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A Complex between C-Methylcalix[4]resorcinarene and Triethylammonium Nitrate

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The synthesis and crystal structure of the complex formed by the all-*cis* epimer of C-methylcalix[4]resorcinarene (1) and triethylammonium nitrate are reported. "1.(HNEt$_3^+$)$_4$ · (NO$_3^-$)$_4$(2)", crystallizes in the monoclinic space group $P2_1/n$, a= 25.796(2), b= 16.6048(11), c= 29.5659(10) Å, β = 94.636(4)°, V= 12623(2) Å^3, Z= 8. Refinement led to a final conventional R_1 value of 0.128 for 12428 reflections and 1473 parameters. The resorcinarene displays the usual bowl-type shape, with four hydroxyl protons involved in intramolecular hydrogen bonds, whereas the remaining four make hydrogen bonds with four bridging nitrate ions, which results in the formation of infinite chains. Those chains are arranged so as to form layers, between which the triethylammonium ions and the remaining nitrate ions are hydrogen-bonded one to another.

Keywords: Calix[4]resorcinarene, hydrogen bonds, supramolecular assembly

INTRODUCTION

Calix[4]resorcinarenes are often used as easily available building blocks in host molecules design based on covalent bonding [1]; more recently, it was shown that their multiple hydrogen-bond donor ability could be used in self-assembling processes, to yield multicomponent species such as resorcinarenes with enlarged cavities [2], a carcerand-like dimer [3] and even a spherical hollow hexamer assembly defining a huge inner cavity [4]. In the light of these results, the calix[4]resorcinarenes can be considered as important basic compounds in supramolecular chemistry. However, if the present work deals also with a self-assembling species involving C-methylcalix[4]resorcinarene and based on hydrogen bonds, it has resulted from a different approach. In the past years, we studied the complexation of uranyl ions with *p-tert*-butylcalix[*n*] arenes (n = 5 – 8) [5], in which the cation is generally located inside the lower rim oxygen atoms array, partially deprotonated with a base, but can also be complexed in an *exo* fashion [5c]. Calix[4]resorcinarenes, whose metal complexing abilities are well known [6], appeared as an interesting ligand to built other uranyl *exo* complexes, which could possibly form multinuclear species. However, the only compound we could isolate as single-crystals in the course

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*Corresponding author. e-mail: thuery@drecam.cea.fr of this work did not contain uranium ions, but appeared instead to be the supramolecular assembly described herein.

RESULTS AND DISCUSSION

In the crystal structure, the asymmetric unit comprises two independent, but identical, resorcinarene moieties, noted A and B. One of them is represented on Figure 1. Selected geometrical parameters are given in Table I. Both calix[4]resorcinarene molecules are in the usual bowl-like or *crown* conformation, the four methyl groups assuming a nearly axial position (all-*cis* epimer) and possess a pseudo-C2*v* symmetry. The four aromatic rings are not equally tilted with respect to the pseudo C2 axis of **1**, as indicated by the dihedral angles they make with the mean plane defined by the four bridging carbon atoms, which is defined within ± 0.11 and ± 0.02 Å in A and B respectively; two of them are in the range 60.9(2) – 67.5(2)° (mean value 64(3)° for the two independent molecules) and the two other ones in the range 40.7(2) – 44.4(2)° (mean value 43(2)°). All the hydroxyl protons have been localized from the Fourier-difference maps and the hydrogen bond pattern is completely determined in this way (Tab. I). It appears that the two most 'vertical' aromatic rings in each molecule correspond to the four hydroxyl protons directed towards the nearest oxygen atom on the neighbouring aromatic ring, whereas the rings more tilted towards the mean

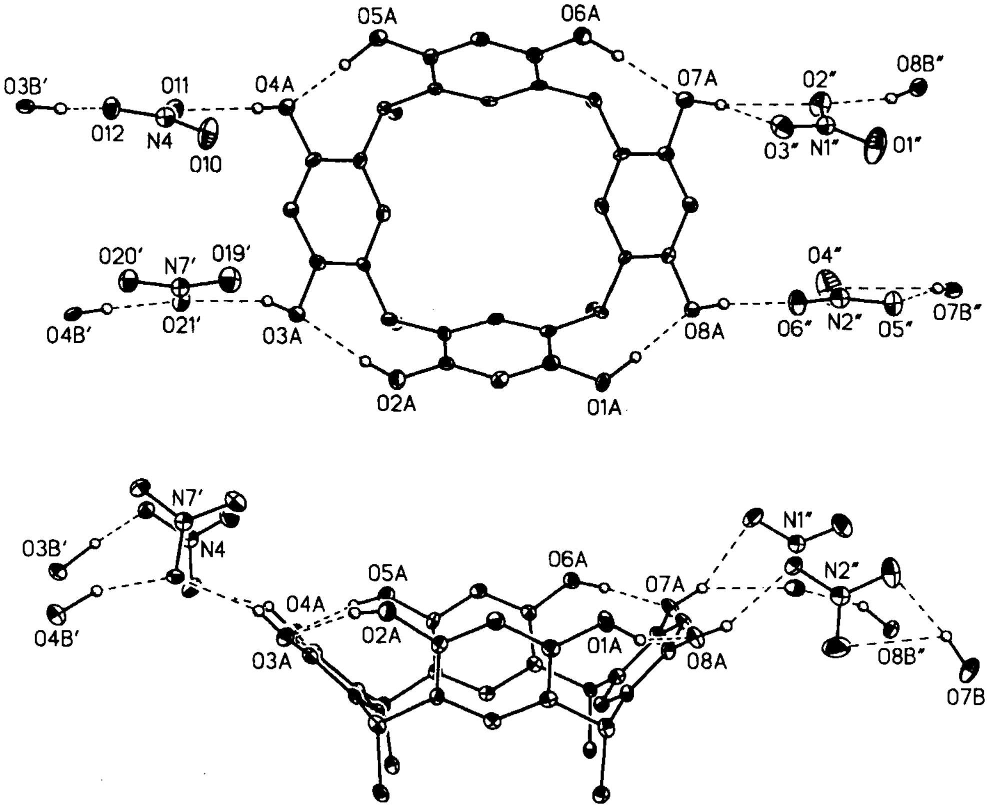

FIGURE 1 Two views of one of the two independent molecular units (A) in **2** (the OH groups of molecule B involved in hydrogen bonding with nitrate ions only are represented). Triethylammonium ions and non-hydroxyl hydrogen atoms omitted for clarity. Hydrogen bonds are shown in broken lines. Ellipsoids drawn at the 20% probability level, hydrogen atoms represented as small spheres of arbitrary radii. Symmetry codes: ′ = 1 – x, – y, 1 – z; ″ = 1 – x, – y, 2 – z.

TABLE I Selected distances (Å) and angles (°) in **1**. Symmetry codes: ' = 1 − x, − y, 1 − z; '' = 1 − x, − y, 2 − z; ''' = 1/2 − x, 1/2 + y, 3/2 − z; '''' = 1/2 + x, 1/2 − y, 1/2 + z; ''''' = − x, − y, 1 − z

Hydrogen bonds					
O1A...O8A	2.690	H...O8A	1.707	O1A-H...O8A	155.3
O2A...O3A	2.846	H...O3A	2.031	O2A-H...O3A	166.2
O4A...O5A	2.778	H...O4A	1.784	O5A-H...O4A	170.5
O6A...O7A	2.812	H...O7A	1.884	O6A-H...O7A	175.1
O3A...O21'	2.816	H...O21'	2.001	O3A-H...O21'	152.8
O4A...O11	2.718	H...O11	1.922	O4A-H...O11	147.1
O7A...O2''	3.051	H...O2''	2.256	O7A-H...O2''	145.2
O7A...O3''	3.026	H...O3''	2.167	O7A-H...O3''	156.4
O8A...O6''	2.692	H...O6''	2.002	O8A-H...O6''	155.6
O1B...O8B	2.806	H...O8B	1.801	O1B-H...O8B	169.9
O2B...O3B	2.778	H...O3B	1.802	O2B-H...O3B	173.2
O4B...O5B	2.740	H...O4B	1.678	O5B-H...O4B	168.5
O6B...O7B	2.794	H...O7B	1.831	O6B-H...O7B	167.3
O3B...O12'	2.660	H...O12'	1.504	O3B-H...O12'	175.0
O4B...O21	2.730	H...O21	1.750	O4B-H...O21	159.5
O7B...O4	2.998	H...O4	2.455	O7B-H...O4	117.6
O7B...O5	2.885	H...O5	1.981	O7B-H...O5	165.3
O8B...O2	2.718	H...O2	1.779	O8B-H...O2	154.2
O3...N9'''	2.977	O7...N11	2.839	O9...N14	2.787
O13...N15	2.945	O14...N13''''	2.795	O15...N15	2.945
O17...N16'	3.037	O20...N10'''''	2.869	O24...N12	2.829

Torsion angles Rings	Molecule A		Molecule B	
	ϕ	χ	ϕ	χ
1-2	94.3	−79.5	−96.2	80.1
2-3	80.5	−99.4	−77.9	101.4
3-4	95.8	−78.0	−100.2	75.0
4-1	82.8	−97.6	−78.0	96.8

plane have their hydroxyl protons directed outwards to make intermolecular hydrogen bonds. The intramolecular hydrogen bond pattern, represented on Figure 1, is the one usually observed for this molecular conformation.

The intermolecular hydrogen bonds involve four nitrate ions out of the eight present in the asymmetric unit. Those ions are bridging alternate A and B molecules, giving rise to infinite chains directed along the **c** axis, with all the calix[4]resorcinarene molecules oriented in the same direction. Two of the nitrate ions are bonded to each calix[4]resorcinarene molecule by one hydrogen bond only, whereas the two other ones make two nearly equal hydrogen bonds with one of the calix[4]resorcinarene molecules and one with the other. As illustrated on the lower part of Figure 1, these four nitrate ions are not equally positioned with respect to the calix[4]resorcinarene molecules. In the case of molecule A, two nitrogen atoms (N1'',N2''), bonded to hydroxyl groups pertaining to the same phenolic ring, are located on one side of the lines defined by the hydrogen bonds O7A...O3'' and O8A...O6'' (below these lines on the figure), whereas the two other ones (N4,N7'), bonded to the hydroxyl groups of the opposite phenolic ring, are located on the other side of the lines defined by the hydrogen bonds O3A...O21' and O4A...O11 (above these lines on the figure). The situation is somewhat different for molecule B, for which, for each phenolic ring, one nitrate is below (N2'', N4) and one above (N1'',N7') the lines defined by hydrogen bonds. This difference is related to the tilt between the mean methylene planes of molecules A and B (7.08(3)°). The overall geometry is reminiscent of the pyridine and 4,4'-bipyridine hydrogen bond complexes of **1**, in which the attached organic molecules extend the calix[4]resorcinarene cavity [2]. However, in place of the large aromatic extension in these compounds, a rather short hydrophilic extension is present in **2** and, furthermore, the resulting assembly is ionic.

The chains described above are arranged so as to form rather irregular layers parallel to the (**b**, c) plane (Fig. 2), in which the neighbouring chains have their lower rims directed alternately upwards and downwards. One repeat unit in a chain bears four negative charges. The four other nitrate ions are located, together with the eight triethylammonium counter-ions, in the interlayer space. Two triethylammonium ions are hydrogen bonded to nitrates from the chains. In the interlayer space itself, each nitrate ion is hydrogen bonded to either one or two cations, in a monodentate or bidentate fashion. This network never extends to more than three ionic species. The present structure can be compared to that of **1**.$(HNEt_3^+)_2(SO_4^{2-})$.4EtOH (**3**) previously reported [7]. The intramolecular hydrogen bonds in the calix[4]resorcinarene unit are the same in both structures; the small differences between the torsion angles in the two compounds (given in Tab. I for **2**, in which ϕ and χ have the same meaning as with calixarenes [8]) may be ascribed to some differences in the intermolecular hydrogen bonding pattern (in **3**, two hydroxyl protons only are hydrogen bonded to the anion). One sulfate and two triethylammonium ions *per* calix[4]resorcinarene molecule are present in **3** and clear-cut hydrophobic and hydrophilic layers are defined in the crystal packing. However, the basic motif is composed of **1**.$(HNEt_3^+)_2(SO_4^{2-})$ which arranges in dimers and not of chains as in our case, since the anion is not bridging two calix[4]resorcinarene units.

In the course of our investigation of uranyl complexes of *p*-*tert*-butylcalix[*n*]arenes ($n = 5-8$), we have used triethylamine as a deprotonating agent. In all cases, the weakly soluble calixarenes become perfectly soluble when triethylamine is added to the organic solvent. In the resulting complexes, as well as in the uranyl complex of *bis* (homo-oxa)-*p*-*tert*-butylcalix[4]arene [9], a fourfold deprotonation is always observed: this deprotonation degree is sometimes higher than predictable on the basis of pK_a values alone, which could indicate a stabilization of the deprotonated form by complexation. In one case,

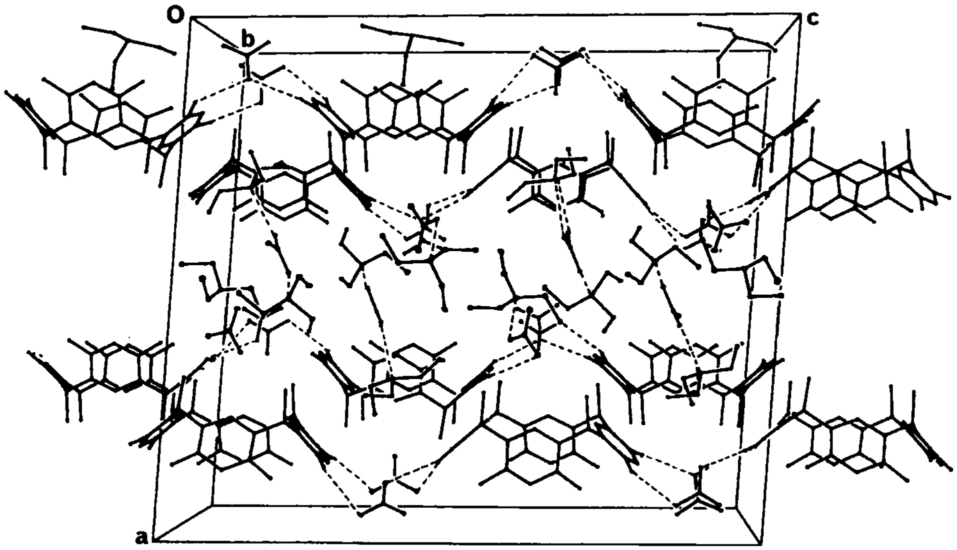

FIGURE 2 View of the crystal packing in 2. Hydrogen bonds in broken lines. For clarity, intramolecular hydrogen bonds are omitted and the triethylammonium and nitrate ions present in the interlayer space have been represented in the forefront (a,c) plane only.

we obtained a doubly deprotonated calixarene ($n = 6$) with two triethylammonium counter-ions [10]. This behaviour of *p-tert*-butylcalix[*n*]arenes is in contrast with that of C-methylcalix[4]resorcinarene as reported here, for which the presence of triethylamine does not result in deprotonation. A NMR investigation of calix[4]resorcinarene in basic medium has shown that four protons are more acidic than those of resorcinol, but that the four remaining ones are much less acidic and are not removed even in presence of $NaOCD_3$, which has been ascribed to the stabilizing effect of intramolecular hydrogen bonds [11]. So it seems surprising that triethylammonium ions are formed but no phenolic group is deprotonated in the process leading to the formation of **2**. A plausible mechanism can be proposed, taking into account the presence of uranyl nitrate hexahydrate (no crystal has been obtained when the experiment was performed in absence of uranyl nitrate). In solution, triethylamine can deprotonate water molecules, either directly, or when they are bonded to uranyl ion, after the uranyl/nitrate ion pair has dissociated. By contrast with the case of *p-tert*-butylcalix[*n*]arenes ($n = 5-8$) which readily form complexes with uranyl ions, the latter is presumably not complexed by calix[4]resorcinarene due to a poor geometrical fit. The presence of hydroxyl ions results in the formation of uranyl hydroxide (included as a precipitate in the tar-like residue which forms during the synthesis), whereas the deprotonation equilibrium of calix[4]resorcinarene is seemingly displaced by nitrate complexation, the resulting complex being the most stable species to be formed.

EXPERIMENTAL

Synthesis

0.7 mmol of C-methylcalix[4]resorcinarene, purchased from *Acros Chimica* and used without further purification, was dissolved in 50 ml of pyridine and 8 ml of triethylamine. A large excess of $UO_2(NO_3)_2 \cdot 6H_2O$ (1.8 mmol) was then added. A dark tar-like residue which has not been further characterized was filtered off and the brownish product was recrystallized from pyridine to yield colourless crystals of **2** suitable for X-ray crystallography.

Crystal Data

1.$4(HNEt_3^+,NO_3^-)$(**2**), $O_{20}N_8C_{56}H_{96}$, $M = 1201.41$; monoclinic, space group $P2_1/n$, $a = 25.796(2)$, $b = 16.6048(11)$, $c = 29.5659(10)$ Å, $\beta = 94.636(4)°$; $V = 12623(2)$ Å^3; $Z = 8$; $D_x = 1.264$ g cm^{-3}; $\mu = 0.096$ mm^{-1}; $F(000) = 5184$; crystal size $0.60 \times 0.35 \times 0.15$ mm.

Data Collection, Structure Determination and Refinement

The diffraction experiment was performed with a Nonius Kappa-CCD area detector diffractometer using graphite monochromated MoK_α radiation (0.71073 Å). The crystal was introduced in a Lindemann glass capillary. The lattice parameters were determined from ten images recorded with 1° ϕ-scans and later refined on all data. The data were recorded at 123 K. A 180° ϕ-range was scanned with 2° steps. The crystal-to-detector distance was fixed at 30 mm. The data were processed with the HKL package [12]. No absorption correction was done. The structure was solved by direct methods with SHELXS-86 [13] and subsequent Fourier-difference synthesis and refined by full-matrix least-squares on F^2 with SHELXL-93 [14]. All non-hydrogen atoms were refined anisotropically unless the nitrogen atoms of the nitrate ions. All the hydroxylic protons were found on the difference-Fourier maps and introduced as riding atoms with a displacement parameter equal to 1.2 times that of the parent oxygen atom. Only two of the hydrogen atoms bonded to nitrogen in the triethylammonium cations were found; these atoms were not introduced in the calculation. All other hydrogen atoms were introduced as riding atoms with a displacement parameter equal to 1.2 (CH, CH_2) or 1.5 (CH_3) times that of the attached carbon atom. Analytical scattering factors for neutral atoms were corrected for the anomalous dispersion terms $\Delta f'$ and $\Delta f''$. 12428 unique observations, out of 83199 measured reflections ($R_{\text{int.}} = 0.157$), were used and 1473 parameters refined. The final R values were $R_1 = 0.128$ ($\sum||F_o| - |F_c||/\sum|F_o|$, calculated on 8224 'observed' $[I > 2\sigma(I)]$ reflections) and $wR_2 = 0.307$ ($\{\sum[w(F_o^2 - F_c^2)^2]/[\sum wF_o^4]\}^{1/2}$ with $w = [\sigma^2(F_o^2) + (0.136P)^2 + 80.834P]^{-1}$ where $P = (F_o^2 + 2F_c^2)/3$). The goodness-of-fit was $S = 1.155$ ($\{\sum[w(F_o^2 - F_c^2)^2]/(n-p)\}^{1/2}$ where n and p are the number of reflections and the number of parameters refined respectively). The maximum positive and negative residual densities were 1.15 (near a nitrate and a triethylammonium ions) and $-0.86\,e\text{Å}^{-3}$. The drawings were done with SHELXTL [15].

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