Functionalized UO2 Salenes: Neutral Receptors for Anions

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Functionalized UO_2 Salenes: Neutral Receptors for Anions

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Abstract: A novel class of neutral receptors for anions that contain a unique combination of an immobilized Lewis acidic binding site (UO_2^{2+}) and additional amide C(O)NH groups, which can form a favorable H-bond with a coordinated anion guest, has been developed. X-ray analysis of free receptor **14b** shows that it is organized in the solid state as dimers, the fifth position of the uranyl being occupied by an oxygen atom of the amide group of a second molecule. Anion complexation has been demonstrated by conductometry, X-ray crystallography, cyclic voltammetry, ^1H and ^{31}P NMR spectroscopy, and FAB mass spectrometry. X-ray structures of **1c**·$H_2PO_4^-$ and **14e**·$H_2PO_4^-$ reveal that anion binding is effected by coordination to the uranyl cation and additional H-bond formation. The **1c**·$H_2PO_4^-$ complex is arranged in centrosymmetric pairs, the core of the dimer consisting of two $H_2PO_4^-$ anions connected by two short H-bonds. In the case of the **14e**·$H_2PO_4^-$ complex, the $H_2PO_4^-$ complexed to the uranyl forms a H-bonded associate with a second $H_2PO_4^-$ anion which itself is not complexed by the ligand. In the case of the preorganized ligands **14b**, **14d**, and **18**, strong ($K_{ass} > 10^5$ M^{-1} in MeCN–DMSO, 99:1) and selective complexation of $H_2PO_4^-$ has been observed. Selectivities of $>10^2$ and $>10^3$ over Cl^- and HSO_4^-, NO_2^-, and SCN^-, respectively, were obtained for receptor **14b**. "Naked" UO_2 salophenes **19a–c**, in which the Lewis acidic binding center contains two vacant positions for guest coordination, have been designed for complexation of dianions like malonate and succinate with K values of 80–460 M^{-1} in DMSO. Salophene **19a** forms a 1:2 complex with $H_2PO_4^-$. Its X-ray structure shows that the complex is organized as a H-bonded ribbon due to the facts that the $H_2PO_4^-$ anions form H-bonded dimers and, in addition, two $H_2PO_4^-$ anions are complexed by one uranyl cation.

Introduction

During the last few decades, supramolecular chemistry has achieved remarkable selectivities in the complexation of cations and neutral molecules.[1] The design and synthesis of neutral macrocyclic receptors are based on the ability to organize the binding sites and size complementarity in a proper way. The recognition in cation complexation is based on Lewis base binding fragments (e.g., crown ether oxygens). For complexation of neutral molecules, in addition to stereoelectronic effects, π–π stacking and H-bond formation play essential roles.[2]

Although macrocycles and clefts with *positively charged* quaternary ammonium groups,[3] guanidinium fragments,[4] or transition-metal cations incorporated into azamacrocycles[5] are known to complex anions, selectivity is not simply introduced. Recently, Beer et al.[6] reported charged and neutral anion receptors which are able to bind anions via mutual Lewis acidic and favorable amide C(O)NH···anion hydrogen bond interactions. *Neutral* macrocyclic and acyclic ligands that contain Lewis acidic binding sites such as boron,[7] silicon,[8] tin,[9] and mercury[10] bind anions, but these structures lack the possibility of subtle structural variation that is the basis for the selectivity in cation and neutral guest complexation.

In nature, the *selective* complexation of anions takes place by hydrogen bonds; the selective recognition of phosphate and sulfate in biological systems by transport receptor proteins has recently been described.[11]

Previously we reported that *metallomacrocycles*[12] and *clefts*[13] containing an immobilized Lewis acidic UO_2 cation are excellent receptors for the complexation of neutral molecules as the result of coordination of a nucleophilic group (C=O, S=O, =N—) to the uranyl center in addition to H-bond formation and π–π stacking. The uranyl cation complexed in a salophene unit prefers a pentagonal bipyramidal coordination, with the two oxygens at the apical positions and with both the four-coordinating sites of the salophene moiety and a *neutral molecule* in the equatorial positions.[14]

Analogously the presence of a uranyl Lewis acidic center and additional H-binding sites like C(O)NH fragments in a preorganized receptor molecule should increase the selectivity and

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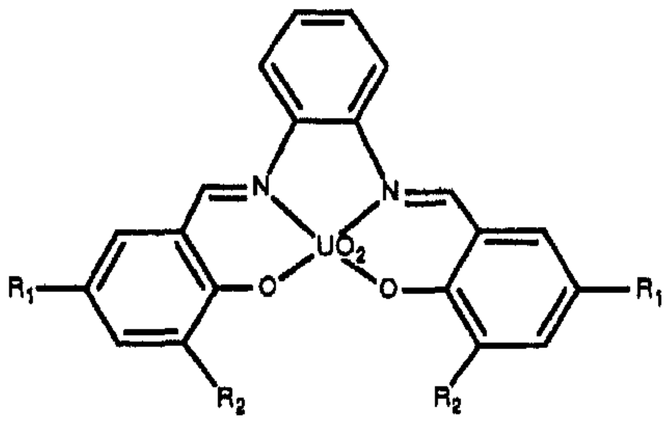
Chart 1



1a : $R_1 = R_2 = H$
1b : $R_1 = NO_2$, $R_2 = H$
1c : $R_1 = H$, $R_2 = OMe$

efficiency of *anion complexation*. In this paper, the synthesis of this novel type of *neutral anion receptor* is described.[15] The complexation of anionic species has been studied by NMR spectroscopy, fast atom bombardment (FAB) mass spectrometry, X-ray crystallography, conductometry, and cyclic voltammetry.

Results and Discussion

Synthesis of Anion Receptors and Solid-State Structures of Anion Complexes. Simple uranyl-containing compounds **1a–c** (Chart 1) were prepared from the corresponding aldehydes, 1,2-benzenediamine, and $UO_2(OAc)_2 \cdot 2H_2O$ in methanol in 60–80% yield.[13,14] The ^1H NMR spectra of **1a–c** show one singlet at 9.3–9.5 ppm, corresponding to the imino groups coordinating to the uranyl moiety.

Stirring of ligand **1a** or **1c** with tetraalkylammonium salts of chloride or dihydrogen phosphate in MeCN overnight followed by evaporation of the solvent gave the corresponding anionic complex as an orange powder. The negative FAB mass spectra of these complexes exhibit, in addition to small peaks of the free ligands, very intense [ligand + anion$^-$]$^-$ signals, while small [ligand + salt]$^-$ peaks are also present.

Red single crystals of the 1:1 complex of salophene **1a** with tetraethylammonium chloride were grown from a dichloromethane solution. As described in a preliminary paper,[15] the uranyl cation is coordinated to two oxygens and two nitrogens of the salophene unit, in addition to the chloride anion with a U···Cl distance of 2.76 Å, which clearly demonstrates the anion complexation.

From the complex of ligand **1c** with tetrabutylammonium dihydrogen phosphate ($Bu_4N^+H_2PO_4^-$), crystals also suitable for X-ray analysis were grown by slow diffusion of diisopropyl ether into a solution of the complex in MeCN. The crystal structure is shown in Figure 1.

In this complex, the uranium atom has approximate pentagonal bipyramidal coordination, with the two oxygens in apical positions. In the equatorial plane, besides coordination with the two nitrogens and two oxygens of the salophene moiety, the fifth coordination position is occupied by an oxygen atom of the dihydrogen phosphate ($H_2PO_4^-$) anion (U···O—P distance 2.28(2) Å). It is evident from Figure 1 that in the solid state the complexes are arranged in centrosymmetric pairs. The "core" of the dimer consists of two $H_2PO_4^-$ anions which are connected by two short H-bonds (O···O distance 2.52(1) Å). Another H-bond (O···O—P distance 2.68(1) Å) is formed between the $H_2PO_4^-$ anion and a methoxy oxygen of the salophene moiety. Although dimerization and polymerization of hydrogen phosphates upon complexation in solution are known,[16] to the best of our knowledge this is the

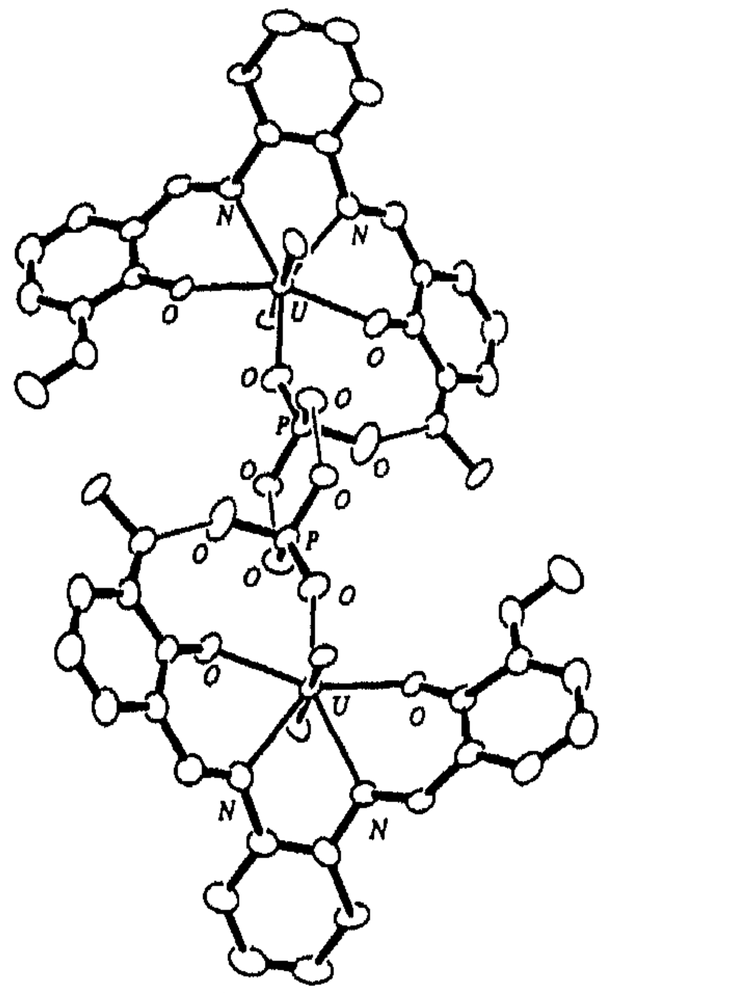


Figure 1. Crystal structure of the complex $1c \cdot H_2PO_4^-$. The dimer shown has a crystallographic center of symmetry. Tetrabutylammonium fragments and solvent molecule are omitted for clarity.

first example of $H_2PO_4^-$ dimerization in the solid state.[17] This result shows the interesting phenomenon that anion binding in this type of compound is effected by coordination to the UO_2 cation and is augmented by hydrogen bonding between anion and ligand.

In order to obtain anion receptors which contain a *combination* of both UO_2 cation and C(O)NH amido functionalities as additional binding sites, we designed cleft-type molecules **5** and **10**.

Aldehyde **3** was synthesized in 63% yield via *o*-lithiation of 1,1′-biphenyl-2,2′-diol monomethoxymethyl ether (**2**) with *t*-BuLi in THF followed by quenching with DMF (Scheme 1). After alkylation of **3** with bromoacetamide, the methoxymethyl group was removed under acidic conditions to give **4** in 54% yield. Subsequently, aldehyde **4** was reacted with *cis*-1,2-cyclohexanediamine[18] and $UO_2(OAc)_2 \cdot 2H_2O$, with formation of metallocleft **5** in 71% yield.

The synthesis of the salicylamide-based metallocleft **10** started with reaction of 2-(tosyloxy)ethyl ether **7** with 2-((2-allyl)oxy)-3-hydroxybenzaldehyde (**6**)[19] to give **8** in 81% yield (Scheme 2). Deallylation of **8** via a Pd-catalyzed reaction with $Et_3N \cdot HCOOH$ in $EtOH_{aq}$[20] afforded aldehyde **9** in 62% yield. Cleft **10** has been prepared by reaction of **9** with *cis*-1,2-cyclohexanediamine and $UO_2(OAc)_2 \cdot 2H_2O$ in methanol in a yield of 51%.

In order to obtain metalloclefts containing a UO_2 center and flexible amido fragments, we synthesized aldehydes **12a–d** in 74–87% yield from the corresponding bromo- or chloroacetamides **11a–d** and 2-((2-allyl)oxy)-3-hydroxybenzaldehyde (**6**) (Scheme 3). Deallylation of **12–d** resulted in the formation of aldehydes **13a–d**, which were used for reaction with *cis*-1,2-cyclohexanediamine or 1,2-benzenediamine and $UO_2(OAc)_2 \cdot 2H_2O$ to give metalloclefts **14a–e** in 64–89% yield. Compounds **14c** and **14d**,

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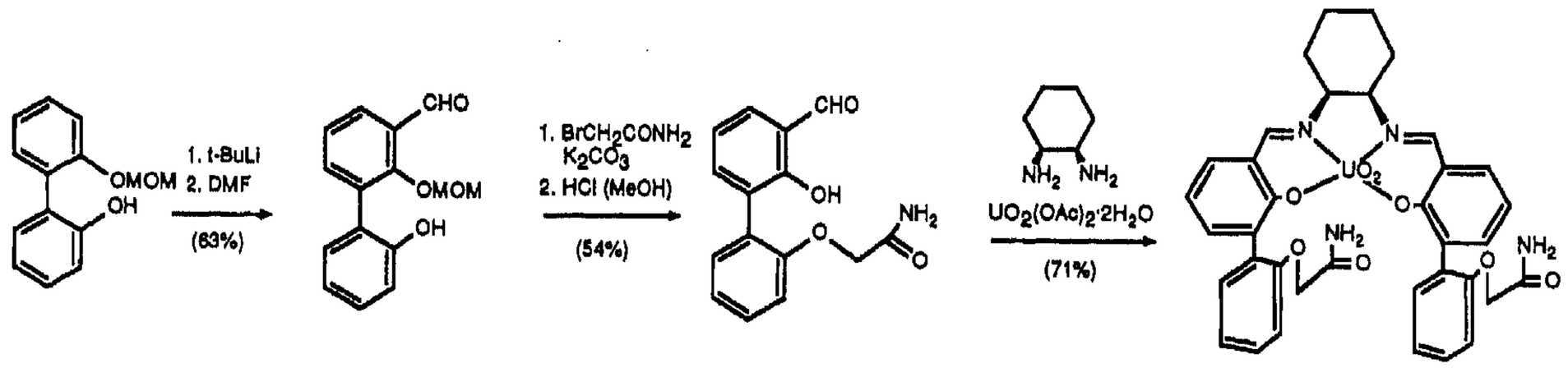
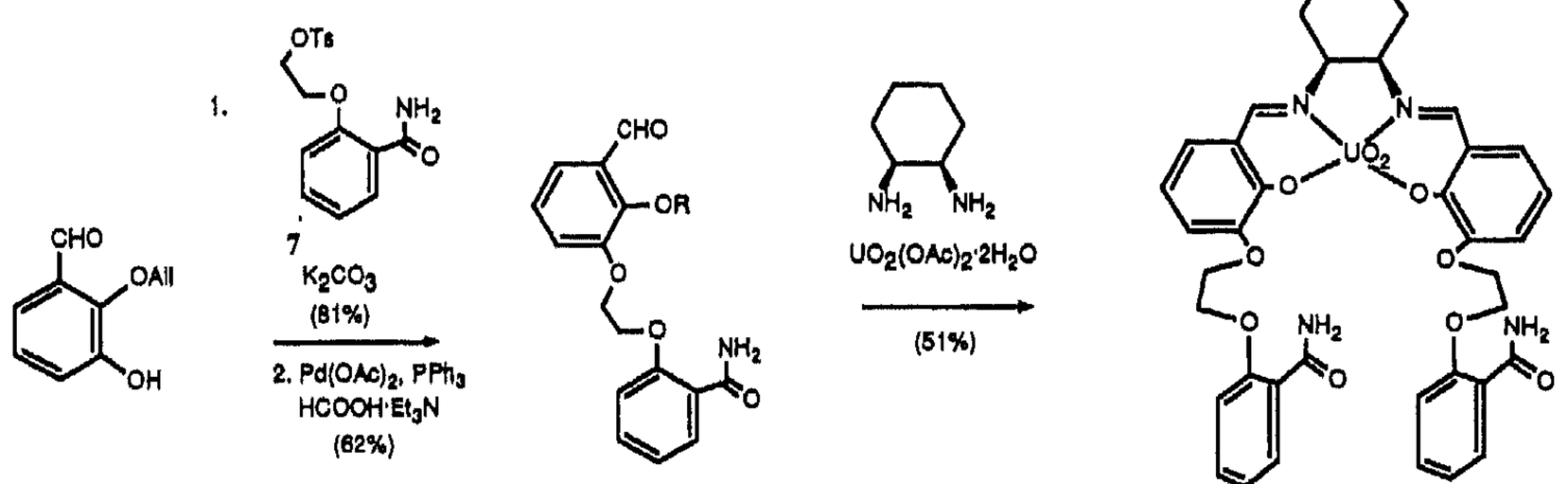
Scheme 1



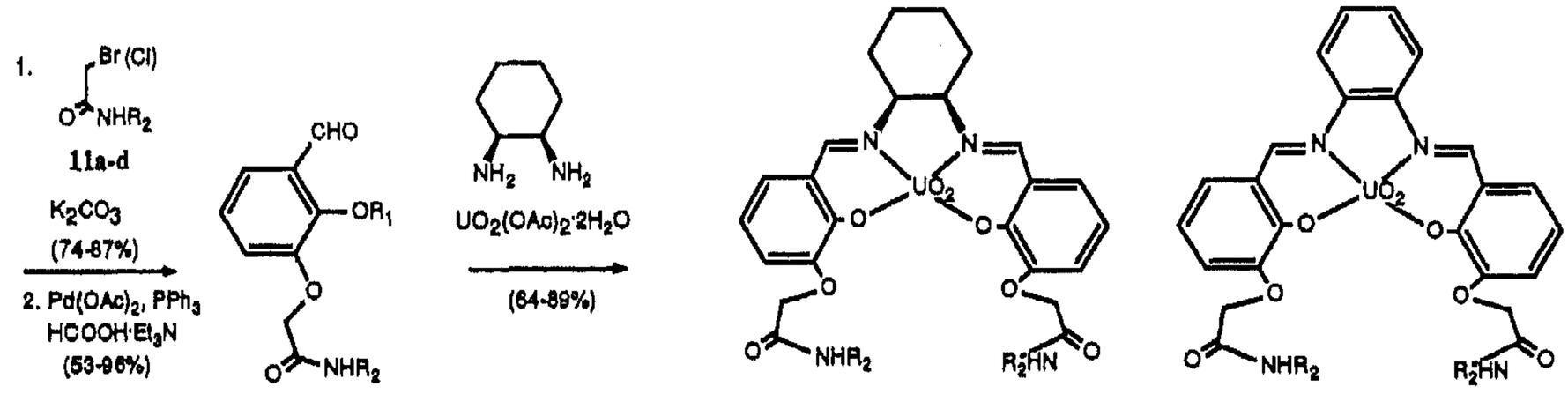
2 3 4 5

Scheme 2



6 7 8: R = All 9: R = H 10

Scheme 3



6

12a: R_1 = All, R_2 = H
12b: R_1 = All, R_2 = 4-MeC_6H_4
12c: R_1 = All, R_2 = n-$C_{18}H_{37}$
12d: R_1 = All, R_2 = 4-(n-$C_8H_{17}O$)C_6H_4
13a: R_1 = R_2 = H
13b: R_1 = H, R_2 = 4-MeC_6H_4
13c: R_1 = H, R_2 = n-$C_{18}H_{37}$
13d: R_1 = H, R_2 = 4-(n-$C_8H_{17}O$)C_6H_4

14a : R_2 = H
14b : R_2 = 4-MeC_6H_4
14c : R_2 = n-$C_{18}H_{38}$
14d : R_2 = 4-(n-$C_8H_{17}O$)C_6H_4

14e : R_2 = 4-MeC_6H_4

containing long lipophilic hydrocarbon chains, have been prepared in order to increase the hydrophobicity compared with the other receptors.

The absorption in the ^1H NMR spectra at 9.40–9.50 ppm and in the IR spectra at 1615–1617 cm^{-1} for clefts **5**, **10**, and **14a–e** proved imino bond formation. The presence of the uranyl moiety is in agreement with the uranium–oxygen vibrations in the IR spectra at 895–904 cm^{-1}. The presence of water in compounds **5**, **10**, and **14a–e** complexed at the fifth equatorial position of the UO_2 cation was confirmed by elemental analyses and Karl Fischer titrations. The $(M + H)^+$ peaks in the FAB mass spectra prove the formation of the UO_2-containing compounds.

From compound **14b**, crystals suitable for X-ray analysis were grown from a hot methanolic solution. A view on the structure is presented in Figure 2.

The structure contains two independent molecules in the asymmetric unit. In the molecules studied so far,[12,13,19] the fifth equatorial position of the UO_2 cation is occupied by an oxygen atom of a *solvent* (H_2O, MeOH) or *guest* (urea, amides, etc.) molecule. Since in **14b**, both the UO_2 center and amido fragments are present, the fifth position of the UO_2 cation is filled by an oxygen atom of the amide group of a second molecule. In this way, molecules are organized in the solid state as dimers. The FAB mass spectrum of **14b** also shows dimer formation, with an intense molecular dimer peak. This phenomenon of *self-complementarity* is very important for self-replication[21] in solution

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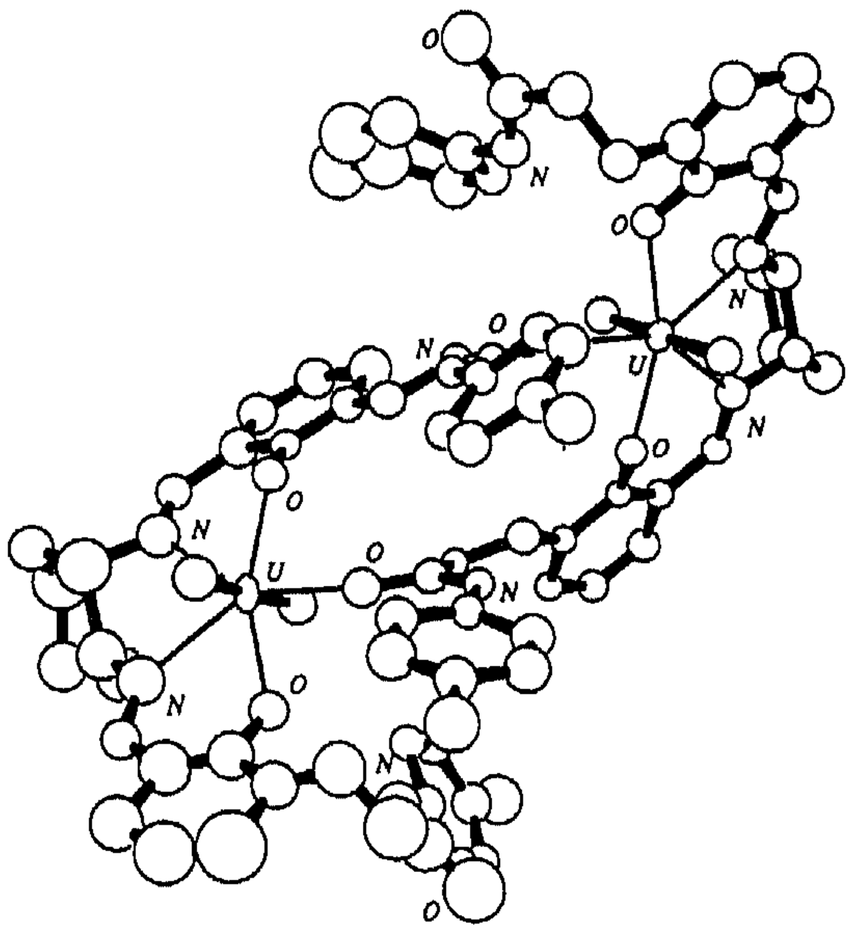

Figure 2. Crystal structure of the dimer of **14b**. The figure shows the two crystallographically independent molecules in the unit cell. The solvent molecule is omitted for clarity.

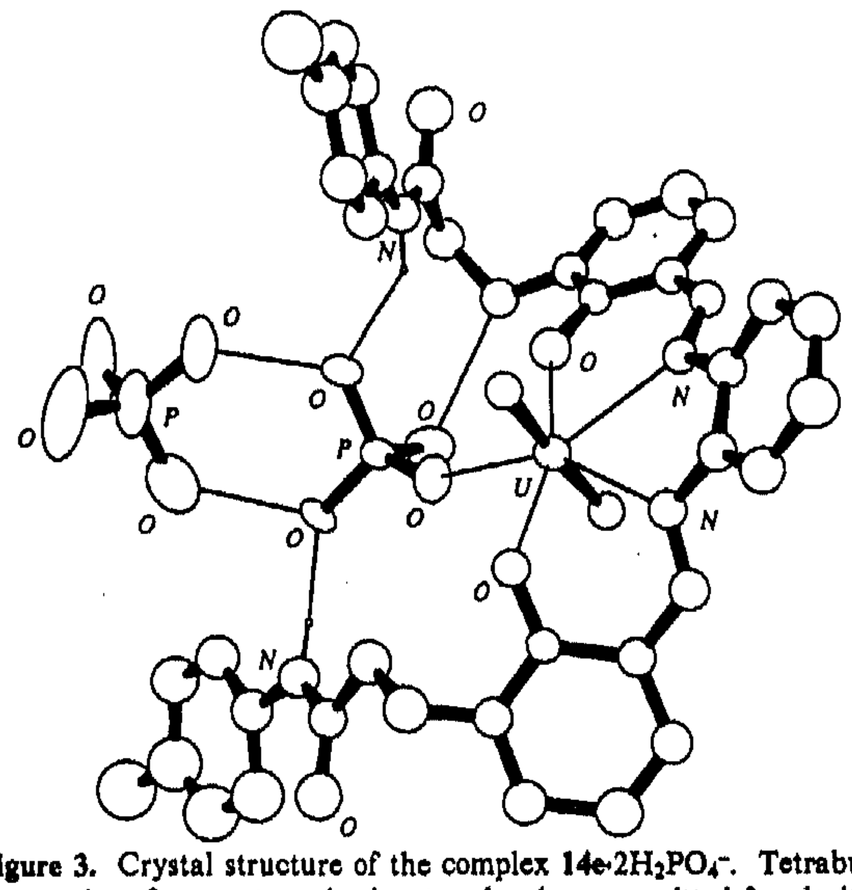

Figure 3. Crystal structure of the complex **14e**·$2H_2PO_4^-$. Tetrabutylammonium fragments and solvent molecules are omitted for clarity.

and for the design of controlled solid-state structures.[22] Due to this type of association, the ^{1}H NMR spectra of the $CDCl_3$ and MeCN-d_3 solutions of ligands **14a–e** show broad signals for all groups of protons. Increasing the solvent polarity prevents this association, and in DMSO-d_6, which is known[23] to form complexes with UO_2 salenes, the ^{1}H NMR spectra are sharp.

Single crystals of the complex of ligand **14e** with $Bu_4N^+H_2PO_4^-$ were also grown by slow diffusion of diisopropyl ether into a solution of **14e** and 2-fold excess of $Bu_4N^+H_2PO_4^-$ in MeCN.[24] The crystal structure is shown in Figure 3.

As in the case of the complex of **1c** with $H_2PO_4^-$ (Figure 1), the $H_2PO_4^-$ anion is tightly complexed to the UO_2 center (U···O—P distance 2.28(2) Å), in addition to a H-bond formation with the acetoxy oxygen of the salene moiety (O···O—P distance 2.84(2) Å). However, in this case two additional H-bonds between the amido groups of the ligand and the complexed anion are present (N···O—P distance 2.79(2) Å), which clearly shows the *participation* of C(O)NH fragments in anion complexation. As in Figure 1, the $H_2PO_4^-$ complexed to the UO_2 cation forms a H-bonded associate with the second $H_2PO_4^-$ anion (O···O distance 2.48(2) Å), which in this case is not complexed itself by ligand **14e**.

We have also synthesized metallomacrocycle **18** containing a polyether bridge. Receptor **18** has been obtained via the same route as **14a–d**, starting from bis(bromoacetamido)triethylene glycol (**15**) via alkylation of 2-((2-allyl)oxy)-3-hydroxybenzaldehyde (**6**) and subsequent deallylation (Scheme 4). Cyclization of dialdehyde **17** with *cis*-1,2-cyclohexanediamine in the presence of $Ba(OTf)_2$ as a template followed by addition of $UO_2(OAc)_2\cdot 2H_2O$ led to **18** in 59% yield.

Stirring of a mixture of ligand **1c**, **14a**, **14b**, **14e**, or **18** and $Bu_4N^+H_2PO_4^-$ in MeCN overnight followed by evaporation of solvent gave the corresponding complex as an orange powder. In all cases, the negative FAB mass spectra of the solid complexes exhibit, in addition to small peaks of the free ligands, very intense [ligand + anion$^-$]$^-$ signals, while small [ligand + salt]$^-$ peaks are also present. In the ^{1}H NMR spectra of all complexes, significant changes of the host were found for the NH amido, the HC═N, and the $CH_2C(O)$ signals which clearly indicate the presence of a guest anion in the cavity. In the ^{31}P NMR spectra of $H_2PO_4^-$ complexes with **1c**, **14a**, **14b**, and **18**, signals of $H_2PO_4^-$ are shifted downfield ($\Delta\delta$ = 1.9–2.3 ppm) in comparison with free $H_2PO_4^-$.

In receptors **5**, **10**, **14a–e**, and **18**, the uranyl center contains only one vacant position. We have also synthesized the so-called "naked" salophenes **19a–c** (Chart 2), which have *two vacant positions* for complexation with guests. "Naked" UO_2 salophenes **19a–c** have been prepared by reaction of the corresponding aldehydes (salicyl aldehyde, **13b**, and **9**, respectively), *o*-aminophenol, and $UO_2(OAc)_2\cdot 2H_2O$ in refluxing MeOH in yields of 91–98%. The ^{1}H NMR spectra of **19a–c** show singlets at 9.53–9.55 ppm, and in the IR spectra, uranium–oxygen vibrations are observed at 904–917 cm^{-1}. Positive FAB mass spectra confirmed the uranyl complexation. Elemental analyses and Karl Fischer titrations show the presence of MeOH or H_2O molecules coordinated to the uranyl center.

Orange single crystals of the complex of "naked" ligand **19a** with $Bu_4N^+H_2PO_4^-$ were grown by slow diffusion of diisopropyl ether into a solution of **19a** and a 2-fold excess of $Bu_4N^+H_2PO_4^-$ in MeCN. The crystal structure is presented in Figure 4 and clearly shows that binding of two $H_2PO_4^-$ anions takes place (U···O—P distance 2.33 Å).

As in previous cases, phosphate anions form H-bonded dimers with phosphates complexed by another molecule of **19a** (O···O distance 2.53 Å). At the same time, due to the unique fact that two phosphates are complexed by the UO_2 cation, molecules of complex **19a**·$(H_2PO_4^-)_2$ are organized as a H-bonded ribbon (Figure 5).

Anion Recognition in Solution. The complexation of anions in solution was studied first by conductometry. Already the simple UO_2 salophenes **1a–c** show strong binding of different anions (e.g., Cl^-, $H_2PO_4^-$, NO_2^-) in MeCN–DMSO (99:1) solutions (Table 1).[25] In all cases, a preference for $H_2PO_4^-$ binding was observed. It is clear from Table 1 that the charge density on the UO_2 fragment is influenced by the presence of substituents in the parent molecule. Due to the presence of the electron-withdrawing

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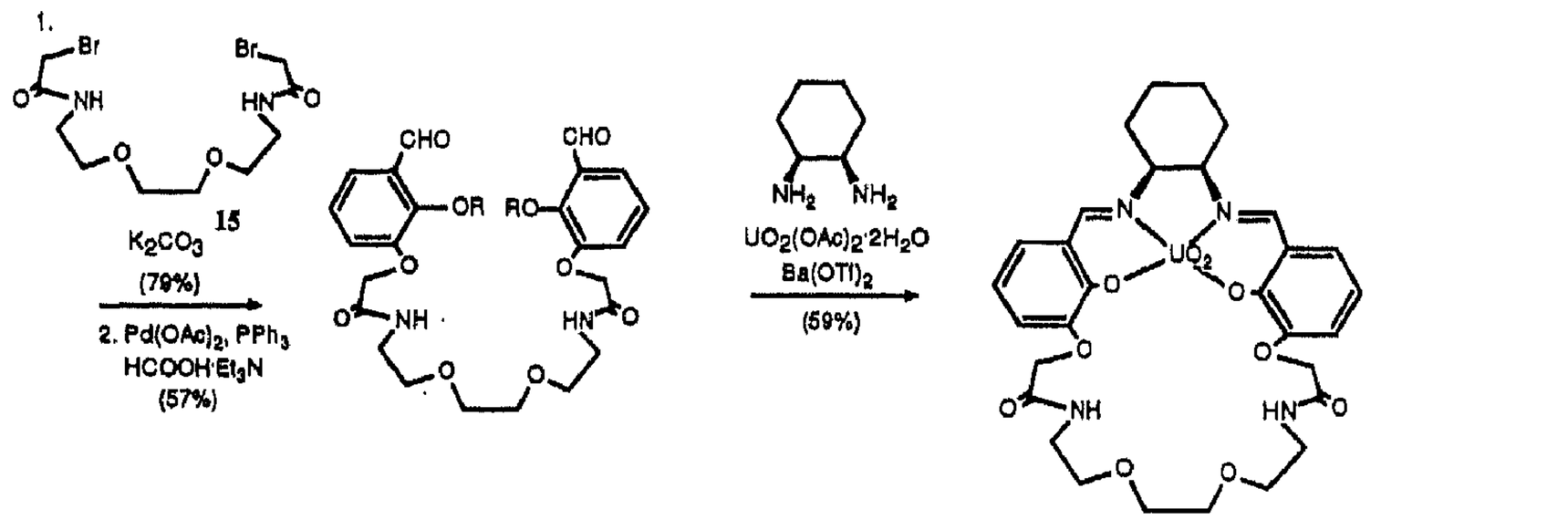
(24) Attempts to obtain single crystals of complexes of salenes **14a–d** with $H_2PO_4^-$ were unsuccessful.

(25) An interesting phenomenon has been observed during temperature-dependent measurements in MeCN–DMSO (99:1) solutions. The binding constants increase as the temperature increases, which demonstrates the importance of the *entropy* in the binding process. For example, ΔH and ΔS parameters for the complexation of $H_2PO_4^-$ by receptors **1a** and **1b** are 4.3 and 7.1 kcal/mol and 92.0 and 99.0 eu, respectively, and for complexation of Cl^-, 9.9 and 5.0 kcal/mol and 84.0 and 87.0 eu, respectively, which may indicate that desolvation plays an important role.

Scheme 4



6

16 : R = All
17 : R = H

18

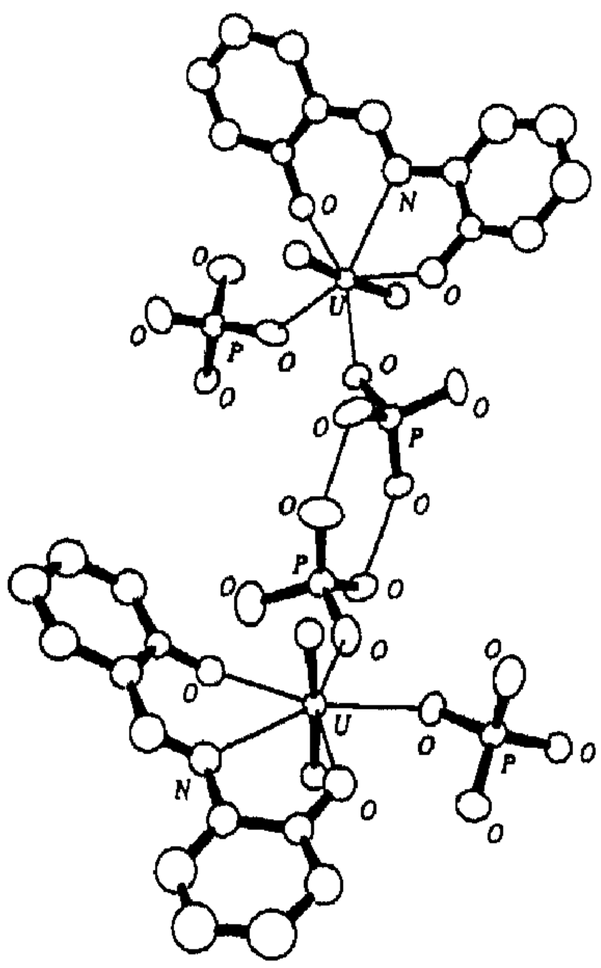
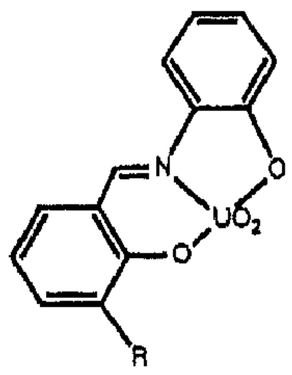


Figure 4. Crystal structure of the complex **19a**·$2H_2PO_4^-$. The structure shown contains a crystallographic center of symmetry. Tetrabutylammonium fragments and solvent molecule are omitted for clarity.

Chart 2



19a : R = H
19b : R = $OCH_2C(O)NH$-C_6H_4-Me-4
19c : R = $O(CH_2)_2O$-C_6H_4-$C(O)NH_2$-2

nitro group, the UO_2 moiety in **1b** is more electropositive, and consequently ligand **1b** binds Cl^- and NO_2^- stronger than ligand **1a**.

In the salophenes **1a–c**, binding exclusively takes place via electrostatic interaction. Therefore, metalloclefts **5** and **10** containing additional amido C(O)NH binding sites seemed to be more effective receptors for anions. Surprisingly, they complex anions weaker than ligands **1a–c**. Probably, in this case the rigid

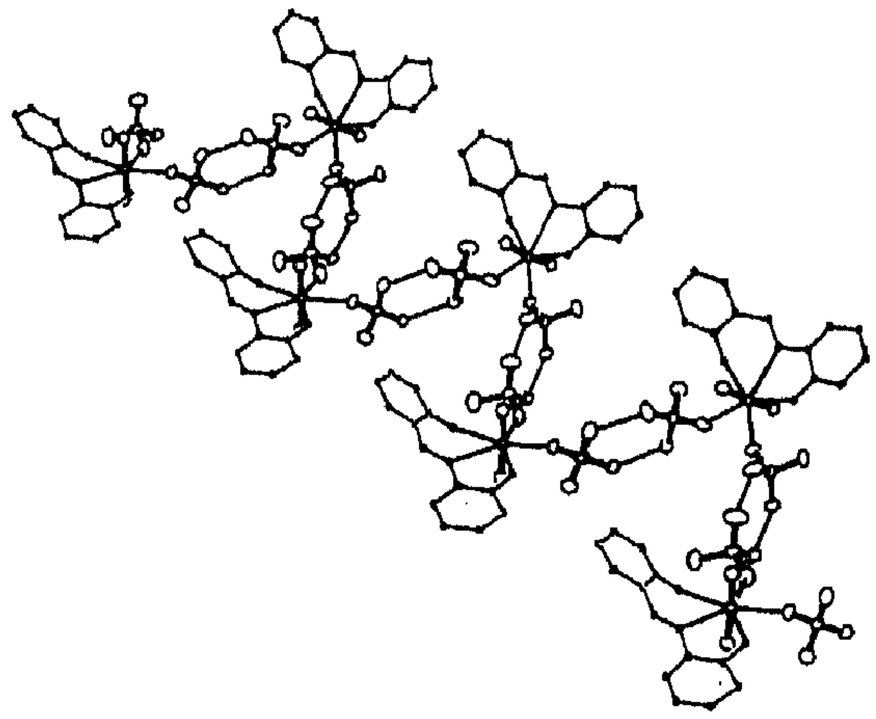


Figure 5. View of the H-bonded ribbon of the complex **19a**·$2H_2PO_4^-$

cavity is too small for complexation; nevertheless, there is selectivity for $H_2PO_4^-$ over the other anions.

In contrast to this, the binding of anions by more flexible clefts **14a, 14b**, and **14d** and metallomacrocycle **18**, which also contain amido C(O)NH functionalities, is very strong. The influence of C(O)NH moieties that are able to form H-bonds is demonstrated (except $H_2PO_4^-$) by comparing the K_{ass} value of compound **1c** with those of **14a, 14b**, and **14d** (Table 1). More preorganized ligands **14b, 14d**, and **18** exhibit a very strong ($K_{ass} > 10^5$ M^{-1}) and selective complexation of $H_2PO_4^-$. Compound **14b** shows for $H_2PO_4^-$ selectivities of $>10^2$ over Cl^- and $>10^3$ over NO_2^-. For HSO_4^- and SCN^-, K_{ass} values of $<3 \times 10^2$ M^{-1} were obtained for all ligands.

The complexation of anions in solution was also studied by NMR spectroscopy. The addition of tetrabutylammonium salts of Cl^- or $H_2PO_4^-$ into solutions of ligands **1a–c** in MeCN-d_3 or MeCN-d_3–DMSO-d_6 (99:1) resulted in significant changes in the ^1H NMR spectra. The HC═N signals of both the free and complexed ligands could be observed separately with $\Delta\delta \sim 0.1$ ppm, the imino peak of the complex shifting upfield. As an example, from ^1H NMR dilution experiments of **1a** with tetrabutylammonium chloride in MeCN-d_3 (with 1% of DMSO-d_6), a K_{ass} of 4.2×10^2 M^{-1} was determined, which is in agreement with conductometry (Table 1).

Analogously, the addition of $Bu_4N^+H_2PO_4^-$ to solutions of **1c**, **5**, **10**, **14a,b,d,e**, and **18** in DMSO-d_6 gave two sets of HC═N, $CH_2C(O)$, and NH signals, both for the free and for the complexed ligand, indicating that the formation of kinetically stable complexes with $H_2PO_4^-$ takes place even in pure DMSO-d_6. The contribution of the C(O)NH···$H_2PO_4^-$ H-bond interaction to the

Table 1. Association Constants (K_{ass}, M^{-1}) of Functionalized UO_2 Salenes Determined by Conductometry in MeCN (99:1)[a]

anion	1a	1b	1c	5	10[b]	14a	14b	14c[c]	14d	18
$H_2PO_4^-$	1.5×10^4	1.9×10^4	2.0×10^4	1.6×10^3	6.5×10^4	1.9×10^4	$>10^5$	8.0×10^3	$>10^5$	$>10^5$
Cl^-	4.0×10^2	5.1×10^3	$<3 \times 10^2$	$<3 \times 10^2$	$<3 \times 10^2$	4.0×10^3	1.7×10^3	<5	2.9×10^3	1.2×10^4
NO_2^-	3.1×10^2	2.1×10^3	$<3 \times 10^2$	$<3 \times 10^2$	4.5×10^2	8.9×10^2	4.5×10^2	<5	4.7×10^3	1.5×10^3

[a] Tetrabutylammonium salts were used. [b] Determined in pure MeCN due to weak complexation. [c] Determined by ^1H NMR in $CDCl_3$–DMSO-d_6 (9:1) due to low solubility in MeCN and DMSO.

Table 2. Association Constants (K_{ass}, M^{-1}) for $H_2PO_4^-$ Anion Complexation with Various Ligands Determined with ^1H NMR in DMSO-d_6[a]

ligand	K_{ass}	ligand	K_{ass}	ligand	K_{ass}
1c	5.1×10^2	14a	8.4×10^2	14d	2.0×10^3
5	$<5.0 \times 10^1$	14b	8.0×10^3	14e	1.5×10^3
10	$<5.0 \times 10^1$	14c	8.0×10^3 [b]	18	1.8×10^3

[a] Tetrabutylammonium salt was used. [b] Determined in $CDCl_3$–DMSO-d_6 (9:1) due to low solubility in DMSO.

Table 3. Association Constants (K_{ass}, M^{-1}) of "Naked" Receptors Determined with ^1H NMR in DMSO-d_6[a]

anion	19a	19b	19c
malonate	80	220	*b*
succinate	165	460	150

[a] Disodium salts were used. [b] No visible changes observed in ^1H NMR spectra.

anion complexation is clearly reflected in the markedly downfield shifts $\Delta\delta = 0.7$–0.9 ppm of the NH signals for **14a,b,d,e**, and **18**. From dilution experiments the K_{ass} values of $H_2PO_4^-$ binding were calculated (Table 2). Addition of more than 1 equiv of $H_2PO_4^-$ did not influence the ^1H NMR signals of the 1:1 complex formed, which indicates that a possible, second phosphate anion is not complexed to the ligand (for the solid state, see Figure 3). Only small shifts ($\Delta\delta \simeq 0.1$ ppm) of NH protons were found for the cleft-type ligands **5** and **10**. Under the same conditions, complexation with Cl^-, HSO_4^-, SCN^-, and ClO_4^- were not observed. No changes in the ^1H NMR spectra of ligands **5**, **10**, **14a–e**, and **18** were found after addition of tetraalkylammonium salts of these anions, which indicates that very selective $H_2PO_4^-$ recognition takes place.

Analogously, in the ^{31}P NMR spectra, the addition of $Bu_4N^+H_2PO_4^-$ to solutions of **1c**, **14a,b,d,e**, and **18** in DMSO-d_6 gave two signals ($\Delta\delta = 1.9$–2.3 ppm) of $H_2PO_4^-$, both for the free and for the complexed anion, the phosphate peak of the complex shifting downfield.

Since the "naked" salophenes **19a–c** contain two free positions for coordination with guests, the complexation of the *dianions* of malonate and succinate was investigated.[26] K_{ass} values for **19a–c** and disodium salts of malonate and succinate dianions were determined by ^1H NMR dilution experiments in DMSO-d_6 (Table 3). The HC=N signals of both the free and the complexed ligand could be observed separately at 9.50–9.55 and 9.40–9.47 ppm, respectively. Under the same conditions, complexation with sodium acetate was not observed.

From Table 3 it is clear that in the cases of **19b** and **19c**, the contribution of the C(O)NH···dianion H-bond interaction increases the strength of binding significantly. In the ^1H NMR spectra, NH signals of both free ligands **19b** and **19c** and their complexes can be separately observed at 10.50 and 11.34 ppm for **19b**, respectively, and at 7.97 and 7.45 ppm and 8.05 and 7.85 ppm for **19c**, respectively. The previously described UO_2 salenes like **14a**, **14b**, and **18** do not bind dianions, as was concluded from the fact that no shifts in the ^1H NMR spectra have been observed after addition of malonate or succinate salts.

(26) ^1H and ^{31}P NMR spectra of "naked" UO_2 salophenes **19a–c**, upon titration of the salophene with *n*-$Bu_4N^+H_2PO_4^-$, show a complex complexation behavior. In this case, two different phosphate binding processes can take place, and consequently the determination of K_{ass} values is difficult.

The presence of electroactive groups in the host molecules allowed us to employ electrochemistry to investigate the complexation of anions. Electrochemical techniques have been already extensively applied to studies of complexation of cations and neutral guest molecules.[27,28] Recently, *qualitative* electrochemical experiments for the characterization of complexes of anions with bipyridinium-based[29] and cobaltizinium-containing[30] receptors have been reported. To the best of our knowledge, we report here the first *quantitative* electrochemical experiments on anion recognition by *neutral* receptors in solution.

For labile complexes, association constants can be derived from the shift of the peak potential, according to the classic de Ford–Hume method.[31] The electrochemical behavior of free ligands **1a**, **5**, and **14b** in DMSO clearly shows two reduction–reoxidation peaks in potential ranges of 0.87–1.05 and 0.80–0.98 V *vs* reference electrode used, respectively. The separation of the reduction and reoxidation peak is approximately 70–80 mV, and this value is almost independent of the scan rate (a change from 0.2 to 1.5 V/s increases the separation by 2–3 mV). There is a slight increase in anodic-to-cathodic current ratio with the increase of scan rate, which might suggest that a very slow, homogeneous reaction follows the electron transfer. The data allow the conclusion that if the scan rate is not too slow, the reaction on the electrode can be regarded as an uncomplicated reversible electron-transfer process.

Since there is a competition in the complexation between $H_2PO_4^-$, ClO_4^- (from the supporting electrolyte, see Experimental Section), and DMSO molecules, only *relative* complexation constants can be estimated, which are valid under conditions of measurements; K values of 120, <10, and 1050 M^{-1} for **1a**, **5**, and **14b**, respectively, were calculated. These values again prove the strong binding ability of functionalized salene **14b** for $H_2PO_4^-$ in comparison with simple salophene **1a**. Also in this case, complexation of cleft **5** is very weak.[32]

Studies of complexation in a DMSO–water mixture (90–10 vol %) show weak complexation constants of 20, ~0, and 40 M^{-1} for **1a**, **5**, and **14b**, respectively. This phenomenon can be explained by increasing the polarity of solution and is in agreement with conclusions published by others.[33]

Conclusions

The unique combination of a Lewis acidic UO_2 center and amide C(O)NH groups, which can form a favorable H-bond with a coordinated anion guest, in one receptor leads to highly specific $H_2PO_4^-$ anion recognition.

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(31) de Ford, D. D.; Hume, D. N. *J. Am. Chem. Soc.* **1951**, *73*, 5321–5322.
(32) Voltammograms of free ligands **19a–c** containing a "naked" cavity show the presence of two reoxidation peaks in the anodic branch, with their height ratio changing with the scan rate. It can be interpreted as an evidence of a chemical process following the reduction and leading to another electroactive species (ECE or more complicated mechanism). In these two cases, no investigation of complexation can be carried out without prior detailed mechanistic studies of the electrode reactions.
(33) Fan, E.; van Arman, S. A.; Kincaid, S.; Hamilton, A. D. *J. Am. Chem. Soc.* **1993**, *115*, 369–370.

The anion complexation has been demonstrated by X-ray analysis, conductometry, cyclic voltammetry, ^1H and ^{31}P NMR spectroscopy, and FAB mass spectrometry. In the case of the preorganized ligands **14b**, **14d**, and **18**, strong ($K_{ass} > 10^5$ M^{-1} in MeCN–DMSO, 99:1) and selective complexation of $H_2PO_4^-$ has been observed. Selectivities of $>10^2$ and $>10^3$ over Cl^- and NO_2^-, respectively, were obtained for receptor **14b**.

"Naked" UO_2 salophenes **19a–c** in which the Lewis acidic binding center contains two positions for guest coordination are good receptors for *dianions*.

Currently we are applying the functionalized UO_2 salenes for detection of $H_2PO_4^-$ anion in Chemically Modified Field Effect Transistors (CHEMFETs)[34] and as carriers in transport studies through supported liquid membranes.[35]

Experimental Section

NMR spectra were recorded in $CDCl_3$ with TMS as internal standard unless stated otherwise. Ion fast atom bombardment (FAB) mass spectra were obtained with *m*-nitrobenzyl alcohol as a matrix. Melting points are uncorrected. CH_2Cl_2 was distilled from CaH_2 and stored over molecular sieves (4 Å). CH_3CN and DMSO were dried over molecular sieves (4 Å) prior to use. Petroleum ether refers to the fraction with bp 40–60 °C. Other chemicals were of reagent grade and were used without purification. Compounds **1a**[36] and **1c**[13] were synthesized according to literature procedures. Column chromatography was performed with silica gel (Merck; 0.015–0.040 mm). All reactions were carried out in an argon atmosphere. If not stated otherwise, the organic layers were dried, after extraction from the water layer, over $MgSO_4$ and concentrated in vacuo. The presence of solvent in the analytical samples was confirmed by ^1H NMR spectroscopy.

Caution: Care should be taken when handling uranyl-containing compounds because of their toxicity and radioactivity.[37]

[[2,2′-[1,2-Phenylenebis(nitrilomethylidyne)]bis[6-nitrophenolato]]-(2–)-*N,N′,O,O′*]dioxouranium (1b). A mixture of 5-nitrosalicylaldehyde (0.79 g, 4.7 mmol) and 1,2-diaminobenzene (0.26 g, 2.4 mmol) was refluxed in MeOH–CH_2Cl_2, 2:1 (75 mL) for 0.5 h. $UO_2(OAc)_2{\cdot}2H_2O$ (1.00 g, 2.4 mmol) in MeOH (25 mL) was added, and reflux was continued for 1 h. After the mixture was cooled, water (100 mL) was added, and **1b** precipitated as an orange solid (1.49 g, 91%): mp > 300 °C; IR (KBr) 1606, 915 cm^{-1}; ^1H NMR (DMSO-d_6) δ 9.92 (s, 2 H), 8.92 (d, J = 8.5 Hz, 2 H), 8.45 (2 × d, J = 8.5 Hz, 2 H), 7.9–7.8 (m, 2 H), 7.6–7.5 (m, 2 H), 7.22 (d, J = 8.5 Hz, 2 H); MS-FAB m/z 674.1 [M^+, calcd 674.1]. Anal. Calcd for $C_{20}H_{12}N_4O_8U{\cdot}0.9H_2O$: C, 34.79; H, 2.01; N, 8.11. Found: C, 34.70; H, 2.04; N, 8.09. Karl Fischer titration calcd for $0.9H_2O$ 2.35, found, 2.60.

2-Hydroxy-2′-(methoxymethoxy)[1,1′-biphenyl] (2). A mixture of 2,2′-biphenol (3.72 g, 20 mmol), BrMOM (1.61 g, 20 mmol), and K_2CO_3 (5.52 g, 40 mmol) in MeCN (200 mL) was refluxed for 8–10 h. The solution was filtered and the solvent evaporated. After addition of water (100 mL) and acidification with 10% HCl_{aq} to pH 5, the product was extracted with CH_2Cl_2 (3 × 100 mL). Column chromatography (CH_2Cl_2) gave compound **2** as a colorless oil (3.13 g, 68%): ^1H NMR δ 7.5–7.1 (m, 8 H), 6.20 (br s, 1 H), 5.18 (s, 2 H), 3.40 (s, 3 H); ^{13}C NMR δ 153.7 (s), 153.6 (s), 132.4 (d), 129.5 (d), 129.3 (d), 128.2 (s), 126.1 (s), 123.5 (d), 120.9 (d), 117.1 (d), 116.4 (d), 95.8 (t); 56.5 (q); MS-EI m/z 230.095 (M^+, calcd 230.094). Anal. Calcd for $C_{14}H_{14}O_3$: C, 73.03; H, 6.13. Found: C, 72.78; H, 6.17.

2-Hydroxy-2′-(methoxymethoxy)[1,1′-biphenyl]-3′-carboxaldehyde (3). To a solution of **2** (2.30 g, 10 mmol) in dry THF (50 mL) was added *t*-BuLi (21 mL in 1.5 M solution in pentane, 20 mmol) at 10 °C. After the mixture was stirred for 2 h, DMF (1.53 mL, 20 mmol) was added, whereupon stirring was continued for 1 h at room temperature. The mixture was quenched with a saturated aqueous solution of NH_4Cl (10 mL) and subsequently extracted with CH_2Cl_2 (3 × 100 mL). The crude reaction mixture was purified by flash chromatography (CH_2Cl_2) to give **3** as a yellow oil (1.63 g, 63%): IR (KBr) 1684 cm^{-1}; ^1H NMR δ 10.41 (s, 1 H), 7.90 (d, J = 8.0 Hz, 1 H), 7.61 (d, J = 8.0 Hz, 1 H), 7.0–6.5 (m, 5 H), 6.27 (br s, 1 H), 4.80 (s, 2 H), 3.29 (s, 3 H); ^{13}C NMR δ 190.2 (d), 156.6 (s), 153.1 (s), 138.5 (d), 133.0 (d), 131.1 (s), 130.1 (s), 128.8 (d), 125.7 (d), 124.8 (d), 121.4 (d), 117.7 (d), 116.7 (s), 101.1 (t), 58.0 (q); MS-EI m/z 258.001 (M^+, calcd 258.000). Anal. Calcd for $C_{15}H_{14}O_4$: C, 69.76; H, 5.46. Found: C, 69.81; H, 5.44.

2-((Aminocarbonyl)methoxy)-2′-hydroxy[1,1′-biphenyl]-3′-carboxaldehyde (4). A mixture of bromoacetamide (0.70 g, 5 mmol), aldehyde **3** (1.30 g, 5 mmol), and K_2CO_3 (1.40 g, 10 mmol) in MeCN (200 mL) was refluxed for 10–12 h. The solution was filtered and the solvent evaporated. The residual oil was treated with MeOH saturated with HCl (prepared in situ from NaCl and concentrated H_2SO_4) (15 mL) and stirred for 0.5 h to remove the ortho-directing dimethyl ether group. Water (20 mL) was added, the pH was adjusted to 7 with 0.1 M NaOH, and the resulting mixture was extracted with CH_2Cl_2 (3 × 100 mL). The product was purified by flash chromatography (CH_2Cl_2–acetone, 10:1) to give **4** as a colorless solid (1.46 g, 54%): mp 114–116 °C (CH_2Cl_2–hexane); IR (KBr) 1693, 1661 cm^{-1}; ^1H NMR δ 11.56 (s, 1 H), 9.95 (s, 1 H), 7.61 (d, J = 7.9 Hz, 1 H), 7.54 (d, J = 7.9 Hz, 1 H), 7.41 (d, J = 7.9 Hz, 1 H), 7.39 (t, J = 7.9 Hz, 1 H), 7.7–7.2 (m, 2 H), 7.00 (d, J = 7.9 Hz, 1 H), 6.90 (br s, 1 H), 6.35 (br s, 1 H), 4.50 (s, 2 H); ^{13}C NMR δ 197.0 (d), 171.6 (s), 158.8 (s), 154.4 (s), 138.6 (d), 133.6 (d), 131.6 (d), 129.8 (d), 127.8 (s), 125.7 (s), 122.0 (d), 120.5 (d), 120.1 (s), 111.9 (d), 66.8 (t); MS-EI m/z 271.104 (M^+, calcd 271.105). Anal. Calcd for $C_{15}H_{13}NO_4{\cdot}0.25H_2O$: C, 65.33; H, 4.93; N, 5.08. Found: C, 65.21; H, 4.96; N, 4.85. Karl Fischer titration calcd for $0.25H_2O$, 1.63, found, 1.67.

[[3,3′-[1,2-Cyclohexanediylbis(nitrilomethylidyne)]bis[2′-((aminocarbonyl)methoxy)][1,1′-biphenyl]-2-olato]](2–)-*N,N′,O,O′*]dioxouranium (5). A solution of aldehyde **4** (0.30 g, 1.1 mmol) and 1,2-*cis*-cyclohexanediamine[18] (0.06 g, 0.55 mmol) in MeOH (100 mL) was refluxed for 1 h. Subsequently a solution of $UO_2(OAc)_2{\cdot}2H_2O$ (0.23 g, 0.55 mmol) in MeOH (10 mL) was added and refluxing was continued for 1 h. The reaction mixture was cooled to room temperature. The precipitate formed after partial evaporation of the solution was filtered and washed with MeOH (2 × 10 mL) to afford **5** as a pale orange solid (0.35 g, 71%): mp 243 °C dec; IR (KBr) 1662, 1615, 895 cm^{-1}; ^1H NMR (DMSO-d_6) δ 9.51 (s, 2 H), 7.65 (d, J = 7.5 Hz, 2 H), 7.53 (d, J = 7.5 Hz, 2 H), 7.5–7.3 (m, 4 H), 7.27 (br s, 2 H), 7.2–7.0 (m, 4 H), 6.90 (br s, 2 H), 6.74 (t, J = 7.5 Hz, 2 H), 4.6–4.5 (m, 2 H), 4.40 (s, 4 H), 2.3–2.2 (m, 2 H), 1.8–1.7 (m, 6 H); ^{13}C NMR (DMSO-d_6) δ 170.4, 168.3, 166.3, 155.7, 136.1, 134.3, 132.0, 129.5, 129.4, 128.2, 123.8, 121.0, 115.8, 112.0, 70.5, 67.0, 27.6, 21.3; MS-FAB m/z 889.4 [$(M + H)^+$, calcd 889.3]. Anal. Calcd for $C_{36}H_{34}N_4O_8U{\cdot}1.3H_2O$: C, 47.40; H, 4.04; N, 6.14. Found: C, 47.04; H, 4.15; N, 5.84. Karl Fischer titration calcd for 1.3 H_2O, 2.57, found, 2.55.

2-(2-Hydroxyethoxy)benzenecarboxamide 4-methylbenzenesulfonate (7). A solution of 2-(2-hydroxyethoxy)benzenecarboxamide[38] (2.20 g, 12 mmol), tosyl chloride (2.30 g, 12 mmol), and Et_3N (2.02 g, 20 mmol) in THF (200 mL) was stirred for 80 h at room temperature. $Et_3N{\cdot}HCl$ was filtered off, and the solvent was evaporated. Recrystallization from *i*-PrOH gave **7** as a colorless solid (3.06 g, 76%): mp 112 °C; ^1H NMR δ 8.19 (d, J = 8.0 Hz, 1 H), 7.80 (d, J = 8.0 Hz, 2 H), 7.55 (br s, 1 H), 7.40 (t, J = 8.0 Hz, 1 H), 7.31 (d, J = 8.0 Hz, 2 H), 7.10 (t, J = 8.0 Hz, 1 H), 6.85 (d, J = 8.0 Hz, 1 H), 5.77 (br s, 1 H), 4.5–4.3 (m, 4 H), 2.32 (s, 3 H); ^{13}C NMR δ 166.5 (s), 156.0 (s), 145.5 (s), 133.2 (d), 132.9 (d), 132.6 (s), 130.1 (d), 127.9 (d), 122.0 (d), 121.5 (s), 112.2 (d), 67.3 (t), 66.4 (t), 21.7 (q); MS-FAB m/z 336.0 [$(M + H)^+$, calcd 336.1]. Anal. Calcd for $C_{16}H_{17}NO_5S$: C, 57.30; H, 5.11; N, 4.18. Found: C, 57.15; H, 5.06; N, 4.09.

General Procedure for the Preparation of Acetamides 11b–d. Chloroacetyl chloride or bromoacetyl chloride (100 mmol) was added dropwise to a solution of the appropriate amine (100 mmol) and K_2CO_3 (13.80 g, 100 mmol) in EtOAc–H_2O, 1:1 (300 mL). The reaction mixture was stirred for 3 h at room temperature, whereupon the organic layer was separated and evaporated. Recrystallization of the residue from *i*-PrOH gave **11b–d** as colorless solids.

2-Chloro-*N*-(4-methylphenyl)acetamide (11b): yield 15.0 g (82%); mp 162 °C; ^1H NMR ($CDCl_3$–DMSO-d_6, 6:1) δ 9.27 (br s, 1 H), 7.13 (d, J = 8.4 Hz, 2 H), 6.77 (d, J = 8.4 Hz, 2 H), 3.79 (s, 2 H), 1.97 (s,

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(38) Faust, J. A.; Jules, L. H.; Sahyun, M. *J. Am. Pharm. Assoc.* **1956**, *45*, 514–518.

3 H); ^{13}C NMR ($CDCl_3$–DMSO-d_6, 6:1) δ 164.4 (s), 135.3 (s), 133.6 (s), 129.1 (d), 119.9 (d), 43.2 (t), 20.6 (q); MS-EI m/z 183.044 (M^+, calcd 183.045). Anal. Calcd for $C_9H_{10}ClNO$: C, 58.87; H, 5.49; N, 7.63. Found: C, 59.06; H, 5.46; N, 7.61.

2-Bromo-*N*-(*n*-octadecyl)acetamide (11c): yield 32.5 g (84%); mp 72–73 °C; ^{1}H NMR δ 6.50 (br s, 1 H), 3.88 (s, 2 H), 3.3–3.2 (m, 2 H), 1.6–1.2 (m, 32 H), 0.87 (t, J = 6.0 Hz, 3 H); ^{13}C NMR δ 165.3 (s), 40.3 (t), 31.9 (t), 29.7 (t), 29.6 (t), 29.5 (t), 29.4 (t), 29.3 (t), 26.8 (t), 22.7 (t), 14.1 (q); MS-EI m/z 388.221 (M^+, calcd 388.220). Anal. Calcd for $C_{20}H_{40}BrNO$: C, 61.66; H, 10.28; N, 3.60. Found: C, 61.77; H, 10.57; N, 3.61.

2-Chloro-*N*-[4-(*n*-octyloxy)phenyl]acetamide (11d): yield 25.2 g (85%); mp 119–120 °C; ^{1}H NMR δ 8.24 (br s, 1 H), 7.40, 6.83 (d, J = 8.0 Hz, 4 H), 4.19 (s, 2 H), 3.96 (t, J = 7.0 Hz, 2 H), 1.9–1.3 (m, 12 H), 0.91 (t, J = 7.0 Hz, 3 H); ^{13}C NMR δ 163.7 (s), 156.7 (s), 129.5 (s), 122.1 (d), 114.9 (d), 68.3 (t), 42.9 (t), 31.8 (t), 29.4 (t), 29.3 (t), 26.0 (t), 22.7 (t), 14.1 (q); MS-FAB m/z 298.2 [$(M + H)^+$, calcd 298.1]. Anal. Calcd for $C_{16}H_{24}ClNO_2$: C, 64.53; H, 8.12; N, 4.70. Found: C, 64.77; H, 8.17; N, 4.61.

General Procedure for the Preparation of Compounds 8 and 12a–d. A mixture of **7** or **11a–d** (10 mmol), 3-hydroxy-2-(2-propenoxy)benzaldehyde[19] (**6**) (1.78 g, 10 mmol), and K_2CO_3 (2.76 g, 20 mmol) in MeCN (200 mL) was refluxed for 10–12 h. The solution was filtered and the solvent evaporated. The residual solid was purified by recrystallization from *i*-PrOH to give pure **8** and **12a–d** as colorless crystals.

2-[2-(3-Formyl-2-((2-propenyl)oxy)phenoxy)ethoxy]benzenecarboxamide (8): yield 2.75 g (81%); mp 137 °C; IR (KBr) 1686 cm^{-1}; ^{1}H NMR δ 10.40 (s, 1 H), 8.20 (d, J = 8.0 Hz, 1 H), 7.83 (br s, 1 H), 7.6–7.1 (m, 5 H), 7.03 (d, J = 8.0 Hz, 1 H), 6.2–6.0 (m, 1 H), 6.00 (br s, 1 H), 5.5–5.3 (m, 2 H), 4.66 (d, J = 6.0 Hz, 2 H), 4.6–4.3 (m, 4 H); ^{13}C NMR δ 190.1 (d), 166.7 (s), 156.6 (s), 151.7 (s), 151.6 (s), 133.3 (d), 132.8 (d), 132.7 (d), 130.7 (s), 124.4 (d), 122.0 (d), 121.6 (s), 120.6 (d), 119.9 (d), 119.3 (t), 112.7 (d), 75.6 (t), 67.5 (t), 67.3 (t); MS-FAB m/z 342.2 [$(M + H)^+$, calcd 342.1]. Anal. Calcd for $C_{19}H_{19}NO_5$: C, 66.85; H, 5.61; N, 4.10. Found: C, 66.67; H, 5.72; N, 4.14.

2-[3-Formyl-2-((2-propenyl)oxy)phenoxy]acetamide (12a): yield 2.05 g (87%): mp 128 °C; IR (KBr) 1684 cm^{-1}; ^{1}H NMR δ 10.40 (s, 1 H), 7.6–7.2 (m, 3 H), 6.85 (br s, 1 H), 6.2–6.0 (m, 1 H), 6.01 (br s, 1 H), 5.5–5.3 (m, 2 H), 4.66 (d, J = 6.0 Hz, 2 H), 4.58 (s, 2 H); ^{13}C NMR δ 189.6 (d), 170.4 (s), 151.3 (s), 151.1 (s), 132.8 (d), 130.8 (s), 124.9 (d), 121.5 (d), 120.5 (d), 119.1 (t), 76.1 (t), 68.3 (t); MS-EI m/z 235.085 (M^+, calcd 235.085). Anal. Calcd for $C_{12}H_{13}NO_4 \cdot 0.15H_2O$: C, 60.57; H, 5.63; N, 5.89. Found: C, 60.30; H, 5.55; N, 5.81. Karl Fischer titration calcd for $0.15H_2O$: 1.14. Found: 1.14.

2-[3-Formyl-2-((2-propenyl)oxy)phenoxy]-*N*-(4-methylphenyl)acetamide (12b): yield 2.47 g (76%); mp 98 °C; IR (KBr) 1685 cm^{-1}; ^{1}H NMR δ 10.46 (s, 1 H), 8.60 (s, 1 H), 7.6–7.2 (m, 3 H), 7.45 (d, J = 8.0 Hz, 2 H), 7.18 (d, J = 8.0 Hz, 2 H), 6.2–6.0 (m, 1 H), 5.5–5.3 (m, 2 H), 4.74 (d, J = 6.0 Hz, 2 H), 4.66 (s, 2 H), 2.32 (s, 3 H); ^{13}C NMR δ 189.5 (d), 165.5 (s), 151.3 (s), 151.2 (s), 134.7 (s), 134.3 (s), 132.6 (d), 130.8 (s), 129.6 (d), 125.2 (d), 121.9 (d), 121.0 (d), 120.1 (d), 119.6 (t), 76.5 (t), 79.4 (t), 20.9 (q); MS-EI m/z 325.131 (M^+, calcd 325.131). Anal. Calcd for $C_{19}H_{19}NO_4 \cdot 0.4H_2O$: C, 68.62; H, 6.00; N, 4.21. Found: C, 68.79; H, 5.68; N, 4.18. Karl Fischer titration calcd for $0.4H_2O$, 2.16, found, 1.91.

2-[3-Formyl-2-((2-propenyl)oxy)phenoxy]-*N*-(*n*-octadecyl)acetamide (12c): yield 3.90 g (80%); mp 80–82 °C; ^{1}H NMR δ 10.40 (s, 1 H), 7.51 (d, J = 7.0 Hz, 1 H), 7.2–7.0 (m, 2 H), 6.82 (br s, 1 H), 6.2–6.0 (m, 1 H), 5.50–5.30 (m, 2 H), 4.66 (d, J = 6.0 Hz, 2 H), 4.50 (s, 2 H), 3.3–3.2 (m, 2 H), 1.5–1.2 (m, 33 H), 0.86 (t, J = 6.4 Hz, 3 H); ^{13}C NMR δ 189.6 (d), 167.4 (s), 152.0 (s), 151.1 (s), 132.8 (d), 130.7 (s), 125.0 (d), 121.3 (d), 120.3 (d), 118.9 (t), 76.0 (t), 68.8 (t), 39.2 (t), 31.9 (t), 29.8 (t), 29.7 (t), 29.6 (t), 29.5 (t), 29.4 (t), 29.3 (t), 26.9 (t), 22.7 (t), 14.2 (q); MS-FAB m/z 448.3 [$(M + H)^+$, calcd 488.4]. Anal. Calcd for $C_{30}H_{49}NO_4$: C, 73.88; H, 10.13; N, 2.87. Found: C, 73.83; H, 10.08; N, 2.86.

2-[3-Formyl-2-((2-propenyl)oxy)phenoxy]-*N*-[4-(*n*-octyloxy)phenyl]acetamide (12d): yield 3.25 g (74%); mp 95 °C; ^{1}H NMR δ 10.42 (s, 1 H), 8.54 (br s, 1 H), 7.6–7.3 (m, 3 H), 7.45 (d, J = 8.0 Hz, 2 H), 6.85 (d, J = 8.0 Hz, 2 H), 6.2–6.0 (m, 1 H), 5.5–5.3 (m, 2 H), 4.69 (d, J = 6.0 Hz, 2 H), 4.67 (s, 2 H), 3.93 (t, J = 6.5 Hz, 2 H), 1.9–1.2 (m, 12 H), 0.88 (t, J = 6.5 Hz, 3 H); MS-FAB m/z 440.1 [$(M + H)^+$, calcd 440.2]. Anal. Calcd for $C_{26}H_{33}NO_5 \cdot 0.1H_2O$: C, 70.76; H, 7.58; N, 3.17. Found: C, 70.36; H, 7.60; N, 3.08. Karl Fischer titration calcd for $0.1H_2O$, 0.41, found, 0.18.

***N,N'*-[1,2-Ethanediylbis(oxy-2,1-ethanediyl)]bis(2-bromoacetamide) (15)**. To a solution of 2-bromoacetyl chloride (7.80 g, 50 mmol) in THF (100 mL) was added dropwise a solution of 1,8-diamino-3,6-dioxaoctane (3.70 g, 25 mmol) and Et_3N (5.05 g, 50 mmol) in THF (25 mL) at 10 °C. The reaction mixture was stirred for 4 h at room temperature and subsequently diluted with water (100 mL). The product was extracted with CH_2Cl_2 (3 × 75 mL). Recrystallization of the residue from toluene gave **15** as a colorless solid (5.55 g, 57%): mp 84–85 °C; ^{1}H NMR δ 6.92 (br s, 2 H), 3.91 (s, 4 H), 3.63 (s, 4 H), 3.6–3.3 (m, 8 H); ^{13}C NMR δ 168.0 (s), 70.6 (t), 69.1 (t), 40.0 (t), 30.0 (t), 29.3 (t); MS-FAB m/z 391.0 [$(M + H)^+$, calcd 390.8). Anal. Calcd for $C_{10}H_{18}Br_2N_2O_4$: C, 30.79; H, 4.65; N, 7.18. Found: C, 31.04; H, 4.71; N, 7.11.

***N,N'*-[1,2-Ethanediylbis(oxy-2,1-ethanediyl)]bis[2-(3-formyl-2-((2-propenyl)oxy)phenoxy)acetamide] (16)**. A mixture of **15** (1.10 g, 2.8 mmol), 3-hydroxy-2-(2-propenoxy)benzaldehyde (**6**) (1.00 g, 5.6 mmol), and K_2CO_3 (1.55 g, 11.2 mmol) in MeCN (200 mL) was refluxed for 10–12 h. The solution was filtered and the solvent evaporated. The residue was purified by flash chromatography (CH_2Cl_2–acetone, 1:1) to give **16** as a colorless solid (1.29 g, 79%): mp 98–102 °C (CH_2Cl_2–hexane); IR (KBr) 1693, 1653 cm^{-1}; ^{1}H NMR δ 10.46 (s, 2 H), 7.50 (d, J = 8.0 Hz, 2 H), 7.2–7.0 (m, 6 H), 6.1–6.0 (m, 2 H), 5.4–5.3 (m, 4 H), 4.61 (d, J = 6.0 Hz, 4 H), 4.53 (s, 4 H), 3.7–3.4 (m, 12 H); ^{13}C NMR δ 189.7 (d), 168.0 (s), 151.2 (s), 151.0 (s), 133.0 (d), 130.8 (s), 124.7 (d), 121.2 (d), 120.2 (d), 76.0 (t), 70.4 (t), 69.7 (t), 68.5 (t), 38.0 (t); MS-FAB m/z 585.3 [$(M + H)^+$, calcd 585.2]. Anal. Calcd for $C_{30}H_{36}N_2O_{10}$: C, 61.63; H, 6.21; N, 4.79. Found: C, 61.66; H, 6.37; N, 4.87.

General Procedure for the Deallylation[20] of Aldehydes 8, 12a–d, and 16. Formation of Aldehydes 9, 13a–d, and 17. A mixture of **8**, **12a–d**, or **16** (3 mmol), $Pd(OAc)_2$ (20 mg, 0.1 mmol), PPh_3 (125 mg, 0.5 mmol), Et_3N (3.7 g, 37 mmol), and HCOOH (1.65 g, 37 mmol) in 80% aqueous EtOH (60 mL) was refluxed for 1 h. The solvent was evaporated, and the total water volume was adjusted to 100 mL. The product was extracted with CH_2Cl_2 (3 × 100 mL). The crude mixture was purified by flash chromatography (acetone) to give **9**, **13a–c** as yellow solids and **13d** and **17** as oils.

2-[2-(3-Formyl-2-hydroxyphenoxy)ethoxy]benzenecarboxamide (9): yield 0.56 g (62%); mp 172–174 °C ($CHCl_3$); IR (KBr) 1663 cm^{-1}; ^{1}H NMR (DMSO-d_6) δ 10.25 (s, 1 H), 7.85 (d, J = 7.6 Hz, 1 H), 7.64 (s, 1 H), 7.56 (s, 1 H), 7.50 (t, J = 7.1 Hz, 1 H), 7.32 (d, J = 7.1 Hz, 2 H), 7.15 (d, J = 7.6 Hz, 1 H), 7.08 (t, J = 7.6 Hz, 1 H), 6.93 (t, J = 7.6 Hz, 1 H), 4.6–4.3 (m, 4 H); ^{13}C NMR (DMSO-d_6) δ 196.6 (d), 166.1 (s), 156.3 (s), 151.0 (s), 147.2 (s), 132.5 (d), 131.0 (d), 122.9 (s), 122.5 (s), 121.5 (d), 120.8 (d), 119.6 (d), 119.2 (d), 113.2 (d), 67.5 (t), 67.1 (t); MS-FAB m/z 301.7 [$(M + H)^+$, calcd 301.1]. Anal. Calcd for $C_{16}H_{15}NO_5 \cdot 0.5H_2O$: C, 61.93; H, 5.20; N, 4.51. Found: C, 61.73; H, 4.92; N, 4.42. Karl Fischer titration calcd for $0.5H_2O$, 3.00, found, 2.81.

2-(3-Formyl-2-hydroxyphenoxy)acetamide (13a): yield 0.32 g (55%); mp 132–133 °C (CH_2Cl_2–hexane); IR (KBr) 1696, 1652 cm^{-1}; ^{1}H NMR (acetone-d_6) δ 10.18 (s, 1 H), 7.46 (d, J = 8.0 Hz, 1 H), 7.34 (d, J = 8.0 Hz, 1 H), 7.30 (br s, 1 H), 7.00 (t, J = 8.0 Hz, 1 H), 6.92 (br s, 1 H), 4.55 (s, 2 H); ^{13}C NMR (acetone-d_6) δ 193.3 (d), 170.4 (s), 151.2 (s), 146.2 (s), 123.3 (s), 122.4 (d), 119.7 (d), 119.3 (d), 68.3 (t); MS-EI m/z 195.054 (M^+, calcd 195.053). Anal. Calcd for $C_9H_9NO_4 \cdot 0.6H_2O$: C, 52.48; H, 4.99; N, 6.80. Found: C, 52.23; H, 4.67; N, 6.63. Karl Fischer titration calcd for $0.6H_2O$, 8.74, found, 8.66.

2-(3-Formyl-2-hydroxyphenoxy)-*N*-(4-methylphenyl)acetamide (13b): yield 0.45 g (53%); mp 84–85 °C (CH_2Cl_2–hexane); IR (KBr) 1688, 1665 cm^{-1}; ^{1}H NMR δ 11.35 (s, 1 H), 9.91 (s, 1 H), 8.87 (s, 1 H), 7.53 (d, J = 8.0 Hz, 2 H), 7.31 (d, J = 7.7 Hz, 1 H), 7.20 (d, J = 7.7 Hz, 1 H), 7.12 (d, J = 8.0 Hz, 2 H), 7.00 (t, J = 7.7 Hz, 1 H), 4.67 (s, 2 H), 2.31 (s, 3 H); ^{13}C NMR δ 196.7 (d), 166.0 (s), 152.2 (s), 146.5 (s), 134.5 (s), 134.4 (s), 129.6 (s), 127.5 (d), 123.0 (d), 121.5 (d), 120.1 (d), 120.0 (d), 70.4 (t), 20.9 (q); MS-EI m/z 285.101 (calcd 285.100). Anal. Calcd for $C_{16}H_{15}NO_4 \cdot 0.6H_2O$: C, 64.90; H, 5.51; N, 4.73. Found: C, 64.62; H, 5.41; N, 4.55. Karl Fischer titration calcd for $0.6H_2O$, 3.64, found, 3.52.

2-(3-Formyl-2-hydroxyphenoxy)-*N*-(*n*-octadecyl)acetamide (13c): yield 1.29 g (96%); mp 75–77 °C (hexane); ^{1}H NMR δ 9.92 (s, 1 H), 7.23 (d, J = 8.0 Hz, 1 H), 7.00 (d, J = 8.0 Hz, 1 H), 6.95 (t, J = 8.0 Hz, 1 H), 4.53 (s, 2 H), 3.4–3.2 (m, 2 H), 1.5–1.2 (m, 32 H), 0.84 (t, J = 7.0 Hz; 3 H); ^{13}C NMR δ 196.4 (d), 167.8 (s), 152.1 (s), 146.5 (s), 126.6 (d), 121.9 (d), 121.5 (s), 119.8 (d), 69.6 (t), 39.1 (t), 29.7–29.3 (15 × t), 26.8 (t), 22.7 (t), 14.1 (q); MS-FAB m/z 448.6 [$(M + H)^+$, calcd 448.3]. Anal. Calcd for $C_{27}H_{45}NO_4$: C, 72.44; H, 10.13; N, 3.13. Found: C, 72.33; H, 10.03; N, 2.86.

2-(3-Formyl-2-hydroxyphenoxy)-*N*-[4-(*n*-octyloxy)phenyl]acetamide (13d):[39] yield 1.12 g (94%); ^{1}H NMR δ 10.16 (br s, 1 H), 9.95 (s, 1 H), 9.15 (br s, 1 H), 7.44 (d, J = 8.5 Hz, 2 H), 7.28 (d, J = 8.0 Hz, 1 H), 7.08 (d, J = 8.0 Hz, 1 H), 6.88 (t, J = 8.0 Hz, 1 H), 6.78 (d, J = 8.5 Hz, 2 H), 4.58 (s, 2 H), 3.88 (t, J = 6.5 Hz, 2 H), 1.9–1.2 (m, 12 H), 0.87 (t, J = 6.5 Hz, 3 H); MS-FAB m/z 399.2 [$(M + H)^+$, calcd for $C_{23}H_{30}NO_5$ 399.2].

***N,N'*-[1,2-Ethanediylbis(oxy-2,1-ethanediyl)]bis[2-(3-formyl-2-hydroxyphenoxy)acetamide] (17)**:[39] yield 0.86 g (57%); IR (KBr) 1672, 1654 cm^{-1}; ^{1}H NMR δ 11.10 (br s, 2 H), 9.90 (s, 2 H), 7.45 (br s, 2 H), 7.22 (d, J = 8.0 Hz, 2 H), 7.09 (d, J = 8.0 Hz, 2 H), 6.93 (t, J = 8.0 Hz, 2 H), 4.52 (s, 4 H), 3.7–3.5 (m, 12 H); ^{13}C NMR δ 196.4 (s), 169.1 (s), 152.0 (s), 149.4 (s), 126.7 (s), 122.0 (d), 121.4 (d), 119.8 (d), 70.4 (t), 69.7 (t), 69.6 (t), 38.9 (t); MS-FAB m/z 505.9 [$(M + H)^+$, calcd for $C_{24}H_{29}N_2O_{10}$ 505.2].

General Procedure for the Synthesis of UO_2 Salenes 10 and 14a–d. A solution of aldehyde **9**, **13a–d** (1.3 mmol), and *cis*-1,2-cyclohexanediamine (0.07 g, 0.65 mmol) in MeOH (100 mL) was refluxed for 1 h. Subsequently a solution of $UO_2(OAc)_2{\cdot}2H_2O$ (0.28 g, 0.65 mmol) in MeOH (10 mL) was added, and refluxing was continued for 1 h. After the solution was cooled, the precipitate formed was filtered off and washed with MeOH (2 × 10 mL) to give **10**, **14a–d** as orange or red solids.

[[2,2'-Bis[1,2-cyclohexanediylbis(nitrilomethylidyne)]-6,6'-bis[2-(2-(aminocarbonyl)phenoxy)ethoxy]phenolato](2–)-*N,N',O,O'*]dioxouranium (10): yield 0.31 g (51%); mp 200–202 °C; IR (KBr) 1685, 1617, 904 cm^{-1}; ^{1}H NMR (DMSO-d_6) δ 9.46 (s, 2 H), 7.7–7.1 (m, 14 H), 7.08 (t, J = 7.4 Hz, 2 H), 6.63 (t, J = 7.4 Hz, 2 H), 4.8–4.4 (m, 10 H), 2.6–2.5 (m, 2 H), 2.0–1.7 (m, 6 H); ^{13}C NMR (DMSO-d_6) δ 168.0 (d), 166.1 (s), 160.1 (s), 156.4 (s), 149.2 (s), 132.7 (d), 131.0 (d), 128.0 (d), 124.5 (s), 122.7 (s), 120.9 (d), 120.4 (d), 115.6 (d), 113.4 (d), 72.0 (d), 67.9 (t), 67.7 (t), 28.1 (t), 21.4 (t); MS-FAB m/z 947.0 [$(M + H)^+$, calcd 947.3]. Anal. Calcd for $C_{38}H_{38}N_4O_{10}U{\cdot}2.2H_2O$: C, 46.18; H, 4.32; N, 5.67. Found: C, 45.86; H, 4.00; N, 5.52. Karl Fischer titration calcd for $2.2H_2O$, 4.00, found, 3.84.

[[2,2'-[1,2-Cyclohexanediylbis[nitrilomethylidyne(2-hydroxy-3,1-phenylene)oxy]]bis[acetamidato]](2–)-*N,N',O,O'*]dioxuranium (14a): yield 0.37 g (77%); mp > 265 °C; IR (KBr) 1666, 1615, 900 cm^{-1}; ^{1}H NMR (DMSO-d_6) δ 9.32 (s, 2 H), 8.05 (br s, 2 H), 7.46 (br s, 2 H), 7.30 (d, J = 8.0 Hz, 4 H), 6.61 (t, J = 8.0 Hz, 2 H), 4.67 (s, 4 H), 4.7–4.6 (m, 2 H), 2.4–2.3 (m, 2 H), 2.0–1.7 (m, 6 H); MS-FAB m/z 737.5 [$(M + H)^+$, calcd 737.2]. Anal. Calcd for $C_{24}H_{26}N_4O_8U{\cdot}2.0H_2O$: C, 37.31; H, 3.91; N, 7.25. Found: C, 36.91; H, 3.66; N, 7.11. Karl Fischer titration calcd for $2.0H_2O$, 4.66, found, 4.41.

[[2,2'-[1,2-Cyclohexanediylbis[nitrilomethylidyne(2-hydroxy-3,1-phenylene)oxy]]bis[*N*-(4-methylphenyl)acetamidato]](2–)-*N,N',O,O'*]dioxouranium (14b): yield 0.47 g (79%); mp 294–251 °C; IR (KBr) 1685, 1617, 904 cm^{-1}; ^{1}H NMR (DMSO-d_6) δ 10.55 (s, 2 H), 9.50 (s, 2 H), 7.60 (d, J = 8.0 Hz, 4 H), 7.55, 7.45 (d, J = 8.0 Hz, 4 H), 6.95 (d, J = 8.0 Hz, 4 H), 6.73 (t, J = 8.0 Hz, 2 H), 5.02 (s, 4 H), 4.7–4.6 (m, 2 H), 2.5–2.4 (m, 2 H), 2.33 (s, 6 H), 2.0–1.7 (m, 6 H); ^{13}C NMR (DMSO-d_6) δ 169.0 (d), 167.5 (s), 160.0 (s), 149.6 (s), 135.6 (s), 132.5 (s), 129.0 (d), 128.7 (d), 125.0 (s), 121.8 (d), 119.7 (d), 115.0 (d), 71.0 (t), 70.5 (d), 27.3 (t), 21.5 (t), 20.3 (q); MS-FAB m/z 917.8 [$(M + H)^+$, calcd 917.3]. Anal. Calcd for $C_{38}H_{38}N_4O_8U{\cdot}1.35H_2O$: C, 48.50; H, 4.36; N, 5.95. Found: C, 48.90; H, 4.11; N, 5.98. Karl Fischer titration calcd for $1.35H_2O$, 2.60, found, 2.91.

[[2,2'-[1,2-Cyclohexanediylbis[nitrilomethylidyne(2-hydroxy-3,1-phenylene)oxy]]bis[*N*-(*n*-octadecyl)acetamidato]](2–)-*N,N',O,O'*]dioxouranium (14c): yield 0.69 g (86%); mp 90–92 °C; IR (KBr) 1686, 1616, 904 cm^{-1}; ^{1}H NMR ($CDCl_3$–DMSO-d_6, 9:1) δ 9.00 (s, 2 H), 8.56 (br s, 2 H), 6.97 (d, J = 8.0 Hz, 4 H), 6.31 (t, J = 8.0 Hz, 2 H), 4.33 (s, 4 H), 4.3–4.2 (m, 2 H), 3.4–3.3 (m, 4 H), 2.2–1.2 (m, 70 H), 0.84 (t, J = 7.0 Hz, 6 H); ^{13}C NMR ($CDCl_3$–DMSO-d_6, 9:1); δ 165.9 (d), 164.2 (s), 157.7 (s), 154.5 (s), 149.5 (s), 128.6 (d), 121.0 (d), 116.2 (d), 71.1 (t), 70.1 (d), 67.3 (t), 35.2–20.4 (18 × t), 13.5 (q); MS-FAB m/z 1239.4 [$(M - H)^-$, calcd 1239.8]. Anal. Calcd for $C_{60}H_{98}N_4O_8U{\cdot}1H_2O$: C, 57.22; H, 8.00; N, 4.45. Found: C, 56.91; H, 7.88; N, 4.36. Karl Fischer titration calcd for $1H_2O$, 1.40, found, 1.40.

[[2,2'-[1,2-Cyclohexanediylbis[nitrilomethylidyne(2-hydroxy-3,1-phenylene)oxy]]bis[*N*-(4-(*n*-octyloxy)phenyl)acetamidato]](2–)-*N,N',O,O'*]dioxouranium (14d): yield 0.66 g (89%); mp 158–160 °C; IR (KBr) 1684, 1616, 906 cm^{-1}; ^{1}H NMR (DMSO-d_6) δ 10.51 (s, 2 H), 9.53 (s, 2 H), 7.66 (d, J = 8.5 Hz, 4 H), 7.45 (d, J = 8.0 Hz, 4 H), 6.8–6.6 (m, 6 H), 4.99 (s, 4 H), 4.8–4.7 (m, 2 H), 3.83 (t, J = 6.0 Hz, 4 H), 2.4–1.7 (m, 8 H), 1.6–1.3 (m, 24 H), 0.87 (t, J = 6.0 Hz, 6 H); ^{13}C NMR (DMSO-d_6) δ 167.9 (d), 167.2 (s), 159.8 (s), 154.8 (s), 149.5 (s), 131.4 (s), 128.7 (d), 124.6 (s), 121.9 (d), 121.1 (d), 116.1 (d), 114.2 (d), 70.9 (t), 70.1 (d), 67.4 (t), 31.2–21.4 (8 t), 13.9 (q); MS-FAB m/z 1145.5 [$(M + H)^+$, calcd 1145.5]. Anal. Calcd for $C_{52}H_{66}N_4O_{10}U{\cdot}4H_2O$: C, 51.31; H, 6.13; N, 4.60. Found: C, 51.54; H, 5.87; N, 4.79. Karl Fischer titration calcd for $4H_2O$, 6.00, found, 6.15.

[[2,2'-[1,2-Phenylenebis[nitrilomethylidyne(2-hydroxy-3,1-phenylene)oxy]]bis[*N*-(4-methylphenyl)acetamidato]](2–)-*N,N',O,O'*]dioxouranium (14e) was synthesized analogously to **14b**, except 1,2-benzenediamine was used instead of *cis*-1,2-cyclohexanediamine: yield 0.38 g (64%); mp 260 °C; IR (KBr) 1676, 1604, 904 cm^{-1}; ^{1}H NMR (DMSO-d_6) δ 10.59 (s, 2 H), 9.70 (s, 2 H), 8.0–7.9 (m, 2 H), 7.65 (d, J = 8.0 Hz, 4 H), 7.58 (d, J = 8.0 Hz, 2 H), 7.6–7.5 (m, 2 H), 7.51 (d, J = 8.0 Hz, 2 H), 6.99 (d, J = 8.0 Hz, 4 H), 6.74 (t, J = 8.0 Hz, 2 H), 4.99 (s, 4 H), 2.20 (s, 6 H); ^{13}C NMR (DMSO-d_6) δ 167.4 (s), 166.9 (d), 160.9 (s), 149.9 (s), 146.6 (s), 135.8 (s), 132.6 (s), 129.8 (d), 129.0 (d), 125.0 (s), 122.9 (d), 120.4 (d), 119.6 (d), 119.5 (d), 116.6 (d), 71.0 (t), 20.4 (q); MS-FAB m/z 911.8 [$(M + H)^+$, calcd 911.3]. Anal. Calcd for $C_{38}H_{32}N_4O_8U{\cdot}1.5H_2O$: C, 48.67; H, 3.76; N, 5.97. Found: C, 48.27; H, 3.57; N, 5.71. Karl Fischer titration calcd for $1.5H_2O$, 2.88, found, 2.91.

[12,13,15,16,19,20,30a,31,32,33,34,34a-Dodecahydro-35,36-dihydroxy-3,7:24,28-dimetheno-9*H*,18*H*-8,14,17,23,1,11,20,30-benzotetraoxatetraazacyclodotriacontine-10,21(11*H*,22*H*)dionato(2–)-N^1,N^{30},O^{35},O^{36}]-dioxouranium (18). To a refluxing solution of $Ba(OTf)_2$[40] (0.7 g, 1.6 mmol) in MeOH (200 mL) were added separate solutions of **17** (0.4 g, 0.8 mmol) in MeOH (30 mL) and 1,2-*cis*-cyclohexanediamine (0.09 g, 0.8 mmol) in MeOH (30 mL) in 0.5 h. After 0.5 h, a solution of $UO_2(OAc)_2{\cdot}2H_2O$ (0.34 g, 0.8 mmol) in MeOH (10 mL) was added, and reflux was maintained for another 0.5 h. The reaction mixture was evaporated in vacuo and washed with a large amount of H_2O. Recrystallization from MeOH gave pure **18** as an orange solid (0.4 g, 59%): mp 240–241 °C; IR (KBr) 1671, 1617, 901 cm^{-1}; ^{1}H NMR (DMSO-d_6) δ 9.50 (s, 2 H), 8.68 (br s, 2 H), 7.41 (d, J = 7.9 Hz, 4 H), 6.69 (t, J = 7.9 Hz, 2 H), 4.72 (d, J = 4.4 Hz, 4 H), 4.6–4.5 (m, 2 H), 3.6–3.4 (m, 12 H), 2.2–2.1 (m, 2 H), 1.9–1.6 (m, 6 H); ^{13}C NMR (DMSO-d_6) δ 169.8 (s), 169.2 (d), 159.6 (s), 149.6 (s), 128.8 (d), 124.6 (s), 121.6 (d), 116.0 (d), 70.8 (t), 70.5 (d), 69.7 (t), 68.8 (t), 38.7 (t), 27.6 (t), 21.3 (t); MS-FAB m/z 851.5 [$(M + H)^+$, calcd 851.0]. Anal. Calcd for $C_{30}H_{36}N_4O_{10}U{\cdot}2H_2O$: C, 40.64; H, 4.55; N, 6.32. Found: C, 40.77; H, 4.49; N, 6.19. Karl Fischer titration calcd for $2H_2O$, 4.05, found, 4.12.

General Procedure for the Synthesis of "Naked" UO_2 Salophenes 19a–c. A mixture of salicyl aldehyde, **9** or **13b** (5 mmol), and 2-aminophenol (0.55 g, 5 mmol) was refluxed in MeOH (50 mL) for 1 h. Subsequently a solution of $UO_2(OAc)_2{\cdot}2H_2O$ (2.12 g, 5 mmol) in MeOH (10 mL) was added, and refluxing was continued for another 1 h. The precipitate formed was filtered off and washed with MeOH (15 mL) to afford deep, dark crystals of **19a–c**.

[[2-[1-(Nitrilomethylidyne)-2-oxyphenylene]phenolato](2–)-*N,O,O'*]-dioxouranium (19a)·2MeOH: yield 2.36 g (98%); mp > 290 °C; IR (KBr) 902 cm^{-1}; ^{1}H NMR (DMSO-d_6) δ 9.53 (s, 1 H), 7.7–6.5 (m, 8 H), 4.12 (q, J = 5.2 Hz, 2 H), 3.19 (d, J = 5.2 Hz, 6 H); ^{13}C NMR (DMSO-d_6) δ 169.1 (s), 167.0 (s), 159.9 (d), 142.2 (s), 135.4 (d), 134.6 (d), 129.0 (d), 124.8 (s), 120.5 (d), 119.2 (d), 116.9 (d), 116.2 (d), 116.0 (d), 48.6 (q); MS-FAB m/z 481.0 [$(M + H)^+$, calcd 481.1]. Anal. Calcd for $C_{13}H_9NO_4U{\cdot}2CH_3OH{\cdot}1.3H_2O$: C, 31.68; H, 3.47; N, 2.46. Found: C, 31.77; H, 3.06; N, 2.49. Karl Fischer titration calcd for $1.3H_2O$, 4.00, found, 4.05.

[[2-[1-(Nitrilomethylidyne)-2-oxyphenylene]-6-[(*N*-(4-methylphenyl)-aminocarbonyl)methoxy]phenolato](2–)-*N,O,O'*-]dioxouranium (19b): yield 3.09 g (96%); mp > 290 °C; IR (KBr) 905 cm^{-1}; ^{1}H NMR (DMSO-d_6) δ 10.56 (s, 1 H), 7.8–7.6 (m, 3 H), 7.50, 7.48 (d, J = 8.0 Hz, 2 H), 7.25 (t, J = 8.0 Hz, 1 H), 7.00 (d, J = 8.0 Hz, 2 H), 6.89 (d, J = 8.0 Hz, 1 H), 6.6–6.5 (m, 2 H), 5.05 (s, 2 H), 2.20 (s, 3 H); MS-FAB m/z 645.3 [$(M + H)^+$, calcd 645.2]. Anal. Calcd for $C_{22}H_{18}N_2O_6U{\cdot}2.5H_2O$: C, 38.33; H, 3.36; N, 4.06. Found: C, 38.30; H, 3.20; N, 3.86. Karl Fischer titration calcd for $2.5H_2O$, 6.50, found, 6.24.

[[2-[1-(Nitrilomethylidyne)-2-oxyphenylene]-6-[2-(2-(aminocarbonyl)-phenoxy)ethoxy]phenolato](2–)-*N,O,O'*]dioxouranium (19c): yield 2.99

(39) No satisfactory elemental analysis could be obtained due to slow decomposition.

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

Table 4. Crystal Data and Data Collection Parameters

formula	**1c**·*n*-$Bu_4N^+H_2PO_4^-$·MeCN	**14e**·2(*n*-$Bu_4N^+H_2PO_4^-$)·3MeCN	**14b**·MeOH	**19a**·2(*n*-$Bu_4N^+H_2PO_4^-$)·MeCN
lattice type	triclinic	triclinic	triclinic	monoclinic
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P2_1/c$
T, K	170	170	195	160
scan width (ω)	1.4 + 0.34 tan θ	1.1 + 0.34 tan θ	1.1 + 0.35 tan θ	1.1 + 0.34 tan θ
cell dimensions				
a, Å	9.569(2)	12.461(2)	13.311(3)	16.366(3)
b, Å	13.190(3)	15.532(1)	14.034(4)	22.891(2)
c, Å	18.423(2)	22.440(3)	21.242(7)	15.280(3)
α, deg	90.22(1)	82.40(1)	96.45(3)	90
β, deg	102.48(1)	76.77(1)	96.93(4)	104.96(1)
γ, deg	106.18(0)	84.76(2)	100.18(5)	90
V, Å^3	2175(1)	4182(1)	3841(5)	5530(3)
Z	2	2	4	4
D_c, g cm^{-3}	1.56	1.36	1.67	1.44
no. of unique obsd data ($F^2 > 3\sigma F^2$)	6446	5468	5848	5368
no. of variables	505	472	435	320
R, %	5.1	8.4	8.5	5.5
R_w, %	6.7	10.1	7.7	6.6

g (91%); mp > 290 °C; IR (KBr) 917 cm^{-1}; ^{1}H NMR (DMSO-d_6) δ 9.54 (s, 1 H), 7.94 (br s, 1 H), 7.38 (br s, 1 H), 7.9–6.6 (m, 11 H), 4.8–4.6 (m, 4 H), 4.11 (q, J = 5.0 Hz, 1 H), 3.12 (d, J = 5.0 Hz, 3 H); ^{13}C NMR (DMSO-d_6) δ 166.9, 166.1, 160.5, 159.9, 156.4, 149.6, 142.2, 132.7, 131.1, 129.1, 128.5, 125.4, 122.8, 121.0, 120.0, 119.2, 117.0, 116.0, 115.4, 113.5, 67.8, 67.7, 48.7; MS-FAB m/z 658.7 [(M – H)$^+$, calcd 659.0]. Anal. Calcd for $C_{22}H_{18}N_2O_7U{\cdot}CH_3OH$: C, 39.89; H, 3.20; N, 4.06. Found: C, 39.63; H, 2.82; N, 4.02.

General Procedure for the Preparation of Solid Complexes. A mixture of **1a** (5 mmol) and Et_4NCl (5 mmol), or **1c**, **14a**, **14b**, **14e**, and **18** (5 mmol) and *n*-$Bu_4NH_2PO_4$ (5 mmol), or **14e**, **19a** (5 mmol), and *n*-$Bu_4NH_2PO_4$ (10 mmol) in MeCN (25 mL) was stirred for 10 h at room temperature. The solvent was evaporated to afford orange solids.

[[2,2′-[1,2-Phenylenebis(nitrilomethylidyne)]bisphenolato](2–)-*N,N′,O,O′*]dioxouranium (1a)·Et_4NCl: mp 275–278 °C, ^{1}H NMR (MeCN-d_3) δ 9.33 (s, 2 H), 7.6–7.4 (m, 4 H), 6.91 (d, J = 8.0 Hz, 4 H), 6.60 (t, J = 8.0 Hz, 2 H), 3.46 (q, J = 6.0 Hz, 8 Hz), 0.97 (t, J = 6.0 Hz, 12 H); MS-FAB m/z 618.8 [(M – H)$^-$, calcd 618.1]. Anal. Calcd for $C_{28}H_{39}ClN_3O_4U$: C, 44.84; H, 4.56; N, 5.60. Found: C, 44.65; H, 4.58; N, 5.58.

[[2,2′-[1,2-Phenylenebis(nitrilomethylidyne)]bis(6-methoxyphenolato)](2–)-*N,N′,O,O′*]dioxouranium (1c)·*n*-$Bu_4NH_2PO_4$: mp 125–128 °C; ^{1}H NMR ($CDCl_3$–MeCN-d_3, 6:1) δ 9.21 (s, 2 H), 7.5–7.3 (m, 4 H), 7.15, 7.04 (d, J = 8.0 Hz, 4 H), 6.51 (t, J = 8.0 Hz, 2 H), 4.09 (s, 6 H), 3.2–3.1 (m, 8 H), 1.8–1.4 (m, 16 H), 0.85 (t, J = 7.2 Hz, 12 H); ^{31}P NMR (DMSO-d_6) δ 0.65; MS-FAB m/z 740.9 [(M – H)$^-$, calcd 741.0 (for **1c** + $H_2PO_4^-$)]. Anal. Calcd for $C_{38}H_{56}N_3O_{10}PU{\cdot}1H_2O$: C, 45.56; H, 5.83; N, 4.19. Found: C, 45.53; H, 5.72; N, 4.08. Karl Fischer titration calcd for 1H_2O, 1.80, found, 1.76.

[[2,2′-[1,2-Cyclohexanediylbis[nitrilomethylidyne(2-hydroxy-3,1-phenylene)oxy]]bis[acetamidato]](2–)-*N,N′,O,O′*]dioxouranium (14a)·*n*-$Bu_4NH_2PO_4$: mp 100–103 °C; ^{1}H NMR (DMSO-d_6) δ 9.40 (s, 2 H), 8.41 (br s, 2 H), 7.29, 7.26 (d, J = 8.0 Hz, 4 H), 6.60 (t, J = 8.0 Hz, 2 H), 4.91 (s, 4 H), 4.6–4.5 (m, 2 H), 3.2–3.1 (m, 8 H), 2.5–2.4 (m, 2 H), 2.1–1.5 (m, 22 H), 0.93 (t, J = 7.2 Hz, 12 H); ^{31}P NMR (DMSO-d_6) δ 0.50; MS-FAB m/z 734.9, 832.9, 1075.2 [(M – H)$^-$, calcd 735.2 (**14a**), 832.2 (**14a** + $H_2PO_4^-$), 1074.5 (**14a** + $Bu_4NH_2PO_4$), respectively]. Anal. Calcd for $C_{40}H_{64}N_5O_{12}PU$: C, 44.65; H, 6.00; N, 6.51. Found: C, 44.28; H, 5.78; N, 6.37.

[[2,2′-[1,2-Cyclohexanediylbis[nitrilomethylidyne(2-hydroxy-3,1-phenylene)oxy]]bis[*N*-(4-methylphenyl)acetamidato]](2–)-*N,N′,O,O′*]dioxouranium (14b)·*n*-$Bu_4NH_2PO_4$: mp 120–123 °C; ^{1}H NMR (DMSO-d_6) δ 11.12 (br s, 2 H), 9.41 (s, 2 H), 7.63 (d, J = 8.0 Hz, 4 H), 7.31, 7.29 (d, J = 8.0 Hz, 4 H), 6.96 (d, J = 8.0 Hz, 4 H), 6.61 (t, J = 8.0 Hz, 2 H), 5.28 (s, 4 H), 4.7–4.6 (m, 2 H), 3.2–3.1 (m, 8 H), 2.5–2.4 (m, 2 H), 2.21 (s, 6 H), 2.1–1.4 (m, 22 H), 0.95 (t, J = 7.2 Hz, 12 H); ^{31}P NMR (DMSO-d_6) δ 0.59; MS-FAB m/z 914.4, 1012.3, 1254.3 [(M – H)$^-$, calcd 915.3 (**14b**), 1012.3 (**14b** + $H_2PO_4^-$), 1254.6 (**14b** + $Bu_4NH_2PO_4$), respectively]. Anal. Calcd for $C_{54}H_{76}N_5O_{12}PU{\cdot}1.8H_2O$: C, 50.33; H, 6.23; N, 5.43. Found: C, 50.54; H, 6.05; N, 5.36. Karl Fischer titration calcd for 1.8H_2O, 2.50, found, 2.53.

[[2,2′-[1,2-Phenylenebis[nitrilomethylidyne(2-hydroxy-3,1-phenylene)oxy]]bis[*N*-(4-methylphenyl)acetamidato]](2–)-*N,N′,O,O′*]dioxouranium (14e)·*n*-$Bu_4NH_2PO_4$: mp 131–135 °C; ^{1}H NMR δ 10.34 (br s, 2 H), 9.30 (s, 2 H), 7.68 (d, J = 8.0 Hz, 4 H), 7.5–7.2 (m, 8 H), 6.93 (d, J = 8.0 Hz, 4 H), 6.64 (t, J = 8.0 Hz, 2 H), 5.28 (s, 4 H), 3.0–2.8 (m, 8 H), 2.20 (s, 6 H), 1.5–1.0 (m, 16 H), 0.65 (t, J = 7.2 Hz, 12 H); ^{31}P NMR (DMSO-d_6) δ 0.39; MS-FAB m/z 908.7, 1007.1, 1249.0 [(M – H)$^-$, calcd 909.3 (**14e**), 1006.3 (**14e** + $H_2PO_4^-$), 1248.6 (**14e** + $Bu_4NH_2PO_4$), respectively]. Anal. Calcd for $C_{54}H_{70}N_5O_{12}PU{\cdot}2H_2O$: C, 50.43; H, 5.80; N, 5.44. Found: C, 50.16; H, 5.59; N, 5.51. Karl Fischer titration calcd for 2H_2O, 2.84, found, 2.64.

[[2,2′-[1,2-Phenylenebis[nitrilomethylidyne(2-hydroxy-3,1-phenylene)oxy]]bis[*N*-(4-methylphenyl)acetamidato]](2–)-*N,N′,O,O′*]dioxouranium (14e)·2*n*-$Bu_4NH_2PO_4$:[39] mp 89–92 °C; ^{1}H NMR and MS-FAB data are identical with those of the **14e**·*n*-$Bu_4NH_2PO_4$ complex; ^{31}P NMR (DMSO-d_6) δ 0.39, –1.62.

[12,13,15,16,19,20,30a,31,32,33,34,34a-Dodecahydro-35,36-dihydroxy-3,7:24,28-dimetheno-9*H*,18*H*-8,14,17,23,1,11,20,30-benzotetraoxatetraazacyclodotriacontine-10,21(11*H*,22*H*)-dionato(2–)-*N*^{31},*N*^{30},*O*^{35},*O*^{36}]dioxouranium (18)·*n*-$Bu_4NH_2PO_4$: mp 95–100 °C; ^{1}H NMR δ 9.23 (s, 2 H), 9.14 (br s, 2 H), 7.24 (d, J = 8.0 Hz, 2 H), 7.16 (d, J = 8.0 Hz, 2 H), 6.64 (t, J = 8.0 Hz, 2 H), 4.92 (d, J = 3.5 Hz, 4 H), 4.7–4.6 (m, 2 H), 3.2–3.1 (m, 8 H), 2.5–2.4 (m, 2 H), 2.1–1.4 (m, 22 H), 0.95 (t, J = 7.2 Hz, 12 H); ^{31}P NMR (DMSO-d_6) δ 0.30; MS-FAB m/z 850.0, 947.0, 1189.1 [M$^-$, calcd 850.0 (**18**), 947.0 (**18** + $H_2PO_4^-$), 1189.5 (**18** + $Bu_4NH_2PO_4$), respectively]. Anal. Calcd for $C_{46}H_{74}N_5O_{14}PU{\cdot}2.75H_2O$: C, 44.57; H, 6.46; N, 5.65. Found: C, 44.51; H, 6.35; N. 5.50. Karl Fischer titration calcd for 2.75H_2O, 4.00, found, 3.77.

[[2-[1-(Nitrilomethylidyne)-2-oxyphenylene]phenolato](2–)-*N,O,O′*]dioxouranium (19a)·2*n*-$Bu_4NH_2PO_4$: mp 175–180 °C; ^{1}H NMR (DMSO-d_6) δ 9.43 (s, 1 H), 7.61 (d, J = 7.8 Hz, 1 H), 7.58 (d, J = 7.8 Hz, 1 H), 7.50 (t, J = 7.8 Hz, 1 H), 7.19 (t, J = 7.8 Hz, 1 H), 7.11 (d, J = 7.8 Hz, 1 H), 6.80 (d, J = 7.8 Hz, 1 H), 6.59 (2 × d, J = 7.8 Hz, 2 H), 3.2–3.0 (m, 16 H), 1.6–1.3 (m, 32 H), 0.95 (t, J = 7.2 Hz, 24 H); MS-FAB m/z 577.6, 675.6 [(M – H)$^-$, calcd 577.3 (**19a** + $H_2PO_4^-$), 675.3 (**19a** + 2$H_2PO_4^-$), respectively]. Anal. Calcd for $C_{45}H_{85}N_3O_{12}P_2U{\cdot}2H_2O$: C, 45.18; H, 7.50; N, 3.51. Found: C, 45.49; H, 7.76; N, 3.51. Karl Fischer titration calcd for 2H_2O, 3.01, found, 3.03.

Crystal Structure Determinations. The crystal structures of **14b**, **1c**·*n*-$Bu_4N^+H_2PO_4^-$, **14e**·2*n*-$Bu_4N^+H_2PO_4^-$, and **19a**·2*n*-$Bu_4N^+H_2PO_4^-$ were determined with X-ray diffraction methods (Table 4). Reflections were measured in the $\omega/2\theta$ scan mode in the range $3 < \theta < 25°$, using graphite monochromated Mo Kα radiation. The structures were solved by heavy atom techniques and refined with full-matrix least-squares methods. Parameters refined were scale factor and positional parameters of all atoms (H-atoms were not included); thermal parameters were refined anisotropically for U-atoms and the atoms of phosphate groups, isotropically for the other atoms. Positions for the H-atoms have been deduced from geometrical considerations, intermolecular distances, and P–O bond lengths. All calculations were done with SDP and DIRDIF,[41]

(41) (a) Structure Determination Package; Frenz, B. A., and Associates, Inc., College Station, TX, and Enraf-Nonius, Delft, 1983. (b) Beurskens, P. T.; Admiraal, G.; Beurskens, G.; Bosman, W. P.; Garcia-Granda, S.; Gould, R. O.; Smits, J. M. M.; Smykalla, C. The DIRDIF program system. Technical Report of the Crystallography Laboratory; University of Nijmegen: The Netherlands, 1992.

An empirical absorption correction using DIFABS[42] was made.

Conductometry. The association constants were determined in MeCN–DMSO (99:1 (v/v)) solutions by conductometric titrations at 25.0 °C. The DMSO was added because the solubility of some host compounds in pure MeCN was too low to allow accurate determination of association constants. Moreover, the presence of 1% (v/v) DMSO reduces the association constants between the host and the anions, which allows the comparison of the association constants of most $H_2PO_4^-$, Cl^-, and NO_2^- complexes. The conductivity was measured in a sample solution of variable concentration of the host and a fixed concentration of the guest, present as the tetrabutylammonium salt. The concentrations of the different stock solutions of the tetrabutylammonium salts were in the range of 0.3–0.7 mM, depending on the expected strength of the association with the host molecule. A sample solution for conductivity measurements was prepared by dissolving 1–18 × 10^{-2} mmol of host compound in 10 mL of the guest anion solution. The starting concentrations of the host and the guest in this sample solution were chosen in such a way that the complexation of the anion was at least 60%. In the titration procedure, the concentration of the host in the sample solution was stepwise reduced, with 10% per step, by removal of 1 mL of the sample solution and addition of 1 mL of the guest stock solution, by using two Metrohm 665 burets (accuracy 0.001 mL). The K_{ass} values were determined by minimization of the calculated and observed conductivity for at least 15 data points by least-squares approximation. The calculated error for the K_{ass} values is less than 6%.

Electrochemistry. The measurements were carried out using a static mercury drop electrode with a radius of approximately 0.25 mm as the working electrode and with a glassy carbon rod as an auxiliary electrode. Potentials were measured with respect to an Ag/AgCl electrode filled with 0.1 M Et_4NCl in DMSO. As a supporting electrolyte, 0.3 M *n*-Bu_4NClO_4 in DMSO or 0.25 M *n*-Bu_4NClO_4 in 90% DMSO–10% H_2O was used. Oxygen was expelled using especially pure (polarographic grade) nitrogen.

Assuming that a 1:1 complex is formed and that the difference in diffusion coefficients of host and the complex is negligible, the association constants can be calculated from the slope of the straight line: $\exp[(E - E^*)nF/RT]$ *vs* $[X^-]$, where E is the voltammetric peak potential in the absence of the anion X^- and E^* is the potential after anion addition. The diffusion coefficients of host and complex were assumed to be equal.

During the determination of K_{ass} in pure DMSO, the initial concentration of the receptor in the cell was 6 × 10^{-4} M, and phosphate solution was added to obtain concentrations in the range 0.002–0.007 M. The electrochemical behavior was studied in the potential range from –0.2 to –1.45 V, and scan rates were varied from 0.1 to 5.0 V s^{-1}.

In experiments in the mixed DMSO–H_2O medium, for each combination of ligand–anion, four series of measurements have been carried out for four different scan rates (0.2, 0.5, 1.0, and 1.5 V s^{-1}). Within each series, the total concentration of anions was kept constant and equal to 0.25 M. The initial concentration of the receptor in the cell was 3 × 10^{-4} M, and it decreased gradually upon addition of the anion solution. Concentration of phosphate was varied from 0.005 to 0.125 M.

^{1}H NMR Measurements. K_{ass} values were determined by integration of the separated signals of the imine protons of both free ligand and complex upon dilution of a receptor solution (10^{-3}–10^{-2} M) by the stock solution of the free salt. On the basis of repetitive measurements, estimated error is <10%.

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Supplementary Material Available: Tables of positional and thermal parameters, bond lengths, and bond angles for **1c**·$H_2PO_4^-$, **14b**, **14e**·$2H_2PO_4^-$, and **19a**·$2H_2PO_4^-$ (23 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

(42) Walker, N.; Stuart, D. *Acta Crystallogr., Sect. A* **1983**, *39*, 158–166.