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Ion Pair Recognition of Quaternary Ammonium and Iminium Salts by Uranyl−Salophen Compounds in Solution and in the Solid State

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Abstract: Efficient ditopic receptors for quaternary ammonium and iminium salts have been obtained upon functionalization of the uranyl−salophen unit with conformationally flexible side arms bearing phenyl or β-naphthyl substituents. Binding affinities in chloroform solution have been measured for a large number of quaternary salts comprising tetramethylammonium (TMA), tetrabutylammonium (TBA), acetylcholine (ACh), *N*-methylpyridinium (NMP), and *N*-methylisoquinolinium (NmiQ) cations. Recognition of the anion partner is ensured by coordination to the hard Lewis acidic uranyl center, whereas cation−π/CH−π interactions of the quaternary ions are established with the aromatic pendants. The role of the cation−anion interactions on the dynamics of exchange between the free and complexed species is discussed. Solid-state structures have been obtained for a few salt−receptor combinations. In the solid state, side-armed receptor molecules form assemblies that enclose ion pair aggregates of varying composition and structure, including AChCl dimers, two different kinds of tetrameric (TMA)Cl clusters, and unidimentional salt strips of (NMP)Br. The lack of side arms as preferential binding sites for the polar quaternary cations prevents association patterns of the kinds formed with the side-armed receptors, as shown by the crystal structure of the complex of (TMA)Cl with the parent uranyl−salophen receptor.

Introduction

In recent years there has been a great interest in the design, synthesis, and investigation of salt-binding receptors.[1] Since either of the charged partners of a salt is a likely site of recognition, a receptor specifically designed for effective salt complexation should consist of at least two subunits, each of which capable per se of binding to one of the partners of the salt.

In apolar organic solvents, salts exist mostly as ion pairs and/or higher aggregates. Thus, high binding affinities are expected when the recognition subunits in the ditopic receptors are connected in such a way that the salt is bound as contact ion pairs, without loss of electrostatic energy arising from charge separation.[2] Several strategies have been devised to achieve recognition of the ionic subunits of the guest salt, most of which make use of crown ethers for cation recognition and hydrogen bond donors for anion recognition.[3] We recently reported on the recognition of alkali-metal halide ion pairs by uranyl−salophen complexes bearing aromatic side arms (e.g., **1**; see Chart 1).[4] Such receptors combine the strong binding of the hard Lewis acidic uranyl center to hard anions (F^-, Cl^-) with cation−π interactions between the flexible aromatic side arms and the alkali-metal countercation.

Cation−π interactions involving organic cations have attracted much attention because their chemical and biological relevance.[5] The present work establishes uranyl−salophen complexes[6] decorated with aromatic side arms as effective

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Chart 1. Chemical Formulas and Crystallographic Numbering of Receptors **1**−**4**

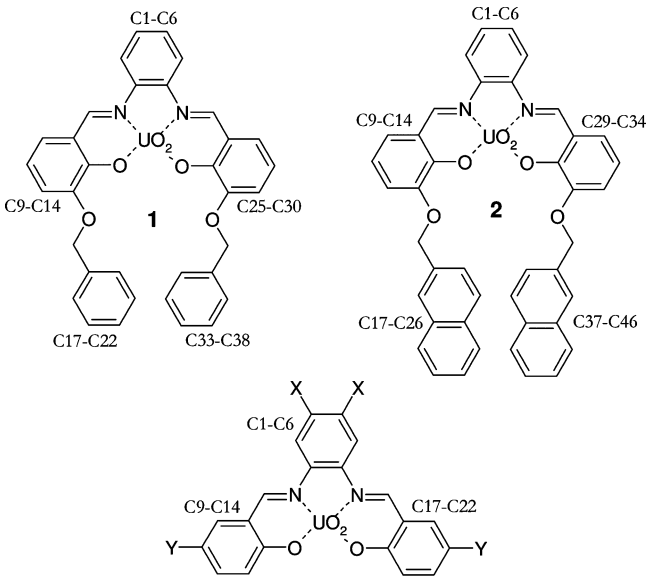
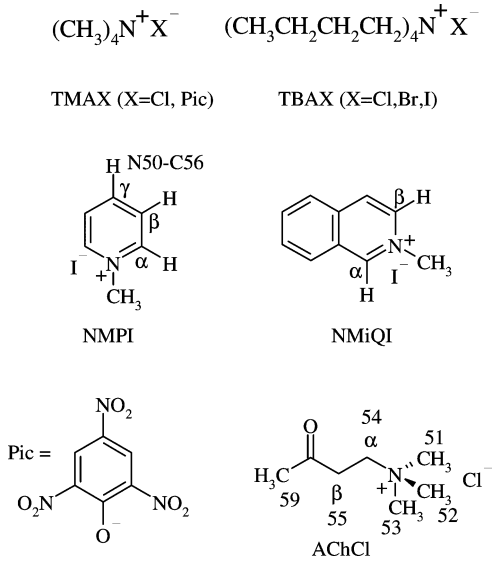


Chart 2. Chemical Formulas and Crystallographic Numbering of Guest Salts



ditopic receptors that recognize associated ion pairs. As an extension of our initial communication in this field,[7] here we show that receptor **1** and **2** make extensive use of cation−π interactions in the formation of strong complexes with a variety of quaternary ammonium and iminium salts in solution and in the solid state. This study also includes the parent uranyl−salophen compound **3** as a control receptor. Whenever appropriate, the moderately soluble **3** was replaced by its more soluble derivative **4**.

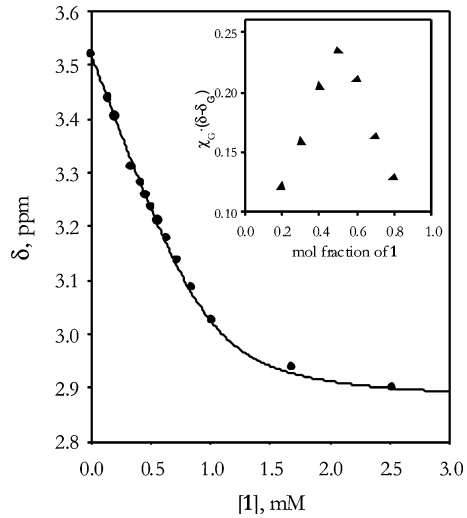


Figure 1. ^{1}H NMR titration of 0.5 mM (TMA)Cl with receptor **1**, in $CDCl_3$ at 25 °C. The inset shows the corresponding Job plot ([**1**] + [(TMA)Cl] = 1 mM).

Results and Discussion

Solution Studies. Binding constants for 1:1 complexes of quaternary ammonium and iminium salts listed in Chart 2 with uranyl−salophen receptors **1**−**3** (Chart 1) were obtained in $CDCl_3$ at 25 °C from ^{1}H NMR titrations in which the time-averaged proton signals of the quats were monitored as a function of increasing receptor concentration. A typical titration curve is shown in Figure 1, together with the corresponding Job plot. Titration data were fitted to a 1:1 binding isotherm by using an iterative procedure. Binding constants (K, M^{-1}) and limiting upfield shifts ($-\Delta\delta_\infty$, ppm) were obtained as best fit parameters (Table 1).[8] In addition to the N−CH_3 and NCH_2 protons, the resonances of other protons were monitored whenever possible. These were the CH_3 protons of Bu_4N, the α-CH_2, β-CH_2, and CH_3CO protons of ACh, the α-, β-, and γ-CH protons of NMP, and the α- and β-CH protons of NMiQ. Multiple titration plots were in all cases internally consistent. Typical examples of such plots are reported in Figure 2.

The signal of the picrate protons experienced small but clearly detectable shifts during titrations of TMAPic (see footnote *b* to Table 1), a finding which is well precedented in previous study of host−guest interactions of picrate salts of quats with aromatic hosts.[9] Interestingly, the signal was shifted downfield in the titration with **3** and shifted upfield in the titrations with **1** and **2**. We interpret the above findings as a result of two opposing effects, namely, a downfield shift due to coordination of picrate to the uranium center and an upfield shift caused by exposure to the aromatic surface of the receptors. It is apparent that the former effect predominates in the complex with **3**, whereas the latter effect predominates in complexes with **1** and **2**.

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Table 1. Binding Constants (K, M^{-1}) and Limiting Upfield Shifts ($-\Delta\delta_\infty$, ppm) for Complexes of Quaternary Salts with Receptors **1**−**3**

entry	salt[a]	1	2	3
1	(TMA)Cl	13 600 ± 600	28 000 ± 2000	1000 ± 130
	$-\Delta\delta_\infty$	0.65 (NCH_3)	0.69 (NCH_3)	0.36 (NCH_3)
2	TMAPic[b]	660 ± 40	950 ± 80	350 ± 40
	$-\Delta\delta_\infty$	1.15 (NCH_3)	1.00 (NCH_3)	0.78 (NCH_3)
3	(TBA)Cl	22 000 ± 3000	23 000 ± 1800	5400 ± 500
	$-\Delta\delta_\infty$	0.30 (NCH_2); 0.25 (CH_3)	0.35 (NCH_2); 0.32 (CH_3)	0.24 (NCH_2); 0.11 (CH_3)
4	(TBA)Br	930 ± 90	1200 ± 180	100 ± 20
	$-\Delta\delta_\infty$	0.17 (NCH_2); 0.12 (CH_3)	0.16 (NCH_2); 0.14 (CH_3)	0.09 (NCH_2); 0.05 (CH_3)
5	(TBA)I	270 ± 70	190 ± 40	30 ± 4[c]
	$-\Delta\delta_\infty$	0.05 (NCH_2); 0.02 (CH_3)	0.12 (NCH_2); 0.05 (CH_3)	0.05 (NCH_2); 0.04 (CH_3)
6	(ACh)Cl	19 000 ± 2600	42 000 ± 5000	6600 ± 600
	$-\Delta\delta_\infty$	0.60 (NCH_3); 0.59 (α-CH_2); 0.66 (β-CH_2); 0.30 (CH_3CO)	0.75 (NCH_3); 0.72 (α-CH_2); 0.80 (β-CH_2); 0.52 (CH_3CO)	0.33 (NCH_3); 0.40 (α-CH_2); 0.43 (β-CH_2); 0.25 (CH_3CO)
7	(NMP)I	130 ± 30	500 ± 100	110 ± 20
	$-\Delta\delta_\infty$	1.07 (NCH_3); 1.10 (α-CH); 0.93 (β-CH_2); 0.38 (γ-CH)	1.09 (NCH_3); 1.17 (α-CH); 1.07 (β-CH); 0.89 (γ-CH)	0.40 (NCH_3); 0.38 (α-CH); 0.35 (β-CH); 0.30 (γ-CH)
8	(NMiQ)I	110 ± 30	800 ± 120	120 ± 40
	$-\Delta\delta_\infty$	0.90 (NCH_3); 1.20 (α-CH_2); 0.74 (β-CH_2)	0.65 (NCH_3); 1.06 (α-CH_2); 0.52 (β-CH_2)	0.52 (NCH_3); 0.60 (α-CH_2); 0.40 (β-CH_2)

[a] Salt concentrations in the titration experiments were in the range 0.5−1 mM, with exception of the sparingly soluble TMAPic for which the concentration was 0.1 mM. [b] Titration plots based on the resonance of the picrate hydrogens are reported in the Supporting Information. Chemical shifts induced by complexation with receptors **1**−**3** ($-\Delta\delta_\infty$) are 0.19, 0.43, and −0.08 ppm in the given order. [c] Titrations carried out with receptor **4**. With the less soluble receptor **3** the percent bound is too low for the titration to be meaningful. The alkoxy groups in **4** exert a very small influence, if any, on the Lewis Acidity of the uranyl center, as shown by the fact that the affinities of **4** toward (TMA)Cl and (TBA)Br (K = 1400 ± 150 and 130 ± 20 M^{-1}, respectively) are almost indistinguishable from those experienced by **3** (entries 1 and 4). See ref 8.

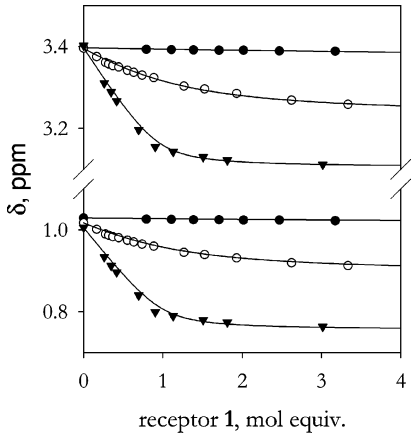

Figure 2. ^{1}H NMR titration of (TBA)X (CH_3− and NCH_2− protons) with receptor **1** in $CDCl_3$ at 25 °C, with X = Cl (▼), Br (○), and I (●). Only the initial portions of the titration curves of (TBA)I are shown. Full titration plots are shown in the Supporting Information.

Inspection of Table 1 shows that uranyl−salophen receptors **1**−**3** form very strong complexes with the chloride salts (entries 1, 3, and 6). The stability orders with TBA and TMA salts, namely, $Cl^- > Br^- > I^-$ (entries 3−5) and $Cl^- > Pic^-$ (entries 1 and 2), are in accordance with the hard Lewis acidic character of the uranyl center and indicate that the large affinities of the investigated chloride salts are dominated by the strong interaction of the hard chloride anion with the metal center. The stabilities of complexes with the control receptor **3** are always lower than those with the side-armed receptor **2** and, with the sole exception of the iminium ions NMP and NMiQ, also lower than those with receptor **1**, which demonstrates that the cation−π interactions of the countercation with the aromatic side arms bear significant contributions to complex stability in almost all cases.

The affinity of receptor **2** toward TMA, ACh, NMP, and NMiQ salts is always higher than that of receptor **1** (entries 1, 2, 6−8), which is a likely consequence of the larger surface and higher quadrupolar moment of naphthalene compared with benzene.[10] Not surprisingly, the largest stability enhancements are shown by the NMP and NMiQ salts, for which π-stacking is a likely additional mode of interaction with the aromatic pendants. Unlike the above salts, TBA salts are quite insensitive to the nature of the side arms as shown by the finding that the binding affinities to receptor **1** and **2** are the same within experimental errors, independent of counteranion nature (entries 3−5). We have already commented on the crystal structure of the complex of **1** with (TBA)Cl, in which the arms of TBA establish a large number of cation−π/CH−π interactions with the counteranion-complexed uranyl−salophen receptor.[7] It seems likely that such a behavior also applies to complexes of TBA salts in solution, as suggested by the observation that the complexation induced shifts of the methyl protons are in all cases comparable to those of the NCH_2 protons. We speculate that the additive nature of a large number of weak, stabilizing interactions in which also the aromatic salophen moiety is presumably involved explains the apparent insensitivity of TBA salts to the presence of naphthalene in place of benzene side arms.

Because of its biological relevance, acetylcholine is an important target in molecular recognition studies. Interestingly, the largest value in Table 1 is the equilibrium constant of 42 000 M^{-1} for the binding of AChCl to receptor **2** (entry 6). Judging from the complexation induced shifts, which are comparable in magnitude for the NCH_3, α-CH_2, and β-CH_2 and still significant for the CH_3CO protons, the whole molecule is involved in the binding. This is at variance with the behavior of typical ACh−receptor complexes, in which the complexation induced shifts grade in the order NCH_3 > α-CH_2, β-CH_2 >> CH_3CO.[11]

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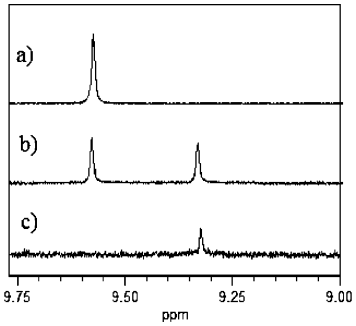
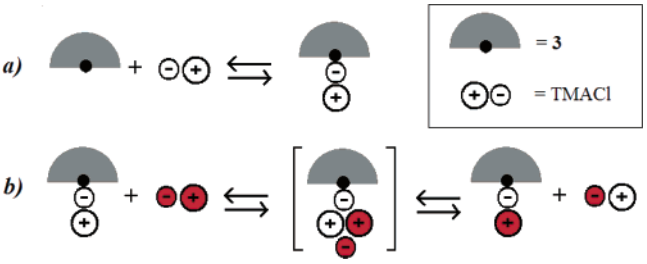


Figure 3. Portion of the ^{1}H NMR spectrum (imine protons) of (a) receptor **3**, (b) receptor **3** plus 1 mol equiv of (TMA)Cl, and (c) receptor **3** plus excess (TMA)Cl.

Scheme 1. Schematic Representations of (a) Complexation−Decomplexation of (TMA)Cl with Receptor **3** and (b) Cation Exchange via Ion Quartet



A last comment is devoted to a number of observations which are related to the dynamics of complexation−decomplexation and, consequently, bear directly on the mechanism of the reversible binding of ion pairs to uranyl−salophen receptors. Upon binding of **3** to (TMA)Cl, the signal of the imine protons of **3** (δ = 9.58 ppm) underwent an upfield shift of 0.3 ppm. Unlike TMA, whose protons appeared as a time-averaged signal during titration, the imine protons of free and complexed **3** appeared as separate signals (Figure 3). A similar behavior was experienced by receptor **4**, but not by receptors **1** and **2**. The imine protons of the side-armed receptors **1** and **2** underwent insignificant chemical shift variations upon titration with (TMA)Cl. Furthermore, the broad singlets of the benzylic protons were downfield shifted upon complexation ($\Delta\delta = +0.4$ ppm), but no separate signals of the free and complexed receptors were observed. Thus, we are faced with the apparently paradoxical evidence that the equilibration with receptors **3** and **4** is either fast or slow on the ^{1}H NMR time scale depending on whether the signal of the cation guest or that of the host is considered. To offer a rationale for the above findings, let us consider the mechanistic picture outlined in Scheme 1. Whereas both pathways a and b lead to exchange of TMA between free and complexed (TMA)Cl, only pathway a equilibrates the receptor between its free and complexed form. We assume that the ion-quartet mechanism b contributes to a very significant extent to the rate of exchange of TMA under the given conditions, which explains the higher rate of equilibration of TMA compared with that of the receptor. In other words, whereas reaction a is slow, reaction b is fast on the ^{1}H NMR time scale under the given experimental conditions. We further speculate that the dissociation of the uranyl-complexed chloride is strongly facilitated by its being tightly ion-paired to its countercation. It seems very likely that such a condition is more easily met by the side-armed receptors **1** and **2** than by the simple receptors **3** and **4**, as suggested by the schematic

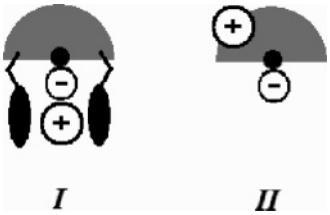


Figure 4. Schematic structures of host−anion−cation ternary complexes of side-armed receptors **1** and **2** (structure I) and parent receptor **3** (structure II) with (TMA)Cl.

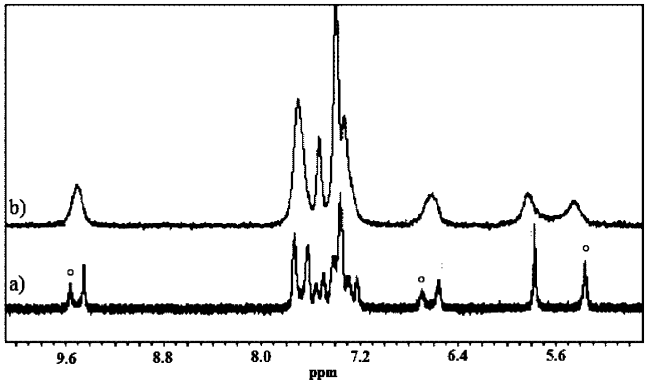


Figure 5. ^{1}H NMR spectrum of receptor **2** in the presence of 0.7 mol equiv of (TMA)Cl in CD_3CN (a, 25 °C; b, 75 °C). Signals at 9.56, 6.69, and 5.35 are due to the imine protons, to the protons *para* to the phenoxide oxygens, and to the benzylic protons of uncomplexed **2** (○), respectively.

structures in Figure 4. Structure I is consistent with the extensive involvement of the side arms in **1** and **2** in cation binding, whereas structure II appears to be more realistic than that in Scheme 1a, in view of the likely involvement of the salophen moiety in **3** and **4** in cation−π interaction.

A definite confirmation that the countercation plays an important role in the dissociation of the uranyl−chloride bond was obtained in CD_3CN solution (Figure 5). In such a polar solvent, cation−anion and cation−π interactions are significantly weakened. Consistently, the proton signal of (TMA)Cl (not shown) undergoes negligible variations upon addition of receptor **2**. On the other hand, the presence of separate signals of free and anion-complexed receptor indicates slow equilibrium on the ^{1}H NMR time scale at room temperature. At 75 °C equilibration is fast enough to produce extensive broadening of the benzylic hydrogens, as well as coalescence of the imine and aromatic hydrogens para to the phenoxide oxygens.

Crystal Structures. The previously reported[7] solid-state structures of complexes of receptor **1** with (TMA)Cl and (TBA)Cl clearly revealed the existence of stabilizing cation−π interactions and CH···O/Cl$^-$ hydrogen bonds. To widen the scope of the above studies and for comparison with ^{1}H NMR solution data, a considerable effort was made to obtain single crystals of host−guest complexes from all combinations of receptors **1**−**3** with the guest salts in Chart 2. Generally, the slow evaporation technique of solutions containing 15−30 mg of receptor in the presence of a 3−10 molar excess of salt was adopted. In many cases the solid materials were either amorphous or powder or contained only bad quality crystals. Crystals of the salt-free receptors coordinated to solvent molecules were obtained in some cases.[12] Good quality crystals were obtained for the 1:1 adducts of receptor **2** with (TMA)Cl and (ACh)Cl,

(12) An example is given in the Supporting Information.

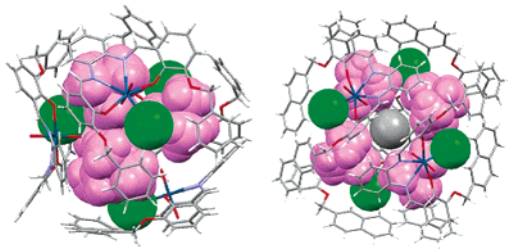


Figure 6. 4:4 assemblies of **1**·(TMA)Cl (left) and **2**·(TMA)Cl (right). Four chloride-bound receptors fully enclose four cations and in the case of **2** also a molecule of disordered acetonitrile. Acetonitrile molecules, cations, and anions outside the capsular assembly are excluded for clarity.

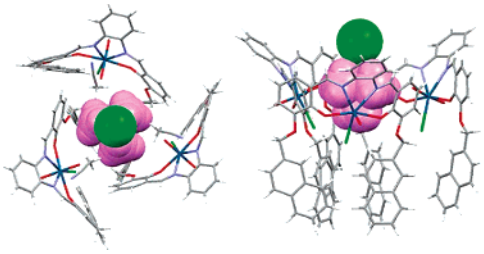


Figure 7. Complex of **2** with (TMA)Cl: Top and side views of one of the (TMA)Cl units located outside the tetrameric assembly shown in Figure 6, right. Each of the three capsule forming receptors belongs to a different assembly. Acetonitrile molecules are excluded for clarity from the side view.

of receptor **3** with (TMA)Cl, and of receptor **1** with (NMP)Br. Notably, no suitable single crystals were obtained whenever the counteranion was either iodide or picrate, which is probably due to the weak binding of such salt anions to the UO_2 center, as shown by solution data (Table 1).

The crystal structure of the complex of **2** with (TMA)Cl showed a very large trigonal unit cell ($V \sim 84\ 000$ Å^3) with four receptors, $5^1/_3$ (TMA)Cl, and five CH_3CN molecules. The four receptors form a spherical assembly which encloses a cluster made of four (TMA)Cl with each chloride bound to an UO_2 center (Figure 6, right). The remaining two (TMA)Cl units (one of which with occupancy of $^1/_3$) are located outside the capsule, where interactions are established with the capsule forming receptors. Formation of 4:4 closed capsulelike assemblies was also observed with receptor **1** (Figure 6, left). Here four receptor units, each coordinated to a chloride ion, form a cage which encloses four TMA cations in a tetrahedral arrangement composed of isosceles triangles. Each cation interacts with three different receptors, with $CH_3\cdots\pi$(centroid) distances of 3.42(6) (C40···Ct(17−22)*), 3.64(6) (C41···Ct(1−6)), and 3.68(6) Å (C42···Ct(33−38)**)[13] and with two chlorides ($CH_3\cdots Cl^-$ = 3.68−3.85 Å). The cations fully occupy the cavity of the assembly so that no room is left for solvent molecules.

In the complex with **2**, the TMA cations and uranyl-coordinated chlorides form cyclic 4:4 arrays. Each cation is connected to nearby naphthyl moieties via $CH_3\cdots\pi$ interactions (C54···Ct(17−26) and C54C···Ct(17B-26B) = 3.42(6) Å; C54B···Ct(37C-46C) and C54D···Ct(37D-46D) = 3.48(4) Å). Additional interactions are established mostly with oxygens of the receptors and with edges of other aromatic moieties. Each cation is connected to two chlorides, one of which is in close contact with two methyl groups (with $CH_3\cdots Cl^-$ distances of 3.62 and 3.86 Å), whereas the other chloride lies on the opposite side of the cation and interacts with only one of its methyl groups at a somewhat longer distance ($CH_3\cdots Cl^- \sim 4.16$ Å). The 4:4 cyclic assembly is large enough to accommodate a disordered acetonitrile molecule exactly in the middle. Clearly, replacement of the benzyl moieties in **1** with the larger naphthyl moieties in **2** is responsible for the different structure of the tetrameric (TMA)Cl aggregates observed in the corresponding complexes. The cavity of the 4-receptor assembly formed by the larger receptor **2** is wide enough to host a cyclic, more extended arrangement of the tetrameric salt guest, instead of the more compact, tetrahedral arrangement found in the complex with receptor **1**. The two independent (TMA)Cl ion pairs are similarly lodged outside the tetrameric capsules and do not interact with naphthyl groups but with core aromatic nuclei. Interestingly, such (TMA)Cl ion pairs are not perturbed by chloride interactions with the UO_2 centers and, consequently, display a cation−anion distance almost 0.4 Å shorter than in the UO_2-bound ion pairs. A closer investigation of the environment around such "nonencapsulated" ion pairs reveals that the outer surfaces of the tetrameric assemblies are arranged in such a way to form cavities suitable to accommodate the ion pairs. Each of the three receptors shown in Figure 7 belongs to a different tetrameric capsule. The bowl-shaped cavity defined by the intercapsule arrangement is capped by acetonitrile molecules weakly bound to the hosted ion pair via $CH\cdots Cl^-$ interactions. The bottom of the cavity is stabilized by π-stacking interactions between the outer sides of the naphthyl moieties. In the structure of **1**·(TMA)Cl no ion pairs or solvent molecules are located outside the capsules. In this case the niches in the outer surfaces are mutually complemented via aromatic interactions.

The solid-state complex of **3** with (TMA)Cl completes the series of (TMA)Cl complexes. The lack of substantial points of similarity between the crystal structure and those of the corresponding complexes of **1** and **2** causes no surprise. The lack of side arms as preferential binding sites for the polar TMA heads prevents association patterns of the kind found in previous cases. The crystal packing shows a group of six receptors forming an open hexameric assembly (Figure 8, top), in which the UO_2-bound chlorides point toward the interior. The polar interior is occupied by disordered acetonitrile molecules and six TMA cations. The six chlorides are located at the vertices of two parallel equilateral triangles, twisted by 60° with respect to each other (Figure 8, bottom left). The side length of the triangles is 5.70 Å, and the distance between them is 3.93 Å. Interactions of TMA with receptor **3** are not as prominent as those with **1** and **2**. Indeed no strong $CH_3\cdots\pi$(centroid) contacts are seen but rather weaker interactions with some aromatic carbons and bonds, with closest distances in the range 3.55−4.03 Å. Additional interactions to the receptor oxygens (in the range 3.35−3.88 Å) are also observed. A more important role is played by interactions with the chloride counterions (Figure 8, bottom right), the shortest distance being remarkably short ($C53\cdots Cl^{-}$* = 3.33(2) Å). Closest contacts to the other two chlorides are also within a clear interaction range ($C53\cdots Cl^{-}$** = 3.74(2) Å and $C53\cdots Cl^-$ = 3.85(2) Å).

Receptor **2** was successfully crystallized with (ACh)Cl, but analogous crystallizations with **1** and **3** failed. The **2**·(ACh)Cl complex crystallizes with two crystallographically independent receptors and acetylcholine molecules in an asymmetric unit. The crystal structure reveals distinctive salt aggregates composed

(13) The one and two asterisks indicate the molecules generated by symmetry.

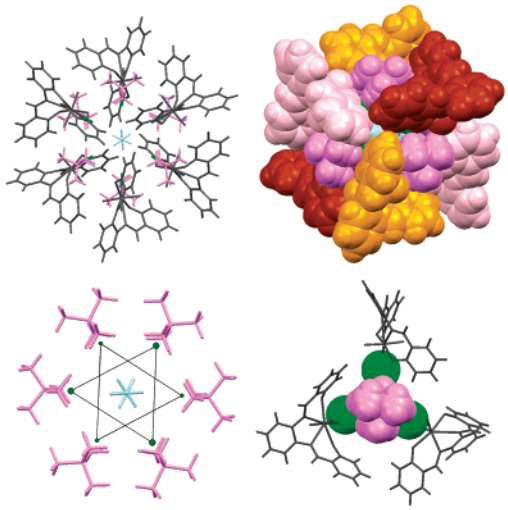


Figure 8. Top: Stick and VDW presentations of the 6:6 assembly of the complex **3** with TMA)Cl. The interior of the assembly is occupied by disordered acetonitrile (pale blue). Bottom: Structural details showing the two parallel triangular arrangements (standing 3.93 Å apart from each other) of the six chloride ions (left) and the interaction of TMA with the closest chloride ions (right).

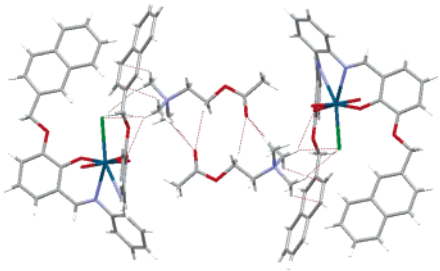


Figure 9. Complex of receptor **2** with (ACh)Cl, showing the weak interactions which join two ACh units together and connect the dimeric pair to the chloride-bound receptors. Only one of the pairs formed by crystallographically independent molecules is shown.

of two salts units surrounded by the receptor molecules (Figure 9). Acetylcholine is arranged in dimeric head-to-tail pairs, in which two $N-CH_3$ and two β-CH_2 groups are CH···O hydrogen bonded to the carbonyl group of the adjacent acetylcholine (C51···O = 3.32 Å, C53···O = 3.41 Å, C55···O = 3.12 Å; C52B···O = 3.45 Å, C53B···O = 3.50 Å, C55B···O = 3.00 Å). The cationic head of acetylcholine is connected to UO_2 bound chloride via two methyl groups (C51···Cl^- = 3.67 Å, C52···Cl^- = 3.71 Å; C51B···Cl^- = 3.68 Å, C52B···Cl^- = 3.79 Å). In one of the crystallographically independent pairs additional contacts to one of the core oxygens and to the edge of the naphthyl side arms are observed, with closest distance of 3.41 and 3.58 Å, respectively. The most significant additional contacts in the other crystallographically independent pair are established to the core oxygens, whereas cation$-\pi$ interactions of the shortest length of 3.68 and 3.84 Å are to the edge of the naphthyl sidearm are also observed. The crystal packing (Figure 10) reveals that the receptors are π-stacked to each other in a layerlike assembly and that the dimeric acetylcholine pairs are arranged in rows. Acetonitrile molecules fill the space between layers.

Among all the attempts at obtaining complexes of receptors **1**−**3** with iminium salts, the crystal structure of **1**·(NMP)Br is the only success. Structural analysis of the monomeric 1:1 adduct reveals that the NMP cation is offset face-to-face

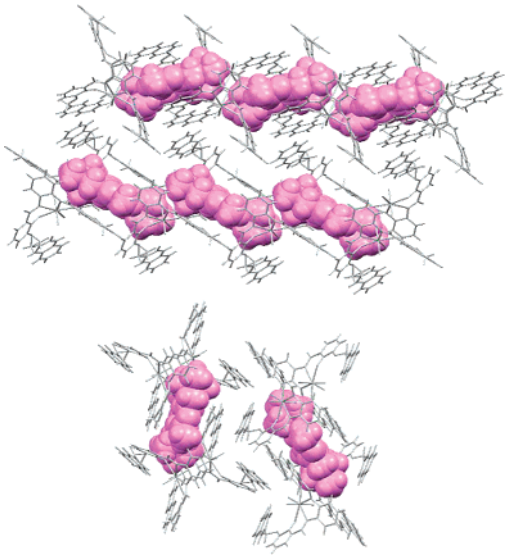


Figure 10. Crystal packing of **2**·(ACh)Cl, two views. Acetylcholine cations are shown as a VDW presentation. Acetonitrile molecules are excluded for clarity.

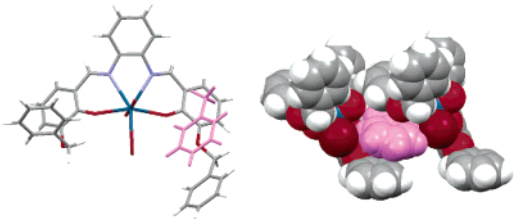


Figure 11. Stick presentation of the asymmetric unit of **1**·(NMP)Br complex. The VDW picture shows the π-stacking of the NMP cation (purple) between two salophen receptors. Acetonitrile molecules are excluded for clarity.

π-stacked between one of the aromatic side arms of one receptor (C33−C38) and the core aromatic ring (C9−C14) of the adjacent receptor (Figure 11). The shortest $\pi-\pi$ contacts vary between 3.34 and 4.05 Å. The polar methyl head is found to be in very close contact with the core aromatic rings of two adjacent receptors (distances of 3.40 Å with C26, 3.47 Å with C11, and 3.55 Å to centroid of ring C9−C14). The ubiquitous short CH···O contacts between cation and receptor oxygens are also seen in this case. The other side arm that is not involved in any interaction with the cationic guest is bent outward from the core of the receptor toward acetonitrile molecules which fill the interstices of the crystal lattice. Bromide anions are, as expected, coordinated to uranyl centers (U···Br^- = 2.90 Å), but unlike previous examples, ion pairs do not aggregate in clusters of definite composition but form infinite salt strips in which each NMP cation is surrounded by three bromide ions and vice versa (Figure 12). The closest CH···Br^- distances between cation and anion are C52···Br^- = 3.86(2) Å, C53···Br^-* = 3.70(2) Å and C54···Br^-** = 3.71(2) Å, C55···Br^-** = 3.52(2) Å. Interestingly, the polymeric salt ribbons are closely and almost completely enveloped by sheaths composed of receptor units, firmly anchored to the ribbons themselves via strong uranyl−bromide bonds.

Concluding Remarks. Consistent with the hard Lewis acid character of the uranyl, binding affinities for complexation of quaternary salts to uranyl−salophen receptors in solution are higher the harder the anion, thus confirming our previous

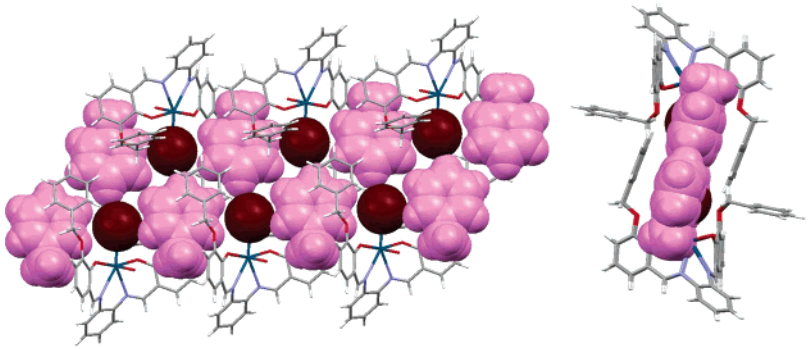


Figure 12. Crystal packing of **1**·(NMP)Br showing the salt strip in VDW style and surrounding receptors in stick presentation, two views. Acetonitrile molecules are omitted for clarity.

suggestion[7] that a major driving force for complexation arises from anion coordination to the metal center. This is in agreement with the finding that in all of the isolated receptor−salt complexes, as well as the previously reported analogues with alkali-metal halides,[4] the anion is firmly coordinated to the uranyl center in its equatorial plane. Less important, yet significant contributions to complex stability in solution arise from cation−π/CH−π interactions of the quaternary ions with the aromatic pendants, with the likely involvement of π-stacking interactions in the case of the NMP and NMiQ cations, which is again consistent with crystal structures.

More elaborate architectures are seen in the solid state compared with the simple receptor−anion−cation ternary complexes formed in the dilute solutions used in the ^{1}H NMR titrations. Thus, whereas simple ion pair recognition is achieved in solution, in the solid-state ion pair aggregates of varying composition and structure are basic elements in the formation of supramolecular assemblies with receptor molecules.

The simplest of such aggregates—an ion quartet featuring an antiparallel arrangement of two acetylcholine units—is found in the structure of the complex of **2** with (ACh)Cl. Higher aggregates are formed by (TMA)Cl in its complexes with receptors **1**−**3**, ranging from tetrameric ((TMA)Cl)$_4$ clusters found in the complexes with **1** and **2** to the hexameric species found in the complex with **3**. The largest, most striking aggregate is the unidimensional, ribbonlike arrangement of infinite composition revealed by the crystal structure of the complex of (NMP)Br with **1**. We conclude therefore that in complexes with the side-armed receptors the salt units aggregate into rather compact clusters that form the core of supramolecular assemblies in which the cluster themselves are enveloped in a sheat of receptor units. In contrast with the above behaviors, no discrete clusters are found in the crystal structure of (TMA)Cl complex with the control receptor **3**, in which the salt units are embedded in a sort of matrix formed by receptor molecules.

The present results, when combined with previous results on alkali-metal halide complexation,[4] demonstrate the high adaptability of salophen receptors **1** and **2**, whose conformationally flexible side arms establish multiple cation−π interactions with the hosted cations. They also illustrate the versatility of the uranyl−salophen unit as a building block in the construction of ditopic salt receptors and emphasize the role of cation−π interactions in the recognition of cation partners of contact ion pairs and ion pair aggregates in solution and in the solid state, respectively.

Experimental Section

Materials. All commercially available compounds were used without further purification. Tetramethylammonium chloride was crystallized from methanol before use. *N*-Methylpyridinium and *N*-methylisoquinolinium iodides were prepared by addition of excess methyl iodide to a concentrated solution in toluene of pyridine and isoquinoline, respectively. Tetramethylammonium picrate was obtained from the corresponding iodide salt by anion exchange with silver picrate. ^{1}H NMR spectra were recorded on Bruker AC 200 and AC 300 spectrometers. Triphenylmethane was used as an internal standard. All ^{1}H NMR titrations were run at 25 °C according to a published procedure.[11b] Receptors **1** and **3** were available from previous work.[7] Receptor **4** was synthesized according to a literature procedure.[14] Synthesis of receptor **2** is given in the Supporting Information.

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[15] or SHELXS-97[16] and refined on F^2 by full-matrix least-squares techniques (SHELXL-97[16]). 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 **1**·(NMP)Br, **2**·(ACh)Cl, and **3**·(TMA)Cl.[17] In **2**·(TMA)Cl the absorption correction worsens the results significantly.

1·(NMP)Br: $C_{34}H_{26}N_2O_6U\cdot C_6H_8N^+Br^-\cdot CH_3CN$, M = 1011.70 g mol^{-1}, monoclinic, $C2/c$ (No. 15), a = 35.560(1) Å, b = 9.6555(3) Å, c = 24.1012(8) Å, β = 112.397(2)°, V = 7650.9(4) Å^3, Z = 8, D_{calc} = 1.757 Mg m^{-3}, μ = 5.341 mm^{-1}, GOF on F^2 = 1.143, R_1 = 0.0729, wR_2 = 0.1458 [$I > 2\sigma(I)$].

2·(TMA)Cl: $4C_{42}H_{30}N_2O_6U\cdot 5^1/_3(CH_3)_4N^+Cl^-\cdot 4.5CH_3CN$, M = 4353.07 g mol^{-1}, trigonal, $R3c$ (No. 161), a = 54.1597(7) Å, c = 33.1332(2) Å, V = 84168(1) Å^3, Z = 18, D_{calc} = 1.546 Mg m^{-3}, μ = 3.600 mm^{-1}, GOF on F^2 = 1.050, R_1 = 0.0451, wR_2 = 0.0857 [$I > 2\sigma(I)$].

2·(ACh)Cl: $2C_{42}H_{30}N_2O_6U\cdot 2C_7H_{16}O_2N^+Cl^-\cdot 4CH_3CN$, M = 2320.95 g mol^{-1}, triclinic, $P\bar{1}$ (No. 2), a = 12.3021(1) Å, b = 16.8778(2) Å, c = 26.4855(3) Å, α = 72.5610(4)°, β = 84.5141(6)°, γ = 75.4356(6)°, V = 5076.67(9) Å^3, Z = 2, D_{calc} = 1.518 Mg m^{-3}, μ = 3.308 mm^{-1}, GOF on F^2 = 1.052, R_1 = 0.0467, wR_2 =0.1053 [$I > 2\sigma(I)$].

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3·(TMA)Cl: $C_{20}H_{14}N_2O_4U\cdot(CH_3)_4N^+Cl^-\cdot{}^1/_3CH_3CN$, $M = 707.64$ g mol^{-1}, trigonal, $R\bar{3}$ (No. 148), $a = 22.5983(5)$ Å, $c = 25.7313(5)$ Å, $V = 11380.0(4)$ Å^3, $Z = 18$, $D_{calc} = 1.859$ Mg m^{-3}, $\mu = 6.560$ mm^{-1}, GOF on $F^2 = 1.274$, $R_1 = 0.0499$, $wR_2 = 0.0931$ [$I > 2\sigma(I)$].

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Supporting Information Available: Crystallographic data (CIF) for **2**·(TMA)Cl, **3**·(TMA)Cl, **2**·(ACh)Cl, **1**·(NMP)Br, and **2**·CH_3CN, text for the synthesis of receptor **2**, the ^{1}H NMR titration of TMA picrate with receptors **1**−**3** in $CDCl_3$ at 25 °C, the ^{1}H NMR titration of (TBA)I with receptor **1** in $CDCl_3$ at 25 °C, the crystal structure of **2**·CH_3CN, and Ortep plots for the complexes **2**·(TMA)Cl, **2**·(ACh)Cl, **1**·(NMP)Br, **2**·CH_3CN, and **3**·(TMA)Cl. This material is available free of charge via the Internet at http://pubs.acs.org.

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