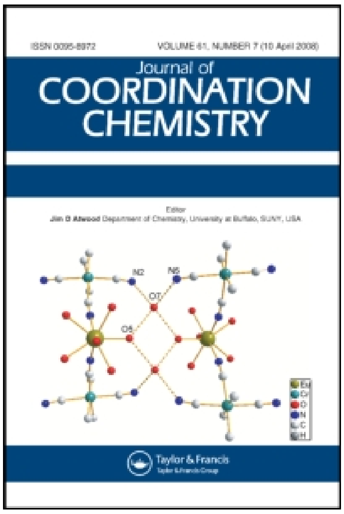

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A MONOMERIC URANYL HYDROXIDE SYSTEM OBTAINED BY INCLUSION IN THE β-CYCLODEXTRIN CAVITY

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Reaction between β-cyclodextrin (β-CD) and diaqua(benzoate)chlorodioxouranium in aqueous solution leads to the formation of the adduct diaqua(benzoate)hydroxydioxouranium(VI)/β-CD. The compound has been characterized from crystallographic studies of two crystal forms. Monometallic uranyl-hydroxide is included in the CD cavity and is stabilized by hydrophobic forces and hydrogen bonds. EXAFS studies of diaqua(benzoate)chlorodioxouranium in aqueous solution with α and β-CD suggest that uranyl insertion compounds are present in both solutions.

Keywords: Uranyl; cyclodextrin; X-ray diffraction; EXAFS

INTRODUCTION

The first investigations of uranium/macrocycle complexes were carried out with crown-ether, cryptand and aza-crown macrocycles.[1–11] Studies of these complexes aimed at determining, *via* the formation of first-sphere coordination compounds, the selectivity of macrocycles with respect to the different oxidation states of uranium, U(III), U(IV), U(V) and U(VI), and to stabilize the oxidation states U(III) and U(V). Systematic structural studies of these compounds have shown that insertion occurs using poorly coordinating counter ions under anhydrous conditions.[12–19] Hydrolysis of the inclusion

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compounds or synthesis in hydrous conditions, leads either to compounds having the crown macrocycle as a second sphere ligand,[14,19] or does not allow any complexation.[20]

Recently, several crystal structures of UO_2^{2+}/calixarenes complexes[21-25] have been reported showing that the σ-bonding character of calixarenes (in basic medium) makes them stronger "uranophiles" than crown-ethers and aza-crowns. In all these compounds the uranyl ion is directly coordinated to phenolic oxygens of the macrocycle, forming inclusion compounds as well as multinuclear sandwich-type complexes, even if binding or non-binding hydroxyl ions or water molecules are present in the crystals.

No crystal structure of a uranium/cyclodextrin (CD) complex has so far been determined. Interactions between uranium–CDs have been only studied in aqueous solution. It was observed that the presence of CD in U(IV) or UO_2^{2+} aqueous solutions hinders the precipitation of the hydrolysis products of uranium to pH 12, whilst in the absence of CD such hydrolysis usually occurs at pH 3.[26] In UO_2^{2+}/β-CD solution, a complex is formed at pH 10; here, the macrocycle would be acting as a first sphere ligand for the uranyl ions, as in UO_2^{2+}/calixarene complexes.[27] Our interest concerning the formation of supramolecular compounds of CDs with neutral uranyl species in aqueous medium led us to study diaqua(benzoato)chlorodioxouranium(VI)/CD systems, because the benzoate ligand is sterically adapted to be included into CDs cavities. Here, we describe the first structural example of a second sphere uranium complex adduct with a CD.

EXPERIMENTAL

EXAFS Analysis

Three different samples were prepared. Solid, benzoato · Cl–UO_2 $U(C_7H_5O_2)ClO_2(H_2O)_2$, diaqua(benzoato)chlorodioxouranium(VI) was obtained during the reaction between UO_2Cl_2 and C_6H_5COOAg. The crystal structure is described in Ref. 28. [Benzoato · Cl–UO_2/α-CD] (1 : 1) solution was prepared by mixing an aqueous solution of α-CD (0.2102 g in 0.5 cm^3 of water) with a methanolic solution of benzoato · Cl–UO_2 (0.1 g in 10 cm^3 of methanol) and stirring at room temperature during 5 h. [Benzoato · Cl–UO_2/β-CD] (1 : 0.5) solution was prepared by dissolving β-CD-hydrate (0.1227 g) in water (10 cm^3) at 40°C and adding solid benzoato · Cl–UO_2 (0.1 g). The mixture was stirred during 5 h at the same temperature and then slowly cooled.

Absorption data were collected at the uranium L_{III} edge on the EXAFS-I station of LURE-DCI (the Orsay-France synchrotron radiation facility). Ring energy: 1.85 Gev; current range: 200–300 mA; monochromator: channel-cut Si (311); step by step transmission mode; energy resolution 2 eV; energy range: 16 900–17 900 eV; room temperature; detectors: two ion chambers filled with argon gas. Powder samples were enclosed between several sheets of adhesive tape; solutions were contained in a cell with mylar windows.

The $\chi(k)$ EXAFS spectra were obtained following the procedure described in Ref. 29. The $k^3\chi(k)$ spectra of the solutions were Fourier transformed in the range 53–625 eV. The two first FT filtered peaks (corresponding to axial and equatorial uranium ligands) were fitted with U–O and U–Cl experimental amplitudes and phases extracted from standard compounds (tetraphenylphosphonium)triacetatedioxouranium(VI) and bis-(tetraethylammonium)tetrachlorodioxouranium(VI).[29] Experimental errors for the fitted parameters, atom number and bond distance, are ±12% and ±0.02 Å, respectively.

X-ray Diffraction

Two different crystalline forms (I and II) of diaqua(benzoate)hydroxydioxouranium(VI) adduct with β-CD were obtained by solvent evaporation at 30°C from [benzoato · Cl–UO_2/β-CD] (1 : 0.5) solution.

Form I

$C_{91}H_{108}O_{77}U \cdot 22H_2O$, $M_r = 3068.1$; crystal dimensions: $0.10 \times 0.10 \times 0.075$ mm; monoclinic, $P2_1$; $a = 16.143(4)$, $b = 24.81(1)$, $c = 19.11(1)$ Å, $\beta = 92.03(3)°$, $V = 7650(9)$ Å^3, $Z = 2$, $\rho_{calc.} = 1.33\ \text{g cm}^{-3}$; $\mu = 1.1\ \text{mm}^{-1}$; Enraf-Nonius CAD4, Mo$K_\alpha$ radiation, graphite monochromator, $\theta_{max} = 18°$, 4076 reflections measured, 3346 independent of which 1712 with $I_{net} > 3\sigma(I_{net})$ were used for the refinement of 258 parameters; structure solution by molecular replacement using a β-CD dimer, and by subsequent difference Fourier maps and refinements. In the first Fourier difference maps, values of the peak intensity of assumed Cl ligand, and its distance to uranyl ion, were smaller than expected; on the basis of this fact and the EXAFS results, one oxygen atom was assigned to the peak. The first refinements of the guest uranyl molecule lead to one UO_2–O equatorial distance corresponding to a U–OH bond length. The guest diaqua(benzoate)hydroxydioxouranium(VI) (benzoato · OH–UO_2), was refined with 50% occupancy. Due to the number of atoms in the asymmetric unit (222 non-hydrogen atoms) and the weak diffraction power of the crystal, the following refinement constraints were applied: CD residues were treated as rigid-bodies and guest molecule with distance constraints ($\sigma = 0.04$), all with global isotropic factors. Hydrogen atoms were placed in calculated positions; $R = 0.116$, $R_\omega = 0.103$, $\omega^{-1} = \sigma^2(F)$, $(\Delta/\sigma)_{max} = 0.2$, $\Delta\rho_{max} = 0.5\,e\text{Å}^3$

Form II

$C_{44.5}H_{52.85}O_{37.5}U_{0.35} \cdot 7.85H_2O$, $M_r = 1410.6$; crystal dimensions: 0.35 × 0.50 × 0.20 mm; monoclinic, *C*2; $a = 18.917(7)$, $b = 24.49(1)$, $c = 15.730(5)$ Å, $\beta = 110.50(2)°$, $V = 6826(8)\,\text{Å}^3$, $Z = 4$, $\rho_{calc.} = 1.37\,g\,cm^{-3}$; $\mu = 3\,mm^{-1}$; Enraf-Nonius CAD4, CuK_α radiation, graphite monochromator, $\theta_{max} = 50°$, 3619 reflections measured, 3060 independent, of which 1979 with $I_{net} > 3\sigma(I_{net})$ were used for the refinement of 413 parameters; semi-empirical absorption correction (average transmission factors: minimum 0.42, maximum 1.67); structure solution by molecular replacement using the β-CD molecular structure; positional disorder affecting the included molecule was solved by fitting of electron density with the benzoato · OH–UO_2 molecule, with 35% occupancy. Hydrogen atoms were not included in the calculations; $R = 0.124$, $R_\omega = 0.081$, $\omega^{-1} = \sigma^2(F)$, $(\Delta/\sigma)_{max} = 0.3$, $\Delta\rho_{max} = 0.6\,e\text{Å}^3$

Because of positional disorder, the amount of water in both crystals is not accurately determined; there are 36 sites for I (3 fully and 33 partially occupied) and 19 partially occupied for II. The occupancy factors were estimated using electron density and contact distance criteria. Final atomic coordinates are listed in Tables I and II. Full lists of crystallographic data are available from the authors upon request.

Programs

EXAFS Locally adapted programs of LURE, running on a Vax 3000 computer.

X-ray diffraction Cell refinements, data collection and data reduction: MolEN software;[30] structure resolution: AMoRe package;[31] refinements: SHELXL-93.[32]

RESULTS AND DISCUSSION

Figure 1 shows differences between the FT (*pseudo*-radial atomic distributions) of the solid compound benzoato · Cl–UO_2 and of the [benzoato · Cl–UO_2]/β-CD (1 : 0.5) and [benzoato · Cl–UO_2]/α-CD (1 : 1) aqueous

TABLE I Final positional and thermal parameters and occupancy factors in the diaqua-(benzoate)hydroxydioxouranium(VI) complex adduct with β-CD (1 : 2), Form I

Atom	*x/a*	*y/b*	*z/c*	*U(iso)*	*s.o.f*
O41A	0.1905(13)	−0.2063(9)	0.2049(9)	0.052(6)	
C11A	0.1574(13)	−0.1660(9)	−0.0054(9)	0.052(6)	
C21A	0.0882(13)	−0.1971(9)	0.0288(9)	0.052(6)	
C31A	0.0977(13)	−0.1904(9)	0.1076(9)	0.052(6)	
C41A	0.1831(13)	−0.2118(9)	0.1312(9)	0.052(6)	
C51A	0.2490(13)	−0.1809(9)	0.0930(9)	0.052(6)	
C61A	0.3364(13)	−0.2040(9)	0.1091(9)	0.052(6)	
O21A	0.0112(13)	−0.1756(9)	0.0047(9)	0.052(6)	
O31A	0.0374(13)	−0.2230(9)	0.1396(9)	0.052(6)	
O51A	0.2354(13)	−0.1854(9)	0.0200(9)	0.052(6)	
O61A	0.3386(13)	−0.2611(9)	0.0928(9)	0.052(6)	
O42A	0.2446(14)	−0.1435(9)	0.4149(12)	0.076(6)	
C12A	0.2079(14)	−0.2503(9)	0.2504(12)	0.076(6)	
C22A	0.1448(14)	−0.2510(9)	0.3081(12)	0.076(6)	
C32A	0.1512(14)	−0.1970(9)	0.3460(12)	0.076(6)	
C42A	0.2375(14)	−0.1939(9)	0.3807(12)	0.076(6)	
C52A	0.3010(14)	−0.1979(9)	0.3237(12)	0.076(6)	
C62A	0.3887(14)	−0.2052(9)	0.3584(12)	0.076(6)	
O22A	0.0645(14)	−0.2550(9)	0.2759(12)	0.076(6)	
O32A	0.0929(14)	−0.1976(9)	0.4003(12)	0.076(6)	
O52A	0.2868(14)	−0.2446(9)	0.2832(12)	0.076(6)	
O62A	0.3958(14)	−0.2482(9)	0.4103(12)	0.076(6)	
O43A	0.2695(14)	0.0260(8)	0.4831(12)	0.071(6)	
C13A	0.2754(14)	−0.1422(8)	0.4891(12)	0.071(6)	
C23A	0.2172(14)	−0.1129(8)	0.5374(12)	0.071(6)	
C33A	0.2004(14)	−0.0570(8)	0.5073(12)	0.071(6)	
C43A	0.2822(14)	−0.0264(8)	0.5106(12)	0.071(6)	
C53A	0.3448(14)	−0.0587(8)	0.4702(12)	0.071(6)	
C63A	0.4327(14)	−0.0349(8)	0.4803(12)	0.071(6)	
O23A	0.1413(14)	−0.1417(8)	0.5382(12)	0.071(6)	
O33A	0.1435(14)	−0.0301(8)	0.5501(12)	0.071(6)	
O53A	0.3492(14)	−0.1117(8)	0.4962(12)	0.071(6)	
O631	0.4668(14)	−0.0376(8)	0.5514(12)	0.071(6)	0.5
O632	0.4639(14)	−0.0645(8)	0.4210(12)	0.071(6)	0.5
O44A	0.2576(13)	0.1749(10)	0.3581(10)	0.067(6)	
C14A	0.3038(13)	0.0728(10)	0.5243(10)	0.067(6)	
C24A	0.2328(13)	0.1125(10)	0.5319(10)	0.067(6)	
C34A	0.2074(13)	0.1334(10)	0.4598(10)	0.067(6)	
C44A	0.2818(13)	0.1598(10)	0.4273(10)	0.067(6)	
C54A	0.3503(13)	0.1180(10)	0.4223(10)	0.067(6)	
C64A	0.4311(13)	0.1439(10)	0.3972(10)	0.067(6)	
O24A	0.1654(13)	0.0834(10)	0.5600(10)	0.067(6)	
O34A	0.1441(13)	0.1724(10)	0.4659(10)	0.067(6)	
O54A	0.3697(13)	0.0973(10)	0.4895(10)	0.067(6)	
O64A	0.4595(13)	0.1830(10)	0.4492(10)	0.067(6)	
O45A	0.2065(12)	0.1931(9)	0.1304(9)	0.056(6)	
C15A	0.2734(12)	0.2269(9)	0.3377(9)	0.056(6)	
C25A	0.1950(12)	0.2529(9)	0.3071(9)	0.056(6)	
C35A	0.1659(12)	0.2203(9)	0.2433(9)	0.056(6)	
C45A	0.2344(12)	0.2218(9)	0.1908(9)	0.056(6)	
C55A	0.3129(12)	0.1981(9)	0.2247(9)	0.056(6)	
C65A	0.3871(12)	0.2060(9)	0.1766(9)	0.056(6)	

TABLE I (*Continued*)

Atom	*x/a*	*y/b*	*z/c*	*U(iso)*	*s.o.f*
O25A	0.1323(12)	0.2511(9)	0.3565(9)	0.056(6)	
O35A	0.0952(12)	0.2463(9)	0.2124(9)	0.056(6)	
O55A	0.3344(12)	0.2270(9)	0.2864(9)	0.056(6)	
O65A	0.4016(12)	0.2611(9)	0.1549(9)	0.056(6)	
O46A	0.1559(14)	0.0651(8)	−0.0278(12)	0.063(6)	
C16A	0.2123(14)	0.2148(8)	0.0574(12)	0.063(6)	
C26A	0.1267(14)	0.2086(8)	0.0216(12)	0.063(6)	
C36A	0.1073(14)	0.1488(8)	0.0158(12)	0.063(6)	
C46A	0.1752(14)	0.1208(8)	−0.0236(12)	0.063(6)	
C56A	0.2577(14)	0.1305(8)	0.0152(12)	0.063(6)	
C66A	0.3301(14)	0.1061(8)	−0.0245(12)	0.063(6)	
O26A	0.0672(14)	0.2329(8)	0.0651(12)	0.063(6)	
O36A	0.0318(14)	0.1424(8)	−0.0233(12)	0.063(6)	
O56A	0.2728(14)	0.1867(8)	0.0187(12)	0.063(6)	
O661	0.3440(14)	0.1493(8)	−0.0735(12)	0.063(6)	0.5
O662	0.4023(14)	0.1189(8)	−0.0003(12)	0.063(6)	0.5
O47A	0.1527(12)	−0.1106(8)	0.0105(11)	0.052(6)	
C17A	0.1594(12)	0.0358(8)	−0.0908(11)	0.052(6)	
C27A	0.0798(12)	0.0032(8)	−0.1010(11)	0.052(6)	
C37A	0.0774(12)	−0.0379(8)	−0.0421(11)	0.052(6)	
C47A	0.1540(12)	−0.0735(8)	−0.0456(11)	0.052(6)	
C57A	0.2302(12)	−0.0379(8)	−0.0352(11)	0.052(6)	
C67A	0.3108(12)	−0.0704(8)	−0.0432(11)	0.052(6)	
O27A	0.0113(12)	0.0385(8)	−0.0953(11)	0.052(6)	
O37A	0.0052(12)	−0.0700(8)	−0.0518(11)	0.052(6)	
O57A	0.2304(12)	0.0021(8)	−0.0877(11)	0.052(6)	
O67A	0.3003(12)	−0.0962(8)	−0.1111(11)	0.052(6)	
C41B	−0.2262(13)	0.1912(10)	0.1444(10)	0.065(6)	
C11B	−0.2813(13)	0.0908(10)	−0.0227(10)	0.065(6)	
C21B	−0.2024(13)	0.1243(10)	−0.0265(10)	0.065(6)	
C31B	−0.1776(13)	0.1424(10)	0.0469(10)	0.065(6)	
C41B	−0.2470(13)	0.1778(10)	0.0740(10)	0.065(6)	
C51B	−0.3263(13)	0.1444(10)	0.0728(10)	0.065(6)	
C61B	−0.4016(13)	0.1802(10)	0.0893(10)	0.065(6)	
O21B	−0.1390(13)	0.0914(10)	−0.0538(10)	0.065(6)	
O31B	−0.1041(13)	0.1733(10)	0.0457(10)	0.065(6)	
O51B	−0.3428(13)	0.1243(10)	0.0047(10)	0.065(6)	
O61B	−0.4031(13)	0.2278(10)	0.0453(10)	0.065(6)	
O42B	−0.1689(13)	0.2009(10)	0.3742(10)	0.075(6)	
C12B	−0.2415(13)	0.2435(10)	0.1715(10)	0.075(6)	
C22B	−0.1570(13)	0.2625(10)	0.1988(10)	0.075(6)	
C32B	−0.1293(13)	0.2276(10)	0.2607(10)	0.075(6)	
C42B	−0.1944(13)	0.2329(10)	0.3163(10)	0.075(6)	
C52B	−0.2764(13)	0.2128(10)	0.2843(10)	0.075(6)	
C62B	−0.3476(13)	0.2181(10)	0.3354(10)	0.075(6)	
O22B	−0.0988(13)	0.2564(10)	0.1454(10)	0.075(6)	
O32B	−0.0528(13)	0.2482(10)	0.2882(10)	0.075(6)	
O52B	−0.2975(13)	0.2470(10)	0.2271(10)	0.075(6)	
O62B	−0.3622(13)	0.2745(10)	0.3509(10)	0.075(6)	
O43B	−0.1521(13)	0.0725(7)	0.5219(12)	0.053(6)	
C13B	−0.1661(13)	0.2258(7)	0.4351(12)	0.053(6)	
C23B	−0.0851(13)	0.2100(7)	0.4729(12)	0.053(6)	
C33B	−0.0809(13)	0.1489(7)	0.4769(12)	0.053(6)	
C43B	−0.1558(13)	0.1293(7)	0.5167(12)	0.053(6)	

TABLE I (*Continued*)

Atom	*x/a*	*y/b*	*z/c*	*U(iso)*	*s.o.f*
C53B	−0.2344(13)	0.1487(7)	0.4788(12)	0.053(6)	
C63B	−0.3116(13)	0.1358(7)	0.5211(12)	0.053(6)	
O23B	−0.0183(13)	0.2300(7)	0.4347(12)	0.053(6)	
O33B	−0.0085(13)	0.1345(7)	0.5172(12)	0.053(6)	
O53B	−0.2326(13)	0.2057(7)	0.4742(12)	0.053(6)	
O63B	−0.3032(13)	0.1550(7)	0.5924(12)	0.053(6)	
O44B	−0.1739(14)	−0.1041(9)	0.4965(12)	0.077(6)	
C14B	−0.1482(14)	0.0475(9)	0.5876(12)	0.077(6)	
C24B	−0.0781(14)	0.0071(9)	0.6006(12)	0.077(6)	
C34B	−0.0845(14)	−0.0360(9)	0.5445(12)	0.077(6)	
C44B	−0.1688(14)	−0.0633(9)	0.5483(12)	0.077(6)	
C54B	−0.2353(14)	−0.0204(9)	0.5368(12)	0.077(6)	
C64B	−0.3227(14)	−0.0435(9)	0.5451(12)	0.077(6)	
O24B	−0.0023(14)	0.0353(9)	0.5949(12)	0.077(6)	
O34B	−0.0218(14)	−0.0752(9)	0.5564(12)	0.077(6)	
O54B	−0.2241(14)	0.0193(9)	0.5893(12)	0.077(6)	
O64B	−0.3416(14)	−0.0737(9)	0.6072(12)	0.077(6)	
O45B	−0.2276(13)	−0.1886(9)	0.3064(9)	0.051(6)	
C15B	−0.1889(13)	−0.1593(9)	0.5177(9)	0.051(6)	
C25B	−0.1273(13)	−0.1964(9)	0.4829(9)	0.051(6)	
C35B	−0.1349(13)	−0.1879(9)	0.4045(9)	0.051(6)	
C45B	−0.2224(13)	−0.2024(9)	0.3786(9)	0.051(6)	
C55B	−0.2844(13)	−0.1717(9)	0.4207(9)	0.051(6)	
C65B	−0.3738(13)	−0.1917(9)	0.4067(9)	0.051(6)	
O25B	−0.0463(13)	−0.1808(9)	0.5068(9)	0.051(6)	
O35B	−0.0792(13)	−0.2235(9)	0.3711(9)	0.051(6)	
O55B	−0.2681(13)	−0.1774(9)	0.4931(9)	0.051(6)	
O65B	−0.4317(13)	−0.1534(9)	0.4354(9)	0.051(6)	
O46B	−0.2618(13)	−0.1234(9)	0.0904(11)	0.058(6)	
C16B	−0.2501(13)	−0.2296(9)	0.2610(11)	0.058(6)	
C26B	−0.1920(13)	−0.2385(9)	0.2007(11)	0.058(6)	
C36B	−0.1840(13)	−0.1852(9)	0.1621(11)	0.058(6)	
C46B	−0.2690(13)	−0.1708(9)	0.1310(11)	0.058(6)	
C56B	−0.3295(13)	−0.1672(9)	0.1903(11)	0.058(6)	
C66B	−0.4198(13)	−0.1635(9)	0.1599(11)	0.058(6)	
O26B	−0.1132(13)	−0.2526(9)	0.2302(11)	0.058(6)	
O36B	−0.1276(13)	−0.1915(9)	0.1075(11)	0.058(6)	
O56B	−0.3269(13)	−0.2158(9)	0.2286(11)	0.058(6)	
O66B	−0.4820(13)	−0.1602(9)	0.2128(11)	0.058(6)	
O47B	−0.2665(14)	0.0471(8)	0.0177(13)	0.072(6)	
C17B	−0.2992(14)	−0.1184(8)	0.0288(13)	0.072(6)	
C27B	−0.2367(14)	−0.0975(8)	−0.0225(13)	0.072(6)	
C37B	−0.2113(14)	−0.0408(8)	−0.0007(13)	0.072(6)	
C47B	−0.2887(14)	−0.0055(8)	−0.0044(13)	0.072(6)	
C57B	−0.3517(14)	−0.0297(8)	0.0439(13)	0.072(6)	
C67B	−0.4356(14)	−0.0001(8)	0.0366(13)	0.072(6)	
O27B	−0.1657(14)	−0.1315(8)	−0.0181(13)	0.072(6)	
O37B	−0.1549(14)	−0.0199(8)	−0.0494(13)	0.072(6)	
O57B	−0.3686(14)	−0.0834(8)	0.0228(13)	0.072(6)	
O67B	−0.4597(14)	−0.0026(8)	−0.0370(13)	0.072(6)	
UB	−0.3977(4)	0.0130(4)	0.2976(5)	0.076(3)	0.5
O1B	−0.4112(4)	0.0327(4)	0.3837(5)	0.076(3)	0.5
O2B	−0.3809(4)	−0.0042(4)	0.2106(5)	0.076(3)	0.5
O3B	−0.4174(4)	0.1056(4)	0.2617(5)	0.076(3)	0.5

TABLE I (*Continued*)

Atom	*x/a*	*y/b*	*z/c*	*U(iso)*	*s.o.f*
O4B	−0.5501(4)	0.0146(4)	0.2794(5)	0.076(3)	0.5
O5B	−0.4254(4)	−0.0771(4)	0.3258(5)	0.076(3)	0.5
O6B	−0.2614(4)	−0.0242(4)	0.3287(5)	0.076(3)	0.5
O7B	−0.2636(4)	0.0600(4)	0.3028(5)	0.076(3)	0.5
C1B	−0.2153(4)	0.0192(4)	0.3214(5)	0.076(3)	0.5
C2B	−0.1273(4)	0.0166(4)	0.3312(5)	0.076(3)	0.5
C3B	−0.0726(4)	0.0617(4)	0.3293(5)	0.076(3)	0.5
C4B	−0.0088(4)	−0.0375(4)	0.3595(5)	0.076(3)	0.5
C5B	0.0418(4)	0.0082(4)	0.3567(5)	0.076(3)	0.5
C6B	0.0087(4)	0.0579(4)	0.3414(5)	0.076(3)	0.5
C7B	−0.0899(4)	−0.0330(4)	0.3469(5)	0.076(3)	0.5
UA	0.3804(5)	−0.0119(4)	0.2001(5)	0.081(4)	0.5
O1A	0.3955(5)	−0.0542(4)	0.1300(5)	0.081(4)	0.5
O2A	0.3690(5)	0.0302(4)	0.2728(5)	0.081(4)	0.5
O3A	0.3921(5)	0.0648(4)	0.1271(5)	0.081(4)	0.5
O4A	0.5305(5)	0.0018(4)	0.2124(5)	0.081(4)	0.5
O5A	0.4168(5)	−0.0847(4)	0.2798(5)	0.081(4)	0.5
O6A	0.2458(5)	−0.0527(4)	0.2194(5)	0.081(4)	0.5
O7A	0.2475(5)	0.0185(4)	0.1513(5)	0.081(4)	0.5
C1A	0.1968(5)	−0.0195(4)	0.1795(5)	0.081(4)	0.5
C2A	0.1064(5)	−0.0237(4)	0.1713(5)	0.081(4)	0.5
C3A	0.0596(5)	−0.0647(4)	0.2031(5)	0.081(4)	0.5
C4A	−0.0217(5)	−0.0687(4)	0.1948(5)	0.081(4)	0.5
C5A	−0.0631(5)	−0.0310(4)	0.1539(5)	0.081(4)	0.5
C6A	−0.0205(5)	0.0103(4)	0.1216(5)	0.081(4)	0.5
C7A	0.0609(5)	0.0133(4)	0.1300(5)	0.081(4)	0.5
O1W	−0.291(3)	0.106(2)	0.723(2)	0.085(9)	0.9
O2W	0.463(3)	−0.219(2)	0.539(3)	0.125(10)	
O3W	0.509(4)	−0.343(3)	0.409(3)	0.101(10)	0.75
O4W	−0.379(3)	0.154(2)	0.813(3)	0.073(9)	0.85
O5W	0.502(4)	0.076(3)	−0.119(3)	0.109(10)	0.8
O6W	0.488(4)	0.226(3)	−0.235(3)	0.092(10)	0.75
O7W	0.424(4)	0.256(2)	0.000(3)	0.097(10)	0.8
O8W	0.330(4)	0.371(3)	0.203(4)	0.096(10)	0.65
O9W	0.529(5)	0.298(3)	0.269(4)	0.103(10)	0.6
O10W	−0.375(6)	0.020(3)	0.702(6)	0.117(10)	0.4
O11W	−0.260(6)	−0.100(5)	0.742(6)	0.093(10)	0.35
O12W	0.514(6)	−0.124(4)	0.602(5)	0.117(10)	0.5
O13W	0.294(7)	0.130(5)	−0.239(6)	0.110(10)	0.35
O14W	−0.400(6)	−0.168(2)	0.631(5)	0.118(10)	0.5
O15W	−0.008(3)	0.360(2)	0.170(3)	0.113(10)	
O16W	−0.041(3)	−0.335(2)	0.178(3)	0.103(9)	
O17W	−0.060(3)	−0.140(3)	0.684(4)	0.098(10)	0.7
O18W	−0.151(4)	−0.144(3)	−0.153(4)	0.119(10)	0.8
O19W	−0.124(3)	−0.005(2)	−0.210(3)	0.114(10)	0.9
O20W	0.096(3)	−0.146(3)	0.665(2)	0.107(10)	0.65
O21W	0.171(6)	−0.050(4)	0.707(6)	0.138(10)	0.5
O22W	0.018(5)	0.169(4)	0.649(4)	0.102(10)	0.6
O23W	0.049(5)	0.053(4)	0.733(5)	0.109(10)	0.55
O24W	−0.144(4)	0.113(3)	−0.197(4)	0.105(10)	0.7
O25W	0.178(7)	0.130(5)	0.697(6)	0.102(10)	0.4
O26W	0.400(7)	0.169(5)	−0.321(6)	0.092(10)	0.25
O27W	0.388(7)	0.176(6)	0.721(7)	0.091(10)	0.25
O28W	−0.682(6)	−0.001(5)	−0.248(6)	0.118(10)	0.6

TABLE I (*Continued*)

Atom	*x/a*	*y/b*	*z/c*	*U(iso)*	*s.o.f*
O29W	0.431(5)	0.205(3)	−0.116(3)	0.114(10)	0.45
O30W	−0.420(6)	−0.040(5)	−0.182(6)	0.135(10)	0.35
O31W	0.358(7)	0.052(6)	−0.221(7)	0.134(10)	0.35
O1WU	0.238(7)	0.490(5)	0.655(6)	0.088(10)	0.45
O2WU	0.009(6)	0.026(4)	0.282(5)	0.093(10)	0.4
O3WU	0.004(6)	0.107(5)	0.219(5)	0.095(10)	0.35
O4WU	−0.700(3)	0.039(3)	0.220(6)	0.092(10)	0.6
O5WU	−0.798(4)	−0.037(3)	0.182(4)	0.090(10)	0.4

Note: All occupancy factors are equal to 1.0 except those indicated.

TABLE II Final positional and thermal parameters and occupancy factors in the diaqua(benzoate)hydroxydioxouranium(VI) complex adduct with β-CD (0.35 : 1), Form II

Atom	*x/a*	*y/b*	*z/c*	*U(iso)*	*s.o.f*
O41	0.4922(10)	−0.2983(11)	0.2640(13)	0.060(6)	
C11	0.7132(11)	−0.3301(12)	0.3134(13)	0.044(7)	
C21	0.6974(11)	−0.2959(13)	0.3852(15)	0.073(8)	
C31	0.6147(10)	−0.3080(12)	0.3733(12)	0.050(8)	
C41	0.5688(10)	−0.2831(12)	0.2819(12)	0.036(7)	
C51	0.5884(11)	−0.3147(13)	0.2098(13)	0.046(7)	
C61	0.5490(14)	−0.2906(13)	0.1147(13)	0.064(8)	
O21	0.7428(10)	−0.3175(11)	0.4714(12)	0.072(6)	
O31	0.5988(12)	−0.2774(11)	0.4417(13)	0.107(7)	
O51	0.6666(10)	−0.3075(11)	0.2301(13)	0.063(6)	
O61	0.5634(13)	−0.2321(12)	0.1162(16)	0.093(7)	
O42	0.2584(12)	−0.3635(11)	0.2182(14)	0.068(6)	
C12	0.4317(12)	−0.2595(12)	0.2384(14)	0.079(8)	
C22	0.3911(13)	−0.2507(12)	0.3067(15)	0.063(8)	
C32	0.3535(12)	−0.3061(11)	0.3100(13)	0.066(8)	
C42	0.2932(13)	−0.3122(12)	0.2155(12)	0.070(8)	
C52	0.3353(13)	−0.3185(12)	0.1483(14)	0.049(8)	
C62	0.2795(16)	−0.3211(15)	0.0497(15)	0.086(8)	
O22	0.4457(12)	−0.2423(12)	0.3956(14)	0.108(7)	
O32	0.3137(11)	−0.2990(11)	0.3720(13)	0.086(7)	
O52	0.3743(11)	−0.2686(11)	0.1519(13)	0.079(7)	
O621	0.225(2)	−0.280(2)	0.012(3)	0.154(9)	0.65
O622	0.307(3)	−0.334(3)	−0.022(3)	0.121(10)	0.35
O43	0.1827(11)	−0.5332(10)	0.2070(12)	0.046(6)	
C13	0.1780(14)	−0.3656(11)	0.1770(14)	0.071(8)	
C23	0.1435(16)	−0.3892(10)	0.2442(16)	0.085(8)	
C33	0.1738(15)	−0.4473(10)	0.2691(14)	0.072(8)	
C43	0.1445(14)	−0.4823(10)	0.1821(13)	0.063(8)	
C53	0.1783(15)	−0.4559(11)	0.1176(15)	0.071(8)	
C63	0.1531(17)	−0.4839(13)	0.0254(16)	0.082(8)	
O23	0.1736(13)	−0.3576(11)	0.3269(14)	0.107(7)	
O33	0.1431(13)	−0.4701(11)	0.3335(13)	0.098(7)	
O53	0.1523(13)	−0.4005(10)	0.1001(14)	0.096(7)	
O631	0.125(4)	−0.478(3)	−0.073(2)	0.117(10)	0.35
O632	0.075(2)	−0.476(2)	−0.0162(26)	0.117(9)	0.65
O44	0.3234(10)	−0.6836(11)	0.2388(12)	0.051(6)	
C14	0.1377(14)	−0.5811(11)	0.1850(14)	0.093(8)	

TABLE II (*Continued*)

Atom	*x/a*	*y/b*	*z/c*	*U(iso)*	*s.o.f*
C24	0.1564(12)	−0.6186(12)	0.2685(15)	0.067(8)	
C34	0.2380(12)	−0.6361(12)	0.2954(14)	0.068(8)	
C44	0.2468(12)	−0.6668(13)	0.2148(12)	0.075(8)	
C54	0.2257(13)	−0.6277(12)	0.1338(14)	0.058(8)	
C64	0.2259(16)	−0.6578(13)	0.0474(16)	0.076(8)	
O24	0.1482(11)	−0.5867(11)	0.3433(13)	0.062(6)	
O34	0.2567(11)	−0.6725(11)	0.3711(12)	0.072(6)	
O54	0.1483(10)	−0.6120(10)	0.1130(13)	0.062(6)	
O64	0.1738(14)	−0.7030(12)	0.0285(16)	0.110(7)	
O45	0.5660(11)	−0.6965(11)	0.2825(14)	0.063(6)	
C15	0.3398(11)	−0.7386(12)	0.2251(14)	0.046(7)	
C25	0.3963(11)	−0.7575(14)	0.3140(16)	0.097(8)	
C35	0.4678(10)	−0.7228(12)	0.3376(13)	0.046(8)	
C45	0.5016(11)	−0.7320(13)	0.2629(13)	0.065(8)	
C55	0.4398(13)	−0.7135(13)	0.1742(14)	0.075(8)	
C65	0.4695(17)	−0.7241(16)	0.0955(17)	0.087(8)	
O25	0.3632(11)	−0.7510(12)	0.3839(13)	0.092(7)	
O35	0.5203(11)	−0.7434(11)	0.4200(13)	0.086(7)	
O55	0.3752(11)	−0.7474(11)	0.1589(13)	0.077(7)	
O651	0.409(2)	−0.740(2)	0.015(3)	0.125(9)	0.5
O652	0.485(2)	−0.778(2)	0.083(3)	0.060(8)	0.5
O46	0.7309(12)	−0.5650(10)	0.3231(14)	0.072(7)	
C16	0.6347(13)	−0.7186(11)	0.2832(13)	0.052(8)	
C26	0.6949(13)	−0.7067(10)	0.3747(14)	0.035(7)	
C36	0.7019(13)	−0.6454(10)	0.3888(12)	0.035(7)	
C46	0.7269(13)	−0.6228(10)	0.3124(12)	0.035(7)	
C56	0.6663(15)	−0.6358(11)	0.2227(13)	0.064(8)	
C66	0.6890(18)	−0.6168(13)	0.1422(15)	0.068(8)	
O26	0.6735(11)	−0.7300(10)	0.4450(12)	0.064(6)	
O36	0.7612(11)	−0.6345(11)	0.4712(12)	0.073(6)	
O56	0.6542(11)	−0.6929(10)	0.2139(13)	0.063(6)	
O661	0.752(2)	−0.652(2)	0.152(3)	0.102(9)	0.5
O662	0.630(2)	−0.636(2)	0.063(2)	0.070(9)	0.5
O47	0.6960(11)	−0.3865(11)	0.3187(15)	0.075(7)	
C17	0.7973(14)	−0.5372(12)	0.3224(14)	0.066(8)	
C27	0.8309(13)	−0.5015(11)	0.4037(15)	0.068(8)	
C37	0.7723(14)	−0.4588(11)	0.4055(13)	0.084(8)	
C47	0.7546(14)	−0.4239(11)	0.3219(13)	0.054(8)	
C57	0.7252(14)	−0.4625(12)	0.2398(14)	0.088(8)	
C67	0.7128(23)	−0.4324(16)	0.1497(17)	0.156(9)	
O27	0.8431(13)	−0.5337(11)	0.4825(14)	0.112(7)	
O37	0.8041(12)	−0.4275(11)	0.4859(13)	0.088(7)	
O57	0.7821(11)	−0.5018(12)	0.2461(13)	0.088(6)	
O671	0.777(2)	−0.399(2)	0.157(3)	0.170(9)	0.65
O672	0.662(4)	−0.457(3)	0.067(4)	0.169(10)	0.35
OW1	0.462(2)	0.8523(13)	0.079(2)	0.080(7)	0.8
OW2	0.104(3)	0.341(2)	0.540(3)	0.071(9)	0.5
OW3	0.057(5)	0.589(4)	0.746(6)	0.113(10)	0.25
OW4	−0.032(5)	0.389(1)	0.323(1)	0.119(10)	0.25
OW5	0.419(3)	0.143(2)	0.504(4)	0.129(9)	0.5
OW6	0.090(2)	0.379(2)	0.796(3)	0.071(9)	0.5
OW7	0.422(4)	0.117(4)	0.132(5)	0.074(10)	0.25
OW8	0.400(3)	0.927(3)	0.176(4)	0.089(9)	0.4
OW9	0.426(3)	0.994(3)	0.192(4)	0.129(9)	0.4

TABLE II (*Continued*)

Atom	*x/a*	*y/b*	*z/c*	*U(iso)*	*s.o.f*
OW10	0.504(4)	0.992(4)	0.367(5)	0.115(10)	0.3
OW11	0.504(4)	0.955(2)	0.469(4)	0.090(9)	0.35
OW12	0.013(3)	0.333(1)	0.511(4)	0.038(8)	0.5
OW13	0.058(2)	0.639(2)	0.413(3)	0.049(8)	0.5
O1WU	0.478(3)	0.504(2)	0.009(4)	0.063(9)	0.35
O2WU	0.482(3)	0.523(6)	0.180(4)	0.093(9)	0.40
O3WU	0.494(5)	0.454(4)	0.160(6)	0.095(10)	0.25
O4WU	0.413(4)	0.527(3)	0.280(5)	0.127(10)	0.35
O5WU	0.425(2)	0.499(2)	0.040(2)	0.079(8)	0.6
O6WU	0.485(4)	0.591(3)	0.063(4)	0.124(10)	0.4
U	0.4414(3)	−0.5014(8)	0.0972(3)	0.087(2)	0.35
O1	0.5368(3)	−0.4909(8)	0.1507(3)	0.087(2)	0.35
O2	0.3447(3)	−0.5146(8)	0.0384(3)	0.087(2)	0.35
O3	0.4663(3)	−0.5963(8)	0.0723(3)	0.087(2)	0.35
O4	0.4585(3)	−0.4969(8)	−0.0495(3)	0.087(2)	0.35
O5	0.4117(3)	−0.4086(8)	0.0496(3)	0.087(2)	0.35
O6	0.4090(3)	−0.4604(8)	0.2203(3)	0.087(2)	0.35
O7	0.4356(3)	−0.5472(8)	0.2336(3)	0.087(2)	0.35
Cl	0.3957(3)	−0.5077(8)	0.2508(3)	0.087(2)	0.35
C2	0.3991(3)	−0.5077(8)	0.3439(3)	0.087(2)	0.35
C3	0.4141(3)	−0.5569(8)	0.3928(3)	0.087(2)	0.35
C4	0.4033(3)	−0.5570(8)	0.4753(3)	0.087(2)	0.35
C5	0.3919(3)	−0.5087(8)	0.5119(3)	0.087(2)	0.35
C6	0.3923(3)	−0.4597(8)	0.4719(3)	0.087(2)	0.35
C7	0.4029(3)	−0.4580(8)	0.3892(3)	0.087(2)	0.35

Note: All occupancy factors are equal to 1.0 except those indicated.

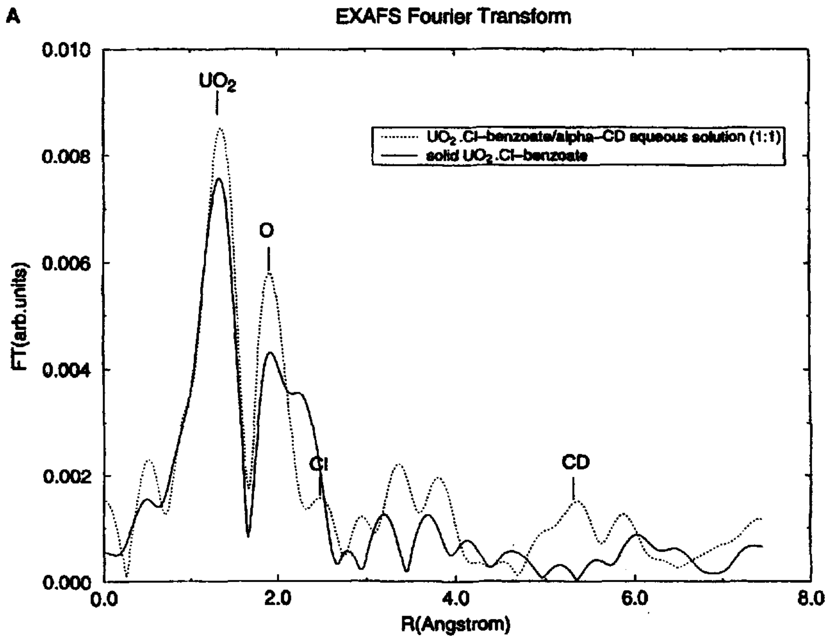

FIGURE 1(A)

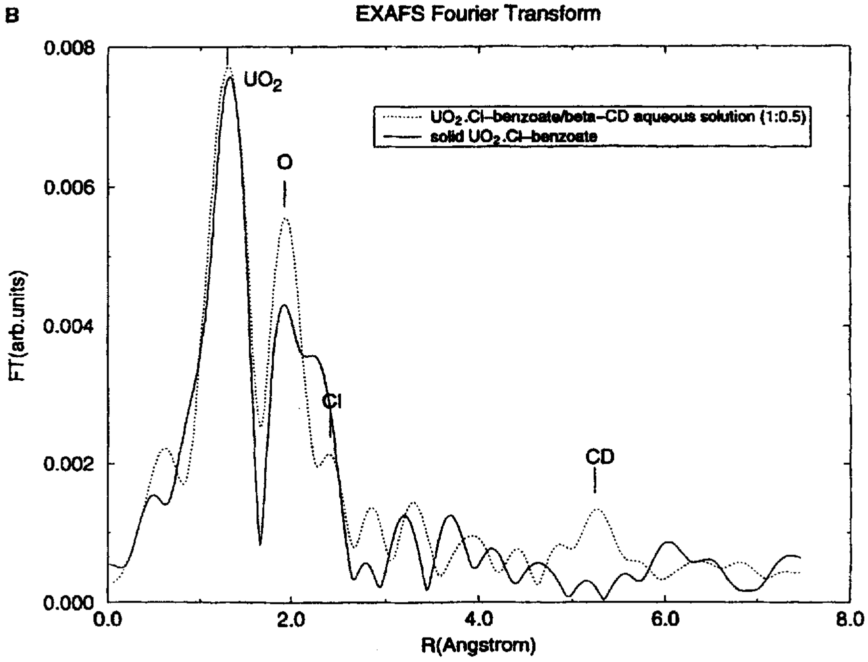

FIGURE 1(B)

FIGURE 1 Superposed $k^3\chi(k)$ Fourier transforms of solid benzoato · Cl–UO$_2$ with A: benzoato · Cl–UO$_2$/α-CD solution; B: benzoato · Cl–UO$_2$/β-CD solution.

solutions. Fit parameters using experimental amplitudes and phases calculated from standard compounds and adjusted on benzoato · Cl–UO$_2$ compound are presented in Table III. The decrease of the chloride and the increase of the oxygen coordination numbers suggest that new species with five oxygen atoms coordinated to the uranyl ion are present in the solutions. The significant peak observed around 5.5 Å on the FT of the solutions point to the formation of an uranyl complex, with CD as second sphere ligand.

Two crystalline forms (I and II) were obtained by evaporation (20 days at 30°C) from [benzoato · Cl–UO$_2$]/β-CD (1 : 0.5) solution and have been analyzed by X-ray crystallography. Both studies show the formation of a diaqua(benzoate)hydroxydioxouranium(VI) adduct with β-CD. Most complexes of native β-CD crystallize as dimers, linked by a network of hydrogen bonds forming *quasi*-invariant layers which stack in four types of crystal packings.[33,34] Forms I and II belong to the channel class (CH) wherein the dimers are aligned on top of each other, forming columns (Figure 2).

The space groups of all β-CD structures classed CH are $C2$ or $P1$,[33] except for an adduct with a complex of the cyclopentadienyl(arene)iron(II) family crystallizing in space group $P2_1$, whose complete structure could not be described due to disorder.[35] Form I is the first completely determined structure in space group $P2_1$. In form II successive layers are shifted by 5.5 Å, giving channels inclined with respect to the dimer plane, whereas in form I they are perpendicular to that plane. This could be related to observed differences in solvent and uranyl-guest occupancy between I and II.

TABLE III Fitted parameters using experimental amplitudes and phases

Sample	*Pairs*	N_i	R_i (Å)	$R_{X\text{-ray}}$ (Å)	$\Delta\sigma_i$ (Å)	E_0 (eV)
Solid benzoato · Cl–UO$_2$	U–O$_{ax}$	2.1	1.76	1.767(9)	0.02	−1.0
	U–O$_{eq}$	3.9	2.44	2.448(9)	0.004	1.3
	U–Cl$_{eq}$	1.0	2.72	2.725(4)	−0.001	
[benzoato · Cl–UO$_2$/β-CD] (1 : 0.5) solution	U–O$_{ax}$	2.0	1.76		0.0007	0.1
	U–O$_{eq}$	4.4	2.41		0.0018	3.0
	U–Cl$_{eq}$	0.6	2.71		−0.05	
[benzoato · Cl–UO$_2$/α-CD] (1 : 1) solution	U–O$_{ax}$	2.0	1.77		−0.0007	0.5
	U–O$_{eq}$	4.7	2.42		−0.0025	3.0
	U–Cl$_{eq}$	0.5	2.75		0.0002	

The fitted parameters are: the atom number N_i of the ith coordination shell, the average distance R_i which separates the absorbing atom from these N_i scattering atoms, the deviation σ_i from this distance R_i and the energy E_0 above which the photoelectron is free. $R_{X\text{-ray}}$ are distances known from X-ray diffraction measurements.

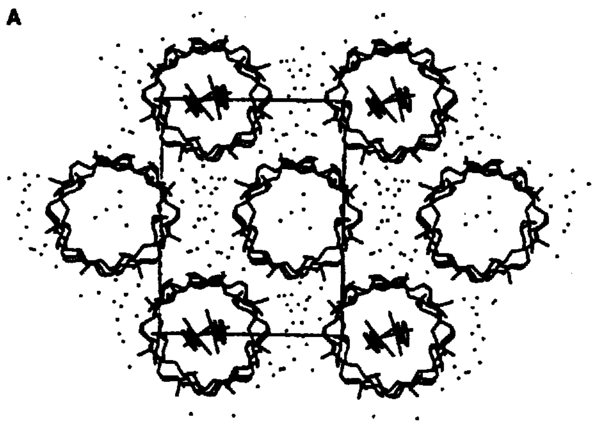

FIGURE 2(A)

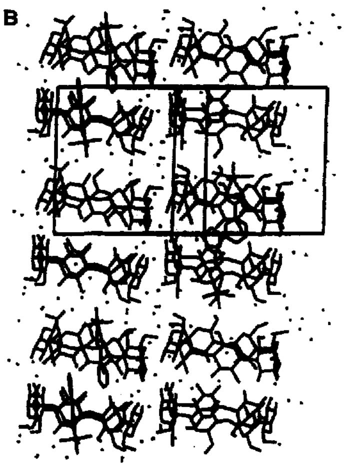

FIGURE 2(B)

FIGURE 2 Channel packing of structure I; A: dimer *pseudo*-centered rectangular layer, plane [*b*, *c*]; B: view along [*b*, *c*] diagonal. The short contacts between the benzoato · OH–UO$_2$ guest with symmetry related molecules, and the presence of water molecules in the β-CD cavity imply that only one of two successive dimers of a channel is complexed with uranyl salts.

Uranyl hydroxide systems have been found in the solid state only as bimetallic complexes having two or one bridging hydroxyl ions.[14,18,36,37] The stabilization of the exceptional monomeric form of the uranyl-guest molecule benzoato · OH–UO$_2$, is due to interactions between this guest and CD. Benzoato · OH–UO$_2$ is inserted into the macrocycle cavity from the narrower primary face (Figure 3) as in the β-CD/platinum phosphine adduct.[38] The hydrophobic benzoate ligand is included in the cavity of the β-CD dimers above the rim of primary hydroxyl groups; the uranyl ion lies on the plane of this rim close to the centre, with average U–OH distances 5.8(2) and 5.9(2) Å in I and 5.66(8) Å in II. The stabilization of the uranyl guest is assured *via* hydrogen-bonds involving primary hydroxyl groups of the CD in *gauche-trans* orientation, and the hydroxyl ligand of the uranyl ion. Distances between the oxygen atoms involved in this host/guest bonding are 2.79 and 2.83 Å in I and 2.64 Å in II. A supplementary stabilization of the uranyl guest is observed in I: hydrogen-bonds are also formed between this molecule and the hydroxyl groups of the uncomplexed neighboring CDs of the same column. These interactions are probably responsible for the new column type observed in the packing of I.

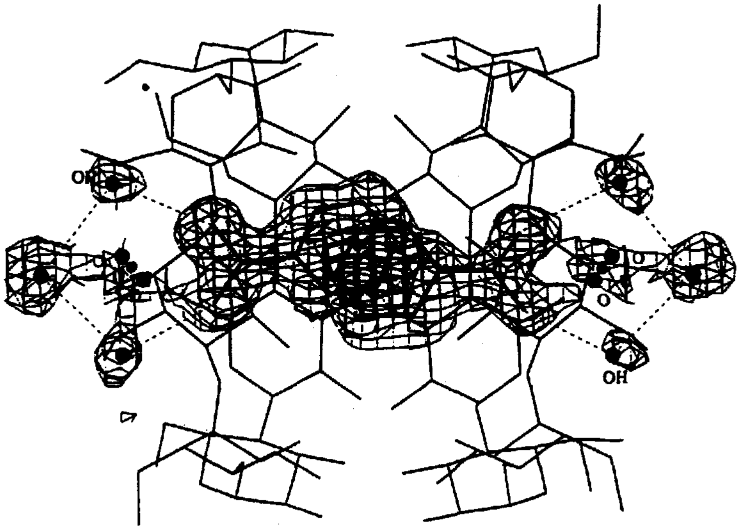

FIGURE 3 View of the two independent units of (benzoato·OH–UO_2/β-CD) in form I showing how the guest penetrates the host. The difference Fourier map has been calculated with only the UO_2^{2+} contribution of the guest molecule. The only difference between the two independent β-CD units is that in one of them, two primary hydroxyl groups point towards the cavity (*gauche-trans* orientation) and in the other, two of the primary hydroxy groups are disordered (two positions).

The present study proves the ability of CDs to act as second sphere ligands toward uranyl complexes with hydrophobic first sphere ligands. The inclusion compound diaqua(benzoate)hydroxydioxouranium(VI)/β-CD is the first uranium complex adduct with a CD. The guest molecule, the monomeric hydroxyl–uranyl complex diaqua(benzoate)hydroxydioxouranium(VI), is stabilized by interactions with the β-CD which, acting as a second sphere ligand, prevents the formation of dimeric uranyl species. Results of EXAFS analysis of [benzoato·Cl–UO_2]/α-CD and [benzoato·Cl–UO_2]/β-CD in aqueous solution suggest that the adducts diaqua(benzoate)hydroxydioxouranium(VI)/CD are present in those solutions.

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