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# Crystal Structures of Uranyl Ion Complexes of Tetrahydroxy[3.1.3.1]metacyclophane (Homocalix[4]arene)

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The first crystal structures of complexes of tetrahydroxy[3.1.3.1]metacyclophanes, also termed homocalix[4]arenes, are reported. In the two uranyl ion complexes obtained, with different *para*-substituents, the complex core is analogous to that in tetrahomodioxacalix[4]arene complexes, with the cation in a tetra-phenoxide, distorted square-planar environment. The packing in one of these complexes comprises two different arrangements, one of them being a columnar stacking of complex molecules with sandwiched triethylammonium counter-ions hydrogen bonded to one complex and held by cation- $\pi$  and CH- $\pi$  interactions within the cavity of the other neighbouring one.

**Keywords:** Uranyl ion; Metacyclophane; Calixarene; Homocalixarene; Crystal structure

## INTRODUCTION

Homocalixarenes are calixarene-like molecules containing a metacyclophane skeleton with at least one bridge larger than methylene [1], which are akin, by their structure if not by their synthesis, to homooxacalixarenes [2]. Up to now, these molecules have been far less investigated than homooxacalixarenes. Although the ionophoric properties of some homocalixarene derivatives have been studied in solution [1,3,4], little is known of the structures of their metal ion complexes. Following the work of Harrowfield [5,6], we have been engaged in the past years in a study of the solid-state structure of uranyl complexes of calixarenes, homooxa- and homoazacalixarenes and a wide range of complexes with macrocycles of variable size is now available [7]. These complexes provide interesting insights into

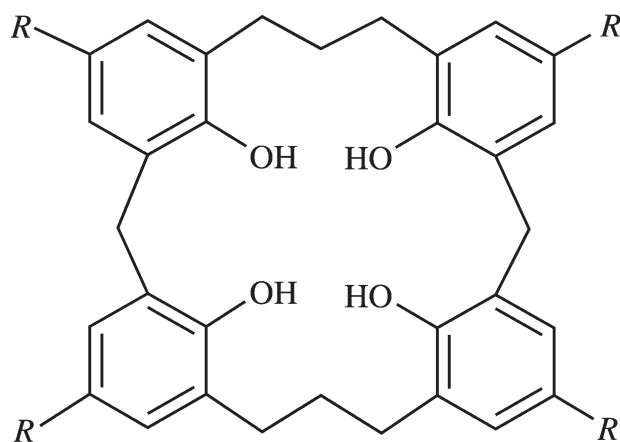
both the solid-state chemistry of the uranyl ion and the complexing preferences of the ligands. As a natural extension of this work, we decided to investigate the complexes formed with this cation by homocalixarenes. As is often with this family of molecules, the main difficulty concerns the obtention of single crystals of suitable quality [8] and, among the homocalixarenes we chose to investigate, few eventually gave compounds suitable for crystallography. We report herein the results obtained with 9,16,25,32-tetrahydroxy[3.1.3.1]metacyclophane, bearing either *tert*-butyl ( $L^1H_4$ ) or H ( $L^2H_4$ ) in the *para* position (Scheme 1). This ligand, which is a homocalix[4]arene with alternating methylene and 1,3-propylene bridges, is closely related to tetrahomodioxacalix[4]arene (or [3.1.3.1]homooxacalixarene), with alternating methylene and 2-oxa-1,3-propylene bridges [2]. The latter, with methyl, *tert*-butyl or phenyl *para*-substituents, has been structurally characterized either free or as a solvate [9,10], or in its uranyl-complexed form [10,11]. We have shown in particular that, depending on the counter-ions used (protonated primary, secondary or tertiary amines) and the *para*-substituents, supramolecular arrangements could be obtained with the uranyl complexes [11]. Further examples of this phenomenon will be described herein.

## EXPERIMENTAL

### Synthesis

The tetrahydroxy[3.1.3.1]metacyclophanes  $L^1H_4$  and  $L^2H_4$  were synthesized as previously reported [12,13].

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$L^1H_4$ :  $R = \textit{tert}$ -Bu

$L^2H_4$ :  $R = H$

SCHEME 1 The tetrahydroxy[3.1.3.1]metacyclophanes under study.

$[HNEt_3]_2[UO_2(L^1)] \cdot CHCl_3 \cdot CH_3CN$  **1** and  $[HNEt_3]_2[UO_2(L^2)] \cdot 2.67H_2O$  **2**:  $L^1H_4$  [resp.  $L^2H_4$ ] (15 mg, 0.021 mmol [resp. 19 mg, 0.040 mmol]) was refluxed in chloroform (100 mL) in the presence of triethylamine (3 mL). Uranyl nitrate hexahydrate in a 1:1 ratio (13 mg, 0.026 mmol [resp. 20 mg, 0.040 mmol]) in acetonitrile (20 mL) was added dropwise, resulting in an orange solution which was refluxed for 5 min, then allowed to cool down, yielding orange single crystals suitable for X-ray crystallography after about 48 h.

### Crystallography

The data were collected on a Nonius Kappa-CCD area detector diffractometer [14] using graphite-monochromated Mo-K $\alpha$  radiation (0.71073 Å). The crystals were introduced in Lindemann glass

capillaries with a protecting "Paratone" oil (Exxon Chemical Ltd.) coating. The unit cell parameters were determined from the reflections collected on ten frames and were then refined on all data. The data were processed with DENZO-SMN [15]. The structures were solved by direct methods with SHELXS-97 [16] and subsequent Fourier-difference synthesis and refined by full-matrix least-squares on  $F^2$  with SHELXL-97 [16]. Absorption effects were empirically corrected with the program DELABS from PLATON [17]. All non-hydrogen atoms were refined with anisotropic displacement parameters, except the disordered ones when present. Special details for each compound are as follows:

**Compound 1.** One *tert*-butyl group was found disordered over two sites which have been refined with occupancy parameters constrained to sum to unity. The ammonium protons were introduced as found on the Fourier-difference map. The structure has been refined as corresponding to a racemic twin [Flack parameter 0.475(7)].

**Compound 2.** Some restraints on displacement parameters have been applied for the atoms of the ammonium ions, which behave badly on refinement. The protons bound to N and O(water) atoms were not found.

All the carbon-bound hydrogen atoms were introduced at calculated positions, except in the disordered parts. All hydrogen atoms were treated as riding atoms with an isotropic displacement parameter equal to 1.2 (NH, CH, CH<sub>2</sub>) or 1.5 (CH<sub>3</sub>) times that of the parent atom. Crystal data and refinement details are reported in Table I and selected bond distances and angles in Table II. The molecular plots were drawn with SHELXTL [18].

TABLE I Crystal data and structure refinement details

	1	2
Empirical formula	C <sub>63</sub> H <sub>96</sub> Cl <sub>3</sub> N <sub>3</sub> O <sub>6</sub> U	C <sub>44</sub> H <sub>65.33</sub> N <sub>2</sub> O <sub>8.67</sub> U
Mol. wt.	1335.81	999.01
T/K	100(2)	100(2)
Crystal system	Orthorhombic	Orthorhombic
Space group	$P2_12_12_1$	$Iba2$
$a/\text{Å}$	12.4046(4)	24.9935(15)
$b/\text{Å}$	16.8657(9)	30.4738(18)
$c/\text{Å}$	30.4608(15)	17.1017(11)
$V/\text{Å}^3$	6372.8(5)	13026(1)
Z	4	12
$\mu/\text{mm}^{-1}$	2.722	3.793
Reflections collected	39661	42477
Independent reflections	11732	12079
Observed reflections [ $I > 2\sigma(I)$ ]	9645	6246
$R_{\text{int}}$	0.103	0.076
Parameters refined	701	764
$R_1$	0.049	0.071
$wR_2$	0.096	0.127

TABLE II Selected distances (Å) and angles (°)

Uranium environment								
1	U–O1	2.328(5)	O1–U–O2	91.3(2)				
	U–O2	2.267(5)	O2–U–O3	89.7(2)				
	U–O3	2.247(5)	O3–U–O4	92.5(2)				
	U–O4	2.285(5)	O4–U–O1	86.6(2)				
	U–O5	1.772(5)	O5–U–O6	178.4(3)				
	U–O6	1.802(5)						
2	U1–O1	2.291(11)	O1–U1–O2	90.4(5)	U2–O7	2.260(10)	O7–U2–O8	92.2(4)
	U1–O2	2.246(11)	O2–U1–O3	87.9(5)	U2–O8	2.219(11)	O8–U2–O7A	87.7(4)
	U1–O3	2.193(14)	O3–U1–O4	95.3(5)	U2–O9	1.855(18)	O9–U2–O10	180.0
	U1–O4	2.238(10)	O4–U1–O1	86.4(5)	U2–O10	1.773(14)		
	U1–O5	1.814(10)	O5–U1–O6	178.8(8)				
	U1–O6	1.805(9)						
Symmetry code: A = x + 0.5, 2.5 – y, z + 0.5								
Hydrogen bonds								
1	N1···O6	2.758(8)	N1–H1	1.05	H1···O6	1.71	N1–H1···O6	172
	N2···O1	2.773(8)	N2–H2	1.01	H2···O1	1.78	N2–H2···O1	168
2*	N1···O6	2.72(2)	N2···O5	2.87(3)	O11···O2	2.87(2)	O12···O3	2.87(2)
	O14···O1	2.61(4)	O13···O11	2.84(3)	O13···O12	2.82(2)	O12···O14A	2.61(3)
	N3···O9B	2.90(2)						
Symmetry codes: A = 1 – x, y, z – 0.5; B = x, –y, z – 0.5								

\*Hydrogen atoms not found.

All calculations were performed on a Silicon Graphics R5000 workstation.

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 192222 for compound **1** and 192223 for compound **2**. Copies of the information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

## RESULTS AND DISCUSSION

The two complexes [HNEt<sub>3</sub>]<sub>2</sub>[UO<sub>2</sub>(L<sup>1</sup>)]·CHCl<sub>3</sub>·CH<sub>3</sub>CN **1** and [HNEt<sub>3</sub>]<sub>2</sub>[UO<sub>2</sub>(L<sup>2</sup>)]·2.67H<sub>2</sub>O **2** present common features in what concerns the complex core itself, and these features are close to those observed in the uranyl complexes of tetrahomodioxacalix[4]arene, denoted L<sup>3</sup>H<sub>4</sub> in the following, whatever its *para*-substituents [10,11]. The repeat unit comprises one complex molecule in compound **1** (Fig. 1) and one and a half in complex **2**, the latter half with its uranyl ion located on a binary axis (Fig. 2). The uranyl ion is located at the centre of the lower rim, perpendicular to the mean O<sub>4</sub> plane and at distances to this plane of 0.011(3) Å in **1** and 0.037(6) and 0.074(8) Å in **2**. The uranium atom is bound to the four phenoxide groups, with U–O distances in the range 2.247(5)–2.328(5) [mean value 2.28(3)] Å in **1** and 2.193(14)–2.291(11) [mean value 2.24(3)] Å in **2** (both U1 and U2 included). These ranges are comparable to that in the complexes of L<sup>3</sup>, 2.225(4)–2.333(4) [mean value 2.28(3)] Å, including the four complexes described. The corresponding O–U–O angles involving adjacent

phenoxide oxygen atoms are larger for phenolic rings separated by a 1,3-propylene bridge [91.3(2), 92.5(2)° in **1**; 90.4(5), 95.3(5) and 92.2(4)° in **2**] than for those separated by a methylene one [89.7(2), 86.6(2)° in **1**; 87.9(5), 86.4(5) and 87.7(4)° in **2**]. The resulting distorted square planar geometry is a common occurrence in tetra-phenoxide complexes of uranyl ions with calixarenes, which indicates its high stability. As a result, the complex molecules in **1** and **2** possess two orthogonal pseudo-symmetry planes perpendicular to the O<sub>4</sub> plane, with the uranyl ion at their intersection and containing either the two methylene bridges or the two central carbon atoms of the 1,3-propylene chains. The same geometry occurs in the L<sup>3</sup> complexes, in which none of the two ether oxygen atoms is bound to uranium, which is not always the case in the family of homooxacalixarenes [19,20]. The separations between the uranium atom and the central carbon atoms of the 1,3-propylene chains are 4.09(1) in **1** and 3.94(2)–4.04(2) Å in **2**, i.e. slightly larger than the non-bonding U–O(ether) contacts in the L<sup>3</sup> complexes [3.715(3)–3.832(4) Å]. The conformation of the three-atoms bridges can be characterized by the two torsion angles they define and the distance of the central atom to the mean plane defined by the four other ones (including the aromatic carbon atoms bound to the bridge). In both **1** and **2**, all these torsion angles are *anti*, as in the L<sup>3</sup> complexes, with values in the range 152(2)–166(2)°, which results in bridges with a “w” shape. The distances of the central carbon atoms to the planes are in the range 0.473(9)–0.501(9) Å in **1** and **2**, whereas the distances of the ether oxygen atoms to the corresponding planes in the L<sup>3</sup> complexes are significantly lower, in the range 0.248–0.319 Å, all these atoms being on the same side of the mean plane, i.e. away from

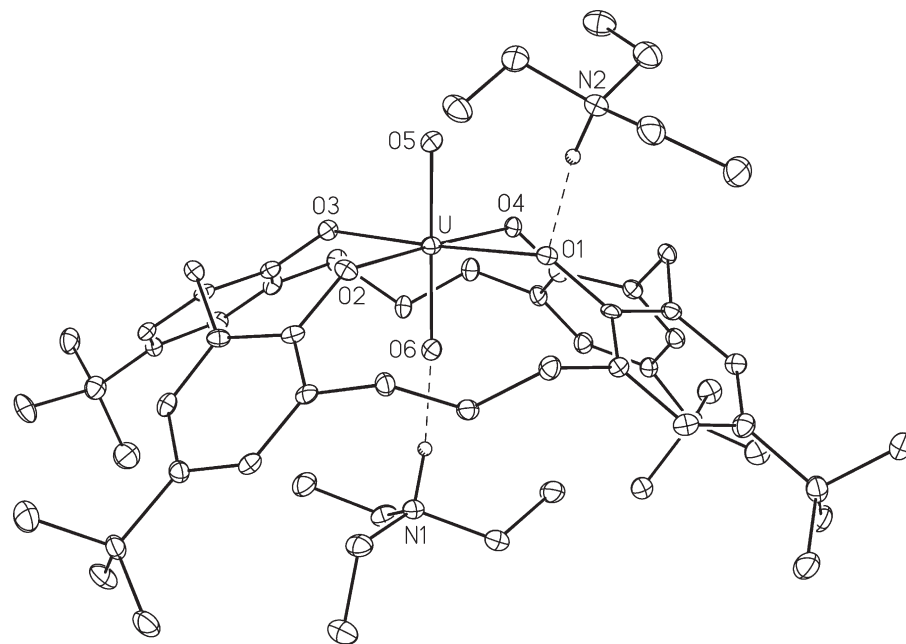


FIGURE 1 View of complex 1. Hydrogen atoms omitted for clarity, except for those involved in hydrogen bonds, which are represented as small spheres of arbitrary radii. Hydrogen bonds represented as dashed lines. Only one position of the disordered *tert*-butyl group is represented. Ellipsoids drawn at the 20% probability level.

the complexed cation. The homocalixarenes are in the *cone* conformation, which is likely imposed by uranyl complexation. The dihedral angles between the four aromatic rings and the  $O_4$  plane are 40.8(3), 46.7(2), 34.4(2) and 48.5(2)° in **1** and 43.9(5), 41.8(5), 35.7(4), 43.6(4), 40.3(3) and 38.0(3)° in **2**. These values lie in the range observed in  $L^3$  complexes [30.3(2)–54.44(9)°]. The crystal structure of the uncomplexed ligand has not been determined, but it can be guessed to be similar to that of  $L^3$  [9,10] with the notable difference that, due to the absence of ether oxygen atoms, hydrogen bonds involving phenolic groups must be simple and not bifurcated.

We have shown previously that, in the uranyl/calixarene family, compounds with the same complex core or at least very similar ones, but differing by other features, such as *para*-substituents and/or counter-ions, could display very different packing arrangements and organize in some cases in supramolecular assemblies based on weak forces such as hydrogen bonds, cation– $\pi$  or CH– $\pi$  interactions. We have given several examples of such architectures built from uranyl ion complexes of *p*-*R*-hexahomotrioxacalix[3]arenes [20] and *p*-*R*-tetrahomodioxacalix[4]arenes [11]. The comparison of complexes **1** and **2** is interesting in this respect. Both complexes possess the same central core, *i.e.* the same coordination around the uranyl ion and identical calixarene shapes, and the same counter-ion is present in both of them. The only significant difference on the molecular level arises from the *para*-substituent, either *tert*-butyl or H. One of the two counter-ions in **1** is located in the homocalixarene

cavity, in which it is held by a hydrogen bond with the oxo atom of the uranyl ion pointing inside, and the second is outside the cavity and involved in a hydrogen bond with a phenoxide group. As shown in Fig. 3, the packing is likely mainly determined by van der Waals interactions. As shown in Fig. 2, the two crystallographically independent molecules in **2** behave in a different way. The first one, corresponding to atom U1, is comparable to that in **1**, with a counter-ion in the cavity (much shallower in this case due to the absence of bulky *para*-substituents) hydrogen bonded to the oxo atom and the second cation outside and bonded to the second oxo atom. However, four water molecules, hydrogen bonded to phenoxide oxygen atoms and/or between themselves, are located on the lower rim side. The second molecule, corresponding to atom U2, displays two counter-ions (related by the binary axis) hydrogen bonded to the same oxo atom and both directed towards the upper rim cavity of a neighbouring homocalixarene. As shown in the two views of Fig. 4, these differences between the two molecules result in two different packings. The interactions of the first molecule with its equivalents, all approximately parallel to the *bc* plane and arranged in an up–down way, may be assumed to be primarily of van der Waals origin, notwithstanding the presence of hydrogen bonded water bridges. On the other hand, the second molecule packs with its equivalents to give columns directed along the *c* axis. The overall packing is thus constituted of two sub-networks with molecules at approximate right angles, the interactions between these two subunits being seemingly

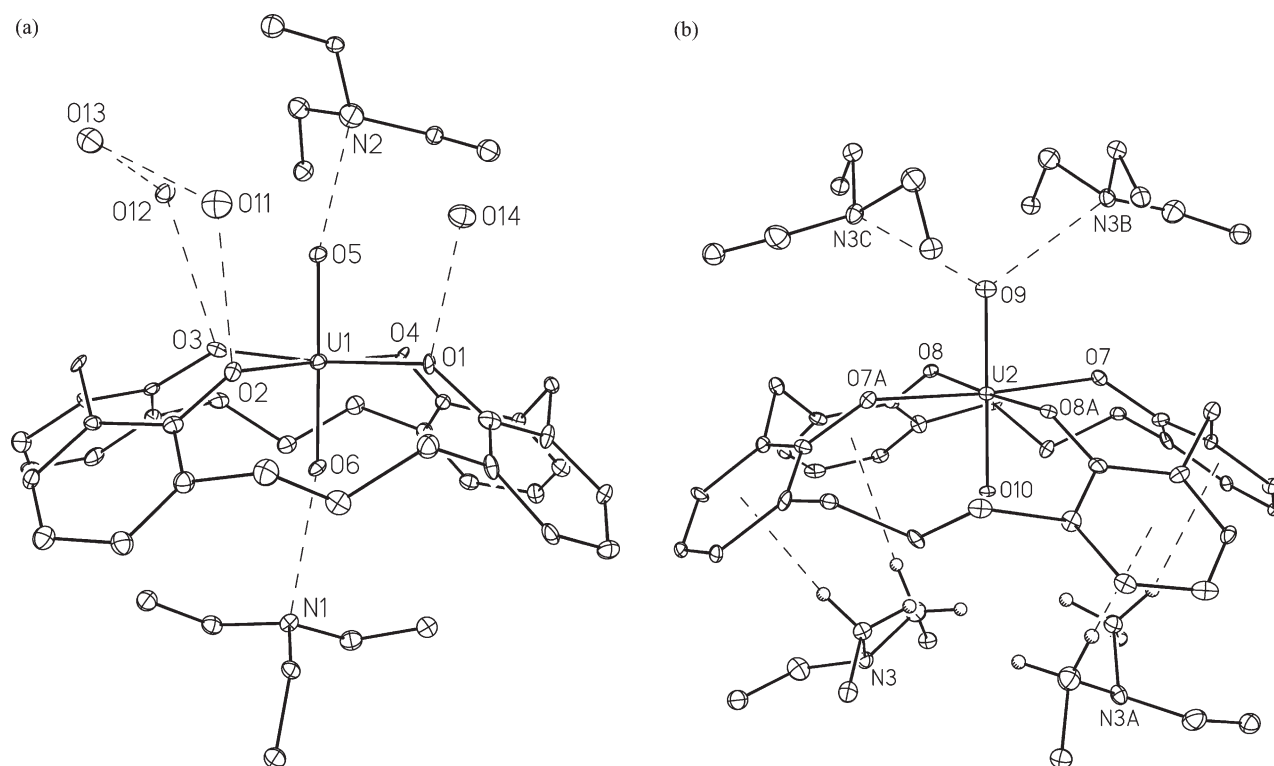


FIGURE 2 (a) and (b) View of the two complex molecules in **2**. Hydrogen atoms omitted for clarity, except for those of the  $\alpha$ -carbon atoms of the counter-ions closer to the aromatic rings in (b). Hydrogen bonds and CH- $\pi$  interactions represented as dashed lines. Ellipsoids drawn at the 5% probability level. Symmetry codes: A  $2 - x, -y, z$ ; B  $x, -y, z + 0.5$ ; C  $2 - x, y, z + 0.5$ .

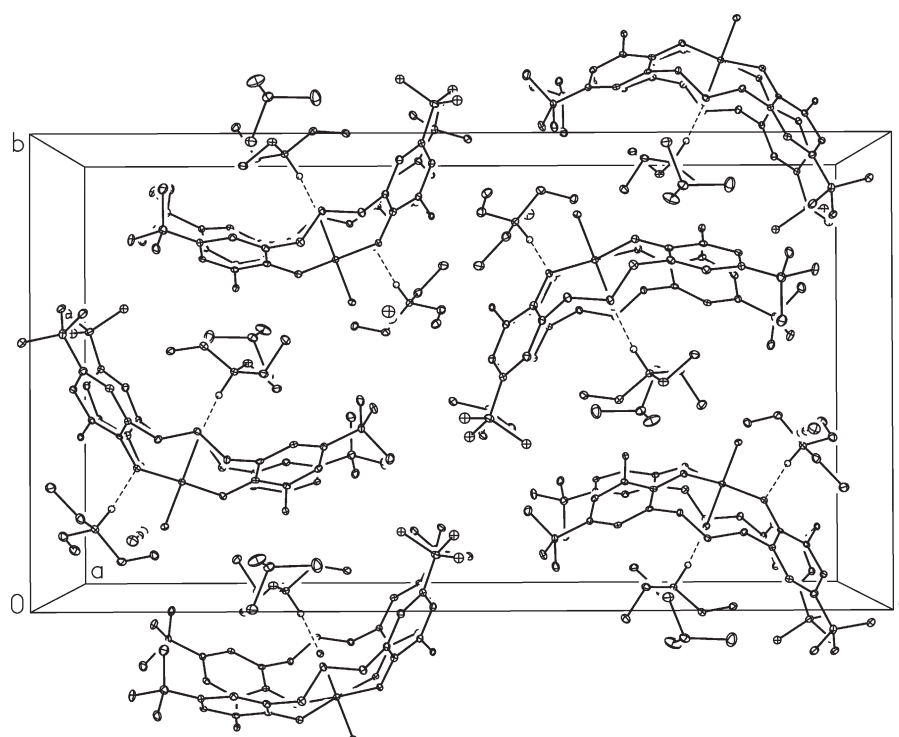


FIGURE 3 View of the packing in complex **1**, with  $c$  axis horizontal and  $b$  axis vertical. Hydrogen atoms omitted for clarity, except for those involved in hydrogen bonds, which are represented as small spheres of arbitrary radii. Hydrogen bonds represented as dashed lines. Only one position of the disordered *tert*-butyl group is represented. Ellipsoids drawn at the 10% probability level.

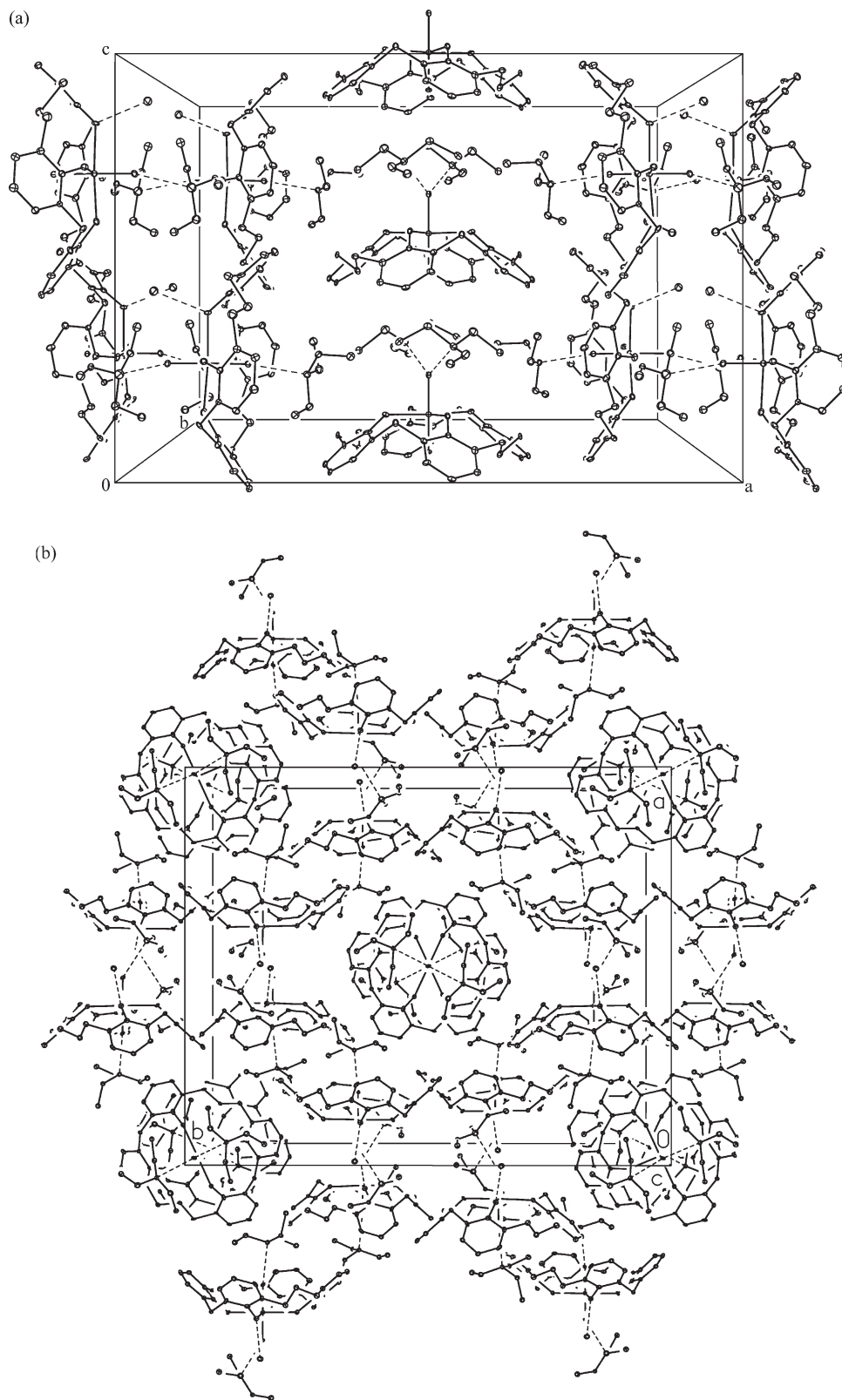


FIGURE 4 Two orthogonal views of the packing in complex 2. Hydrogen atoms omitted for clarity. Hydrogen bonds represented as dashed lines. (a): *a* axis horizontal, *c* axis vertical, ellipsoids drawn at the 5% probability level; (b): *b* axis horizontal, *a* axis vertical, ellipsoids drawn at the 3% probability level. The columnar arrangements are parallel to the *c* axis.

of the van der Waals type. It is interesting to note that a columnar arrangement with an alternate stacking of anionic complexes and groups of two triethylammonium counter-ions has previously been found in the uranyl ion complex of *p*-phenyltetrahomodioxacalix[4]arene [11]. The shortest distances between the counter-ions and the aromatic rings in the columns of **2**, which involve two  $\alpha$ -carbons of the former, are 3.71 and 3.73 Å, the corresponding distances with the centroids being 3.66 and 3.53 Å. Shorter distances were observed in the previous columnar arrangement (C $\cdots$ C contacts as short as 3.39 Å). Such values, together with a N $\cdots$ centroid shortest distance of 4.5 Å, are compatible with the existence of cation– $\pi$  interactions [20,21]. Each of the two  $\alpha$ -carbons involved in the shortest contacts has a hydrogen atom pointing towards an aromatic ring, with H $\cdots$ centroid distances of 2.69 and 2.70 Å. Although such interactions cannot easily be distinguished from cation– $\pi$  ones, this geometry seems to indicate with reasonable certainty the presence of CH– $\pi$  interactions as well [22–24].

The columnar stacking mode based on the sequence complex/hydrogen bonded counterion(s)/cavity of the neighbouring complex, with possible variants corresponding to double hydrogen bonding to both calixarenes in the case of secondary amines, appears as a very general trend in uranyl complexes of calixarenes and related homooxa- and now homocalixarenes. Apart from the regular columns reported herein and in the previous *p*-phenyltetrahomodioxacalix[4]arene complex, with two ammonium ions involved and parallel complex molecules, tilted chain arrangements have been observed, with only one counter-ion sandwiched between neighbouring calixarenes [5,20]. As shown by the coexistence in complex **2** of two largely different stacking modes from the same constituting molecules, the obtention of a particular arrangement is however hardly predictable, so subtle are the weak interactions (cation– $\pi$ , CH– $\pi$ ) governing the packing.

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