	.7888(5)	.5600(4)	0.062
Me(5)	-.0187(8)	.8547(7)	.4753(5)	0.076
Me(6)	.0389(8)	.8445(6)	.6115(6)	0.076
Me(7)	.0962(9)	.7018(7)	.5408(6)	0.085
Me(8)	-.0978(8)	.7604(8)	.6072(6)	0.088
N(3)	1.2800(6)	.5331(5)	.1027(5)	0.072
Me(9)	1.2288(9)	.6262(7)	.1380(7)	0.102
Me(10)	1.3166(9)	.5541(9)	.0066(6)	0.100
Me(11)	1.2030(9)	.4693(9)	.1263(9)	0.120
Me(12)	1.3840(8)	.4832(7)	.1402(6)	0.082
N(4)	1.0984(6)	.9779(5)	.1629(4)	0.071
Me(13)	1.135(1)	1.065(1)	.1538(9)	0.183
Me(14)	1.191(1)	.891(1)	.174(1)	0.175
Me(15)	1.018(1)	.970(1)	.2421(7)	0.132
Me(16)	1.048(1)	.979(1)	.0869(8)	0.167
N(5)	.6299(7)	1.2358(5)	.2865(5)	0.077
Me(17)	.6153(9)	1.3219(7)	.2172(6)	0.088
Me(18)	.535(1)	1.1920(9)	.3023(8)	0.115
Me(19)	.740(1)	1.1627(9)	.2622(9)	0.128
Me(20)	.6378(9)	1.2696(8)	.3672(6)	0.095
W(1)	.2069(7)	.7221(5)	.3199(5)	0.121
W(2)	.264(1)	.208(1)	.2014(9)	0.114
W(3)	.768(1)	.121(1)	.065(1)	0.116
W(4)	.877(2)	.1983(9)	.060(1)	0.154

Table 3 Ring centroid...centroid, O...O and S...S distances (Å) and angles (°) between distal rings

Centroid 1...Centroid 3	6.84
Centroid 2...Centroid 4	6.75
O11...O21	2.61
O11...O31	3.63
O11...O41	2.50
O21...O41	3.78
O31...O41	2.58
O21...O31	2.80
S1...S2	7.46
S2...S3	7.13
S3...S4	7.43
S1...S3	10.53
S1...S4	7.37
S2...S4	10.24
Plane angle* (rings 1,3)	73.3
Plane angle (rings 2,4)	67.1

*Plane angle is defined by the dihedral angle between distal rings

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