

Functionalized UO₂ 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 (UO₂²⁺) 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 ³¹P NMR spectroscopy, and FAB mass spectrometry. X-ray structures of **1c**·H₂PO₄⁻ and **14e**·H₂PO₄⁻ reveal that anion binding is effected by coordination to the uranyl cation and additional H-bond formation. The **1c**·H₂PO₄⁻ complex is arranged in centrosymmetric pairs, the core of the dimer consisting of two H₂PO₄⁻ anions connected by two short H-bonds. In the case of the **14e**·H₂PO₄⁻ complex, the H₂PO₄⁻ complexed to the uranyl forms a H-bonded associate with a second H₂PO₄⁻ anion which itself is not complexed by the ligand. In the case of the preorganized ligands **14b**, **14d**, and **18**, strong (*K*_{ass} > 10⁵ M⁻¹ in MeCN–DMSO, 99:1) and selective complexation of H₂PO₄⁻ has been observed. Selectivities of >10² and >10³ over Cl⁻ and HSO₄⁻, NO₂⁻, and SCN⁻, respectively, were obtained for receptor **14b**. "Naked" UO₂ 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 H₂PO₄⁻. Its X-ray structure shows that the complex is organized as a H-bonded ribbon due to the facts that the H₂PO₄⁻ anions form H-bonded dimers and, in addition, two H₂PO₄⁻ 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 azamacrocycles⁵ 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 mercury¹⁰ 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 UO₂ 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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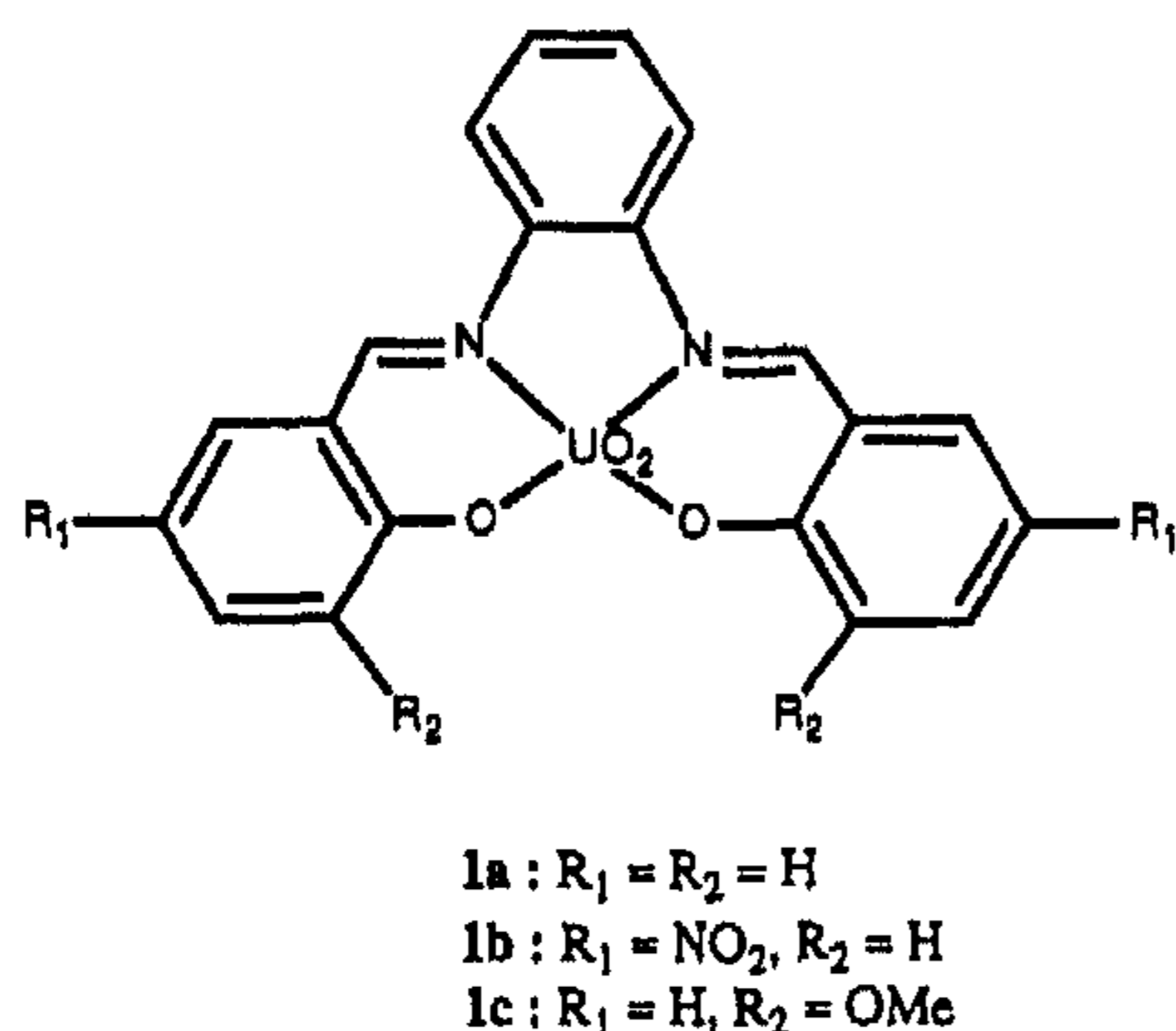
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Chart 1



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 UO₂(OAc)₂·2H₂O 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 (Bu₄N⁺H₂PO₄[−]), 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 (H₂PO₄[−]) 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 H₂PO₄[−] 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 H₂PO₄[−] 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

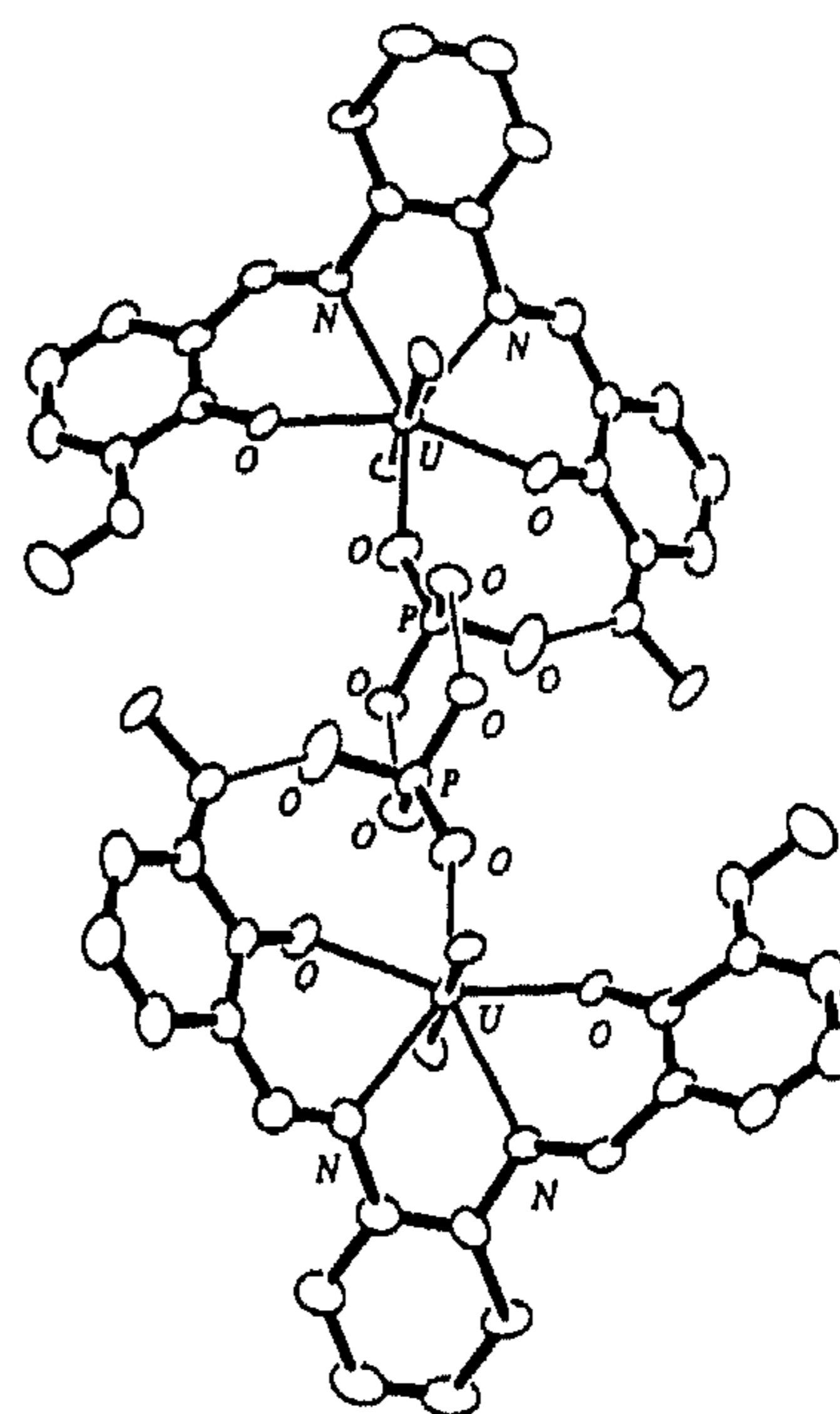


Figure 1. Crystal structure of the complex **1c**·H₂PO₄[−]. The dimer shown has a crystallographic center of symmetry. Tetrabutylammonium fragments and solvent molecule are omitted for clarity.

first example of H₂PO₄[−] 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 UO₂ cation and is augmented by hydrogen bonding between anion and ligand.

In order to obtain anion receptors which contain a *combination* of both UO₂ 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-cyclohexanediamine¹⁸ and UO₂(OAc)₂·2H₂O, with formation of metalocleft **5** in 71% yield.

The synthesis of the salicylamide-based metalocleft **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 Et₃N·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 UO₂(OAc)₂·2H₂O in methanol in a yield of 51%.

In order to obtain metaloclefts containing a UO₂ 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 UO₂(OAc)₂·2H₂O to give metaloclefts **14a–e** in 64–89% yield. Compounds **14c** and **14d**,

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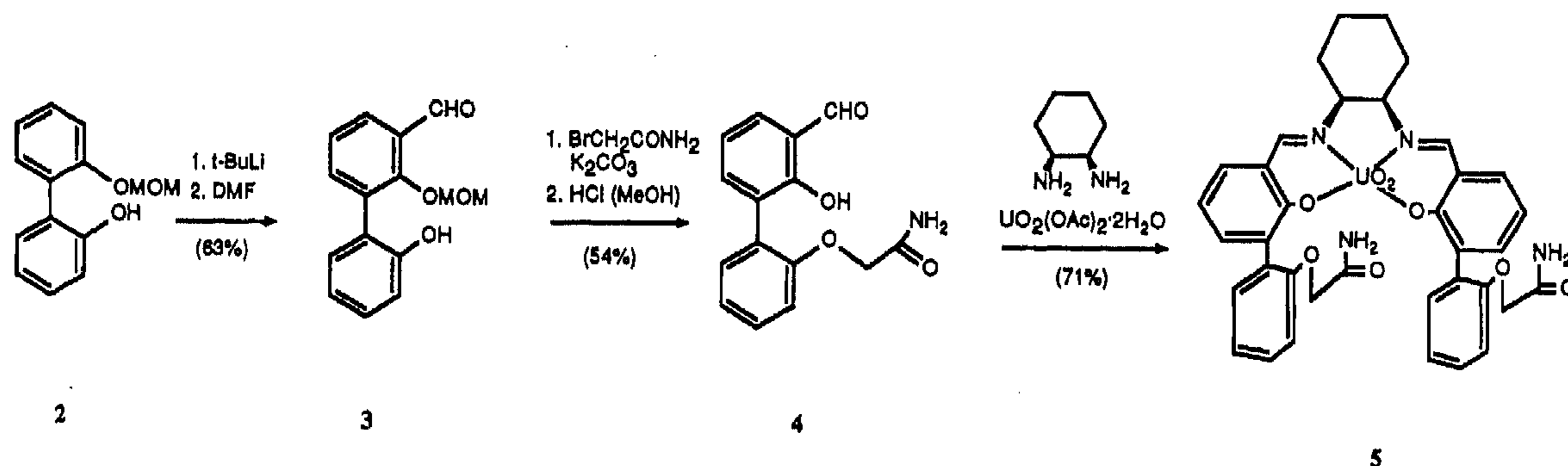
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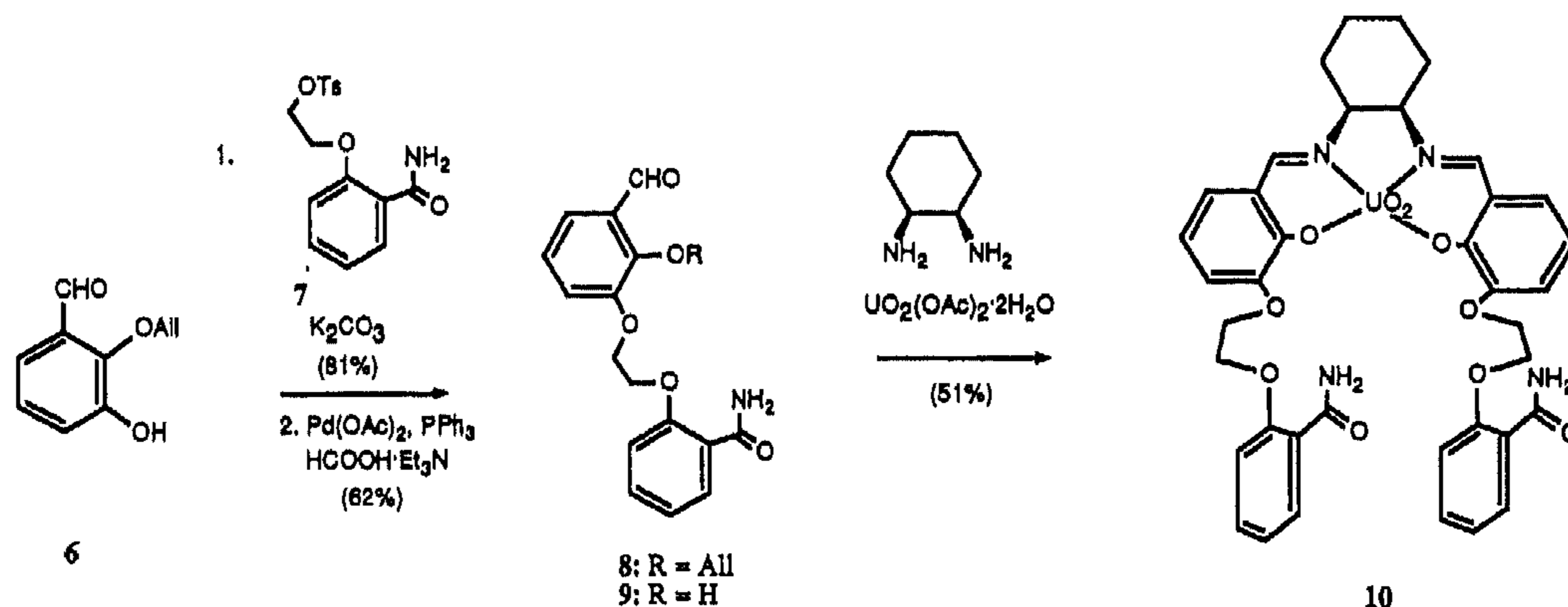
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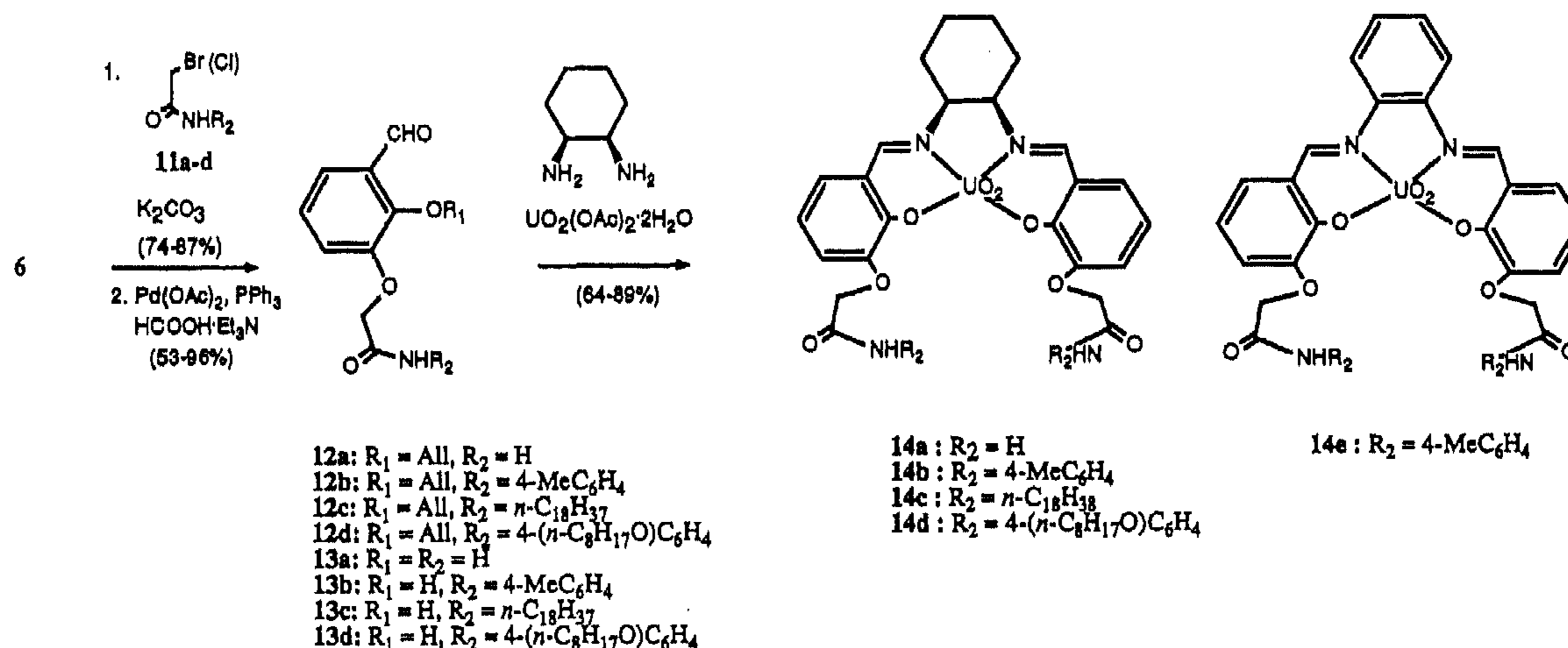
Scheme 1



Scheme 2



Scheme 3



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 UO₂ cation was confirmed by elemental analyses and Karl Fischer titrations. The (M + H)⁺ peaks in the FAB mass spectra prove the formation of the UO₂-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 UO₂ cation is occupied by an oxygen atom of a solvent (H₂O, MeOH) or guest (urea, amides, etc.) molecule. Since in 14b, both the UO₂ center and amido fragments are present, the fifth position of the UO₂ 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-replication²¹ in solution

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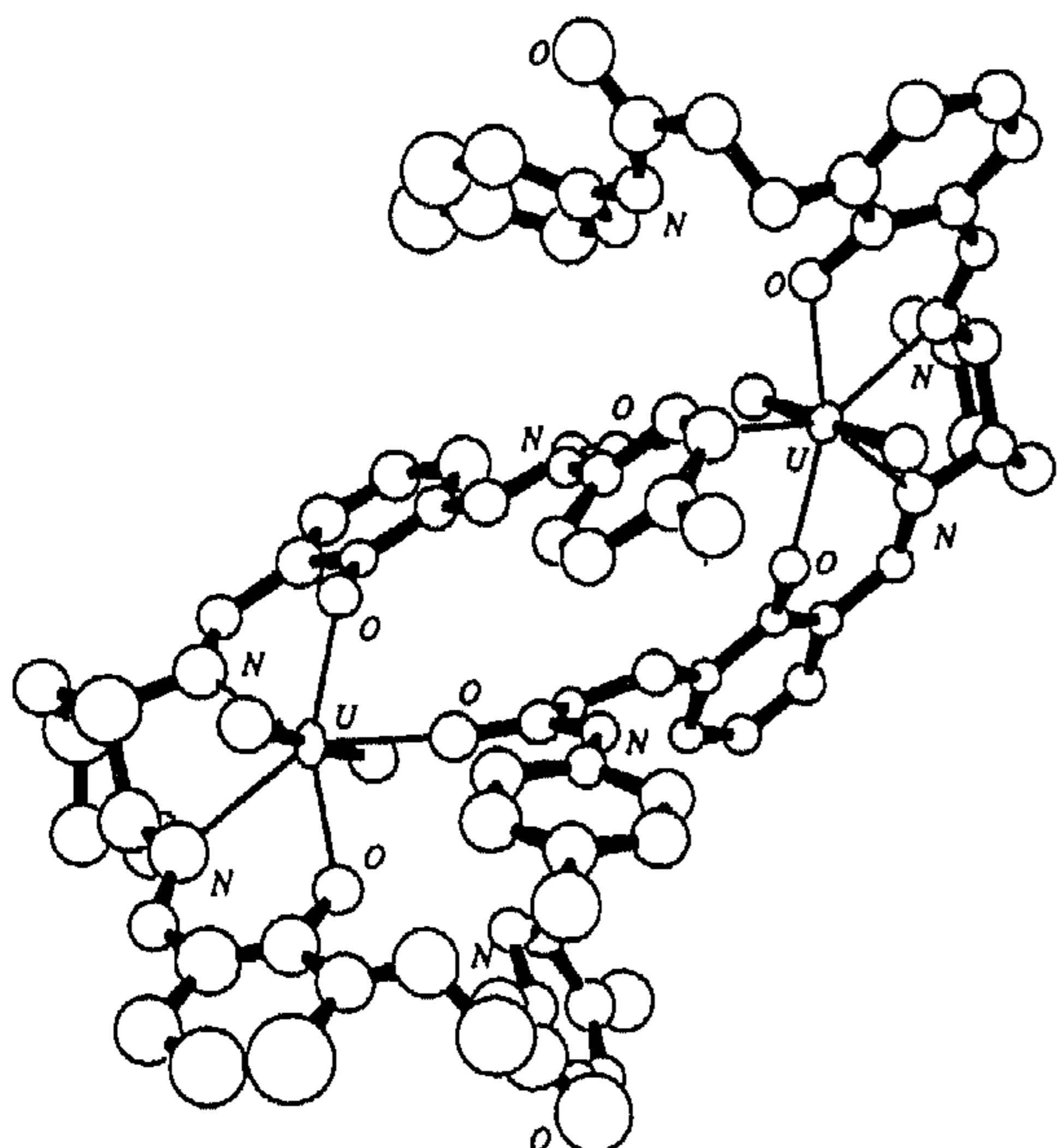


Figure 2. Crystal structure of the dimer of 14b. The figure shows the two crystallographically independent molecules in the unit cell. The solvent molecule is omitted for clarity.

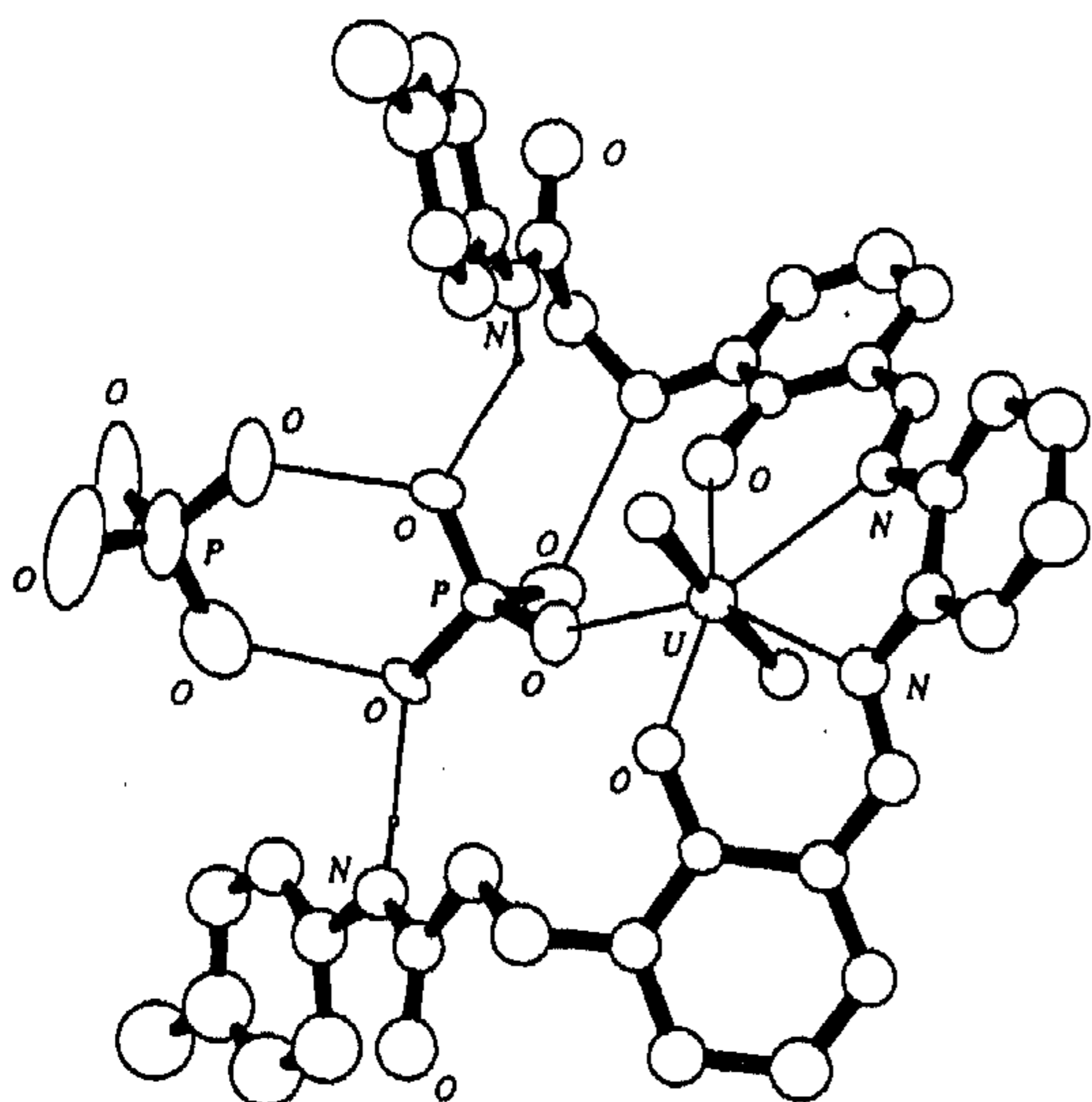


Figure 3. Crystal structure of the complex 14e·2H₂PO₄⁻. Tetrabutylammonium fragments and solvent molecules are omitted for clarity.

and for the design of controlled solid-state structures.²² Due to this type of association, the ¹H NMR spectra of the CDCl₃ 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 known²³ to form complexes with UO₂ salenes, the ¹H NMR spectra are sharp.

Single crystals of the complex of ligand 14e with Bu₄N⁺H₂PO₄⁻ were also grown by slow diffusion of diisopropyl ether into a solution of 14e and 2-fold excess of Bu₄N⁺H₂PO₄⁻ in MeCN.²⁴ The crystal structure is shown in Figure 3.

As in the case of the complex of 1c with H₂PO₄⁻ (Figure 1), the H₂PO₄⁻ anion is tightly complexed to the UO₂ center (U...O—P distance 2.28(2) Å), in addition to a H-bond formation

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(24) Attempts to obtain single crystals of complexes of salenes 14a–d with H₂PO₄⁻ were unsuccessful.

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 H₂PO₄⁻ complexed to the UO₂ cation forms a H-bonded associate with the second H₂PO₄⁻ anion (O...O distance 2.48(2) Å), which in this case is not complexed itself by ligand 14e.

We have also synthesized metallomacrocyclic 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-allyloxy)-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 UO₂(OAc)₂·2H₂O led to 18 in 59% yield.

Stirring of a mixture of ligand 1c, 14a, 14b, 14e, or 18 and Bu₄N⁺H₂PO₄⁻ 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 ¹H NMR spectra of all complexes, significant changes of the host were found for the NH amido, the HC=N, and the CH₂C(O) signals which clearly indicate the presence of a guest anion in the cavity. In the ³¹P NMR spectra of H₂PO₄⁻ complexes with 1c, 14a, 14b, and 18, signals of H₂PO₄⁻ are shifted downfield (Δδ = 1.9–2.3 ppm) in comparison with free H₂PO₄⁻.

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" UO₂ salophenes 19a–c have been prepared by reaction of the corresponding aldehydes (salicyl aldehyde, 13b, and 9, respectively), *o*-aminophenol, and UO₂(OAc)₂·2H₂O in refluxing MeOH in yields of 91–98%. The ¹H 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 H₂O molecules coordinated to the uranyl center.

Orange single crystals of the complex of "naked" ligand 19a with Bu₄N⁺H₂PO₄⁻ were grown by slow diffusion of diisopropyl ether into a solution of 19a and a 2-fold excess of Bu₄N⁺H₂PO₄⁻ in MeCN. The crystal structure is presented in Figure 4 and clearly shows that binding of two H₂PO₄⁻ 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 UO₂ cation, molecules of complex 19a·(H₂PO₄⁻)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 UO₂ salophenes 1a–c show strong binding of different anions (e.g., Cl⁻, H₂PO₄⁻, NO₂⁻) in MeCN–DMSO (99:1) solutions (Table 1).²⁵ In all cases, a preference for H₂PO₄⁻ binding was observed. It is clear from Table 1 that the charge density on the UO₂ fragment is influenced by the presence of substituents in the parent molecule. Due to the presence of the electron-withdrawing

(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, Δ*H* and Δ*S* parameters for the complexation of H₂PO₄⁻ 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

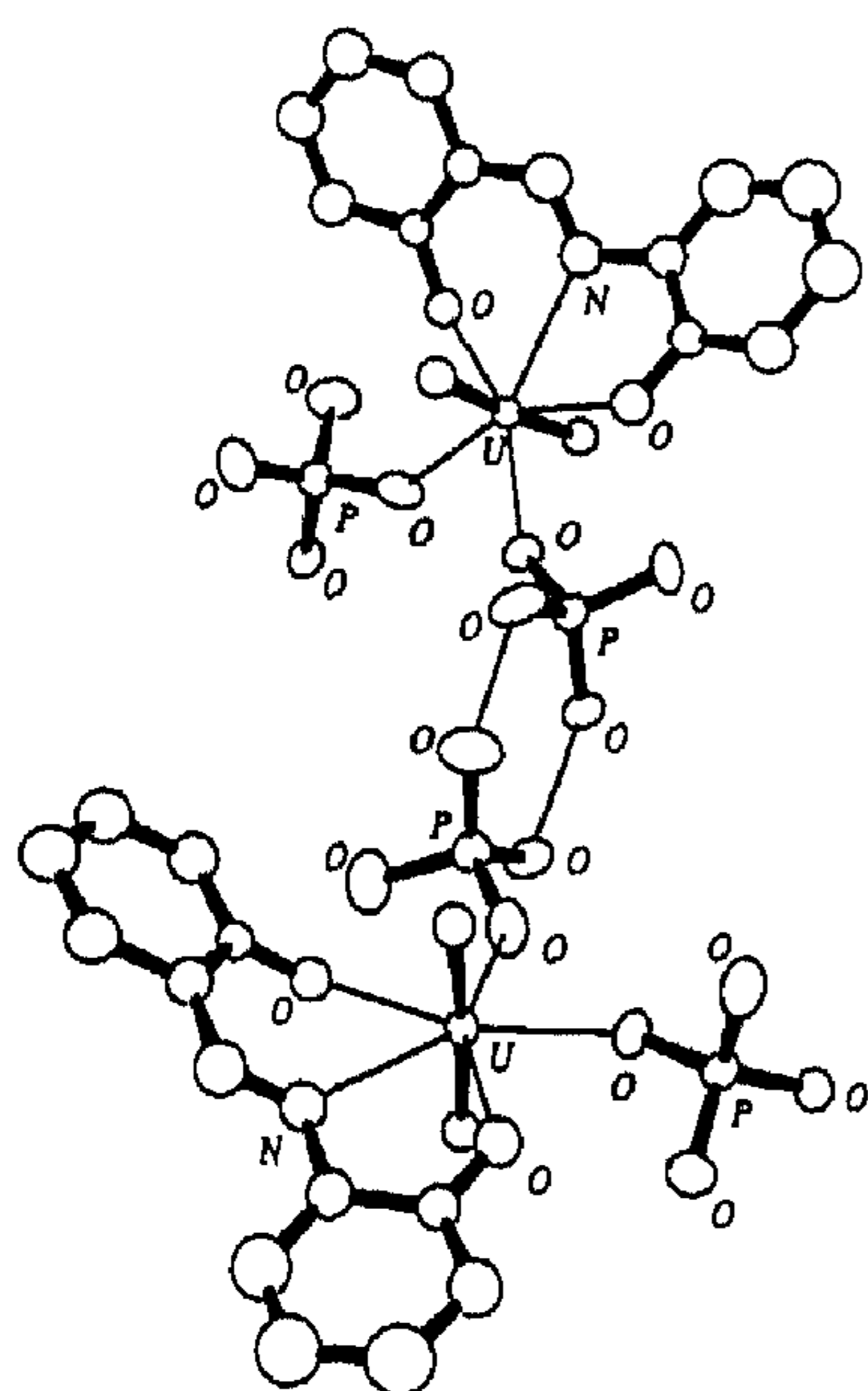
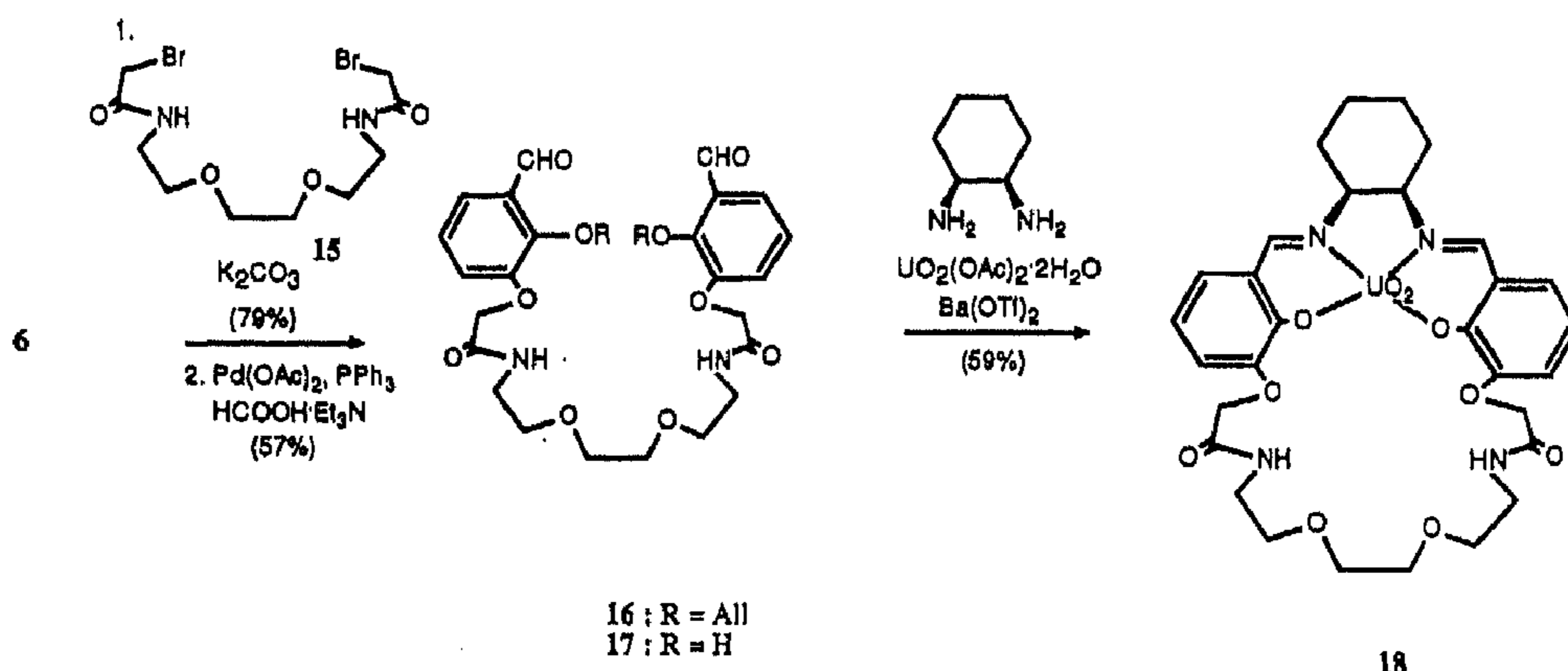
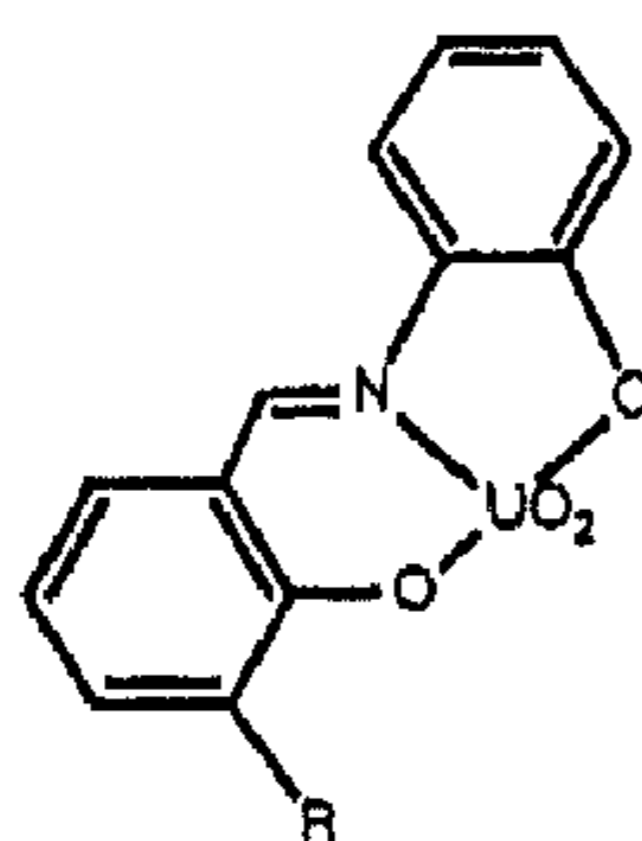


Figure 4. Crystal structure of the complex $19a \cdot 2H_2PO_4^-$. The structure shown contains a crystallographic center of symmetry. Tetrabutylammonium fragments and solvent molecule are omitted for clarity.

Chart 2



19a: R = H
19b: R = OCH₂C(O)NH-C₆H₄-Me-4
19c: R = O(CH₂)₂O-C₆H₄-C(O)NH₂-2

nitro group, the UO₂ moiety in **1b** is more electropositive, and consequently ligand **1b** binds Cl⁻ and NO₂⁻ stronger than ligand **1a**.

In the salophenes **1a-c**, binding exclusively takes place via electrostatic interaction. Therefore, metallolefts **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

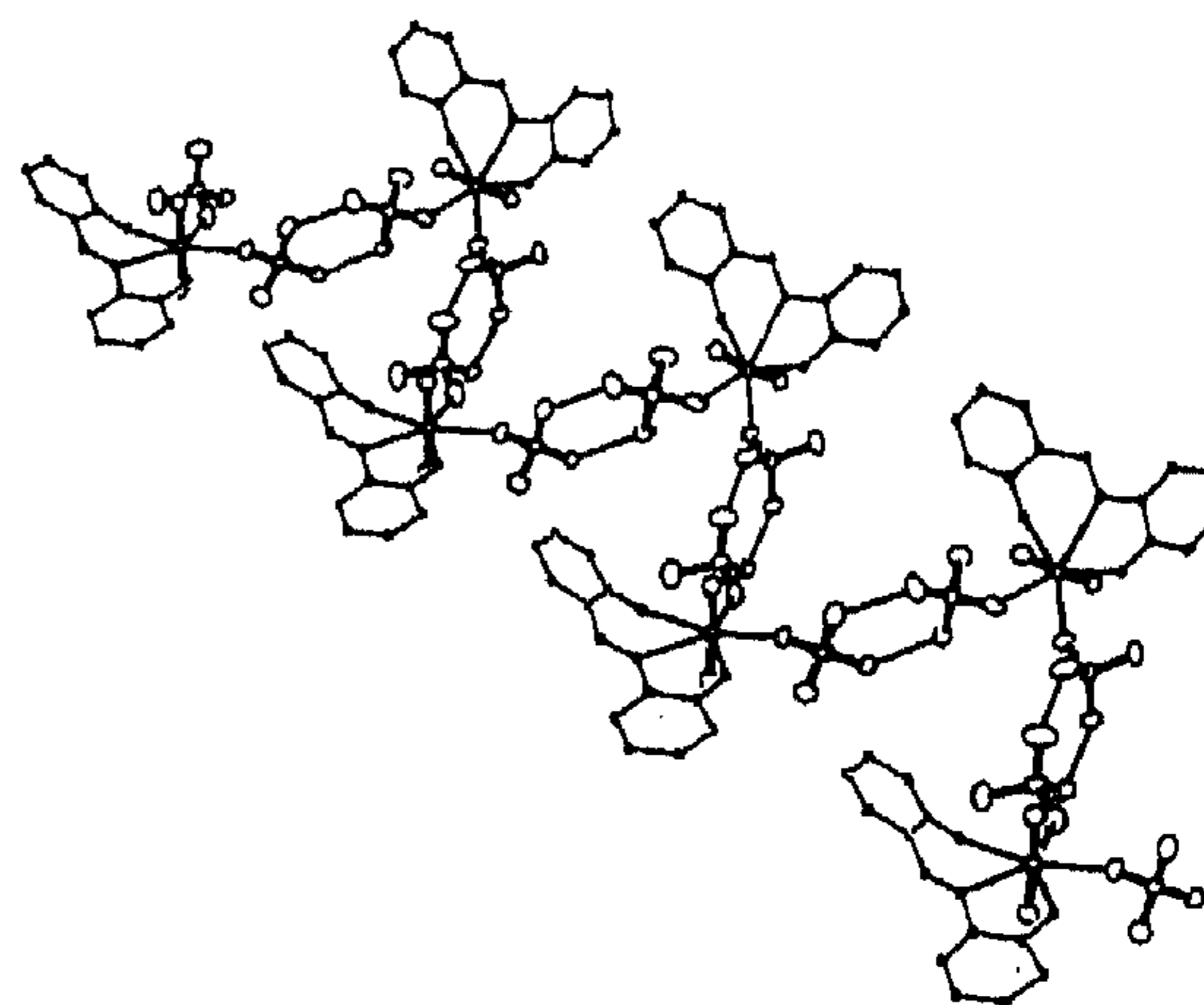


Figure 5. View of the H-bonded ribbon of the complex $19a \cdot 2H_2PO_4^-$.

cavity is too small for complexation; nevertheless, there is selectivity for H₂PO₄⁻ over the other anions.

In contrast to this, the binding of anions by more flexible clefts **14a**, **14b**, and **14d** and metallomacrocyclic **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 H₂PO₄⁻) 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 H₂PO₄⁻. Compound **14b** shows for H₂PO₄⁻ selectivities of $>10^2$ over Cl⁻ and $>10^3$ over NO₂⁻. For HSO₄⁻ 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 salt of Cl⁻ or H₂PO₄⁻ 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 $4.2 \times 10^2 M^{-1}$ was determined, which is in agreement with conductometry (Table 1).

Analogously, the addition of Bu₄N⁺H₂PO₄⁻ to solutions of **1c**, **5**, **10**, **14a,b,d,e**, and **18** in DMSO-*d*₆ gave two sets of HC=N, CH₂C(O), and NH signals, both for the free and for the complexed ligand, indicating that the formation of kinetically stable complexes with H₂PO₄⁻ takes place even in pure DMSO-*d*₆. The contribution of the C(O)NH...H₂PO₄⁻ 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	<i>b</i>
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 ($\Delta\delta \approx 0.1$ 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 $\text{Bu}_4\text{N}^+\text{H}_2\text{PO}_4^-$ 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 \cdots 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 $n\text{-Bu}_4\text{N}^+\text{H}_2\text{PO}_4^-$, 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-based²⁹ and cobaltizinium-containing³⁰ 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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(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 ³¹P NMR spectroscopy, and FAB mass spectrometry. In the case of the preorganized ligands **14b**, **14d**, and **18**, strong ($K_{\text{ext}} > 10^5 \text{ M}^{-1}$ in MeCN–DMSO, 99:1) and selective complexation of H₂PO₄⁻ has been observed. Selectivities of >10² and >10³ over Cl⁻ and NO₂⁻, respectively, were obtained for receptor **14b**.

"Naked" UO₂ 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 UO₂ salenes for detection of H₂PO₄⁻ 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 CDCl₃ 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. CH₂Cl₂ was distilled from CaH₂ and stored over molecular sieves (4 Å). CH₃CN 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 MgSO₄ 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(nitrilomethylidene)]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–CH₂Cl₂, 2:1 (75 mL) for 0.5 h. UO₂(OAc)₂·2H₂O (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 C₂₀H₁₂N₄O₈U·0.9H₂O: C, 34.79; H, 2.01; N, 8.11. Found: C, 34.70; H, 2.04; N, 8.09. Karl Fischer titration calcd for 0.9H₂O 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 K₂CO₃ (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 CH₂Cl₂ (3 × 100 mL). Column chromatography (CH₂Cl₂) 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); ¹³C 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 C₁₄H₁₄O₃: 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 NH₄Cl (10

mL) and subsequently extracted with CH₂Cl₂ (3 × 100 mL). The crude reaction mixture was purified by flash chromatography (CH₂Cl₂) 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); ¹³C 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 C₁₅H₁₄O₄: 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 K₂CO₃ (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 H₂SO₄) (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 CH₂Cl₂ (3 × 100 mL). The product was purified by flash chromatography (CH₂Cl₂–acetone, 10:1) to give **4** as a colorless solid (1.46 g, 54%); mp 114–116 °C (CH₂Cl₂–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); ¹³C 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 C₁₅H₁₃NO₄·0.25H₂O: C, 65.33; H, 4.93; N, 5.08. Found: C, 65.21; H, 4.96; N, 4.85. Karl Fischer titration calcd for 0.25H₂O, 1.63, found, 1.67.

[[[3,3'-[1,2-Cyclohexanedylbis(nitrilomethylidene)]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*-cyclohexanediamine¹⁸ (0.06 g, 0.55 mmol) in MeOH (100 mL) was refluxed for 1 h. Subsequently a solution of UO₂(OAc)₂·2H₂O (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); ¹³C 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 C₃₆H₃₄N₄O₈U·1.3H₂O: 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 H₂O, 2.57, found, 2.55.

2-(2-Hydroxyethoxy)benzenecarboxamide 4-methylbenzenesulfonate (7). A solution of 2-(2-hydroxyethoxy)benzenecarboxamide³⁸ (2.20 g, 12 mmol), tosyl chloride (2.30 g, 12 mmol), and Et₃N (2.02 g, 20 mmol) in THF (200 mL) was stirred for 80 h at room temperature. Et₃N·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); ¹³C 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 C₁₅H₁₇NO₅S: 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 K₂CO₃ (13.80 g, 100 mmol) in EtOAc–H₂O, 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 (CDCl₃–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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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 $\text{C}_9\text{H}_{10}\text{ClNO}$: 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; ^1H 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 $\text{C}_{20}\text{H}_{40}\text{BrNO}$: 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; ^1H 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 [($\text{M} + \text{H}$) $^+$, calcd 298.1]. Anal. Calcd for $\text{C}_{16}\text{H}_{24}\text{ClNO}_2$: 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)benzaldehyde¹⁹ (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} ; ^1H 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 [($\text{M} + \text{H}$) $^+$, calcd 342.1]. Anal. Calcd for $\text{C}_{19}\text{H}_{19}\text{NO}_5$: 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} ; ^1H 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 $\text{C}_{12}\text{H}_{13}\text{NO}_4 \cdot 0.15\text{H}_2\text{O}$: C, 60.57; H, 5.63; N, 5.89. Found: C, 60.30; H, 5.55; N, 5.81. Karl Fischer titration calcd for 0.15 H_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} ; ^1H 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 $\text{C}_{19}\text{H}_{19}\text{NO}_4 \cdot 0.4\text{H}_2\text{O}$: C, 68.62; H, 6.00; N, 4.21. Found: C, 68.79; H, 5.68; N, 4.18. Karl Fischer titration calcd for 0.4 H_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; ^1H 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 [($\text{M} + \text{H}$) $^+$, calcd 448.4]. Anal. Calcd for $\text{C}_{30}\text{H}_{49}\text{NO}_4$: 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; ^1H 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 [($\text{M} + \text{H}$) $^+$, calcd 440.2]. Anal. Calcd for $\text{C}_{26}\text{H}_{33}\text{NO}_5 \cdot 0.1\text{H}_2\text{O}$: C, 70.76; H, 7.58; N, 3.17. Found: C, 70.36; H, 7.60; N, 3.08. Karl Fischer titration calcd for 0.1 H_2O , 0.41, found, 0.18.

***N,N'*-[1,2-Ethanediybis(oxy-2,1-ethanediy)]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 \times 75 mL). Recrystallization of the residue from toluene gave 15 as a colorless solid (5.55 g, 57%); mp 84–85 °C; ^1H 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 [($\text{M} + \text{H}$) $^+$, calcd 390.8]. Anal. Calcd for $\text{C}_{10}\text{H}_{18}\text{Br}_2\text{N}_2\text{O}_4$: C, 30.79; H, 4.65; N, 7.18. Found: C, 31.04; H, 4.71; N, 7.11.

***N,N'*-[1,2-Ethanediybis(oxy-2,1-ethanediy)]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} ; ^1H 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 [($\text{M} + \text{H}$) $^+$, calcd 585.2]. Anal. Calcd for $\text{C}_{30}\text{H}_{36}\text{N}_2\text{O}_{10}$: C, 61.63; H, 6.21; N, 4.79. Found: C, 61.66; H, 6.37; N, 4.87.

General Procedure for the Deallylation²⁰ 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), $\text{Pd}(\text{OAc})_2$ (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 \times 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} ; ^1H 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 [($\text{M} + \text{H}$) $^+$, calcd 301.1]. Anal. Calcd for $\text{C}_{16}\text{H}_{15}\text{NO}_5 \cdot 0.5\text{H}_2\text{O}$: C, 61.93; H, 5.20; N, 4.51. Found: C, 61.73; H, 4.92; N, 4.42. Karl Fischer titration calcd for 0.5 H_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} ; ^1H 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 $\text{C}_9\text{H}_9\text{NO}_4 \cdot 0.6\text{H}_2\text{O}$: C, 52.48; H, 4.99; N, 6.80. Found: C, 52.23; H, 4.67; N, 6.63. Karl Fischer titration calcd for 0.6 H_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} ; ^1H 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 $\text{C}_{16}\text{H}_{15}\text{NO}_4 \cdot 0.6\text{H}_2\text{O}$: C, 64.90; H, 5.51; N, 4.73. Found: C, 64.62; H, 5.41; N, 4.55. Karl Fischer titration calcd for 0.6 H_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); ^1H 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 \times t), 26.8 (t), 22.7 (t), 14.1 (q); MS-FAB m/z 448.6 [($\text{M} + \text{H}$) $^+$, calcd 448.3]. Anal. Calcd for $\text{C}_{27}\text{H}_{45}\text{NO}_4$: 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%); ¹H 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 C₂₃H₃₀NO₃ 399.2].

N,N'-[1,2-Ethanedilybis(oxy-2,1-ethanedily)]bis[2-(3-formyl-2-hydroxyphenoxy)acetamide] (17):³⁹ yield 0.86 g (57%); IR (KBr) 1672, 1654 cm⁻¹; ¹H 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); ¹³C 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 C₂₄H₂₉N₂O₁₀ 505.2].

General Procedure for the Synthesis of UO₂ 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 UO₂(OAc)₂·2H₂O (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-cyclohexanedilybis(nitrilomethylidene)]-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; ¹H 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); ¹³C 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 C₃₈H₃₈N₄O₁₀U·2.2H₂O: C, 46.18; H, 4.32; N, 5.67. Found: C, 45.86; H, 4.00; N, 5.52. Karl Fischer titration calcd for 2.2H₂O, 4.00, found, 3.84.

[[2,2'-[1,2-Cyclohexanedilybis(nitrilomethylidene)(2-hydroxy-3,1-phenyleneoxy)]bis[acetamidato]](2-)-*N,N',O,O'*-dioxouranium (14a): yield 0.37 g (77%); mp > 265 °C; IR (KBr) 1666, 1615, 900 cm⁻¹; ¹H 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 C₂₄H₂₆N₄O₈U·2.0H₂O: C, 37.31; H, 3.91; N, 7.25. Found: C, 36.91; H, 3.66; N, 7.11. Karl Fischer titration calcd for 2.0H₂O, 4.66, found, 4.41.

[[2,2'-[1,2-Cyclohexanedilybis(nitrilomethylidene)(2-hydroxy-3,1-phenyleneoxy)]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; ¹H 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); ¹³C 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 C₃₈H₃₈N₄O₈U·1.35H₂O: C, 48.50; H, 4.36; N, 5.95. Found: C, 48.90; H, 4.11; N, 5.98. Karl Fischer titration calcd for 1.35H₂O, 2.60, found, 2.91.

[[2,2'-[1,2-Cyclohexanedilybis(nitrilomethylidene)(2-hydroxy-3,1-phenyleneoxy)]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; ¹H NMR (CDCl₃-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); ¹³C NMR (CDCl₃-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 C₆₀H₉₈N₄O₈U·1H₂O: C, 57.22; H, 8.00; N, 4.45. Found: C, 56.91; H, 7.88; N, 4.36. Karl Fischer titration calcd for 1H₂O, 1.40, found, 1.40.

[[2,2'-[1,2-Cyclohexanedilybis(nitrilomethylidene)(2-hydroxy-3,1-phenyleneoxy)]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; ¹H 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); ¹³C 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 C₅₂H₆₆N₄O₁₀U·4H₂O: C, 51.31; H, 6.13; N, 4.60. Found: C, 51.54; H, 5.87; N, 4.79. Karl Fischer titration calcd for 4H₂O, 6.00, found, 6.15.

[[2,2'-[1,2-Phenylenebis(nitrilomethylidene)(2-hydroxy-3,1-phenyleneoxy)]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; ¹H 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); ¹³C 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 C₃₈H₃₂N₄O₈U·1.5H₂O: C, 48.67; H, 3.76; N, 5.97. Found: C, 48.27; H, 3.57; N, 5.71. Karl Fischer titration calcd for 1.5H₂O, 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,N',O,O'*-dioxouranium (18). To a refluxing solution of Ba(OTf)₂⁴⁰ (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 UO₂(OAc)₂·2H₂O (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 H₂O. 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; ¹H 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); ¹³C 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 C₃₀H₃₆N₄O₁₀U·2H₂O: C, 40.64; H, 4.55; N, 6.32. Found: C, 40.77; H, 4.49; N, 6.19. Karl Fischer titration calcd for 2H₂O, 4.05, found, 4.12.

General Procedure for the Synthesis of "Naked" UO₂ 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 UO₂(OAc)₂·2H₂O (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-(Nitrilomethylidene)-2-oxyphenylene]phenolato](2-)-*N,O,O'*-dioxouranium (19a)·2MeOH: yield 2.36 g (98%); mp > 290 °C; IR (KBr) 902 cm⁻¹; ¹H 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); ¹³C 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 C₁₃H₉NO₄U·2CH₃OH·1.3H₂O: C, 31.68; H, 3.47; N, 2.46. Found: C, 31.77; H, 3.06; N, 2.49. Karl Fischer titration calcd for 1.3H₂O, 4.00, found, 4.05.

[[2-[1-(Nitrilomethylidene)-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; ¹H 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 C₂₂H₁₈N₂O₆U·2.5H₂O: C, 38.33; H, 3.36; N, 4.06. Found: C, 38.30; H, 3.20; N, 3.86. Karl Fischer titration calcd for 2.5H₂O, 6.50, found, 6.24.

[[2-[1-(Nitrilomethylidene)-2-oxyphenylene]-6-[2-(2-(aminocarbonyl)-phenoxy)thoxy]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· <i>n</i> -Bu ₄ N ⁺ H ₂ PO ₄ ⁻ ·MeCN	14e·2(<i>n</i> -Bu ₄ N ⁺ H ₂ PO ₄ ⁻)·3MeCN	14b·MeOH	19a·2(<i>n</i> -Bu ₄ N ⁺ H ₂ PO 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; ¹H 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); ¹³C 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 C₂₂H₁₈N₂O₇·U·CH₃OH: 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 Et₄NCl (5 mmol), or 1c, 14a, 14b, 14e, and 18 (5 mmol) and *n*-Bu₄NH₂PO₄ (5 mmol), or 14e, 19a (5 mmol), and *n*-Bu₄NH₂PO₄ (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(nitrilomethylidene)bisphenolato)](2-)-*N,N',O,O'*-dioxouranium (1a)·Et₄NCl: mp 275–278 °C; ¹H 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 H), 0.97 (t, *J* = 6.0 Hz, 12 H); MS-FAB *m/z* 618.8 [(M – H)⁺, calcd 618.1]. Anal. Calcd for C₂₈H₃₉ClN₃O₄U: C, 44.84; H, 4.56; N, 5.60. Found: C, 44.65; H, 4.58; N, 5.58.

[[2,2'-(1,2-Phenylenebis(nitrilomethylidene)bis(6-methoxyphenolato)](2-)-*N,N',O,O'*-dioxouranium (1c)·*n*-Bu₄NH₂PO₄: mp 125–128 °C; ¹H NMR (CDCl₃-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); ³¹P NMR (DMSO-*d*₆) δ 0.65; MS-FAB *m/z* 740.9 [(M – H)⁺, calcd 741.0 (for 1c + H₂PO₄⁻)]. Anal. Calcd for C₃₈H₅₆N₃O₁₀PU·1H₂O: C, 45.56; H, 5.83; N, 4.19. Found: C, 45.53; H, 5.72; N, 4.08. Karl Fischer titration calcd for 1H₂O, 1.80, found, 1.76.

[[2,2'-(1,2-Cyclohexanedilyl)bis(nitrilomethylidene(2-hydroxy-3,1-phenyleneoxy))bis[acetamidato]](2-)-*N,N',O,O'*-dioxouranium (14a)·*n*-Bu₄NH₂PO₄: mp 100–103 °C; ¹H 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); ³¹P 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 + H₂PO₄⁻), 1074.5 (14a + Bu₄NH₂PO₄), respectively]. Anal. Calcd for C₄₀H₆₄N₃O₁₂PU: C, 44.65; H, 6.00; N, 6.51. Found: C, 44.28; H, 5.78; N, 6.37.

[[2,2'-(1,2-Cyclohexanedilyl)bis(nitrilomethylidene(2-hydroxy-3,1-phenyleneoxy))bis[*N*-(4-methylphenyl)acetamidato]](2-)-*N,N',O,O'*-dioxouranium (14b)·*n*-Bu₄NH₂PO₄: mp 120–123 °C; ¹H 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); ³¹P 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 + H₂PO₄⁻), 1254.6 (14b + Bu₄NH₂PO₄), respectively]. Anal. Calcd for C₅₄H₇₆N₃O₁₂PU·1.8H₂O: C, 50.33; H, 6.23; N, 5.43. Found: C, 50.54; H, 6.05; N, 5.36. Karl Fischer titration calcd for 1.8H₂O, 2.50, found, 2.53.

[[2,2'-(1,2-Phenylenebis(nitrilomethylidene(2-hydroxy-3,1-phenyleneoxy))bis[*N*-(4-methylphenyl)acetamidato]](2-)-*N,N',O,O'*-dioxouranium (14e)·*n*-Bu₄NH₂PO₄: mp 131–135 °C; ¹H 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); ³¹P 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 + H₂PO₄⁻), 1248.6 (14e + Bu₄NH₂PO₄), respectively]. Anal. Calcd for C₅₄H₇₀N₃O₁₂PU·2H₂O: C, 50.43; H, 5.80; N, 5.44. Found: C, 50.16; H, 5.59; N, 5.51. Karl Fischer titration calcd for 2H₂O, 2.84, found, 2.64.

[[2,2'-(1,2-Phenylenebis(nitrilomethylidene(2-hydroxy-3,1-phenyleneoxy))bis[*N*-(4-methylphenyl)acetamidato]](2-)-*N,N',O,O'*-dioxouranium (14e)·2*n*-Bu₄NH₂PO₄: mp 89–92 °C; ¹H NMR and MS-FAB data are identical with those of the 14e·*n*-Bu₄NH₂PO₄ complex; ³¹P 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,N',O,O'*-dioxouranium (18)·*n*-Bu₄NH₂PO₄: mp 95–100 °C; ¹H 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); ³¹P 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 + H₂PO₄⁻), 1189.5 (18 + Bu₄NH₂PO₄), respectively]. Anal. Calcd for C₄₆H₇₄N₃O₁₄PU·2.75H₂O: C, 44.57; H, 6.46; N, 5.65. Found: C, 44.51; H, 6.35; N, 5.50. Karl Fischer titration calcd for 2.75H₂O, 4.00, found, 3.77.

[[2-[1-(Nitrilomethylidene)-2-oxophenylene]phenolato](2-)-*N,N',O,O'*-dioxouranium (19a)·2*n*-Bu₄NH₂PO₄: mp 175–180 °C; ¹H 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 + H₂PO₄⁻), 675.3 (19a + 2H₂PO₄⁻), respectively]. Anal. Calcd for C₄₅H₈₃N₃O₁₂P₂U·2H₂O: C, 45.18; H, 7.50; N, 3.51. Found: C, 45.49; H, 7.76; N, 3.51. Karl Fischer titration calcd for 2H₂O, 3.01, found, 3.03.

Crystal Structure Determinations. The crystal structures of 14b, 1c·*n*-Bu₄N⁺H₂PO₄⁻, 14e·2*n*-Bu₄N⁺H₂PO₄⁻, and 19a·2*n*-Bu₄N⁺H₂PO₄⁻ were determined with X-ray diffraction methods (Table 4). Reflections were measured in the $\omega/2\theta$ scan mode in the range $3 < \theta < 25^\circ$, using graphite monochromated Mo K α 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 DIFABS⁴² 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 H₂PO₄⁻, Cl⁻, and NO₂⁻ 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*_{1:1} 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*_{1:1} 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 Et₄NCl in DMSO. As a supporting electrolyte, 0.3 M *n*-Bu₄NClO₄ in DMSO or 0.25 M *n*-Bu₄NClO₄ in 90% DMSO–10% H₂O 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*_{1:1} 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–H₂O 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.

¹H NMR Measurements. *K*_{1:1} 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·H₂PO₄⁻, 14b, 14e·2H₂PO₄⁻, and 19a·2H₂PO₄⁻ (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.