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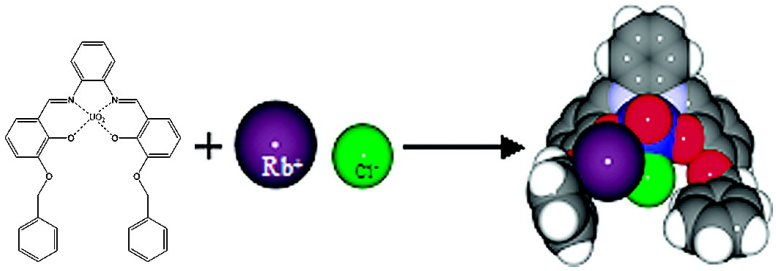

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Recognition of Alkali Metal Halide Contact Ion Pairs by Uranyl−Salophen Receptors Bearing Aromatic Sidearms. The Role of Cation−π Interactions

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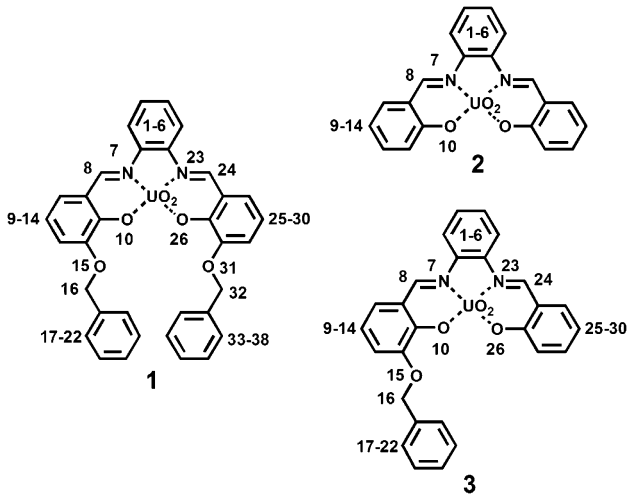
Abstract: Hard anions have long been known to bind strongly to the uranium of uranyl−salophen complexes. Upon functionalization of the salophen framework with one or two benzyloxy substituents, efficient ditopic receptors for alkali metal ions are obtained. The solid-state structures of complexes formed by the two-armed receptor **1** with CsF and with the chlorides of K^+, Rb^+, and Cs^+ reported here reveal the existence of dimeric supramolecular assemblies in which two receptor units assemble into capsules fully enclosing $(MX)_2$ ion quartets. In addition to the strong coordinative binding of the anion to the uranyl center and to electrostatic cation−anion interactions, stabilizing interactions arise from coordination of each cation to six oxygens, three from each receptor, and most importantly, to two aromatic sidearms belonging to different receptors. There are marked differences in organization at the supramolecular level in the CsCl complex of the one-armed receptor **3**, in that four uranyl−salophen units instead of two are assembled in a capsule-like arrangement housing a $(CsCl)_2$ ion quartet. However, both receptors achieve the common goal of having each metal cation in close contact with carbon atoms of two aromatic rings. ^{1}H NMR data provide strong evidence that cation−π(arene) interactions with the sidearms participate in binding also in solution.

Introduction

The search for neutral ditopic receptors capable of simultaneous complexation of both of the counterions in a target salt is a subject of great current interest in the general field of molecular recognition.[1−3] High binding affinity is expected when the salt is bound to the receptor as a contact ion pair.[1f]

Our previous contribution to this field was based on the use of uranyl−salophen complexes endowed with aromatic pendants (e.g., **1**) as ditopic receptors for quaternary ammonium halide contact ion pairs (Chart 1).[3] Recognition of hard anions is ensured by strong binding to the hard Lewis acidic uranyl center in the equatorial plane of the uranium,[1b] whereas cation−π interactions[4] are established between the aromatic sidearms and the cation partner of the ion pair, as nicely exemplified by the molecular structure of the 1:1 complex of receptor **1** with tetramethylammonium chloride (Figure 1).[5]

Chart 1. Chemical Formulas and Crystallographic Numbering of Uranyl−Salophen Receptors **1**−**3**



There is a wide current interest in the cation−π interactions of alkali metal ions because of their chemical and biological

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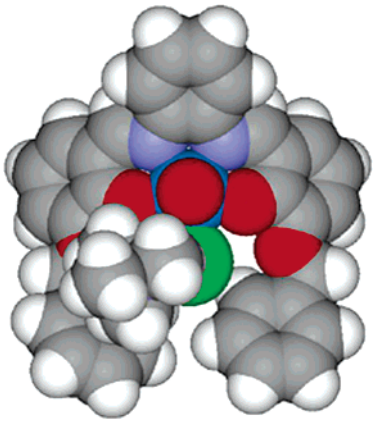

Figure 1. Crystal structure of the 1:1 complex of receptor **1** with tetramethylammonium chloride. $CH_3\cdots\pi$ (centroid) distance is 3.42 Å.[3]

relevance.[4,6] Much of our present knowledge in this area derives from gas-phase investigations[7] and theoretical studies.[8] As to the condensed phase, there has been a general difficulty of addressing the interactions experimentally, and most of the earlier evidences consist in episodic discoveries of unanticipated cation$-\pi$ interactions in a number of crystal structures.[6a] Only during the past decade have systematic investigations provided useful insights into the general significance of alkali metal cation$-\pi$ binding. Popular ligands for such studies have been lariat ethers having aromatic sidearms[6] and calixarene derivatives.[9,10]

We felt that uranyl−salophen derivatives such as **1** had the potential to behave as ditopic receptors also for alkali metal ion pairs owing to the possible interactions of the aromatic sidearms with the cation. We report here the preparation and characterization of the complexes formed by the uranyl−salophen receptors **1** and **3** with halides of the larger alkali metals (K^+, Rb^+, and Cs^+). The results of such an investigation further substantiate the general occurrence of the alkali metal cation$-\pi$ interaction and underscore its role in the formation of supramolecular assemblies.

Results and Discussion

Crystallization Experiments. A large number of cocrystallization attempts of receptor **1** with the series of alkali metal chlorides or fluorides from Li^+ to Cs^+ were carried out in mixtures of **1** (10 mg) and salt in proportions variable from 1:1 to 1:10, dissolved in various solvent mixtures including $CHCl_3$/MeOH, $CHCl_3$/MeOH/MeCN, and H_2O/MeOH (3−4 mL). The solid materials obtained upon slow evaporation (from days to several weeks) at ambient temperature were in many cases either amorphous or powder, or contained no suitable crystals for X-ray analysis. In a number of cases crystals of the salt-free receptor coordinated to different solvent molecules were obtained. Occasional attempts at inducing crystallization from the above solutions by means of slow diffusion of diisopropyl ether were unsuccessful. Analogous cocrystallization attempts carried out on the parent uranyl−salophen receptor **2** (Chart 1) in no case yielded crystals of the salt complexes. Good quality crystals were obtained for the 1:1 adducts of receptor **1** with KCl, RbCl, CsCl, and CsF, and for the MeCN and MeOH complexes of the salt-free receptor **1**. All these crystals were subjected to X-ray analysis.

RbCl, CsCl, and CsF Complexes of 1. RbCl, CsCl, and CsF all form structurally similar 1:1 complexes, which are, however, best described as 2:2 complexes owing to their evident dimeric nature (Figure 2). Complexes **1**·RbCl and **1**·CsCl crystallize with similar unit cells and nearly isomorphous structures. Each uranyl strongly binds to a halide ion, which is located in its equatorial plane and two negatively charged **1**·X^- units are connected through coordination to alkali metal cations which are placed above the aromatic sidearms similarly to the Me_4NCl complex (Figure 1).[3]

Coordination of rubidium and cesium cations is similar in all structures; that is, each cation is coordinated to six oxygens, three from each receptor, thus creating a pseudo-crown ether-like environment for the cation.[11] Additionally, each metal ion in the dimeric unit is coordinated to both halide ions and, most importantly, to two aromatic sidearms, one from each of the receptors giving decacoordination for the cation. Thus, the two uranyl−salophen units are combined in a centrosymmetric arrangement featuring a dimeric capsule in which an ion quartet is enclosed. The relevant distances fall within typical ranges of Cs^+ and Rb^+ coordinative bonds, namely, 3.03−3.86 Å for $Cs^+\cdots O$, 2.94−3.63 Å for $Rb^+\cdots O$, 3.33−3.49 Å for $Cs^+\cdots Cl^-$, 3.22−3.32 Å for $Rb^+\cdots Cl^-$, and 2.94−3.03 Å for $Cs^+\cdots F^-$ bonds.[12]

As shown by theoretical studies, an optimal cation$-\pi$ interaction is one in which the cation approaches the ring centroid along the normal to the carbon plane in η^6 coordination mode.[8] Indeed, there is evidence from X-ray crystal studies that simple aromatics such as benzene are η^6-coordinated to alkali metal ions.[13] However, off-center geometries are more the rule than the exception when the cation-coordinated arenes are part structures of more elaborate receptors and where other weak interactions also contribute to the complexation. Notable examples are provided by Cs^+ complexes of calix[4]arene-crown-6 derivatives[14] and by the K^+, Rb^+, and Cs^+ complexes of hexakis(methoxymethyl)benzene.[15] In our complexes with

(5) In the crystalline state, the complex is better described as a 4:4 complex in which four uranyl−salophen receptors enclose four tetramethylammonium cations. Each cation interacts with aromatic rings of three different receptor units. In addition to the interaction shown in Figure 1, the cation interacts with the other sidearm of a second receptor molecule and with the *o*-phenylenediamine ring of a third one, with $CH_3\cdots\pi$ (centroid) distances of 3.64 and 3.68 Å, respectively (Data from ref 3).

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(12) Detailed coordination distances and distances between the alkali metals and aromatic carbons are given as a Supporting Information.

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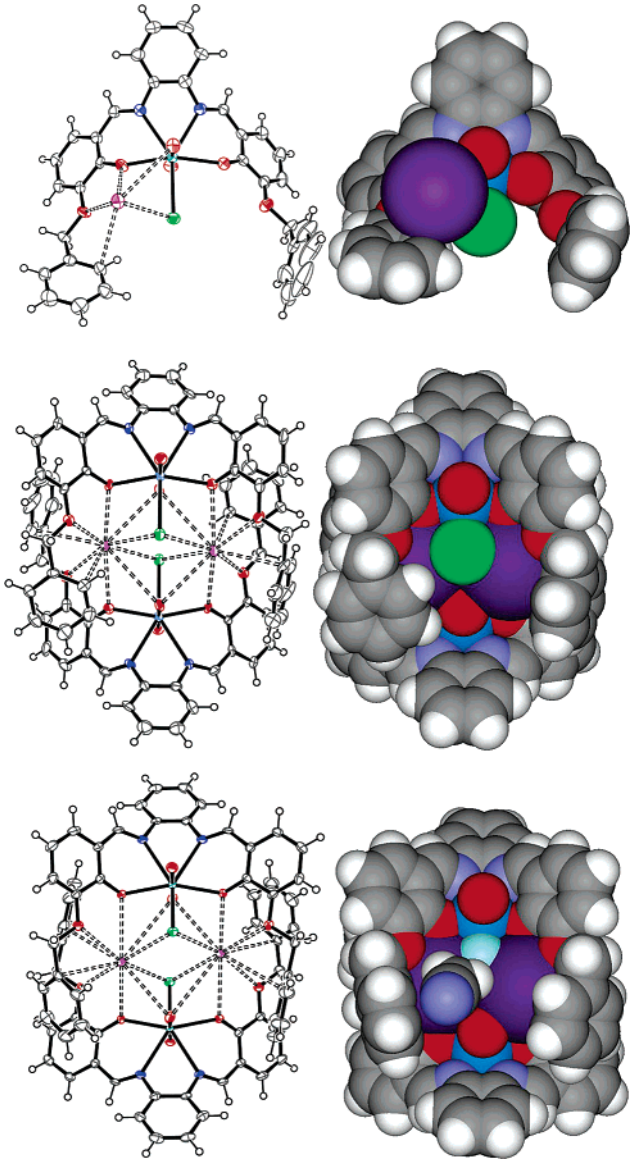

Figure 2. Top: Asymmetric unit of the RbCl complex of **1** drawn as Ortep plot (50% probability level) and as VDW presentation (chloride: green). Middle: Dimeric assembly of the CsCl complex of **1**, which is isomorphous to the RbCl complex. Bottom: CsF complex of **1** showing the acetonitrile inclusion within the dimer in the VDW picture (fluoride: light blue).

receptor **1** the closest metal ion−aromatic carbon distances of 3.44(1) Å for CsCl, 3.34−3.38(1) Å for RbCl, and 3.58(1) Å for CsF fall within the criteria of van der Waals contacts between ten-coordinated Cs^+ or Rb^+ [16] and aromatic carbon[17] and are in accordance with those observed in systems where $M^+\cdots$arene interactions have been documented.[6,14,15,18] These coordinative $M^+\cdots C$ distances indicate either η^1 or η^2 type of bonding. Longer, yet significant $M^+\cdots C$ distances in the range of 3.60−3.80 Å are also observed, which makes it difficult to determine

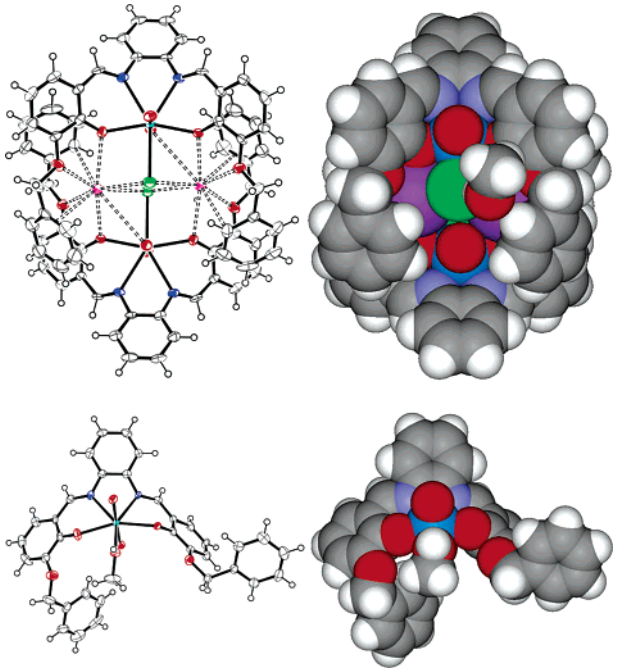

Figure 3. Ortep (50% probability level) and VDW presentations of the KCl complex of **1** (top) and of the MeOH complex of **1** (bottom), which cocrystallizes with the KCl complex. The VDW picture of the KCl complex **1** (top) shows the methanol molecule hydrogen bonded to chloride anion.

the coordination mode with accuracy. Nevertheless, the shortest $M^+\cdots$arene distances definitely signify the operation of binding interactions between metal cation and arene donors, which play an important role in the formation of the dimeric supramolecular assembly.

The smaller size and more electronegative nature of fluoride compared to chloride provide an explanation for the marked difference observed in the shortest $Cs^+\cdots C$ distances in CsCl and CsF complexes (3.44 versus 3.58 Å, respectively). There is more space "inside" the dimeric assembly of the latter, which is occupied by an acetonitrile solvent molecule hydrogen bonded to fluoride with a C···F distance of 3.09 Å. Inclusion of such solvent molecule prevents the aromatic sidearms from approaching to the metal ion as close as in the chloride complex (Figure 2, bottom).

KCl Complex of 1. There are similarities, but also significant differences, between the solid-state structure of the KCl·**1** complex and those of the corresponding complexes of rubidium and cesium. The asymmetric unit contains a 1:1 complex, which forms 2:2 dimers similar to the larger alkali metals, but additionally there is another receptor with solvent methanol coordinated to the UO_2 center in the crystal lattice (Figure 3).

This MeOH-coordinated receptor is placed between dimeric assemblies via edge-to-face and face-to-face π interactions between the aromatic units of the receptor molecule (Figure 4). The role as well as the reason for the crystallization of the additional MeOH coordinated receptor is unclear. It is possibly related to the fact that the crystallization solvent used in this case was MeOH/H_2O, while other complexes were obtained

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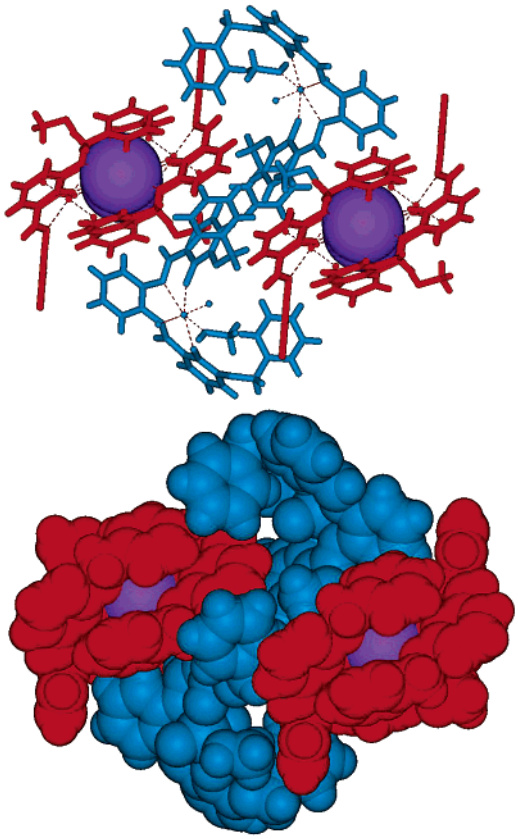

Figure 4. Stick and VDW presentations of the crystal packing showing **1**·KCl dimers (red) and **1**-MeOH complexes (blue) between the dimers.

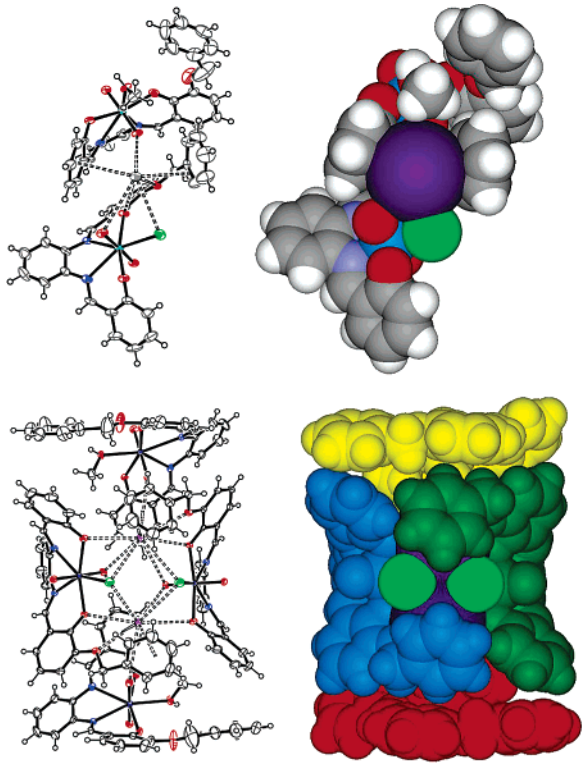

Figure 5. Ortep (50% probability level) and VDW presentations of the crystal structure of the CsCl complex of **3**. The top view shows half of the tetramer and cation···π interactions. The bottom view shows the noncentrosymmetric tetramer of the centrosymmetric crystal lattice, with the four salophen units in different colors.

from $CHCl_3$/MeOH/MeCN mixtures, but the operation of closest packing effects cannot be excluded.

The structure of the dimeric potassium complex resembles closely the structures of the corresponding rubidium and cesium complexes (Figure 2). However, there are minor differences in the coordination. The cation is coordinated to six oxygens with K^+···O distances of 2.85−3.87 Å, to two chlorides with K^+···Cl distances of 3.12−3.15 Å, and to carbons of the aromatic sidearms by η^1 and η^2 coordination (η^1 to C38 and η^2 to the bond C17−C22, distances 3.269(8) Å and 3.286(8) Å, respectively). The distances are in accordance with those of M^+−arene interactions documented earlier.[6,13−15,18] The smaller cation size allows the sidearms to bend toward the interior of the dimeric assembly and yet there is enough space for a methanol molecule to hydrogen bond to chloride anion, shown in the VDW picture of the KCl complex of **1** (Figure 3, top).

CsCl Complex of 3. Given that in the capsule-like dimeric complexes both sidearms of **1** are engaged in π-interactions with the complexed alkali metal ion, it was of interest to investigate the behavior of uranyl−salophen receptors with either no aromatic sidearm (receptor **2**) or with one sidearm (receptor **3**). Several cocrystallizations of receptor **2** with various alkali metal salts in various solvents were attempted but only powderlike precipitates or crystal structures of salt-free solvent-receptor **2** complexes were obtained,[19] which strengthens the view that cation−π interactions with the aromatic sidearms play a significant role in complexation of alkali metals. Receptor **3**, however, showed successful complexation with CsCl, but the stoichiometry and the structure of the complex are different than those of the corresponding complex of the two-armed receptor **1**. With receptor **3** a 2:1 complex of receptor and salt was obtained, in which one receptor binds to chloride and the other to a solvent methanol molecule, and both participate in cesium complexation (Figure 5). The stoichiometry of the complex is best described as 4:2, in which four receptor molecules are assembled in a capsule-like arrangement in which a $(CsCl)_2$ ion quartet is enclosed. The reason for this stoichiometry relates to the coordination of the cesium: owing to the only one aromatic sidearm the coordination sphere is not complete unless three separate uranyl−salophen units coordinate to each cesium. Each cesium is thus coordinated to altogether six oxygens of three receptors (3:2:1), to two chlorides bound to the two middle units of the tetrameric assembly (blue and green units in Figure 5) and to two aromatic rings belonging to different receptors in a tilted-sandwich arrangement. The type of coordination is η^2 to the bond C17−C18 (ring C17−C22) and η^6 to ring C25−C30.[12] The relevant closest distances are 3.53(1) Å to the bond C17−C18, 3.66(1) Å to the centroid of the same aromatic ring, and 3.650(8) Å to the ring C25−C30. Interestingly, the "core" aromatic ring (C25−C30) of the parent salophen unit also participates in complexation, while in complexes of **1** only aromatic sidearms were responsible for cation···π interactions.

MeCN and MeOH Complexes of 1. The structures of **1**·MeCN and **1**·MeOH complexes are not only interesting in their own rights, but also in connection with the question of why the complexation of the smallest alkali metal ions Li^+ and Na^+ was not successful. Both acetonitrile and methanol are bound to the uranyl center in the equatorial plane (Figure 6) and crystallize with similar unit cells and isomorphous structures

(19) Crystallographic details of these **2**·solvent complexes are provided as a Supporting Information.

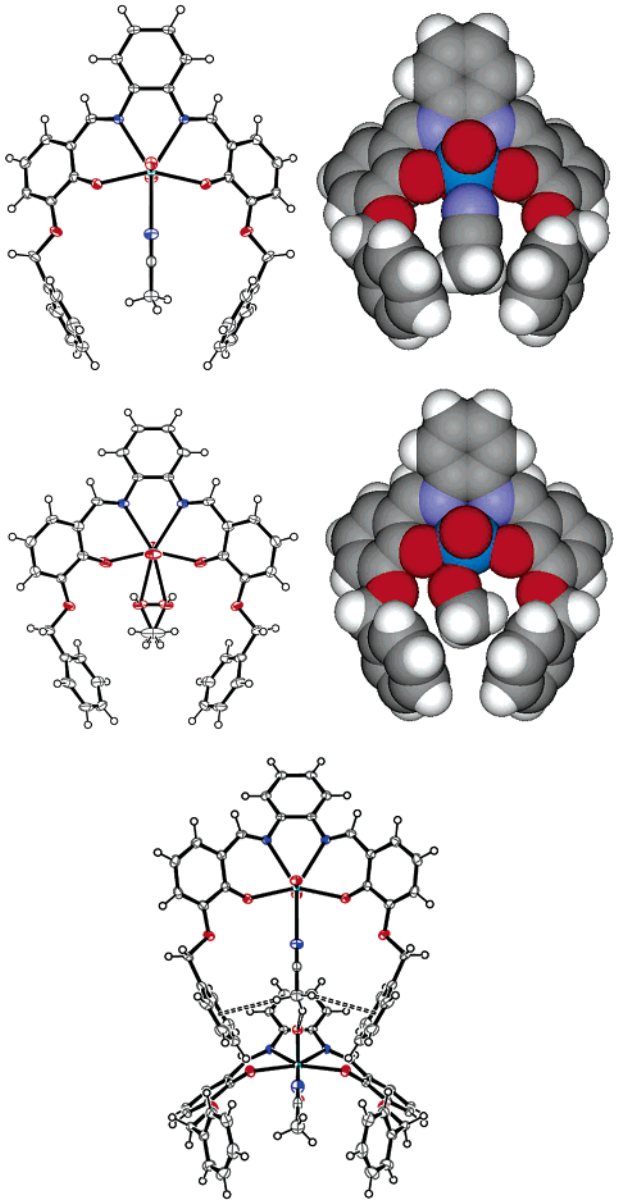

Figure 6. Top: Crystal structure of uranyl−salophen receptor **1** crystallized with acetonitrile. Middle: Isomorphous structure crystallized with methanol. Bottom: Acetonitrile is coordinated to the uranium center and interacts with the aromatic sidearms via C−H···π interactions (3.63 Å) and with the uranyl oxygen of the adjacent complex via weak C−H···O hydrogen bonds (3.77 Å).

despite their different size. In the acetonitrile complex the sidearms of **1** are turned inward in a quasimacrocyclic conformation that fully encloses a CH···π (3.63 Å) bonded CH_3CN molecule. Corroborating evidence comes from the observation that **1** and CH_3CN form a complex of definite stability in $CDCl_3$ solution ($K = 23 \pm 5$ M^{-1}, 25 °C). The upfield shift suffered by the ^{1}H NMR signal of MeCN upon complexation ($-\Delta\delta_\infty =$ 0.06 ppm) demonstrates that the methyl group is under the influence of the ring currents of the aromatic walls[20] and provides a strong indication that the structure of the complex in solution closely resembles the molecular structure in the solid state.

Unlike acetonitrile, the hosted methanol molecule is too small to fill the cavity completely and therefore is disordered over two positions inside the quasimacrocyclic cavity, where very weak C−H···π interactions (3.88 Å) between the hosted methanol and one of the aromatic sidearms are established in each orientation. It is of interest to compare the structure of **1**·MeOH in Figure 6 with the structure of the methanol-coordinated **1** crystallized with KCl (Figure 3). In the latter, the aromatic sidearms do not interact with methanol at all, but are turned away to interact with aromatic parts of nearby receptors. It appears therefore that CH···π interactions with the unsuitably sized methanol are not strong enough to keep the quasimacrocyclic conformation as the most stable arrangement in all cases.

The difference in π-interactions with the complexed solvent molecules emphasizes the significance of guest size for effective binding through π-interactions. It seems therefore likely that, despite its high flexibility, receptor **1** is not geometrically suited to provide the smallest Li^+ and Na^+ cations with a favorable environment made up of a suitable pseudocrown ether arrangement and aromatic sidearms available for cation−π interactions.

Solution Studies. Experimental studies in which the existence of alkali metal cation−π(arene) interactions in solution has been convincingly demonstrated are extremely rare.[21] A major reason for this difficulty is the large penalty due to cation desolvation and counterion separation, which is hardly offset by weak cation−π interactions. Since counterion separation is not a problem with our receptors, we decided to ascertain whether the sidearms of **1** participate in binding also in solution.

An indication was obtained by ESI-TOF mass spectrometric analysis of a mixture of **1** and CsCl. The mass spectrum revealed peaks due to **1**·Cs^+, **1**·CsCl·Cs^+, $\mathbf{1}_2$·CsCl·Cs^+, and (**1**·CsCl)$_2$·Cs^+. We suggest that the structure of the last species is a dimeric assembly similar to that found in the solid state (Figure 2), complexed with a Cs^+ cation in exo-mode. Similarly peaks due to (**3**·$Cs)^+$, (**3**·CsCl·$Cs)^+$, and ($\mathbf{3}_2$·CsCl·$Cs)^+$ species are found in the mass spectrometric analysis of a mixture of **3** and CsCl.

Solubilization into an organic solvent of an otherwise insoluble alkali metal salt upon treatment with a suitable receptor is a well-known phenomenon since Pedersen's discovery of the crown ethers.[22] Contrary to expectations, no dissolution of the chloroform insoluble CsCl took place upon treatment with a chloroform solution of **1**. Instead, the red-orange color typical of uranyl−salophen compounds passed from the solution to the solid phase. The red-orange material was separated and shown by scanning electron microscopy (SEM)/EDS analysis to consist of crystals containing Cs, Cl, and U in a 1:1:1 stoichiometric ratio, grown on a matrix of CsCl (Figure 7). Identical results were obtained using CsF, but when receptor **1** was replaced by the parent compound **2** no precipitation took place.

This markedly different behavior is well illustrated by the competition experiment reported in Figure 8. An equimolar mixture of **1** and **2** in $CDCl_3$ was exposed to the action of excess CsCl in an NMR tube. After 2 days, about 3/4 of **1** was transformed into the insoluble CsCl complex, whereas the concentration of **2** in the solution remained unchanged.

The different behavior of the two receptors is remarkable. Nevertheless, it does not demonstrate unequivocally that **1** has

(20) The deshielding by ring currents of the aromatic walls is strong enough to more than offset the presumably large downfield shift caused by coordination to the uranyl.

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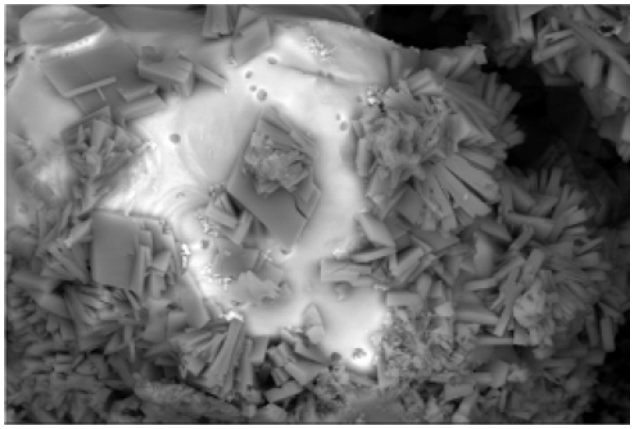

Figure 7. SEM image of crystals of the complex of **1** with CsCl formed by precipitation from a solution of **1** in $CHCl_3$ on excess solid CsCl (shown as a white zone surrounding the large crystal in the center of the picture).

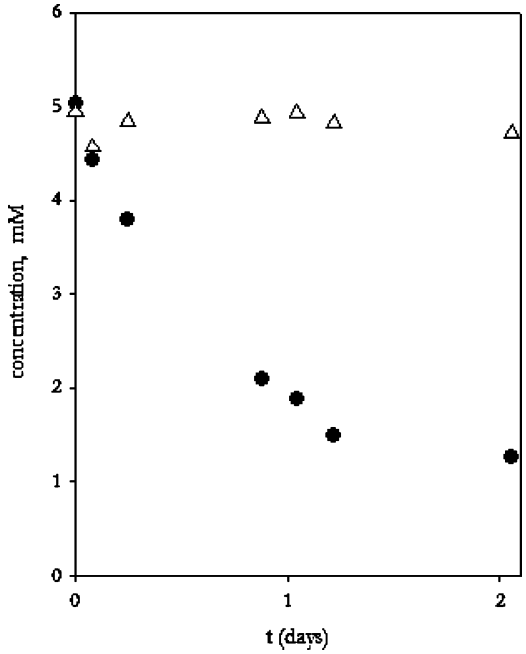

Figure 8. Time−concentration profile of a mixture of **1** (●) and **2** (△) in $CDCl_3$ exposed to the action of solid CsCl. Concentration data from ^1H NMR analysis (internal standard: 1,1,2,2-tetrachloroethane).

a higher affinity for CsCl than **2**. It might simply mean that the complex formed by the former is much less soluble than that formed by the latter. Therefore, additional evidence was sought. Given the insolubility of the salt complexes of **1** in chloroform, a more polar solvent was used. A portion of the ^1H NMR spectrum of 1 in CD_3COCD_3 is shown in Figure 9a. Addition of ca. 0.4 molar equivalent of solid Bu_4NCl caused the appearance of a second species (Figure 9b), whose imine and aromatic protons were upfield shifted relative to free **1**, whereas the benzyl protons were strongly downfield shifted. We interpret these results in terms of a virtually quantitative formation of a complex of **1** with chloride anion, whose complexation−decomplexation rate is slow on the ^1H NMR time scale. At variance with the large upfield shifts observed in chloroform solution,[3] the chemical shifts of the Bu_4N^+ countercation (not shown) were practically the same as those of pure tetrabutylammonium chloride, which indicates that the chloride-bound species **1**·Cl^- is not ion-paired to Bu_4N^+ ion, but a free species.

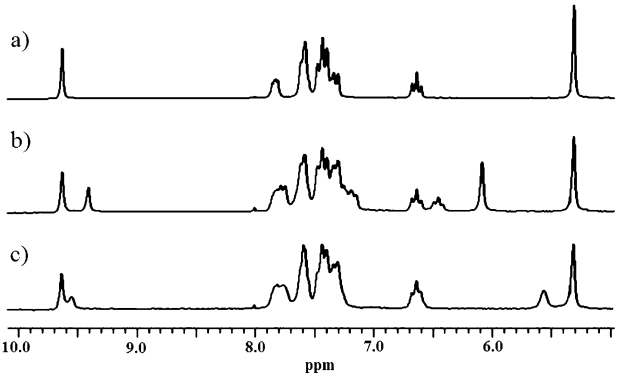

Figure 9. Portions of the ^1H NMR spectra in CD_3COCD_3 of: (a) 5 mM **1**. Singlets at 9.64 and 5.32 δ are due to the imine and benzyl protons, respectively, whereas the triplet at 6.64 δ is due to aromatic hydrogens para to the phenoxide oxygens; (b) solution a and 0.4 mol equiv of Bu_4NCl; (c) solution b and excess $CsPF_6$.

Addition of excess solid $CsPF_6$ caused precipitation of the red-orange complex of **1** with CsCl, leaving after few minutes receptor **1** as the sole detectable species in solution. However, in a spectrum taken immediately after the addition of $CsPF_6$ (Figure 9c), in addition to free **1** a second species is clearly visible, which is interpreted as a Cs^+-associated **1**-Cl^- entity, present in solution as a transient species before precipitation. When the one-armed receptor **3** was subjected to the same treatments similar results were obtained, with the sole significant difference that no precipitation occurred upon addition of $CsPF_6$. The Cs^+-bound species obtained thereupon had very nearly the same ^1H NMR spectral features as those observed with receptor **1**.

A control experiment was carried out on receptor **2**. Addition of tetrabutylammonium chloride caused as before upfield shifts of the imine and aromatic hydrogens, showing again strong complexation with chloride. However, addition of $CsPF_6$ caused the immediate formation of a white precipitate of CsCl, uncontaminated by the receptor. We conclude therefore that the affinity of CsCl toward **1** and **3** is much higher than toward the parent receptor **2** and that the observed increase in binding affinity is a manifestation of cation−π interactions with the sidearms of **1** and **3**.

Concluding Remarks

Our search for contact ion pair recognition resulted in the discovery of ion-quartet recognition. In all of the isolated complexes of receptor and salt an ion quartet having composition of a dimeric ion pair $(MX)_2$ constitutes the core of a supramolecular assembly in which either two two-armed or four one-armed receptor molecules assemble into capsules fully enclosing the ion quartets. Thus, the objective of alkali metal halide recognition without any penalty arising from counteranion separation was fully achieved.

^1H NMR solution studies of the complex of **1** with MeCN indicate close contacts of the aromatic sidearms with the methyl group of the guest. Furthermore, in CD_3COCD_3 solution Cs^+ ion binds to **1**·Cl^- and **3**·Cl^- much more strongly than to **2**·Cl^-. Therefore, solution data indicate that the structure of the above complexes correlate with the solid-state structures, thus reinforcing the view that the sidearms participate in binding both in solution and in the solid state. Although the primary interaction between receptor **1** and **3** with alkali metal halides is anion

Table 1. Crystallographic Data for Uranyl−Salophen Complexes

	1·CsF	**1**·CsCl	**1**·RbCl	**1**·KCl	**3**·CsCl	**1**·MeCN	**1**·MeOH
formula	$C_{34}H_{26}N_2O_6U$· CsF·$2CH_3CN$	$C_{34}H_{26}N_2O_6U$· $CsCl$·$2CH_3CN$	$C_{34}H_{26}N_2O_6U$· $RbCl$·$2CH_3CN$· $0.25H_2O$	$2C_{34}H_{26}N_2O_6U$· KCl·$2CH_3OH$	$2C_{27}H_{20}N_2O_5U$· $CsCl$·$2CH_3CN$· CH_3OH·H_2O	$C_{34}H_{26}N_2O_6U$· CH_3CN	$C_{34}H_{26}N_2O_6U$· CH_3OH
crystallization solvent mixture	$CHCl_3$/MeCN/ MeOH = 4:1:1	$CHCl_3$/MeCN/ MeOH = 1:1:1	$CHCl_3$/MeCN/ MeOH = 1:1:0.5	MeOH/H_2O = 4:1	$CHCl_3$/MeCN/ MeOH = 3:3:0.5	$CHCl_3$/MeCN/ MeOH = 1:2:1	MeOH/$CHCl_3$ = 2:1
formula weight	1030.62	1047.07	1004.15	1731.83	1681.51	837.65	828.64
crystal system	monoclinic	triclinic	triclinic	triclinic	monoclinic	orthorhombic	orthorhombic
space group	$P2_1/n$ (No. 14)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$C2/c$ (No.15)	*Pnam* (No. 62)	*Pnam* (No. 62)
crystal color	red	red	orange	red	red	red	orange
a/Å	16.3779(7)	12.0338(3)	11.8754(4)	14.3905(2)	32.4597(7)	9.6034(1)	9.5634(2)
b/Å	13.9653(6)	12.3620(3)	12.2205(5)	15.2086(3)	15.9145(4)	13.3230(2)	13.7333(4)
c/Å	16.6928(5)	14.5835(5)	14.6154(7)	15.5041(3)	26.1849(4)	23.3439(3)	22.4731(7)
α/deg	90	108.135(2)	107.790(2)	93.258(1)	90	90	90
β/deg	107.568(2)	97.069(1)	96.735(2)	107.142(1)	120.983(1)	90	90
γ/deg	90	108.179(2)	108.296(2)	100.843(1)	90	90	90
V/Å^3	3639.9(2)	1899.66(9)	1863.4(1)	3161.7(1)	11596.6(4)	2986.76(7)	2951.6(1)
Z	4	2	2	2	8	4	4
final R indices[a]	0.027/0.062	0.052/0.096	0.058/0.140	0.038/0.083	0.034/0.076	0.017/0.038	0.042/0.095
GOF	1.190	1.065	1.088	1.125	1.087	1.111	1.105

[a] $I > 2\sigma I$.

binding to the uranyl and, in turn, the primary interaction between uranyl−salophen-complexed halide anion and the cation is electrostatic in nature, the appropriately positioned sidearms reinforce the binding through cation−π interactions.

The results presented here, added to our previous results of tetralkylammonium halide complexation,[3] show that uranyl−salophen **1** is quite adaptable a receptor, in that upon guest complexation its conformationally flexible sidearms adapt to achieve a stable arrangement, in which multiple CH−π or cation−π interactions are established. The sidearms positions and, consequently, the molecular and crystal structures of the resulting complexes are controlled by interactions of the aromatic sidearms with the different guests. This work opens the way toward the development of novel zwitterion receptors, a matter which has received until now a limited attention.[23] Thanks to their high adaptability, we are presently exploiting sidearmed uranyl−salophen complexes as neutral ditopic receptors in the recognition of a number of zwitterions, including betaine and related compounds, and phospholipids.

Experimental Section

Materials. Receptors **1** and **2** were available from previous investigations.[3]

Receptor 3. *o*-Phenylenediamine (0.7 g, 6.6.mmol) in 25 mL of CH_3-OH was added dropwise to a solution of salycilaldehyde (1.1 g, 8.8 mmol) and 2-hydroxy-3-(phenylmethoxy)benzaldehyde[24] (1.0 g, 4.4 mmol) in 50 mL of CH_3OH. The mixture was refluxed for 2 h, and $UO_2(OAc)_2$·2 H_2O (2.8 g, 6.6 mmol) was added. After 15 h the solvent was evaporated, and the desired product was obtained by column chromatography on neutral Al_2O_3 using first $CHCl_3$ and then adding 2% and 4% of CH_3OH. The purification yielded 1.1 g of an orange solid (25% yield, to be compared with a 44% yield calculated on a purely statistical basis). ^{1}H NMR (300 MHz, DMSO) δ 9.54 (s, 2H), 7.77−7.26 (m, 13H), 6.97 (d, J = 8.5 Hz, 1H), 6.72 (t, J = 7.5 Hz, 1H), 6.60 (t, J = 7.8 Hz, 1H), 5.29 (s, 2H). ^{13}C NMR (75 MHz, DMSO) δ 170.2, 167.1, 161.6, 150.4, 147.3, 138.2, 137.1, 136.6, 129.3, 129.0, 128.8, 128.7, 125.1, 124.8, 121.4, 120.9, 118.2, 117.4, 71.3. ESI-MS m/z mass calcd for $C_{27}H_{20}N_2O_5UK$ [M + K$^+$], 729.59; found, 729.26. Anal. Calcd. for $C_{27}H_{20}N_2O_5U$·H_2O: C, 45.77; H, 3.13; N, 3.95. Found: C, 45.72; H, 3.21; N, 3.84.

Warning! Care should be taken when handling uranyl-containing compounds because of their toxicity and radioactivity.

NMR Measurements. The experiments were performed at 25 °C on a Bruker AC 300 instrument.

Scanning Electron Microscopy. The measurements were performed with a LEO1450VP microscope equipped with an INCA300 EDS system.

X-ray Data Collection and Crystal Structure Determinations. X-ray data for all complexes were collected on a Nonius Kappa CCD diffractometer using graphite monochromatized Mo Kα radiation and the temperature of 173.0 K. Structure solution was performed by SIR-92 or SHELXS-97 and refined on F^2 by full-matrix least-squares techniques (SHELXL-97).[25] Hydrogen atoms were calculated to their idealized positions and refined as riding atoms (temperature factor 1.2 or 1.5 times C temperature factor). Absorption correction was applied to all structures.[26] Crystallographic details are presented in Table 1.

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Supporting Information Available: Coordinative distances between alkali metal cations and uranyl−salophen receptors **1** and **3**, crystal structures of solvent-receptor complexes of **2**, and crystallographic information in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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