Actinide Complexes of the Calixarenes. Part 1. Syntheses and Crystal Structures of Bis(homo-oxa)-*p*-*tert*-butylcalix[4]arene and its Uranyl Ion Complex*

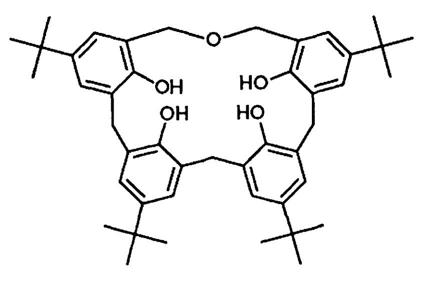
Jack M. Harrowfield, Mark I. Ogden and Allan H. White

Department of Physical and Inorganic Chemistry, The University of Western Australia, Nedlands, 6009, Western Australia

Interaction of the uranyl ion with the potentially quinquedentate calixarene bis(homo-oxa)-*p*-*tert*-butylcalix[4]arene, $C_{45}H_{58}O_5$ (H_4L), in the presence of amine bases results in the formation of the red-brown, anionic complex $[UO_2(L)]^{2-}$. Crystal-structure determinations of the hydrated triethylammonium salt of this complex [monoclinic, space group $C2/c$ (C_{2h}^6, no. 15), $a = 29.81(2)$, $b = 16.653(7)$, $c = 26.38(2)$ Å, $\beta = 115.47(4)°$, $Z = 8$, $R = 0.049$ for 6608 'observed' reflections] and of the dimethylformamide adduct of the free ligand [monoclinic, space group $P2_1/m$ (C_{2h}^2, no. 11), $a = 9.701(1)$, $b = 25.108(9)$, $c = 9.230(3)$ Å, $\beta = 95.97(2)°$, $Z = 2$, $R = 0.067$ for 1749 'observed' reflections] show that the ligand adopts a very similar 'cone' conformation in both instances, and that the uranium–ligand interaction is primarily through the four phenoxide donor atoms, with only a remote (and presumably weak) contact between the uranium and ether-oxygen atoms. One of the triethylammonium counter cations is included within the cone of the co-ordinated ligand in a very similar way to the inclusion of dimethylformamide by the free ligand, and ^1H NMR spectroscopy indicates that this inclusion persists in solution. Uranyl ion luminescence is quenched completely in solutions of the complex at room temperature.

In examining the co-ordination chemistry of the calixarenes[1] with rare-earth ions, we have demonstrated[2–5] that both the complex ion stoichiometry and the ligand binding mode are strongly dependent upon the calixarene ring size. Interestingly, from the limited comparisons that are possible with other metal ions,[6–9] it seems that a given calixarene may adopt preferentially a single conformation when co-ordinated, regardless of the particular metal ion. Were this to be generally true, it might well carry significant implications with respect to any possible selectivity in metal ion binding by the calixarenes.[2] Hence, it is necessary to carry out thorough and systematic studies of calixarene co-ordination chemistry, and one of the metal-ion groups for which we have now accumulated relevant information is that of the actinides.

Some study has, of course, already been made of uranyl ion complexes of calixarene derivatives,[10] though these species may involve co-ordination through pendant-arm substituents rather than solely through the calixarene phenoxo groups. Nonetheless, the principle applied therein, that selective binding to the uranyl ion may be attained by exploiting the proclivity of the UO_2^{2+} ion to form an equatorial garland of four, five or six ligand donor atoms held in a near-planar array,[11] may also be applied with the simple calixarenes. In particular, bis(homo-oxa)-*p*-*tert*-butylcalix[4]arene (see below) would appear to provide an array of five oxygen donor atoms well suited to the pentagonal-bipyramidal geometry at uranium so commonly observed in uranyl ion complexes.[12,13] We report herein aspects of the chemistry of the interaction of uranyl ion with this ligand, and the structure of a crystalline complex which has been isolated.



Experimental

Syntheses.—*Bis(homo-oxa)-*p-tert-*butylcalix[4]arene* (H_4L). Crude H_4L was obtained as a minor product from the synthesis of *p*-*tert*-butylcalix[8]arene as described in the literature.[14] Purification was simplified by the observation that the solubility of H_4L in acetone was very much greater than any other product. Hence, the crude H_4L was recrystallised twice from acetone–water giving colourless needles which effloresced slowly, becoming opaque when dry. Average yield was of the order of 10%, although there was a wide variation, presumably due to subtle changes in the reaction conditions. Proton NMR measurements on an air-dried sample suggested that the product had crystallised as a 1:1 complex with acetone. Recrystallisation from dimethylformamide (dmf) produced colourless prisms that were stable in the laboratory atmosphere and hence were preferred for X-ray diffraction studies (Found: C, 76.5; H, 8.5; N, 2.1. H_4L·dmf requires C, 76.65; H, 8.70; N, 1.85%).

$[NHEt_3]_2[UO_2(L)]\cdot 2H_2O$. A slurry of H_4L·dmf (0.39 g) in acetonitrile (10 cm³) was heated to 60 °C, and triethylamine (0.3 g) added in excess, forming a clear, colourless solution. The compound $[UO_2(dmso)_5][ClO_4]_2$ (0.50 g) (dmso = dimethyl sulphoxide) was added to this solution to give a slightly cloudy red solution which was filtered. On slow cooling to room temperature the filtrate deposited large red crystals (0.48 g,

---

* Bis(homo-oxa)-*p*-*tert*-butylcalix[4]arene = 7,13,19,25-tetra-*tert*-butyl-27,28,29,30-tetrahydroxy-2,3-dihomo-3-oxacalix[4]arene.

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii–xxii.

Table 1 Non-hydrogen atomic coordinates for $[NHEt_3]_2[UO_2(L)]\cdot 2H_2O$

Atom	*x*	*y*	*z*	*x*	*y*	*z*
Anion	Section a			Section b		
U	0.152 27(1)	0.063 20(2)	0.207 27(2)			
O(1U)	0.169 7(2)	0.166 1(3)	0.218 0(2)			
O(2U)	0.135 4(3)	−0.041 1(3)	0.197 1(3)			
O(1)	0.071 9(2)	0.099 6(4)	0.172 5(3)	0.144 1(2)	0.063 7(4)	0.288 1(3)
C(11)	0.059 7(3)	0.179 5(6)	0.166 0(4)	0.155 5(4)	0.130 2(6)	0.318 7(4)
C(12)	0.056 0(3)	0.222 0(6)	0.210 0(4)	0.119 5(3)	0.190 5(6)	0.309 7(4)
C(13)	0.043 2(3)	0.301 9(6)	0.202 8(4)	0.132 5(3)	0.261 1(6)	0.342 1(4)
C(14)	0.033 7(3)	0.341 6(6)	0.153 5(4)	0.180 6(4)	0.274 3(6)	0.384 1(4)
C(141)	0.017 6(4)	0.429 8(7)	0.147 0(5)	0.191 9(4)	0.350 9(6)	0.419 8(4)
C(142)	−0.029 5(5)	0.437 3(8)	0.155 8(6)	0.164 3(4)	0.346 7(7)	0.457 1(4)
C(143)	0.007 2(6)	0.464 4(7)	0.090 3(6)	0.247 7(5)	0.362 1(7)	0.457 8(5)
C(144)	0.057 5(5)	0.480 0(8)	0.191 9(6)	0.174 5(5)	0.423 8(6)	0.381 4(5)
C(15)	0.037 7(3)	0.299 8(7)	0.111 1(4)	0.215 4(3)	0.214 0(6)	0.392 6(4)
C(16)	0.050 8(3)	0.218 1(6)	0.116 3(4)	0.204 2(4)	0.141 6(6)	0.361 3(4)
C(1)	0.066 5(3)	0.181 2(6)	0.265 0(4)			
O(2)	0.142 4(2)	0.073 9(4)	0.117 6(3)	0.232 2(2)	0.026 4(4)	0.262 0(3)
C(21)	0.144 2(4)	0.139 6(6)	0.088 0(4)	0.270 5(3)	0.076 2(5)	0.292 3(4)
C(22)	0.103 0(4)	0.188 3(6)	0.061 1(4)	0.279 6(3)	0.099 9(6)	0.347 2(4)
C(23)	0.106 6(4)	0.250 3(7)	0.027 4(4)	0.323 1(4)	0.141 4(6)	0.378 5(4)
C(24)	0.148 1(4)	0.266 0(7)	0.020 4(4)	0.357 7(4)	0.164 3(6)	0.358 3(4)
C(241)	0.149 6(6)	0.335(1)	−0.016 4(6)	0.406 0(4)	0.205 9(8)	0.396 5(5)
C(242)	0.196 8(7)	0.376(1)	0.003 8(9)	0.439 8(5)	0.221(1)	0.368 3(7)
C(243)	0.143(2)	0.303(2)	−0.066 6(9)	0.432 9(6)	0.155(1)	0.446 9(7)
C(244)	0.113(1)	0.395(2)	−0.027(2)	0.394 3(6)	0.286(1)	0.414 9(8)
C(25)	0.188 4(4)	0.218 8(6)	0.049 2(4)	0.346 5(4)	0.143 1(6)	0.303 9(4)
C(26)	0.187 9(4)	0.155 8(6)	0.083 2(4)	0.303 7(3)	0.099 8(6)	0.270 0(4)
C(2)	0.054 8(4)	0.174 4(6)	0.067 2(4)	0.244 3(3)	0.078 7(6)	0.371 8(4)
C(3)	0.232 4(4)	0.106 8(6)	0.115 9(4)	0.292 6(3)	0.079 2(6)	0.211 5(4)
O(3)	0.250 0(2)	0.125 9(4)	0.174 4(3)			
Triethylammonium cation (1)				Triethylammonium cation (2)		
N	−0.257 5(5)	0.142 3(7)	−0.285 1(6)	−0.083 2(5)	0.018 7(9)	0.074 9(7)
C(1)	−0.303(1)	0.158(2)	−0.331(1)	−0.065(2)	0.100(3)	0.099(2)
C(2)	−0.338 6(7)	0.108(1)	−0.342(1)	−0.078 7(7)	0.160(1)	0.073 3(9)
C(3)	−0.210(1)	0.182(2)	−0.286(1)	−0.062(—)	−0.057(—)	0.076(—)
C(4)	−0.203(1)	0.159 (1)	−0.325 1(9)	−0.012(1)	−0.061(2)	0.083(2)
C(5)	−0.247(1)	0.181(2)	−0.231(2)	−0.128(—)	0.000(—)	0.063(—)
C(6)	−0.242(1)	0.154(1)	−0.189(1)	−0.168 3(8)	−0.040(1)	0.057(1)
Water (1)				Water (3)		
O	−0.110(1)	0.038(1)	−0.042(1)	O 0.072(1)	0.046(2)	0.213(1)
Water (2)						
O	0.027(2)	0.025(3)	−0.289(2)			

79%). For X-ray diffraction studies, crystals were sealed in capillaries wet with supernatant solution. Crystals collected, washed with acetonitrile, and dried by vacuum desiccation effloresced slowly and became opaque. Microanalyses were consistent with loss of water relative to the stoichiometry implied by the structure determination {Found: C, 59.8; H, 7.4; N, 2.5. $[NHEt_3]_2[UO_2(L)]$ requires C, 59.55; H, 7.55; N, 2.45%}.

$[NH_2Et_2]_2[UO_2(L)]$. The procedure followed was as described for the synthesis of $[NHEt_3]_2[UO_2(L)]$, substituting diethylamine for triethylamine. The product precipitated as small red crystals (0.34 g, 58%) which were washed with acetonitrile and dried by vacuum desiccation {Found: C, 58.0; H, 7.1; N, 2.6. $[NH_2Et_2]_2[UO_2(L)]$ requires C, 58.2; H, 7.2; N, 2.55%}.

Structure Determinations.—Unique data sets were measured at ≈295 K within the limit $2\theta_{max} = 50°$ using an Enraf-Nonius CAD-4 diffractometer (2θ–θ scan mode; monochromatic Mo-Kα radiation, λ = 0.71069 Å). *N* Independent reflections were obtained, N_o with $I > 3\sigma(I)$ being considered 'observed' and used in the full-matrix least-squares refinement after Gaussian absorption correction (uranium complex only). Anisotropic thermal parameters were refined for the non-hydrogen atoms, excepting some of those associated with the cation and solvent molecules, where amplitudes were excessively high and anisotropic or disordered. Residuals on $|F|$ at convergence, *R*, *R′* are quoted, statistical weights derivative of $\sigma^2(I) = \sigma^2(I_{diff}) + 0.0004\sigma^4(I_{diff})$ being employed. Neutral atom scattering factors were employed;[15] computation used the XTAL 2.6 program system[16] implemented by S. R. Hall. Atomic co-ordinates for the two structures are given in Tables 1 and 2, selected bond lengths and angles in Tables 3 and 4.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters and remaining bond lengths and angles.

Crystal data. $[NHEt_3]_2[UO_2(L)]\cdot 2H_2O$. $C_{57}H_{86}N_2O_7U\cdot 2H_2O$, *M* = 1185.4. monoclinic, space group $C2/c$ (C_{2h}^6, no. 15). *a* = 29.81(2), *b* = 16.653(7), *c* = 26.38(2) Å, β = 115.47(4)°, *U* = 11820 Å^3, $D_c(Z = 8)$ = 1.33 g cm^{-3}, *F*(000) = 4880, μ_{Mo} = 26.5 cm^{-1}; specimen: 0.5 × 0.5 × 0.2 mm (capillary);

Table 2 Non-hydrogen atomic coordinates for $H_4L\cdot dmf$

Atom	*x*	*y*	*z*
O(1)	0.0871(3)	0.1953(2)	0.5327(3)
C(11)	0.2215(5)	0.1750(2)	0.5427(5)
C(12)	0.3258(5)	0.2002(2)	0.6288(5)
C(13)	0.4598(6)	0.1801(2)	0.6321(5)
C(14)	0.4926(5)	0.1362(2)	0.5520(5)
C(141)	0.6429(6)	0.1169(3)	0.5524(7)
C(142)	0.741(1)	0.1413(6)	0.657(2)
C(143)	0.652(1)	0.0553(4)	0.573(2)
C(144)	0.687(1)	0.1247(6)	0.396(1)
C(145)	0.726(2)	0.1697(9)	0.518(3)
C(146)	0.690(3)	0.106(1)	0.727(3)
C(147)	0.660(3)	0.076(1)	0.464(4)
C(15)	0.3834(6)	0.1108(2)	0.4721(5)
C(16)	0.2477(5)	0.1286(2)	0.4665(5)
C(1)	0.3023(7)	$\frac{1}{4}$	0.7136(7)
O(2)	0.0036(4)	0.1892(1)	0.2388(3)
C(21)	0.0552(5)	0.1500(2)	0.1556(6)
C(22)	0.1190(5)	0.1052(2)	0.2198(5)
C(23)	0.1698(5)	0.0671(2)	0.1309(6)
C(24)	0.1593(5)	0.0712(2)	−0.0203(6)
C(241)	0.2167(6)	0.0290(2)	−0.1174(6)
C(242)	0.2297(7)	−0.0250(3)	−0.0445(6)
C(243)	0.1207(7)	0.0223(3)	−0.2609(6)
C(244)	0.3591(7)	0.0475(3)	−0.1554(8)
C(25)	0.0952(6)	0.1168(2)	−0.0790(5)
C(26)	0.0424(5)	0.1557(2)	0.0045(6)
C(2)	0.1316(5)	0.0971(2)	0.3828(5)
C(3)	−0.0307(6)	0.2027(2)	−0.0650(5)
O(3)	0.0388(5)	$\frac{1}{4}$	−0.0102(5)
Dimethylformamide			
O	0.6246(8)	0.2372(5)	−0.0371(9)
C(1)	0.560(2)	0.2320(7)	0.062(2)
N	0.465(1)	0.2345(4)	0.122(1)
C(2)	0.384(1)	0.2366(8)	0.229(1)
C(3)	0.443(2)	0.1835(7)	0.078(2)

Table 3 Uranium environment in $[NHEt_3]_2[UO_2(L)]\cdot 2H_2O$: *r* is the uranium–ligand atom distance (Å); other entries in the matrix are the angles subtended at the uranium by the relevant atoms at the head of the row and column (°)

Atom	*r*	O(2U)	O(1a)	O(2a)	O(1b)	O(2b)
O(1U)	1.778(5)	179.3(3)	89.5(3)	89.3(3)	89.4(3)	90.3(2)
O(2U)	1.796(6)		91.1(3)	91.0(3)	90.4(3)	89.0(2)
O(1a)	2.247(6)			85.1(3)	81.7(2)	166.5(3)
O(2a)	2.261(7)				166.8(2)	108.4(3)
O(1b)	2.249(8)					84.8(2)
O(2b)	2.275(6)					

Table 4 Ring dihedral angles (°) for $[NHEt_3]_2[UO_2(L)]\cdot 2H_2O$ and $H_4L\cdot$ dmf; atoms are denoted by number, O atoms are italicized

	$[NHEt_3]_2[UO_2(L)]\cdot 2H_2O$		
Atoms	Section a	Section b	$H_4L\cdot dmf$
12–1–12–11	94(1)	−97(1)	−91.3(6)
1–12–11–16	−178.9(6)	−179(6)	−179.5(5)
11–16–2–22	−100(1)	101(1)	102.7(6)
16–2–22–21	89(1)	−91(1)	−79.0(6)
2–22–21–26	−177.6(9)	177.8(8)	−178.5(5)
22–21–26–3	175.3(9)	−176.3(8)	177.7(5)
21–26–3–*3*	−70(1)	69(1)	59.3(6)
26–3–*3*–3	177.7(8)	−175.1(8)	−176.2(4)

$A^*_{\text{min,max}} = 1.62,\ 2.61$; $N = 10\,018$, $N_o = 6608$; $R = 0.049$, $R' = 0.057$.

Abnormal features. After consideration of difference maps and refinement behaviour, site occupancies of solvent water molecules 2 and 3 were set at 0.5 each; large thermal parameters associated with the peripheries of the cations and some Bu^t groups may also encompass real or incipient disorder.

$H_4L\cdot dmf$. $C_{45}H_{58}O_5\cdot C_3H_7NO$, $M = 752.05$, monoclinic, space group $P2_1/m(C_{2h}^2$, no. 11), $a = 9.701(1)$, $b = 25.108(9)$, $c = 9.230(3)$ Å, $\beta = 95.97(2)°$, $U = 2236$ Å^3, $D_c(Z = 2) = 1.12$ g cm^{-3}, $F(000) = 816$, $\mu_{Mo} = 0.4$ cm^{-1}; specimen: $0.15 \times 0.20 \times 0.40$ mm; $N = 4014$, $N_o = 1749$; $R = 0.067$, $R' = 0.064$.

Abnormal features. The residual is rather high, seemingly in consequence of high thermal motion, and disorder and possible space group ambiguity. The methyl substituents on one of the Bu^t groups are rotationally disordered; after consideration of the behaviour of site occupancies during refinement, they were modelled in terms of two sets of components, one with anisotropic thermal parameter refinement and occupancy 0.72(1), the other with isotropic thermal parameter refinement and occupancy 1 − 0.72(1). The dimethylformamide (dmf) molecule is disordered about a mirror plane; the possibility that this was indicative of the proper space group being $P2_1$ was considered but discarded as unworkable. Protonating hydrogen atoms were not located; in view of the quasi-square O_4 (phenolic) array (see below) and the lack of similarly close interspecies contacts, it is likely that they are disordered.

Results and Discussion

Although the known chemistry of U^{VI} with aryloxide ligands appears to be limited,[17] there is little reason to expect that such an oxophilic cation would not bind well to aryloxides, and certainly it is easy to demonstrate a ready interaction between uranyl ion and various calixarenes. Thus, following the same procedure as used to prepare calixarene complexes of the lanthanides,[2–5] deep red-brown complexes of UO_2^{2+} with the *p-tert*-butylcalix[*n*]arenes, *n* = 6 or 8, are deposited readily from dmf or dmso solutions. Unfortunately, the use of triethylamine to deprotonate the calixarenes results in microcrystalline materials which have proved very difficult to characterise both stoichiometrically and structurally. Attempts to synthesise the UO_2^{2+} complex of *p-tert*-butylcalix[4]arene by similar means result in the formation of highly insoluble gelatinous green precipitates, despite the initial formation of red-brown solutions. It was, in fact, because of these difficulties that efforts were made to characterise the uranyl ion complex of bis(homo-oxa)-*p-tert*-butylcalix[4]arene, in the belief that the 'fit' of this ligand to the equatorial geometry of mononuclear uranyl ion might allow a simple complex to be isolated.

When a source of anhydrous UO_2^{2+}, such as $[UO_2(dmso)_5][ClO_4]_2$[13] is added to a solution of bis(homo-oxa)-*p-tert*-butylcalix[4]arene and an excess of alkyl- or aryl-amine in solvents such as CH_3CN, dmf or dmso, a red-brown solution results. Careful spectrophotometric monitoring of titration of the ligand (plus excess triethylamine) with uranyl ion in dmso indicates that a 1:1 complex is the only species produced at significant concentrations. Crystals of the complex deposit readily from CH_3CN solutions when triethylamine or diethylamine is the base employed. Microanalyses and ^1H NMR spectroscopy (see below) both show that these crystals incorporate amine as well as the calixarene and uranium, suggesting that the complex may be an anionic species, precipitating as the protonated amine salt. In the case of lanthanide ion complexes of *p-tert*-butylcalix[*n*]arenes (*n* = 4,6 or 8) and of bis(homo-oxa)-*p-tert*-butylcalix[4]arene, the precipitated species are neutral and contain no amine. This may be indicative of a greater acid-enhancing effect on phenolic hydrogen of UO_2^{2+} relative to tripositive lanthanides, for which there is some evidence that this effect may be quite small (in multidentate ligands incorporating a phenolic group both phenol and phenolate forms for their lanthanide complexes

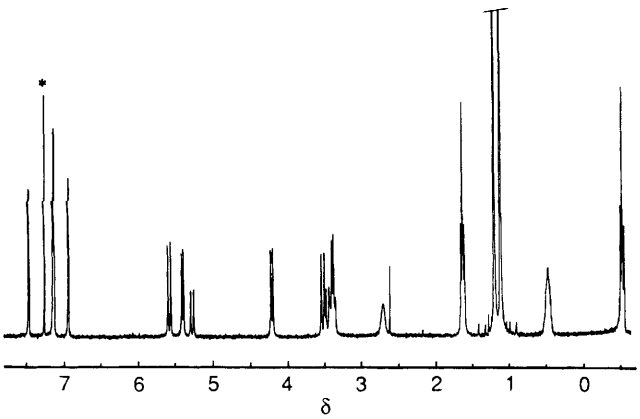


Fig. 1 The 300 MHz ^{1}H NMR spectrum of the diethylammonium salt of the uranyl ion complex of bis(homo-oxa)-*p*-*tert*-butylcalix[4]arene in $CDCl_3$ (* indicates solvent peak; the two Bu^t resonances have been truncated to facilitate viewing of methylene and aromatic proton peaks)

Table 5 Resonances in the 300 MHz ^{1}H NMR spectrum of $[NH_2Et_2]_2[UO_2(L)]$ in $CDCl_3$*

δ	Assignment
−0.55, −0.52, −0.50	'included' $Et_2NH_2^+$: $-CH_3$ triplet
0.48	: $-CH_2$ broad quartet
1.12, 1.21	$(CH_3)_3C$ singlets (36 H)
1.61, 1.63, 1.66	'free' $Et_2NH_2^+$: $-CH_3$ triplet
3.35, 3.37, 3.40, 3.42	: $-CH_2$ quartet
2.71	NH singlet
3.44, 3.48, 5.25, 5.29	RCH_2R AB doublet pair (2 H)
3.50, 3.54, 5.56, 5.60	RCH_2R AB doublet pair (4 H)
4.20, 4.22, 5.39, 5.41	RCH_2O doublet pair (4 H)
6.93_4, 6.94_3 7.12_4, 7.13_2, 7.14_2, 7.15_1, 7.46_8, 7.47_7	Aromatic CH

* R = Aryl.

have been isolated).[18] Again as observed with europium ion complexes of the calixarenes,[19] quenching of the metal ion luminescence is very effective and no detectable emission was observed for room-temperature chloroform solutions of the isolated complex of uranyl ion with bis(homo-oxa)-*p*-*tert*-butylcalix[4]arene.

While the visible spectra of uranyl ion–bis(homo-oxa)-*p*-*tert*-butylcalix[4]arene complexes isolated with the use of different amines are identical, suggesting that the amine is not incorporated into the solid by co-ordination to uranium, ^{1}H NMR spectroscopy shows that, in $CDCl_3$ solution, two types of amine species are present. The spectrum of the diethylamine derivative, for example, is shown in Fig. 1; chemical shifts and peak assignments are given in Table 5. It is obvious that there is a very marked upfield shift of one set of amine ethyl group resonances, consistent with inclusion of one of the amine moieties in such a way that the ethyl groups are placed in close proximity to the face of calixarene phenyl rings.* Remarkably, this shift is approximately an order of magnitude greater than, and in the opposite direction to shifts observed in the spectra of amines interacting with uncomplexed calixarenes.[20] The Nuclear Overhäuser Enhancement spectrum shows cross-peaks indicative of exchange between the two amine moieties but the rate of this process is so slow that even at the highest temperature at which the ^{1}H NMR spectrum could be recorded (55 °C) only a slight broadening of the methylene and methyl resonances was observed. It is also noteworthy that the complex appears to be considerably more rigid in solution than does the free calixarene, as indicated by the resolution of the methylene proton resonances into three pairs of doublets. Variable-temperature studies over the range −60 to 55 °C showed no significant changes in these resonances.†

The results of the structure determination of the uranium complex of bis(homo-oxa)-*p*-*tert*-butylcalix[4]arene are fully consistent with the expectations based on the analytical and spectroscopic experiments. The uranyl group lies within the co-ordination environment offered by the calixarene in an unsymmetrical manner dictated by the connectivity between four nearby phenolic oxygen atoms and/or the fifth ether oxygen atom [Fig. 2(*a*) and (*b*)]. The uranyl, UO_2^{2+}, moiety itself is unremarkable, with O–U–O 179.3(3)° and U–O 1.778(5) and 1.796(6) Å. In the equatorial co-ordination plane, in which the relatively unusual array of only four co-ordinated oxygen atoms is found,[12] the U–O distances differ noticeably, U–O(1a,b) being similar and short at 2.247(6) and 2.249(8) Å, with O(1a)–U–O(1b) only 81.7(2)°; U–O(2a,b) are slightly longer [2.261(7) and 2.275(6) Å], with a larger angle between them [108.4(3)°]. Although there is a distant approach of the ether oxygen O(3) at 3.534(8) Å, it is noteworthy that its lone pairs are oriented away from the uranium. The conformation adopted by the ligand is the anticipated 'calyx' cone. In association with the asymmetries in co-ordination about the uranyl group, however, and in consequence of the incorporation of the ether oxygen, the cup is disposed unsymmetrically [Fig. 2(*b*)], with dihedral angles of the aromatic C_6 planes relative to the central O(1a,b; 2a,b) plane (χ^2, 4.9) of 60.0(3), 62.9(3)° (rings 1 a,b) and 45.4(3), 46.6(3)° (rings 2 a,b), with the uranium atom lying 0.013(3) Å out of the plane away from the cup. The uranium atom lies 1.92(2), 2.01(2), 1.47(2) and 1.47(2) Å out of the planes of the phenoxide aromatic rings 1 a,b; 2 a,b respectively.

The disposition of the cations is of particular interest in regard to explaining their inequivalence in solutions of the complex. Although it has high thermal amplitudes at its periphery, cation 1 lies within the cup of the ligand, with a configuration at the (presumably) protonated nitrogen such that the proton is directed outwards to contact O(2b) of the adjacent ($\frac{1}{2} - x$, $\frac{1}{2} + y$, $\frac{1}{2} - z$) ligand of the next molecule [N ··· O, 2.90(1) Å], as shown in Fig. 3. Oxygen atom O(2a) of the ligand is approached by the fully populated solvent molecule 1 [O(W1) ··· O(2a)(*x*,*y*,*z*), 2.59(2) Å], which is also approached by the apex, presumably protonated, of the second cation [O(W1) ··· N, 2.85(3) Å], Fig. 3. The atoms O(1a,b) of the ligand have associations with symmetry related disordered/partially occupied solvent fragments 2 and 3 at distances of 2.88(5) and 2.80(3) Å, while the distance between the two solvent fragments is 3.00(6) Å. Maintenance of the inclusion of one cation on dissolution is suggested by the solution ^{1}H NMR spectra of both the di- and tri-ethylammonium salts of the complex, though there are no indications of inequivalences attributable to association of the included cation with a second anion as in the solid state.

The structure of the free ligand shows it to adopt the expected 'calyx' form,[1] though the method of crystallisation used involves the incorporation of a dimethylformamide (dmf) molecule within the cup, and this must influence the conformation to some extent.[22] Interestingly, the dmf molecule is found in the 'off-centre' position occupied by cation 1 in the uranyl ion complex. In space group $P2_1/m$, there is crystallographically imposed *m* symmetry, so that the dmf molecule, modelled in terms of a pair of equally occupied, symmetry related, superimposed components, is disordered, as is the Bu^t group associated with ring 1. The structure of the ligand is shown in comparison with that of the uranyl ion complex in the side-by-

---

* Similar very marked upfield shifts of resonances due to included ligands have been observed in both diamagnetic and paramagnetic complexes of lanthanide ions with the calixarenes.[19]

† Uncomplexed bis(homo-oxa)-*p*-*tert*-butylcalix[4]arene in chloroform shows a coalescence temperature of −2 °C for the CH_2OCH_2 resonances and −8 °C for the RCH_2R resonances (R = aryl).[21]

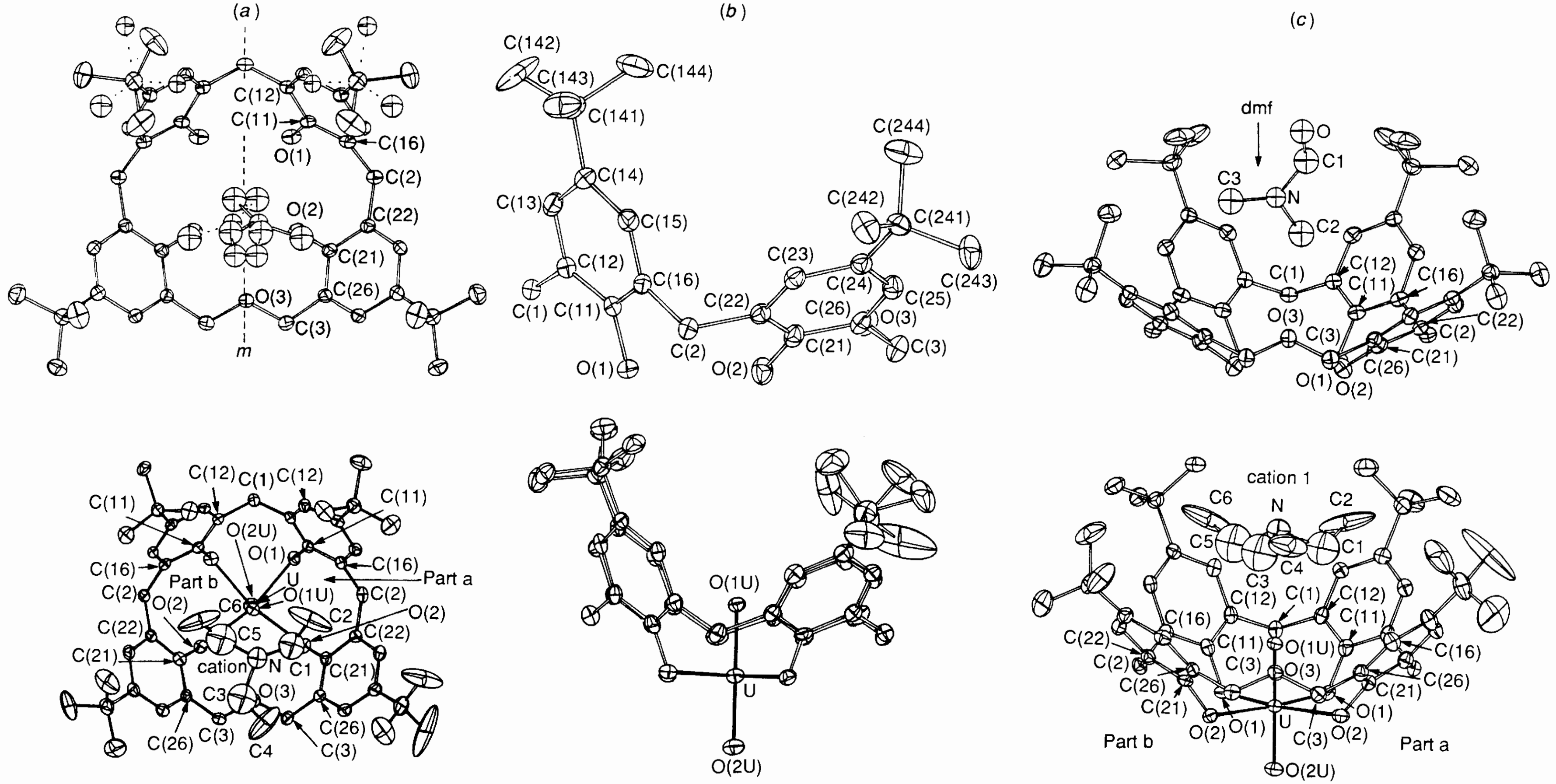


Fig. 2 Views of the uranyl ion complex in various projections in association with the uncomplexed ligand in similar orientation; 20% thermal envelopes are shown for the non-hydrogen atoms. (*a*) Projection normal to the co-ordination plane; the two components of the disordered Bu^t are shown, as also of the enclosed dmf molecule. For the uranyl ion complex, the enclosed alkylammonium cation which is hydrogen-bonded to one of the oxygen atoms of an adjacent ligand is shown. (*b*) Projection normal to the mirror plane of the system; the plane is exact in the case of the ligand. Full atom numbering for the ligand is shown; for the complex, section b lies nearest the reader. (*c*) Projection down the mirror plane of the system. A single deconvoluted included solvent molecule is shown within the free ligand

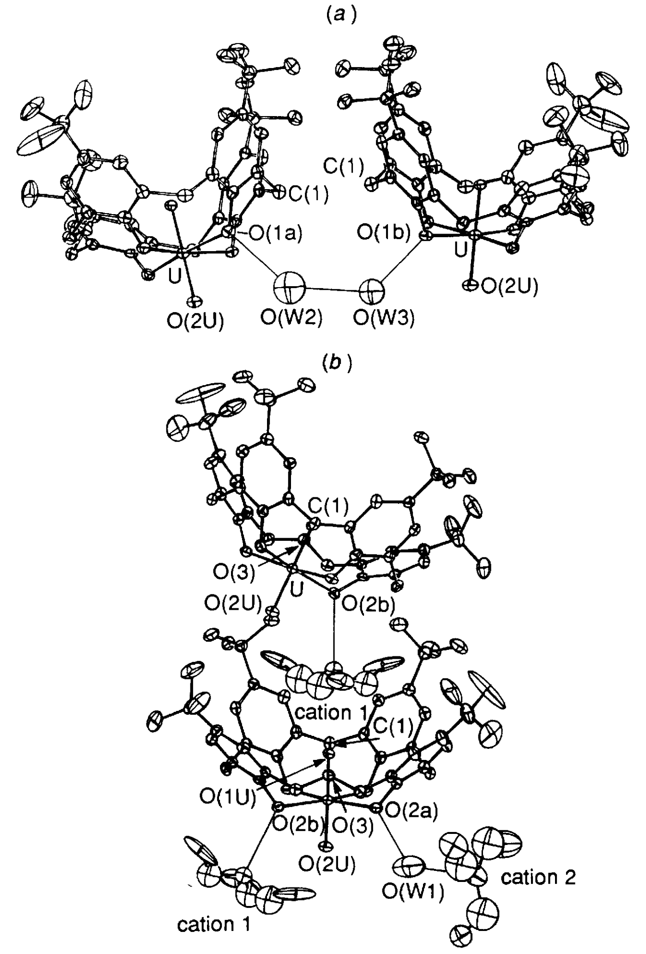


Fig. 3 Hydrogen-bonding interactions of the uranyl ion complex with nearby cations and solvent molecules (see text)

side, similar projections of Fig. 2. These show that the conformations differ only in a matter of degree and suggest, therefore, that while the ligand may indeed be conformationally labile,[1] there is a strong preference for the cone conformation. In the dmf adduct, the O_4 (phenoxide) core atoms are necessarily planar; dihedral angles of rings 1 and 2 relative to the O_4 plane are 67.4(1) and 31.8(1)°, respectively. The O $\cdots$ O separations are O(1) $\cdots$ O(1′), 2.746(5); O(2) $\cdots$ O(2′), 3.053(5); O(1) $\cdots$ O(2), 2.753(4) and O(1) $\cdots$ O(2′), 3.995(5) Å; counterpart distances in the uranyl ion complex are 2.941(8); 3.678(8); 3.050(12), 3.051(11) and 4.491(9), 4.480(11) Å, showing an expansion of the O_4 core on complexation. Possibly significant in relation to the co-ordination modes known for other calixarenes,[1–9] the O(2) $\cdots$ O(3) distances in the ligand [2.810(5) Å] and its uranyl ion complex [3.023(9) and 3.069(10) Å] are suggestive of a compact tridentate moiety which might form the basis of, for example, a bridged binuclear species.

Inclusion by means other than co-ordination to the phenolic oxygens is, of course, a notable feature of calixarene chemistry.[1] Inclusion of a cation in this way is, however, unique to the uranyl ion complex of bis(homo-oxa)-*p*-*tert*-butylcalix[4]arene, though it would appear from the similar positionings of the dmf and triethylammonium species in, respectively, the free and co-ordinated ligand derivatives, that interactions between apolar moieties are responsible for the association in both cases. The orientations of included dmso in its adduct with *p*-*tert*-butylcalix[4]arene and of included dmf in its adduct with the europium(III) complex of *p*-*tert*-butylcalix[4]arene[5] are indicative of similar interactions, though the latter case contrasts with dmf bound to the europium(III) complex of *p*-*tert*-butylcalix[8]-arene,[2,4] where, in the case of two of the solvent molecules, they can be considered included as well as co-ordinated (*via* oxygen) to Eu^{III}, so that the carbonyl group penetrates furthest into the 'calyx'. This orientation nonetheless results in the *N*-methyl groups occupying a similar position relative to the peripheral Bu^t groups to that in the other systems.

Obviously, bis(homo-oxa)-*p*-*tert*-butylcalix[4]arene cannot be regarded as a ligand ideally suited to a pentagonal-bipyramidal geometry at the uranium atom of its uranyl ion complex, and this is seemingly because it is not possible to render all five oxygen donor atoms coplanar. Interaction between the uranium and ether-oxygen atoms is so slight that the ligand can be considered to provide essentially four phenolic-oxygen donor atoms. In this context it is interesting to note the apparent instability of the uranyl ion complex of *p*-*tert*-butylcalix[4]arene, which has not as yet been characterised. This may indicate that the four potential donor atoms in this ligand are unable to encompass the uranyl ion easily, and hence the greater stability of the uranyl ion complex of bis(homo-oxa)-*p*-*tert*-butylcalix[4]arene may be due to the relative increase in the size and flexibility of the macrocycle rather than the introduction of a fifth donor atom.

Acknowledgements

We gratefully acknowledge support of this work by the Australian Research Council.

References

1 C. D. Gutsche, *Calixarenes*, Monographs in Supramolecular Chemistry, No. 1, ed. J. F. Stoddart, Royal Society of Chemistry, Cambridge, 1989.
2 B. M. Furphy, J. MacB. Harrowfield, D. L. Kepert, B. W. Skelton, A. H. White and F. R. Wilner, *Inorg. Chem.*, 1987, **26**, 4231.
3 L. M. Engelhardt, B. M. Furphy, J. MacB. Harrowfield, D. L. Kepert, A. H. White and F. R. Wilner, *Aust. J. Chem.*, 1988, **41**, 1465.
4 J. MacB. Harrowfield, M. I. Ogden, A. H. White and F. R. Wilner, *Aust. J. Chem.*, 1989, **42**, 949.
5 B. M. Furphy, J. MacB. Harrowfield, M. I. Ogden, B. W. Skelton, A. H. White and F. R. Wilner, *J. Chem. Soc., Dalton Trans.*, 1989, 2217.
6 See ref. 1, chs. 4 and 6.
7 G. E. Hofmeister, F. E. Hahn and S. F. Pedersen, *J. Am. Chem. Soc.*, 1989, **111**, 2318.
8 F. Corazza, C. Floriani, A. Chiesi-Villa and C. Guastini, *J. Chem. Soc., Chem. Commun.*, 1990, 640.
9 A. W. Coleman, S. G. Bott, S. D. Morley, C. M. Means, K. D. Robinson, H. Zhang and J. L. Atwood, *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 1361; J. L. Atwood, A. W. Coleman, H. Zhang and S. G. Bott, *J. Incl. Phenom.*, 1989, **7**, 203.
10 S. Shinkai, *Pure Appl. Chem.*, 1986, **58**, 1523; S. Shinkai, H. Koreishi, K. Ueda, T. Arimura and O. Manabe, *J. Am. Chem. Soc.*, 1987, **109**, 6371; see also ref. 1, ch. 7, pp. 190–191.
11 I. Tabushi, Y. Kobuke, K. Ando, M. Kishimoto and E. Ohara, *J. Am. Chem. Soc.*, 1980, **102**, 5947; I. Tabushi, Y. Kobuke and A. Yoshizawa, *J. Am. Chem. Soc.*, 1984, **106**, 2481.
12 K. W. Bagnall, in *Comprehensive Coordination Chemistry*, eds. J. C. McCleverty, R. D. Gillard and G. Wilkinson, Pergamon, Oxford, 1987, vol. 3, ch. 40, pp. 1192–1209.
13 J. MacB. Harrowfield, D. L. Kepert, S. F. Lincoln, J. M. Patrick and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1983, 393.
14 C. D. Gutsche, B. Dhawan, K. H. No and R. Muthukrishnan, *J. Am. Chem. Soc.*, 1981, **103**, 3782.
15 *International Tables for X-Ray Crystallography*, eds. J. A. Ibers and W. C. Hamilton, Kynoch Press, Birmingham, 1974, vol. 4.
16 'The XTAL System – Version 2.6,' Users' Manual, eds. S. R. Hall and J. M. Stewart, Universities of Western Australia and Maryland, 1989.
17 See ref. 12, p. 1194.
18 See D. E. Fenton and P. A. Vigato, *Chem. Soc. Rev.*, 1988, **17**, 69; S. Sitran, D. Fregona and G. Faraglia, *J. Coord. Chem.*, 1988, **18**, 269.

19 J.-C. G. Bünzli and J. MacB. Harrowfield, in *Calixarenes – A New Class of Catalysts*, eds. J. Vicens and V. Böhmer, Kluwer, Dordrecht, 1990, pp. 223–244.
20 L. J. Bauer and C. D. Gutsche, *J. Am. Chem. Soc.*, 1985, **107**, 6063; C. D. Gutsche, M. Iqbal and I. Alam, *J. Am. Chem. Soc.*, 1987, **109**, 4314.
21 C. D. Gutsche and L. J. Bauer, *J. Am. Chem. Soc.*, 1985, **107**, 6052.
22 P. D. J. Grootenhuis, P. A. Kollman, L. C. Groenen, D. N. Reinhoudt, G. J. van Hummel, F. Ugozzoli and G. D. Andreetti, *J. Am. Chem. Soc.*, 1990, **112**, 4165.

Received 9*th August* 1990; *Paper* 0/03674I