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ARTICLE *in* JOURNAL OF THE CHEMICAL SOCIETY PERKIN TRANSACTIONS 2 · JUNE 1994

DOI: 10.1039/p29940001167

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Calix Salophen Crown Ethers as Receptors for Neutral Molecules

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The calix[4]arene based salophen crown ethers **7** and **8** were synthesized as lipophilic carriers for neutral molecules. The X-ray structures of the H_2O, CH_3OH and $(CH_3)_2SO$ complexes of **8a** have been determined.

Calix[4]arene (**1**) has attracted much attention as a useful building block [1] for the synthesis of receptor molecules for both cations [2] and neutral molecules.[3] The possibility selectively to functionalize either the upper or the lower rim and to control their conformation makes calix[4]arenes valuable platforms for the positioning of functional groups in space.

In view of our work on the complexation of neutral molecules by uranyl salophen crown ethers,[4] it was interesting to incorporate a calix[4]arene moiety in such a metallomacrocycle. The resulting receptor molecules **7** and **8** are highly lipophilic, making them useful as carriers for urea in supported liquid membranes.[5] Furthermore, they have a phenolic group on either side of the crown ether ring, which can be used for the incorporation of functional groups either as additional binding sites for the substrate molecule or for catalysing reactions of the complexed substrate.

In this paper, the synthesis of calix[4]arene-based metallomacrocycles **7** and **8** is described. The X-ray structures of the water, the methanol and the $(CH_3)_2SO$ complexes of **8a** are presented.

Results and Discussion

Synthesis.—The synthesis of metallomacrocycles **7** and **8** is shown in Scheme 1. Alkylation of calix[4]arene (**1**)[6] with tosylates **2**[4e] in CH_3CN in the presence of 1 equiv. of K_2CO_3 as a base gave protected dialdehydes **3** in 60–65% yield.† Only the 1,3-dialkylated product was isolated, which is in agreement with the literature.[7] The doublets in the ^1H NMR spectra of **3** at 4.37 and 3.32 ppm for the methylene protons and around 31.0 ppm in the ^{13}C NMR spectra for the methylene-bridge carbon atoms of the calix[4]arene moiety reveal that the dialdehydes have a cone conformation.[8] This conformation ascertains that both aldehyde groups are on the same side of the molecule, which is a prerequisite for cyclization to be possible.

Protected dialdehydes **3** were reductively deallylated with $Pd(PPh_3)_4$ and $HCOONHEt_3$ in quantitative yield. The ^1H NMR spectra of **4** revealed no signals for the allyl ethers. Singlets for the 2-OH groups of the benzaldehyde moieties are observed at 10.87 ppm in the ^1H NMR spectra, whereas the signals for the aldehyde groups were shifted from 10.4 (**3**) to 9.9 (**4**) ppm in the ^1H and from around 190 (**3**) to 196 (**4**) ppm in the ^{13}C NMR spectra.

Cyclization of the dialdehydes **4** was performed by the addition of 1 equiv. of benzene-1,2-diamine **5** or *cis*-cyclohexane-1,2-diamine **6** to a solution of **4** and 2 equiv. of $Ba(OTf)_2$,‡ which served as a template ion,[4b,9] in THF. Addition of $UO_2(OAc)_2 \cdot 2H_2O$ gave the crude uranyl salophen crown ethers **7** and **8**. Metallomacrocycles **7** were purified by precipitation from a solution in CH_2Cl_2 with cyclohexane,§ whereas salophen crown ethers **8** could be purified by column chromatography on silica gel, followed by precipitation.

Table 1 Selected distances (Å) of the X-ray structures

	8a·$2H_2O$	**8a**·MeOH	**8a**·Me_2SO
$U–O_{apical}$	1.792(8) 1.802(8)	1.36(3) 1.85(3)	1.764(11) 1.812(11)
$U–O_{phenolate}$	2.219(9) 2.250(8)	2.25(2) 2.18(2)	2.256(12) 2.253(12)
$U–N_{imine}$	2.56(1) 2.55(1)	2.56(4) 2.55(4)	2.525(15) 2.632(15)
$U–O_{guest}$	2.556(8)	2.47(3)	2.378(15)

In the IR spectra of metallomacrocycles **7** and **8**, absorptions were observed for both the imine bonds and the uranyl cations, which revealed that cyclization and complex formation had occurred. The FAB mass spectra showed M + 1 peaks, indicating that the uranyl cations are tightly bound.

The ^1H NMR spectrum of **7a** exhibits two doublets for the methylene bridge protons at 4.41 and 3.39 ppm. This shows that the calix[4]arene moiety is in the cone conformation, which positions the two remaining phenolic OH groups on both sides of the crown ether ring. In the ^1H NMR spectra of **8**, the 'sidedness' which results from the presence of the cyclohexane ring is observed: two singlets are observed for the phenolic OH groups and either the low-field half (**8a**) or the high-field half (**8b**) of the AB system for the methylene bridge protons appears as two doublets. In the ^{13}C NMR spectra, only three signals are observed for the carbons of the cyclohexyl ring, indicating that the cyclohexyl ring has C_s-symmetry on the NMR timescale.

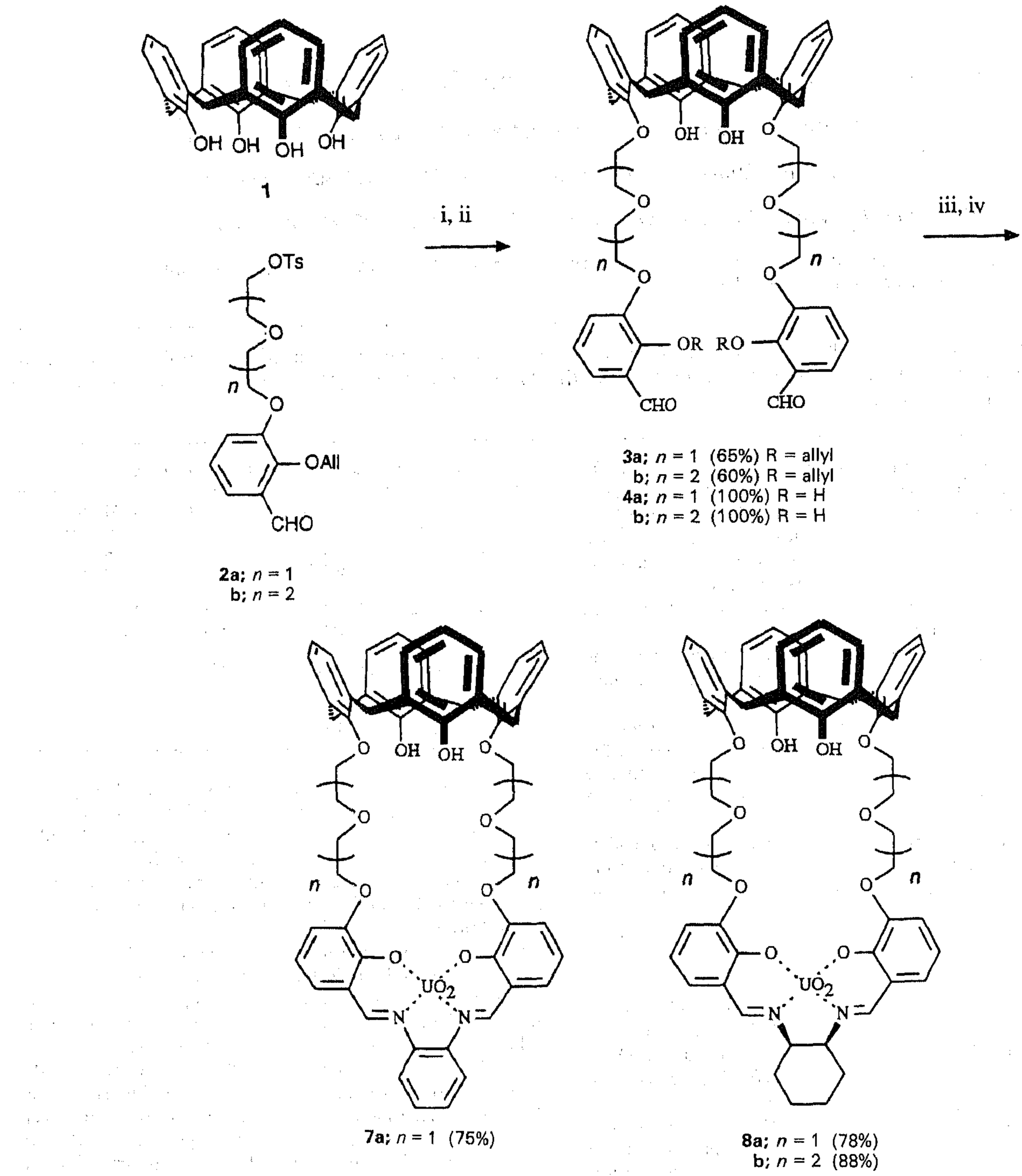
X-Ray Analysis.—Crystals of **8a**·$2H_2O$, suitable for X-ray analysis, were obtained by crystallization from hot CH_3CN. A PLUTON view of this structure is shown in Fig. 1.

Selected bond distances are presented in Table 1. The X-ray

† Approximately 10% of the monoalkylated calix[4]arene was obtained.

‡ Barium triflate was prepared by reaction of trifluoromethanesulfonic acid with barium hydroxide in MeOH. Evaporation of the solvent gave the product as white crystals.

§ **7b** could not be freed from a small amount of polymeric material.



Scheme 1 *Reagents and conditions:* i, K_2CO_3, CH_3CN; ii, $Pd(PPh_3)_4$, $HCOONHEt_3$, THF–EtOH–H_2O; iii, $Ba(OTf)_2$, benzene-1,2-diamine (**5**) or *cis*-cyclohexane-1,2-diamine (**6**), THF; iv, $UO_2(OAc)_2{\cdot}2H_2O$

structure clearly shows that only one of the complexed water molecules is coordinated to the uranyl cation. The distance between the oxygen atom of the guest and the uranyl cation (2.56 Å) is slightly larger than that reported for similar H_2O (2.44 Å),[10] MeOH (2.45 Å),[4c,11] and EtOH (2.46 Å)[12] complexes. The second water molecule fills the cavity and is probably complexed by hydrogen bonds. The calix[4]arene moiety is in a cone conformation, which positions the two phenolic OH groups close to the cavity of the metallomacrocycle.

The X-ray structure of **8a**·MeOH, obtained by diffusion of MeOH into a solution of **8a** in CH_2Cl_2, shows an MeOH molecule coordinated to the complexed uranyl cation (Fig. 2).

Diffusion of MeOH into a solution of **8a** in a mixture of CH_2Cl_2 and $(CH_3)_2SO$ gave crystals suitable for X-ray analysis. Although complexes of uranyl salophen crown ethers with $(CH_3)_2SO$ are already known,[3b,c] this is, to the best of our knowledge, the first X-ray structure of a $(CH_3)_2SO$ complex (Fig. 3). The distance between the oxygen of the complexed $(CH_3)_2SO$ molecule and the uranyl cation (2.38 Å) is very similar to the distance between the carbonyl oxygen atom of urea and the uranyl cation in the known urea complexes (2.37 Å,[4a,b] 2.36[4c]).

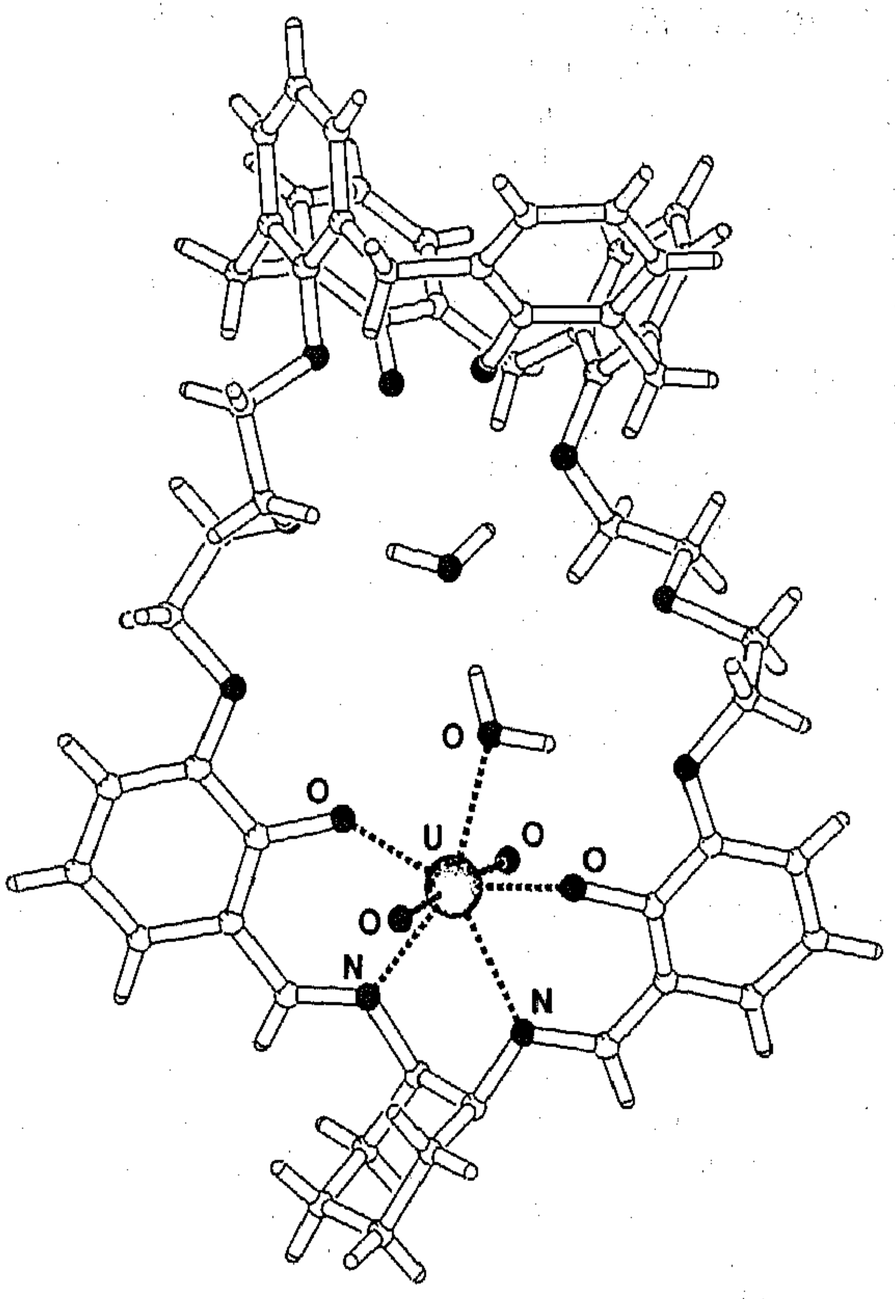


Fig. 1 X-Ray crystal structure of **8a**·2H_2O

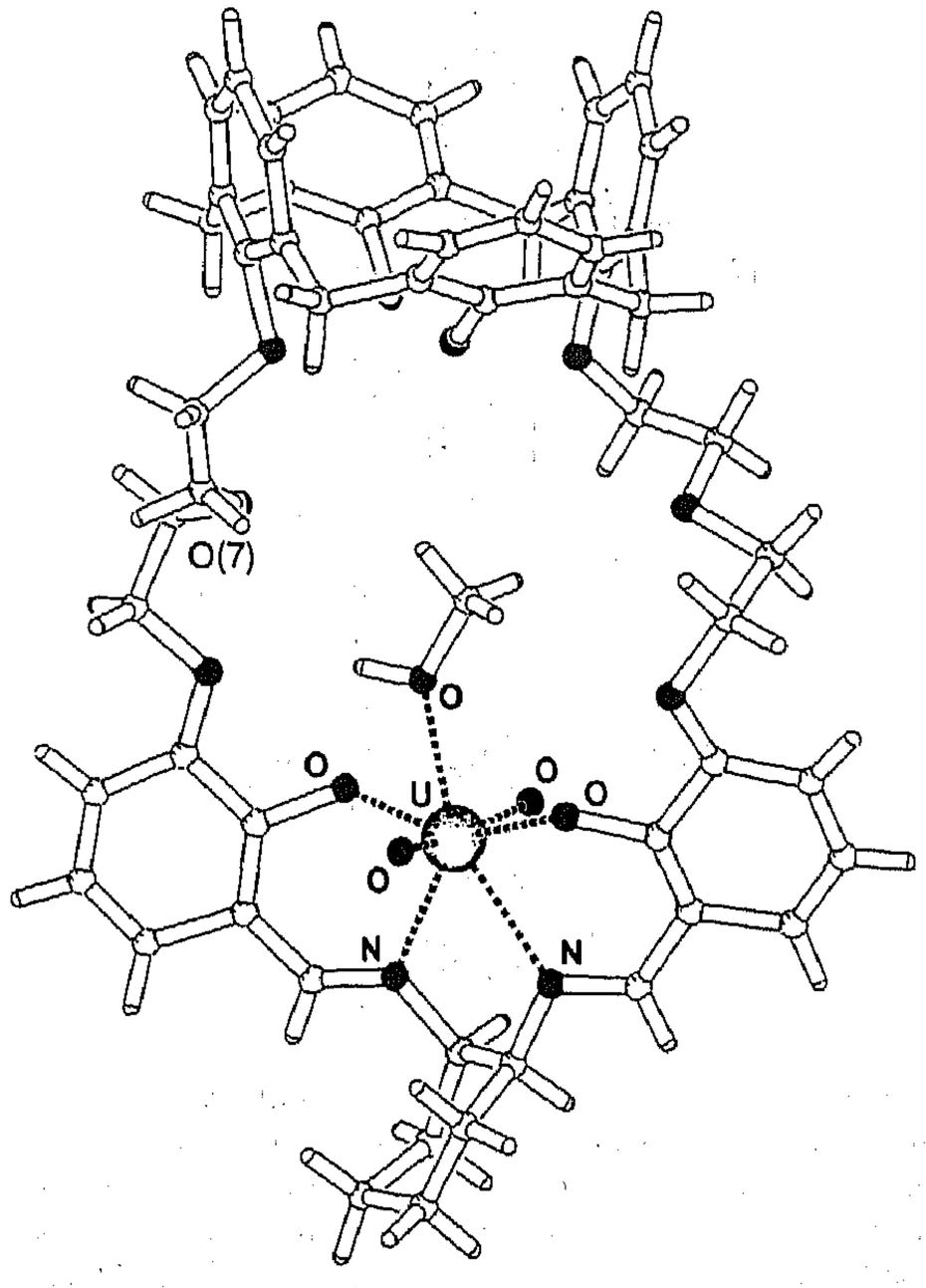


Fig. 2 X-Ray crystal structure of **8a**·MeOH

*Extraction of Urea.**—Solid–liquid extraction experiments were performed by equilibrating a 4 mmol dm^{-3} solution of metallomacrocycles **7a** and **8** in $CDCl_3$ with solid urea. In all cases, significant changes in chemical shift and pattern were found for the signals of the polyether moiety.

Addition of free host to the solution of urea complex showed that a rapid exchange on the NMR timescale occurred, because only the averaged spectra were observed. The dynamic exchange made the interpretation of liquid–liquid extraction experiments at different urea concentrations (0.05, 0.1 and 1.0 mol dm^{-3}) very difficult.

The use of these receptor molecules in carrier-mediated transport of urea through a supported liquid membrane has been reported previously.[5]

Conclusions

A convenient synthesis of the new calix salophen crown ethers **7** and **8** has been developed. The solid-state structures of **8a**·2H_2O, **8a**·MeOH and **8a**·$(CH_3)_2SO$ were determined showing that the guest molecules are coordinated to the uranyl cation.

Experimental

NMR spectra were recorded on a Bruker AC 250 spectrometer in $CDCl_3$ with Me_4Si as an internal standard unless stated otherwise. *J*-values are given in Hz. Assignments of the NMR spectra are according to the numbering illustrated below. Mass spectra were obtained with a Finnigan MAT 90 spectrometer. Positive-ion fast atom bombardment (FAB) mass spectra were recorded using *m*-nitrobenzyl alcohol as the matrix. IR spectra were recorded with a Nicolet SCX FT spectrophotometer. Melting points were determined using a Reichert melting point apparatus and are uncorrected. Elemental analyses were carried out by use of a Model 1106 Carlo Erba Strumentazione elemental analyser. CH_2Cl_2, EtOAc and hexane were distilled

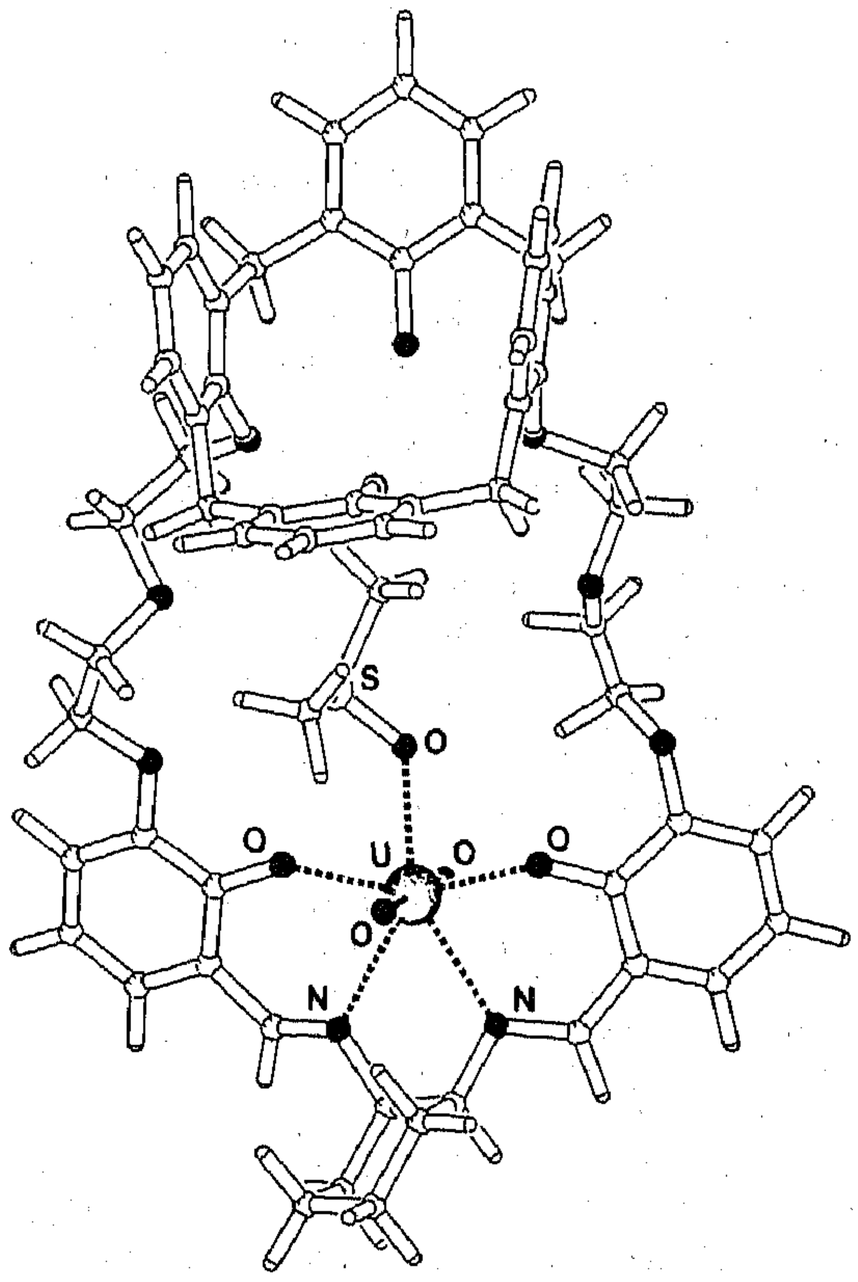
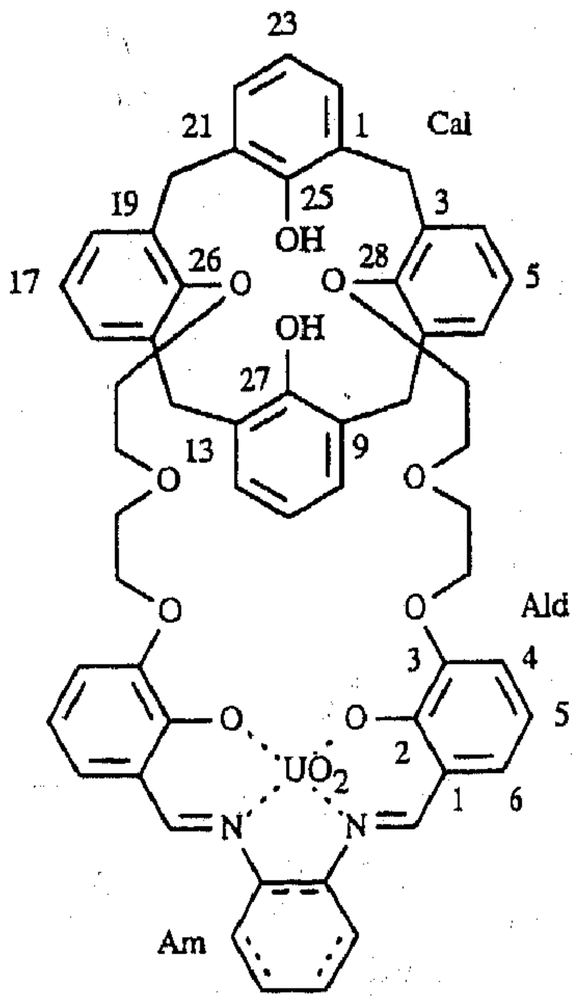


Fig. 3 X-Ray crystal structure of **8a**·Me_2SO

* Formamide and acetamide are too soluble in $CHCl_3$ to use them in these extraction experiments: more than one equivalent of guest is extracted.



before use. CH_2CN was stored over molecular sieves (4 Å) prior to use. Other chemicals were of reagent grade and were used without purification. Column chromatography was performed with silica gel (Merck: 0.040–0.063 mm). All reactions were carried out under an argon atmosphere. Calix[4]arene **1**[6] (R = H) was prepared according to the literature.

Care should be taken when handling uranyl-containing compounds because of their toxicity and radioactivity.[13]

General Procedure for the Dialkylation of Calix[4]arene **1**

Synthesis of Dialdehydes **3**.—A mixture of calix[4]arene **1** (1.06 g, 2.5 mmol), tosylate **2**[4e] (5.0 mmol), and K_2CO_3 (0.35 g, 2.5 mmol) in dry CH_3CN (25 cm^3) was refluxed for 48 h. NaI (0.2 g) and NEt_3 (2 cm^3) were added and refluxing was continued for 30 min. The reaction mixture was cooled, diluted with CH_2Cl_2 (50 cm^3), and filtered through Celite. The solvent was evaporated off and the residue was redissolved in CH_2Cl_2 (100 cm^3). The organic layer was washed with 1 mol dm^{-3} hydrochloric acid (50 cm^3) containing a few drops of concentrated aqueous $NaHSO_3$, dried ($MgSO_4$), and evaporated to dryness. After flash column chromatography of the residue, the products **3** were obtained as oils.

$3^2,7^2$-*Bis*[5-(2-*allyloxy*-3-*formylphenoxy*)-3-*oxapentyloxy*]-1(1,3),3(1,3),5(1,3),7(1,3)-*tetrabenzenacyclooctaphane*-$1^2,5^2$-*diol* (**3a**).—Eluent EtOAc–hexane (2:3), yield 65%; ν_{max}/cm^{-1} 3352 (OH) and 1686 (HC=O); δ_H(250 MHz; $CDCl_3$) 3.32 (4 H, d, *J* 13.0, $ArCH_2Ar$), 3.9–4.0 (8 H, m, CH_2O), 4.1–4.25 (8 H, m, CH_2O), 4.37 (4 H, d, *J* 13.0, $ArCH_2Ar$), 4.63 (4 H, d, *J* 6.0, $OCH_2CH{=}CH_2$), 5.1–5.35 (4 H, m, $OCH_2CH{=}CH_2$), 5.9–6.1 (2 H, m, $OCH_2CH{=}CH_2$), 6.56 (2 H, t, *J* 7.5, CalH), 6.65 (2 H, t, *J* 7.4, CalH), 6.78 (4 H, d, *J* 7.5, CalH), 6.9–7.1 (4 H, m, $AldC_{4,4',5,5'}H$), 7.03 (4 H, d, *J* 7.4, CalH), 7.35 (2 H, dd, *J* 7.7 and 1.5, $AldC_{6,6'}H$), 7.78 (2 H, s, OH) and 10.39 (2 H, s, CHO); δ_C(63 MHz; $CDCl_3$) 31.0 (t, $ArCH_2Ar$), 68.6–75.3 (t, CH_2O), 118.6 (t, $OCH_2CH{=}CH_2$), 119.3, 119.7, 123.9 (d, $AldC_{4,4',5,5',6,6'}$), 118.9, 125.2 (d, $CalC_{5,11,17,23}$), 128.4, 128.8 (d, $CalC_{4,6,10,12,16,18,22,24}$), 129.9 (s, $AldC_{1,1'}$), 127.8, 132.9 (s, $CalC_{1,3,7,9,13,15,19,21}$), 133.1 (d, $OCH_2CH{=}CH_2$), 151.3, 151.5, 152.0, 153.0 (s, $AldC_{2,2',3,3'}$ and $CalC_{25,26,27,28}$) and 190.2 (d, CHO); *m/z* (FAB) 920.2 (M^+, calc. for $C_{56}H_{56}O_{12}$ 920.4).

$3^2,7^2$-*Bis*[8-(2-*allyloxy*-3-*formylphenoxy*)-3,6-*dioxaoctyloxy*]-1(1,3),3(1,3),5(1,3),7(1,3)-*tetrabenzenacyclooctaphane*-1^2,5^2-*diol* (**3b**).—Eluent EtOAc–hexane (1:1), yield 60%; ν_{max}/cm^{-1} 3357 (OH) and 1687 (HC=O); δ_H(250 MHz; $CDCl_3$) 3.33 (4 H, d, *J* 13.0, $ArCH_2Ar$), 3.75–4.05 (20 H, m, CH_2O), 4.15–4.2 (4 H, m, CH_2O), 4.39 (4 H, d, *J* 13.0, $ArCH_2Ar$), 4.7 (4 H, dd, *J* 6.1 and 1.1, $OCH_2CH{=}CH_2$), 5.2–5.4 (4 H, m, $OCH_2CH{=}CH_2$), 5.95–6.15 (2 H, m, $OCH_2CH{=}CH_2$), 6.6–6.75 (4 H, m, CalH), 6.85 (4 H, d, *J* 7.5, CalH), 7.0–7.15 (4 H, m, $AldC_{4,4',5,5'}H$), 7.04 (4 H, d, *J* 7.4, CalH), 7.41 (2 H, dd, *J* 7.3 and 2.1, $AldC_{6,6'}H$), 7.70 (2 H, s, OH) and 10.43 (2 H, s, CHO); δ_C(63 MHz, $CDCl_3$) 31.1 (t, $ArCH_2Ar$), 68.4–75.4 (t, CH_2O), 118.9 (t, $OCH_2CH{=}CH_2$), 119.3, 119.5, 124.0 (d, $AldC_{4,4',5,5',6,6'}$), 119.0, 125.3 (d, $CalC_{5,11,17,23}$), 128.5, 128.9 (d, $CalC_{4,6,10,12,16,18,22,24}$), 130.1 (s, $AldC_{1,1'}$), 128.1, 133.2 (s, $CalC_{1,3,7,9,13,15,19,21}$), 133.4 (d, $OCH_2CH{=}CH_2$), 151.5, 151.8, 152.1, 153.2 (s, $AldC_{2,2',3,3'}$ and $CalC_{25,26,27,28}$) and 190.5 (d, CHO); *m/z* (FAB) 1008.5 (M^+, calc. for $C_{60}H_{64}O_{14}$ 1008.4).

General Procedure for the Deallylation of Protected Dialdehydes **3**

Synthesis of Dialdehydes **4**.—A solution of **3** (2 mmol), $Pd(PPh_3)_4$ (11.5 mg, 10 μmol), and $HCOONHEt_3$ (1.76 g, 12 mmol) in a mixture of THF (20 cm^3), EtOH (20 cm^3) and H_2O (4 cm^3) was refluxed until the reaction had finished according to TLC (2–3 h). The solvent was evaporated off and the residue was dissolved in CH_2Cl_2 (100 cm^3) and washed with 1 mol dm^{-3} hydrochloric acid (100 cm^3). The organic phase was dried ($MgSO_4$) and evaporated to give the products as oils in quantitative yield.

$3^2,7^2$-*Bis*[5-(3-*formyl*-2-*hydroxy*)*phenoxy*]-3-*oxapentyloxy*]-1(1,3),3(1,3),5(1,3),7(1,3)-*tetrabenzenacyclooctaphane*-1^2,5^2-*diol* (**4a**).—ν_{max}/cm^{-1} 3380 (OH), 1681 and 1655 (HC=O); δ_H(250 MHz; $CDCl_3$) 3.32 (4 H, d, *J* 13.1, $ArCH_2Ar$), 4.0–4.35 (16 H, m, CH_2O), 4.36 (4 H, d, *J* 13.0, $ArCH_2Ar$), 6.55–6.9 (10 H, m, ArH), 7.02 (4 H, m, *J* 7.5, CalH), 7.11 (4 H, d, *J* 7.9, CalH), 7.80 (2 H, s, CalOH), 9.87 (2 H, s, CHO) and 10.86 (2 H, s, AldOH); δ_C(63 MHz; $CDCl_3$) 31.1 (t, $ArCH_2Ar$), 69.1–75.4 (t, CH_2O), 121.0 (s, $AldC_{1,1'}$), 119.4, 120.5, 124.9 (d, $AldC_{4,4',5,5',6,6'}$), 118.9, 125.3 (d, $CalC_{5,11,17,23}$), 128.4, 128.9 (d, $CalC_{4,6,10,12,16,18,22,24}$), 128.0, 133.2 (s, $CalC_{1,3,7,9,13,15,19,21}$), 147.3 (s, $AldC_{2,2'}$), 151.7, 151.9, 153.1 (s, $AldC_{3,3'}$ and $CalC_{25,26,27,28}$) and 196.1 (d, CHO); *m/z* (FAB) 840.4 (M^+, calc. for $C_{50}H_{48}O_{12}$ 840.3).

$3^2,7^2$-*Bis*[8-(3-*formyl*-2-*hydroxyphenoxy*)-3,6-*dioxaoctyloxy*]-1(1,3),3(1,3),5(1,3),7(1,3)-*tetrabenzenacyclooctaphane*-1^2,5^2-*diol* (**4b**).—ν_{max}/cm^{-1} 3359 (OH), 1681 and 1655 (HC=O); δ_H(250 MHz; $CDCl_3$) 3.33 (4 H, d, *J* 13.1, $ArCH_2Ar$), 3.75–4.2 (24 H, m, CH_2O), 4.40 (4 H, d, *J* 13.0, $ArCH_2Ar$), 6.6–6.9 (10 H, m, ArH), 7.0–7.05 (6 H, m, ArH), 7.16 (2 H, dd, *J* 7.7 and 1.5, $AldC_{6,6'}H$), 7.79 (2 H, s, CalOH), 9.92 (2 H, s, CHO) and 10.87 (2 H, br s, AldOH); δ_C(63 MHz; $CDCl_3$) 31.1 (t, $ArCH_2Ar$), 68.9–75.5 (t, CH_2O), 121.1 (s, $AldC_{1,1'}$), 119.4, 120.4, 124.7 (d, $AldC_{4,4',5,5',6,6'}$), 118.9, 125.3 (d, $CalC_{5,11,17,23}$), 128.4, 128.9 (d, $CalC_{4,6,10,12,16,18,22,24}$), 128.1, 133.3 (s, $CalC_{1,3,7,9,13,15,19,21}$), 147.4 (s, $AldC_{2,2'}$), 151.8, 152.0, 153.2 (s, $AldC_{3,3'}$ and $CalC_{25,26,27,28}$) and 196.0 (d, CHO); *m/z* (FAB) 928.4 (M^+, calc. for $C_{54}H_{56}O_{14}$ 928.4).

General Procedure for the Cyclization of Dialdehydes **4**

Synthesis of the Calix Salophen Crown Ethers **7** *and* **8**.—A solution of dialdehyde **4** (2.5 mmol), $Ba(OTf)_2$ (2.18 g, 5.0 mmol), and either benzene-1,2-diamine **5** (270 mg, 2.5 mmol)

or *cis*-cyclohexane-1,2-diamine **6** (285 mg, 2.5 mmol) in THF (250 cm^3) was refluxed for 30 min. After cooling slightly, $UO_2(OAc)_2 \cdot 2H_2O$ (1.59 g, 3.75 mmol) was added and refluxing was continued for about 30 min. The solvent was evaporated off and the residue was dissolved in CH_2Cl_2 (200 cm^3) and washed consecutively with water (2 × 100 cm^3), aqueous Na_2SO_4 (50 cm^3) and water (100 cm^3). After drying ($MgSO_4$) and evaporation of the solvent the crude products were obtained, which were purified by precipitation (**7**: CH_2Cl_2–cyclohexane) or by flash column chromatography followed by precipitation (**8**: eluent see below, CH_2Cl_2–cyclohexane).

{25²,28²-*Dihydroxy*-10,11:13,14-*didehydro*-2,5,8,16,19,22-*hexaoxa*-11,13-*diaza*-1(2,1,3),9(1,3),12(1,2),15(1,3),23(2,1,3),25-(1,3),28(1,3)-*heptabenzenabicyclo*[21.3.3]*nonacosacyclophane*-9²,15²-*diolato*(2−)-κ⁴O,O′,N,N′}*dioxouranium* (**7a**).—Yield 75%; m.p. (from CH_2Cl_2–cyclohexane) 260–265 °C (Found: C, 57.85; H, 4.75; N, 2.35. $C_{56}H_{50}N_2O_{12}U \cdot C_6H_{12} \cdot 2H_2O$ requires * C, 57.23; H, 5.11; N, 2.15%); Karl Fischer titration: Found: 3.35. Calc. for 2 H_2O: 2.77; ν_{max}/cm^{-1} 3413 (OH), 1603 (HC=N) and 905 (O–U–O); δ_H(250 MHz; CD_2Cl_2) 3.39 (4 H, d, *J* 13.1, $ArCH_2Ar$), 4.1–4.35 (12 H, m, CH_2O), 4.41 (4 H, d, *J* 13.1, $ArCH_2Ar$), 4.45–4.5 (4 H, m, CH_2O), 6.6–6.8 (6 H, m, $AldC_{5,5'}H$ and $CalC_{5,11,17,23}H$), 6.92 and 7.06 (2 × 4 H, d, *J* 7.5, $CalC_{4,6,10,12,16,18,22,24}H$), 7.26 and 7.35 (2 × 2 H, d, *J* 7.8, $AldC_{4,4',6,6'}H$), 7.4–7.6 (4 H, m, AmH), 7.88 (2 H, s, CalOH) and 9.37 (2 H, s, HC=N); δ_C(63 MHz; CD_2Cl_2) 31.4 (t, $ArCH_2Ar$), 69.9–75.0 (t, CH_2O), 117.1 (d, $AldC_{5,5'}$), 147.2 (s, $AmC_{1,1'}$), 150.1 (s, $AldC_{3,3'}$), 152.1, 153.1 (s, $CalC_{25,26,27,28}$), 162.7 (s, $AldC_{2,2'}$) and 165.8 (d, HC=N); *m/z* (FAB) 1181.1 ($[M + H]^+$. Calc. for $[C_{56}H_{50}N_2O_{12}U + H]$ 1181.4).

{25²,28²-*Dihydroxy*-10,11:13,14-*didehydro*-2,5,8,16,19,22-*hexaoxa*-11,13-*diaza*-1(2,1,3),9(1,3),15(1,3),23(2,1,3),25(1,3),28(1,3)-*hexabenzena*-12(1,2)-*cyclohexanabicyclo*[21.3.3]*nonacosaphane*-9²,15²-*diolato*(2−)κ⁴O,O′,N,N′}*dioxouranium* (**8a**).—Yield 78%; m.p. (from CH_2Cl_2–cyclohexane) 255–259 °C (Found: C, 55.1; H, 5.05; N, 2.4. $C_{56}H_{56}N_2O_{12}U \cdot 0.5C_6H_{12} \cdot 2.75H_2O$ requires C, 55.42; H, 5.32; N, 2.19%); Karl Fischer titration: Found: 3.89. Calc. for 2.75 H_2O: 3.87; ν_{max}/cm^{-1} 3404 (OH), 1614 (HC=N) and 901 (O–U–O); δ_H(250 MHz; CD_2Cl_2) 1.65–1.9 (4 H, m, $AmC_{3,3'}$), 1.9–2.05 and 2.35–2.5 (2 × 2 H, m, $AmC_{2,2'}H$), 3.41 (4 H, d, *J* 13.1, $ArCH_2Ar$), 4.1–4.5 (20 H, m, CH_2O and $ArCH_2Ar$), 4.6–4.7 (2 H, m, $AmC_{1,1'}H$), 6.6–6.85 (6 H, m, $AldC_{5,5'}H$ and $CalC_{5,11,17,23}H$), 6.96 and 7.06 (2 × 4 H, d, *J* 7.5, $CalC_{4,6,10,12,16,18,22,24}H$), 7.2–7.3 (4 H, m, $AldC_{4,4',6,6'}H$), 8.04 and 8.09 (2 H, s, OH) and 9.30 (2 H, s, HC=N); δ_C(63 MHz; CD_2Cl_2) 22.2 (t, $AmC_{3,3'}$), 28.1 (t, $AmC_{2,2'}$), 31.6 (t, $ArCH_2Ar$), 70.2–75.0 (t, CH_2O), 71.9 (d, $AmC_{1,1'}$), 116.8 (d, $AldC_{5,5'}$), 124.7 (s, $AldC_{1,1'}$), 150.1 (s, $AldC_{3,3'}$), 152.3, 153.3, 153.4 (s, $CalC_{25,26,27,28}$), 161.3 (s, $AldC_{2,2'}$) and 167.9 (d, HC=N); *m/z* (FAB) 1187.8 ($[M + H]^+$. Calc. for $[C_{56}H_{56}N_2O_{12}U + H]$ 1187.4).

31²,34²-*Dihydroxy*-13,14:16,17-*didehydro*-2,5,8,11,19,22,-25,28-*octaoxa*-14,16-*diaza*-1(2,1,3),12(1,3),18(1,3),29(2,1,3),31(1,3), 34(1,3)-*hexabenzena*-15(1,2)-*cyclohexanabicyclo*-[27,3,3]*pentatriacontaphane*-12²,18²-*diolato*(2−)κ⁴O,O′,N,-N′}*dioxouranium* (**8b**).—Yield 88%; m.p. (from CH_2Cl_2–cyclohexane) 202–205 °C (Found: C, 54.9; H, 5.15; N, 1.95. $C_{60}H_{64}N_2O_{14}U \cdot 2H_2O$ requires C, 54.96; H, 5.23; N, 2.14%). Karl Fischer titration: Found: 2.61. Calc. for 2 H_2O: 2.75; ν_{max}/cm^{-1} 3388 (OH), 1614 (HC=N) and 899 (O–U–O); δ_H(250 MHz; $CDCl_3$) 1.6–1.85 (4 H, m, $AmC_{3,3'}H$), 1.85–2.0 and 2.35–2.5 (2 × 2 H, m, $AmC_{2,2'}H$), 3.33 and 3.34 (2 × 2 H, d, *J* 13.0, $ArCH_2Ar$), 4.0–4.2 (20 H, m, CH_2O), 4.3–4.4 (8 H, m, CH_2O and $ArCH_2Ar$), 4.6–4.7 (2 H, m, $AmC_{1,1'}$), 6.6–6.75 (6 H, m, $AldC_{5,5'}H$ and $CalC_{5,11,17,23}H$), 6.86, 7.04 and 7.05 (4 + 2 × 2 H, d, *J* 7.5, $CalC_{4,6,10,12,16,18,22,24}H$), 7.2–7.3 (4 H, m, $AldC_{4,4',6,6'}H$), 7.98 and 7.99 (2 × 1 H, s, OH) and 9.25 (2 H, s, HC=N); δ_C(63 MHz; $CDCl_3$) 21.7 (t, $AmC_{3,3'}$), 27.7 (t, $AmC_{2,2'}$), 31.3 (t, $ArCH_2Ar$), 70.4–75.9 ($AmC_{1,1'}$ and CH_2O), 116.6 (d, $AldC_{5,5'}$), 124.7 (s, $AldC_{1,1'}$), 149.9 (s, $AldC_{3,3'}$), 152.0, 153.4 (s, $CalC_{25,26,27,28}$), 161.6 ($AldC_{2,2'}$) and 167.6 (d, CH=N); *m/z* (FAB) 1275.9 ($[M + H]^+$, calc. for $[C_{60}H_{64}N_2O_{14}U + H]$ 1275.5).

X-Ray Crystallography †

X-Ray Crystal Structure Analysis of the Water Complex of **8a**.—*Crystal data.* $C_{56}H_{56}N_2O_{10} \cdot UO_2 \cdot 4CH_3CN \cdot 2H_2O$, M = 1387.4. Orange monoclinic crystals, space group $P2_1$, a = 10.374(2), b = 15.062(6), c = 19.613(6) Å, β = 101.79(2)°, V = 3000(3) Å³ (average of least-squares refinement of repeated measurements of 25 reflection angles), Z = 2, d_{calc} = 1.54 g cm^{-3}, μ = 26.3 cm^{-1}.

Data collection and processing. Reflections were measured on a CAD4 diffractometer, T = 110 K, $\omega/2\theta$ scan mode, using graphite-monochromated Mo-Kα radiation [scan width (ω) (1.1 + 0.35 tan θ)°; $3 < \theta < 27.5°$; $-14 < h < 14$, $0 < k < 19$; $0 < l < 23$]; 8475 reflections were measured of which 8016 were unique (R_{merge} = 2.7% after an empirical absorption correction with DIFABS).[14] A total of 6608 reflections with $F_o^2 > 3\sigma(F_o^2)$ were used in the refinement.

Structure analysis and refinement. The structure was solved by Patterson methods and refined with full-matrix least-squares. In one of the crown ether parts disorder was found for one of the carbon atoms. This could be resolved by refining two atoms with partial occupancies of 0.8/0.2. The neighbouring atoms of this carbon have been refined with anisotropic thermal parameters, which showed rather large apparent thermal motion in one direction. The number of parameters refined was 362 [scale factor, extinction parameter, positional parameters of all atoms, isotropic thermal parameters, anisotropic thermal parameters for U and the two atoms described above; H-atoms not included; origin in the *y*-direction fixed by the position of the U-atom]. The final *R*-factors were R = 5.5%, R_w = 7.5%. All calculations were done with SDP[15] and the illustration with PLUTON.[16]

X-Ray Crystal Structure Analysis of the Methanol Complex of **8a**.—*Crystal data.* $C_{56}H_{56}N_2O_{10} \cdot UO_2 \cdot 3CH_4O \cdot 2H_2O$, M = 1319.3. Red monoclinic crystals, space group $P2_1/c$, a = 9.642(4), b = 15.785(8), c = 38.01(2) Å, β = 93.59(5)°, V = 5774(5) Å³ (from 19 SET4 setting angles), Z = 4, d_{calc} = 1.518 g cm^{-3}, μ(Mo-Kα) = 27.3 cm^{-1}. Plate-shaped crystal [0.10 × 0.40 × 0.70 mm].

Data collection and processing. TurboCAD4/Rotating anode diffractometer, 60 kV, 150 mA, T = 150 K, $\omega/2\theta$-scan mode, graphite-monochromated Mo-Kα radiation, $\Delta\omega$ = (1.0 + 0.35 tan θ)°; $1.1 < \theta < 23°$; *hkl*: 0, 8; −17, 0; −41, 41; 8003 reflections scanned of which 7127 unique. The data were corrected for L_p and absorption (DIFABS).[14]

Structure analysis and refinement. The structure was solved with DIRDIF92[17] and refined in F^2 by full-matrix least-squares with SHELXL-93.[18] Hydrogen atoms were introduced at calculated positions. Convergence was reached at R_1 = 0.19 (wR_2 = 0.48), S = 1.05, $w^{-1} = \sigma^2(F^2) + (0.1938\ P^2) +$

* The presence of cyclohexane in the precipitated product was confirmed by ^1H NMR spectroscopy.

† Tables of fractional atomic coordinates, bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See 'Instructions for Authors (1994)', in the January issue of *J. Chem. Soc., Perkin Trans. 2*, 1994.

909.8 *P*. The relatively high *R* value is due to the fact that the crystals reflect poorly and with broad reflection profiles. The non-coordinating solvents are disordered and were modelled. Geometrical calculations were done with PLATON[19] and the illustration with PLUTON.[16] Scattering factors were taken from the International Tables.[20]

X-Ray Crystal Structure Analysis of the Me_2SO *Complex of* **8a**.—*Crystal data.* $C_{56}H_{56}N_2O_{10}\cdot UO_2\cdot C_2H_6SO\cdot 3.5CH_4O\cdot 3H_2O$, $M = 1431.42$. Orange monoclinic crystals, space group $P2_1/c$; $a = 18.011(1)$, $b = 24.517(2)$, $c = 14.241(2)$ Å, $\beta = 107.86(1)°$, $V = 5985.7(8)$ Å^3 (from 25 SET4 setting angles in the range $10 < \theta < 14°$), $Z = 4$, $d_{calc} = 1.588$ g cm^{-3}, μ(Mo-Kα) = 26.8 cm^{-1}. Block-shaped crystal [0.25 × 0.38 × 0.50 mm].

Data collection and processing. TurboCAD4/Rotating anode diffractometer, 60 kV, 150 mA, $T = 150$ K, $\omega/2\theta$-scan mode, graphite-monochromated Mo-Kα radiation, $\Delta\omega = (0.68 + 0.35 \tan\theta)°$; $1 < \theta < 26.5°$; *hkl*: −16, 17; 0, 29; −22, 0; 11 806 reflections scanned of which 11 104 unique. The data were corrected for L_p and absorption (DIFABS).[14] 5859 reflections with $I > 2.5\ \sigma(I)$ were used in the subsequent calculations.

Structure analysis and refinement. The structure was solved with DIRDIF92[17] and refined in *F* by full-matrix least-squares (SHELX-76).[21] Hydrogen atoms were taken into account at calculated positions. Convergence was reached at $R = 0.069$, $wR = 0.082$, $w = 1$, $S = 2.06$. The S atom was found to be disordered over two positions (0.75, 0.25). The disordered solvent areas were modelled. Geometrical calculations were done with PLATON[19] and the illustration with PLUTON.[16] Scattering factors were taken from Cromer and Mann,[22] corrected for anomalous dispersion.[23]

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Paper 3/06894C
Received 18*th November* 1993
Accepted 7*th February* 1994