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A Calix[4]arene Strapped Calix[4]pyrrole: An Ion-Pair Receptor Displaying Three Different Cesium Cation Recognition Modes

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Abstract: An ion-pair receptor, the calix[4]pyrrole-calix[4]arene pseudodimer **2**, bearing a strong anion-recognition site but not a weak cation-recognition site, has been synthesized and characterized by standard spectroscopic means and *via* single-crystal X-ray diffraction analysis. In 10% CD_3OD in $CDCl_3$ (v/v), this new receptor binds neither the Cs^+ cation nor the F^- anion when exposed to these species in the presence of other counterions; however, it forms a stable 1:1 solvent-separated CsF complex when exposed to these two ions in concert with one another in this same solvent mixture. In contrast to what is seen in the case of a previously reported crown ether "strapped" calixarene−calixpyrrole ion-pair receptor **1** (*J. Am. Chem. Soc.* **2008**, *130*, 13162−13166), where Cs^+ cation recognition takes place within the crown, in **2**·CsF cation recognition takes place within the receptor cavity itself, as inferred from both single-crystal X-ray diffraction analyses and ^1H NMR spectroscopic studies. This binding mode is supported by calculations carried out using the MMFF94 force field model. In 10% CD_3OD in $CDCl_3$ (v/v), receptor **2** shows selectivity for CsF over the Cs^+ salts of Cl^-, Br^-, and NO_3^- but will bind these other cesium salts in the absence of fluoride, both in solution and in the solid state. In the case of CsCl, an unprecedented 2:2 complex is observed in the solid state that is characterized by two different ion-pair binding modes. One of these consists of a contact ion pair with the cesium cation and chloride anion both being bound within the central binding pocket and in direct contact with one another. The other mode involves a chloride anion bound to the pyrrole NH protons of a calixpyrrole subunit and a cesium cation sandwiched between two cone shaped calix[4]pyrroles originating from separate receptor units. In contrast to what is seen for CsF and CsCl, single-crystal X-ray structural analyses and ^1H NMR spectroscopic studies reveal that receptor **2** forms a 1:1 complex with $CsNO_3$, with the ions bound in the form of a contact ion pair. Thus, depending on the counteranion, receptor **2** is able to stabilize three different ion-pair binding modes with Cs^+, namely solvent-bridged, contact, and host-separated.

Introduction

The importance of supramolecular interactions in nature has been increasingly recognized in recent years, as has the utility of artificial receptors capable of recognizing selectively ions or neutral substrates.[1−3] Most ion-pair receptors studied thus far have been designed to recognize selectively either cations or anions, but not both.[2−4] However, as the importance of counterion effects have come to be increasingly appreciated, attention has turned to the synthesis of so-called ion-pair receptors that permit the concurrent complexation of both cations and anions.[5] Compared to simple ion receptors, ion-pair receptors generally display significantly enhanced affinities for ions as the result of, e.g., allosteric effects and enhanced electrostatic interactions between the cobound ions. As such, they are potentially attractive for use

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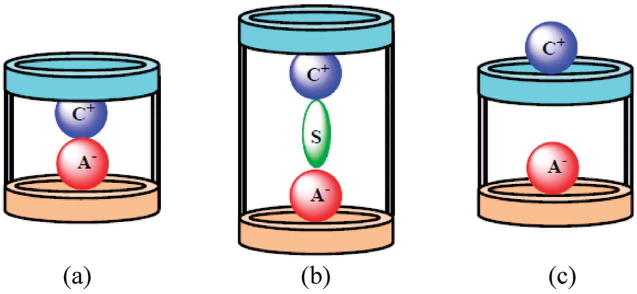

Figure 1. Limiting ion-pair interactions relevant to receptor-mediated ion-pair recognition: (a) Contact, (b) solvent-bridged, and (c) host-separated. In this schematic, the anion is shown as "A$^-$", the cation as "C$^+$", and the solvent as "S".

in such areas as salt solublization, ion extraction, and through-membrane transport.[6−9]

Ion-pair receptors generally bind cations and anions in three limiting modes depending on the size of the ions, distance between the anion and cobound cation, the nature of the constituent recognition sites, and solvent, among other effects. These different ion-pair binding arrangements are shown schematically in Figure 1. They are conveniently defined as (i) contact ion pairs, where the anion and cation are held in close proximity (Figure 1a);[8] (ii) solvent-bridged ion pairs, in which solvent molecules help link the anion to the cobound cation (Figure 1b),[8a−c,11] and (iii) host-separated ion pairs, an arrangement characterized by ostensibly independent anion and cation recognition sites (Figure 1c).[10] Examples of all three host−guest arrangements are now known. However, as a general rule, these arrangements have been defined in the context of different receptor systems. Indeed, most ion-pair receptors reported to date operate on the basis of only one or, in very rare cases, two of the binding modes shown in Figure 1.[8a−c,10c] To the best of our knowledge, we are unaware of any synthetic receptor with which it has proved possible to stabilize all three limiting interactions using a single molecular framework. Here, we report the first receptor that binds ion pairs in accord with all three limiting modes shown in Figure 1. This flexibility in binding, which has been fully documented *via* single-crystal X-ray diffraction analyses, is of particular interest because the underlying ion-pair recognition behavior can be modified by simply changing the counteranion.

We recently reported the synthesis of the ion-pair receptor **1**, a system that is characterized by the presence of two strong ion-binding sites (a calix[4]pyrrole and calix[4]arene crown-6 subunits for anion and cation recognition, respectively).[12] In the solid state, X-ray diffraction analysis revealed the presence of a 1:1 CsF complex that was characterized by a large (>10 Å) Cs^+ and F^- separation. In spite of this large separation, in 10% methanol−chloroform (v/v), compound **1** was found to bind both the F^- anion and Cs^+ cation strongly, and to do so in a sequential manner.[12] In order to gain greater insights into the nature of the binding interactions in **1**, we have now prepared, and report here, the crown-free ion-pair receptor (**2**). This new system, which lacks the calix[4]-crown-6 cation recognition site,[13] displays anion-dependent ion-pair binding that differs dramatically from that observed in the case of **1** or, indeed, any other synthetic receptor system of which we are aware. As will be discussed further below, we have found that, in 10% methanol−chloroform, receptor **2** fails to bind either Cs^+ or F^- when exposed to these ions in the form of salts containing other counterions (i.e., ClO_4^- and tetrabutylammonium (TBA^+), for Cs^+ and F^-, respectively). However, it forms a very strong and selective complex with CsF, when mixed with CsF or with various combinations of salts that provide a source of CsF *in situ*. Further, in contrast to what is true for **1**, the binding of the Cs^+ and F^- ions takes place concurrently, rather than sequentially, on the NMR time scale in 10% $CD_3OD:CDCl_3$. Also noteworthy is that in **1** the Cs^+ cation is bound in the crown ether strap, whereas in **2** it is bound closer to the F^- anion and within the receptor pocket. The result is a solvent-bridged ion-pair structure in the case of **2** wherein the cation and anion are separated by roughly 5.6 Å in the solid state. This binding mode is protean and can be modified by the choice of counteranion. For instance, no solvent bridging is seen in the case of the $CsNO_3$ complex; here, solid-state structural analysis confirms the existence of a contact ion pair within the receptor cavity. Finally, in the case of CsCl, single-crystal X-ray structural analysis reveals the existence of an unprecedented 2:2 complex characterized by two different ion-pair binding modes, including one that is best described as host-separated. Such host-separated ion pairing has been observed recently in

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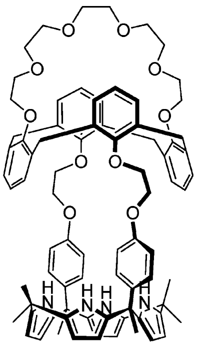
the case of Cs$^+$ salts of simple calix[4]pyrrole, **3**.[10c] However, the ability to "adjust" the ion-pair recognition as a function of specific conditions is, to the best of our knowledge, a unique feature of receptor **2** and could make this new system of interest as a selective ion-recognition agent, in accord with very recent literature suggestions.[14]



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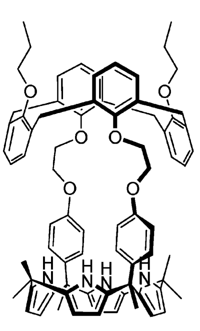

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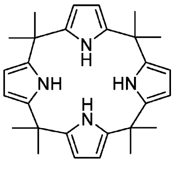

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Results and Discussion

Receptor **2** was synthesized using a synthetic procedure similar to that used to prepare compound **1**.[12] As shown in Scheme 1, the reaction of calix[4]arene ditosylate **4**[15] with 4′-hydroxyacetophenone in the presence of excess K$_2$CO$_3$ in acetonitrile under reflux gave the calix[4]arene diketone **5** in its 1,3-alternate conformation in 80% yield; subsequent condensation with pyrrole in the presence of excess trifluoroacetic acid ($\sim$23 equiv) at 65 °C then gave the dipyrromethane **6** in 48% yield. Compound **6** was further condensed with acetone in the presence of a catalytic amount of BF$_3$·OEt$_2$ to give the target compound (**2**) in 12% yield.[12,16]

Compound **2** was fully characterized by standard spectroscopic means, as well as by single-crystal X-ray diffraction analysis (Figure 2). The datum crystal used for this latter analysis was obtained by subjecting **2** in its ion-free form to slow evaporation from a chloroform−methanol (1:1, v/v) solvent mixture. The resulting structure revealed that, in the solid state, the calix[4]arene moiety adopts the expected 1,3-alternate conformation, while the calix[4]pyrrole moiety is in a partial cone conformation with two methanol molecules bound to the four pyrrolic NH protons.

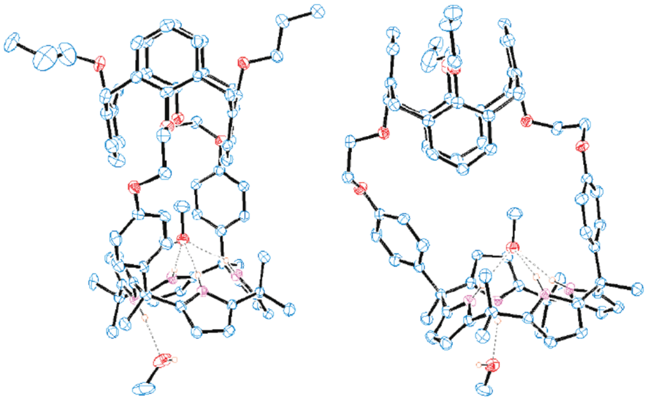


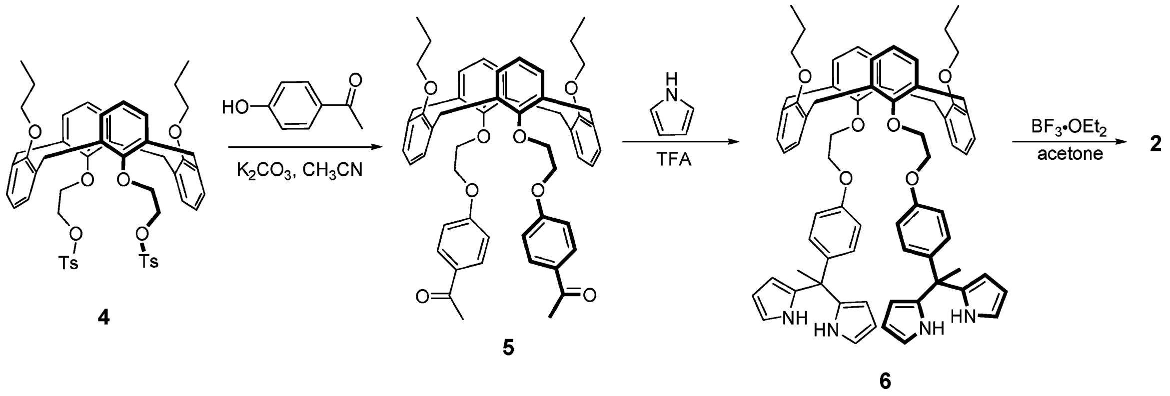
Figure 2. Two different views of the single-crystal structure of **2**·(CH$_3$OH)$_2$. Displacement ellipsoids are scaled to the 30% probability level. Most hydrogen atoms have been removed for clarity. Dashed lines are indicative of H-bonding interactions.

As a first step toward analyzing the ion recognition properties of **2**, its ability to bind halide anion salts in CDCl$_3$ solution was investigated *via* ^{1}H NMR spectroscopy. In analogy to what was found to be true in the case of the ion-pair receptor **1**,[12] significant chemical shift changes in the NMR spectrum of **2** were observed when the receptor was treated with fluoride anion salts (e.g., tetrabutylammonium fluoride, TBAF), but not other analogous halide anion salts (Figures S1 and S2, Supporting Information). Such findings lead us to suggest that, like the earlier system **1**, receptor **2** is selective for the fluoride anion. This stands in contrast to what is true for normal calix[4]pyrrole **3**, which is able to bind other halide anions in CDCl$_3$ (Figures S3 and S4, Supporting Information) and other solvent systems.[17] As shown in Figure S1, Supporting Information, the ^{1}H NMR spectrum of free **2** is characterized by a broad singlet at $\delta = 6.75$ ppm for the NH protons, as well as two triplets, resonating at about $\delta = 6.03$ ppm and $\delta = 5.95$ ppm, for the β-pyrrolic protons, respectively.

Upon subjecting compound **2** to titration with TBAF in CDCl$_3$, two sets of resonances were seen for all observable proton signals in the various ^{1}H NMR spectra recorded before saturation was achieved. The deconvoluted spectra were found to reflect, as expected, the presence of both the ion-free and fluoride-bound forms of **2**. As such, these studies serve to indicate that the kinetics of fluoride anion binding/release is slow on the NMR time scale (Figure S1, Supporting Information). They also provide support for the notion that fluoride anion is strongly bound by receptor **2** in this solvent medium.

The presumed strong complexation between receptor **2** and fluoride anion in CDCl$_3$ was further supported by the observation of significant chemical shift changes in the β-pyrrolic proton signals and, especially, the pyrrolic NH protons (Figure S1, Supporting Information). Upon reaching saturation, the NH proton signal in the ^{1}H NMR spectrum was shifted downfield

Scheme 1. Synthesis of Compound **2**



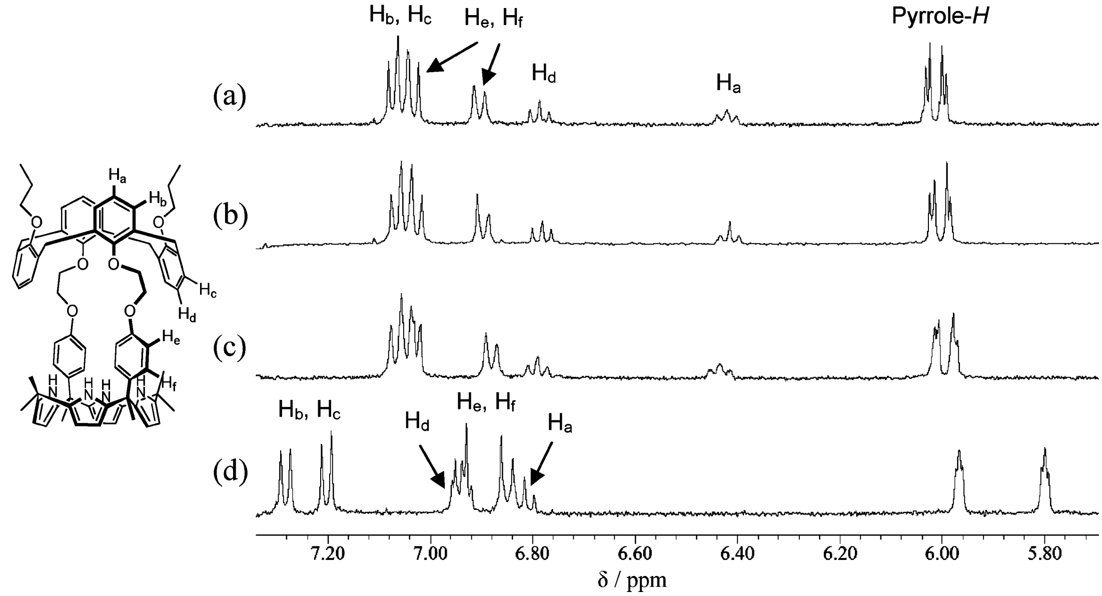


Figure 3. Partial ^{1}H NMR spectra of (a) **2** only, (b) **2** + 5 equiv of TBAF (tetrabutylammonium fluoride), (c) **2** + 5 equiv of $CsClO_4$, and (d) **2** + 5 equiv of CsF in $CD_3OD/CDCl_3$ (1:9, v/v).

to $\delta \approx 13.0$ ppm ($\Delta\delta \approx 6.3$ ppm). This resonance, initially a singlet, was also split into a doublet ($J = 45.6$ Hz), a finding ascribed to coupling between the NH protons and the bound fluoride anion (Figure S1, Supporting Information).[18] In contrast, the triplet peaks corresponding to the β-pyrrolic protons were shifted upfield and appear as two singlets (at 5.85 ppm and 5.67 ppm, respectively; cf. Figure S1, Supporting Information) at the end of the titration; this is as would be expected given the anion-induced changes in the electronic features of the calix[4]pyrrole portion of receptor **2**.

Very different binding behavior was observed when experiments analogous to those described above were carried out in 10% CD_3OD in $CDCl_3$ (v/v). In this more polar medium, no appreciable change in any of the chemical shifts was seen in the ^{1}H NMR spectrum of receptor **2**, even upon treatment with 5.0 equiv of TBAF. This result, interpreted in terms of receptor **2** not binding the fluoride anion under these particular experimental conditions, is ascribed to the strong solvation of fluoride anions by the CD_3OD present in this solvent mixture (Figures 3, 4, and S5, Supporting Information).

Simple calix[4]pyrrole **3** is known to complex the cesium cation weakly, if at all, in organic media.[10c] Therefore, as expected, little evidence of an interaction between compound **2** and the Cs^+ cation was seen when this receptor was treated with 5.0 equiv of $CsClO_4$ in 10% CD_3OD in $CDCl_3$ (v/v), as evidenced by the absence of chemical shift changes in the ^{1}H NMR spectrum (Figures 3c and S5, Supporting Information).

In contrast to what is seen with TBAF or $CsClO_4$, the addition of CsF (5.0 equiv) to a solution of **2** in 10% CD_3OD in $CDCl_3$ causes significant changes in the proton signals of both the calix[4]arene and the calix[4]pyrrole moiety in the ^{1}H NMR spectrum (Figure 3d). Such findings are consistent with the CsF being bound to receptor **2** as an ion pair. Further, since the combination of both ionic species is required to trigger both Cs^+ and F^- complexation, the binding process mimics a cooperative *AND* logic gate.[19] Specifically, in accord with the logic rules governing such devices, only the combined presence of two inputs induces CsF binding by **2** (i.e., both the Cs^+ cation and the F^- anion, but neither the Cs^+ cation nor the F^- anion alone, triggers the change); presumably, this complexation leads to formation of a solvent separated-ion pair, just as it does in the solid state (cf. discussion below). As discussed later on, this logic behavior was found to extend to other cesium salts.

A noteworthy feature of the spectra shown in Figure 3d, is the CsF-induced downfield shift in all the proton signals associated with the calix[4]arene subunit. Such a finding is fully consistent with the 1,3-alternate calix[4]arene moiety, which is known to be a weak Cs^+ receptor,[13] being involved in Cs^+ cation complexation. The fact that changes are seen in the signals ascribed to protons H_a and H_b confirms that the oxygen atoms of the calix[4]arene phenoxy groups participate in Cs^+ cation recognition. In contrast, the upfield shift seen for both the β-pyrrolic and *meso*-aromatic proton signals of the calix[4]pyrrole moiety, as well as the significant downfield shift and splitting (into a doublet) observed for the pyrrolic N*H* resonance, are taken as strong evidence that F^- anion binding takes place within the calix[4]pyrrole moiety (Figures 3d and S5d, Supporting Information). These findings are consistent with the structure of **2**·CsF determined in the solid state *via* X-ray diffraction analysis (*vide infra*).

Further evidence that receptor **2** forms a strong complex with CsF came from ^{1}H NMR spectroscopic titrations carried out with CsF. Specifically, addition of 0.57−1.79 equiv of CsF to a solution of **2** in $CD_3OD/CDCl_3$ (1:9, v/v) was found to give rise to two sets of distinguishable resonances for all proton signals. These sets of peaks are attributed to the ion-free and

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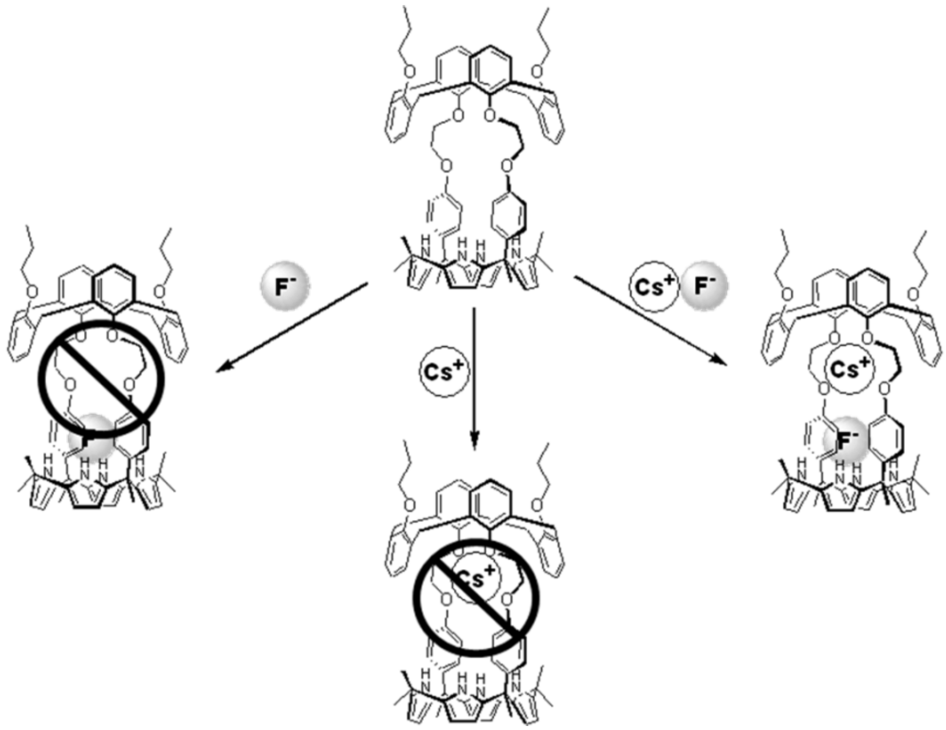

Figure 4. Proposed *AND* logic gate binding behavior of **2** toward a CsF ion pair in $CD_3OD/CDCl_3$ (1:9, v/v).

CsF bound forms of **2**, respectively. The presence of two separate signals is consistent with the ion-pair binding/decomplexation equilibrium being slow on the ^1H NMR time scale, as noted above. As proved true after the titration was complete (cf. discussion of Figure 3d above), a detailed analysis of the signals associated with the CsF complex (Figure S6, Supporting Information) revealed that shifts are seen for both the pyrrolic N*H* and protons H_a and H_b of the calix[4]arene. This is consistent with the Cs^+ cation and F^- anion being bound concurrently, at least on the ^1H NMR time scale (eq 1).

The binding behavior for the new receptor **2** is very different for what is seen for compound **1**. In the case of the latter species, addition of 0.57−1.79 equiv of CsF gives rise at first to changes in the proton signals of the calix[4]arene moiety and the crown-6 ring, but *not* those of the calix[4]pyrrole moiety (Figure S7, Supporting Information). Such a finding is consistent with the Cs^+ cation being bound to the calix[4]crown-6 ring *before* the F^- anion is bound to the calix[4]pyrrole (eq 2). Only after the Cs^+ cation is bound to the calix[4]arene crown-6 ring of **1** does complexation of the F^- counteranion occur;[12] as expected, this gives rise to two distinct (and distinguishable) sets of pyrrolic β-proton signals during the course of the titration (Figure S7, Supporting Information, and eq 3).

$$[\mathbf{2}] + \mathrm{CsF} \rightarrow [\mathbf{2}\cdot\mathrm{CsF}] \qquad (1)$$

$$[\mathbf{1}] + \mathrm{CsF} \rightarrow [\mathbf{1}\cdot\mathrm{Cs}]\mathrm{F} \qquad (2)$$

$$[\mathbf{1}\cdot\mathrm{Cs}]\mathrm{F} + \mathrm{CsF} \rightarrow [\mathbf{1}\cdot\mathrm{CsF}] + \mathrm{CsF} \qquad (3)$$

ITC was utilized to quantify the CsF affinity of receptor **2**. To maintain consistency with the prior ^1H NMR spectroscopic analyses, a solvent mixture consisting of 10% MeOH in $CHCl_3$ (v/v) was employed (Figure S8, Supporting Information). This choice reflects the fact that no other solvent systems allowed for interpretable data to be obtained for either this salt or other combinations of F^- and Cs^+ and various counterions (see Table S1, Supporting Information). In 10% CH_3OH in $CHCl_3$ (v/v), the titration of CsF [1.0 mM] with **2** [11.2 mM] is characterized by a highly favorable enthalpic term ($\Delta H = -14.4$ kcal/mol), with a strong opposing entropy term ($T\Delta S = -8.7$ kcal/mol). The overall binding energy, $\Delta G = -5.7$ kcal/mol, corresponds to a $K_a = 1.3 \times 10^4$ M^{-1}, when fit to a 1:1 binding equation (Figure S8, Supporting Information). This affinity is an order of magnitude lower than what was observed for compound **1**, which contains a calix[4]arene crown-6 ring ($\Delta H = -16.2$ kcal/mol, $T\Delta S = -8.6$ kcal/mol, $\Delta G = -7.6$ kcal/mol, and $K_a = 3.77 \times 10^5$ M^{-1}).[12] The lower CsF affinity of **2** presumably reflects the absence of the strong calix[4]crown-6 cesium binding site, but may also be the result of reduced flexibility and associated steric limitations to either anion or cation binding. Nevertheless, even if the binding is reduced compared to **1**, it is to be appreciated that in absolute terms, compound **2** is a highly effective receptor for CsF, at least in this moderately polar solvent mixture.

The binding behavior of **2** toward the Cs^+ cation and the F^- anion was further studied in the presence of various cations and anions. The concurrent addition of both TBAF and $CsClO_4$, neither of which is individually bound to compound **2**, gives rise to ^1H NMR spectral changes in 10% CD_3OD in $CDCl_3$ (v/v) that are very similar to those seen upon the addition CsF (Figures S5e, Supporting Information). Such observations provide support for the conclusion that compound **2** is able to capture selectively the Cs^+ cation and the F^- anion (as an ion pair) through a process involving counterion exchange (eq 4). By contrast, in the presence of perchlorate salts of other metal ions (i.e., Li^+, Na^+, K^+, Rb^+ and NH_4^+, as opposed to Cs^+), no spectral changes are observed; this lends credence to the notion that the F^- anion is bound by compound **2**, but only in the presence of Cs^+.

$$[\mathbf{2}] + \mathrm{CsClO_4} + \mathrm{TBAF} \rightarrow [\mathbf{2}\cdot\mathrm{CsF}] + \mathrm{TBAClO_4} \qquad (4)$$

In the presence of TBA salts of other anions (Cl^-, Br^-, and NO_3^-), the Cs^+ cation is strongly complexed by receptor **2**, as inferred from ^{1}H NMR spectral measurements (cf. Figures S5, S9, S10, and S11, Supporting Information). However, even though such complexes are formed when CsCl, CsBr, and $CsNO_3$ are added independently (Figure S9, Supporting Information), receptor **2** binds only CsF when a mixture of cesium salts (CsF, CsCl, CsBr, and $CsNO_3$) is used. Thus, selectivity for CsF is seen (Figure S12, Supporting Information). As such, our work serves to extend the findings of Beer and co-workers who noted that appropriately designed heteroditopic calix[4]diquinone receptors will form complexes with several ions and/or contact ion pairs, albeit not with the selectivity demonstrated by **2**.[20]

The strong preference for CsF displayed by **2** in 10% CD_3OD in $CDCl_3$ (v/v) stands in marked contrast to what is true for simple calix[4]pyrrole **3**. This latter system has been observed to bind a number of different anions under a wide variety of conditions and thus high selectivity for CsF was not expected.[17] Indeed, when tested under conditions identical to those used above (i.e., exposure to a mixture of cesium salts), this unfunctionalized "parent" system was found to interact with a variety of anions in 10% CD_3OD in $CDCl_3$ (v/v), rather than just fluoride, as seen for **2** (cf. Figure S13, Supporting Information).

The high selectivity for CsF seen in the case of **2** relative to **3** is thought to reflect favorable ion pairing interactions. However, it may also reflect a reduced accessibility to the anion binding site compared to simple calix[4]pyrrole **3**.[10c] Presumably, this reduced accessibility is a consequence of the greater rigidity of the calix[4]pyrrole core that results from the use of relatively inflexible ethylene glycol spacers between the calix[4]pyrrole and calix[4]arene subunits. The phenoxy groups flanking the calix[4]pyrrole binding site may also serve to limit accessibility to the cavity.

Single crystals of the CsF complex of **2** (**2**·CsF) were obtained by subjecting a chloroform/methanol solution of receptor **2** to slow evaporation in the presence of excess cesium fluoride. The resulting structure revealed that **2** forms a 1:1 complex with cesium fluoride, and that the latter is bound in the form of an ion pair wherein the constituent ions are separated by a water molecule. As expected, the Cs^+ cation is bound strongly to the 1,3-alternate conformation of the calix[4]arene through ion-dipole interactions with two phenoxy oxygen atoms and π−cation interactions involving the two arene rings:[21] $Cs^+\cdots O$ distances of 2.98 and 3.09 Å; $Cs^+\cdots$arene centroid distances of 3.28 and 3.40 Å (Figure 5). The Cs^+ cation is also coordinated by a molecule of methanol ($Cs^+\cdots O$ distance = 3.04 Å) and a water molecule ($Cs^+\cdots O$ distance = 3.22 Å). The distal oxygen atoms of the ethylene glycol spacers exhibit long $Cs^+\cdots O$ distances, 3.66 and 4.25 Å, leading us to suggest that they do not play a significant role in cation binding (*vide infra*). The F^- anion is bound to the NH protons of the calix[4]pyrrole with distances of 2.79−2.81 Å ($N\cdots F^-$ interaction), and is also bound to the water molecule with a distance of 2.52 Å ($O\cdots F^-$ interaction). The distance between the Cs^+ cation and the F^- anion in **2**·CsF is found to be 5.62 Å, which is much shorter than the distance (10.92 Å) seen in the CsF complex of **1**. It is also much longer than the intra- (3.69 Å) and intercomplex (2.77 Å) distances seen in the solid-state structure of the CsF complex of simple *meso*-octamethylcalix[4]pyrrole **3** (Figure 6).[10c] In the previously reported CsF complex of **3**, the Cs^+ cation is symmetrically encapsulated with the cone-like cavity of the calix[4]pyrrole *via* apparent π−cation interactions with a distance of 3.39 Å between the Cs^+ ion and the centroids of the pyrrole rings.[10c]

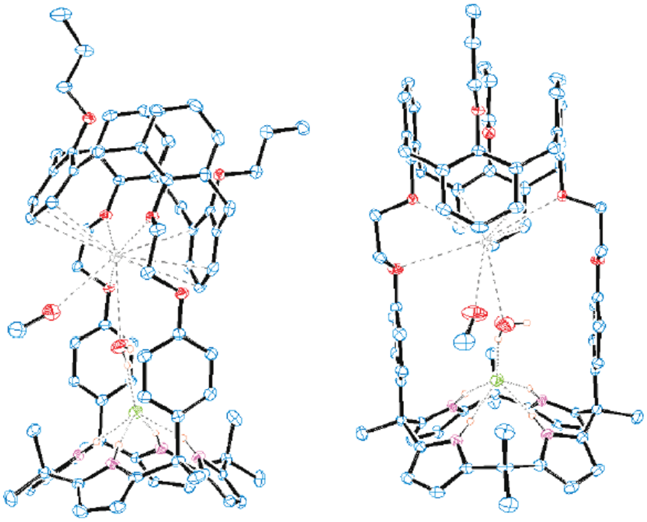

Figure 5. Two different views of the single-crystal structure of **2**·CsF·CH_3OH·H_2O. Displacement ellipsoids are scaled to the 50% probability level. Most hydrogen atoms have been removed for clarity.

Molecular mechanics calculations were performed to gain further insight into the ion-pair binding interactions (see Supporting Information for coordinates of all structures). Definition of van der Waals parameters for the Cs^+ cation,[22] allowed calculations to be performed with the MMFF94 force field model.[23] Starting from the X-ray coordinates, geometry optimization of the solvated (**2**·CsF) complex resulted in only minor changes to the structure. Figure 7a shows the superposition of the optimized geometry on the X-ray geometry, yielding a root mean squared displacement for heavy atom positions of 0.24 Å. After removal of the two solvent molecules, further optimization results in a displacement of the Cs^+ cation from the calix[4]arene pocket toward the F^- anion, going from a water-separated ion-pair $Cs\cdots F$ distance of 5.33 Å to a contact ion-pair distance of 2.79 Å (see Figure 7b). Thus, the addition of a water spacer is required in order for both the cation and anion of this ion pair to contact their corresponding binding sites within **2**.

Further calculations were performed to evaluate the participation of the distal ethylene glycol oxygen atoms in Cs^+ binding. Conformational analysis of the methoxy-substituted analog of (**2**·CsF) yielded a C_2 symmetric conformer as the global minimum, 1.9 kcal/mol lower in energy than the X-ray conformation. On removal of F^- followed by optimization, the Cs^+ cation moves into the internal calix[4]arene cavity (Figure 8a) with a binding energy of −39.8 kcal/mol. As with the X-ray structure, the $Cs^+\cdots O$ distances to the calix[4]arene oxygen atoms (2.91 Å) are significantly shorter than the distances to the distal oxygen atoms (3.31 Å). Figure 8b shows the optimized structure obtained after moving the Cs^+ to the external

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(21) (a) Hay, B. P.; Nicholas, J. B.; Feller, D. *J. Am. Chem. Soc.* **2000**, *122*, 10083–10089. (b) Nicholas, J. B.; Hay, B. P. *J. Phys. Chem. A* **1999**, *103*, 9815–9820.

(22) MMFF94 van der Waals parameters for the Cs^+ cation were adapted from the default values used for the K^+ cation by altering the atomic polarizability from 1.0 to 2.0 Å^3.

(23) Halgren, T. A. *J. Comput. Chem.* **1996**, *17*, 490–519.

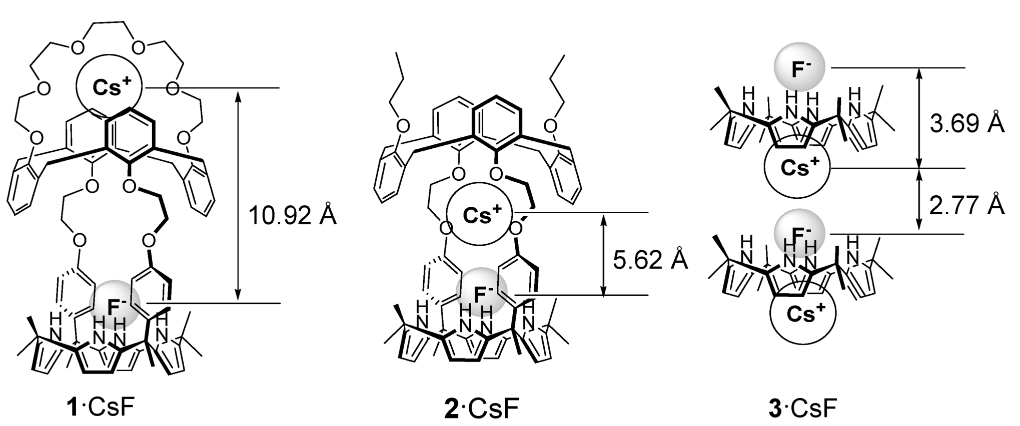
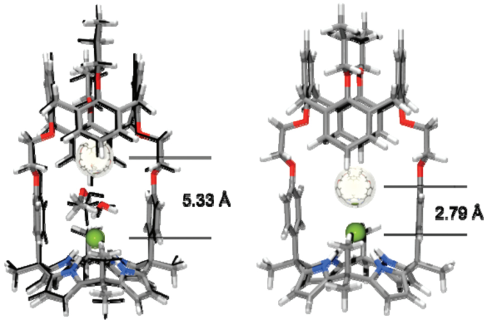
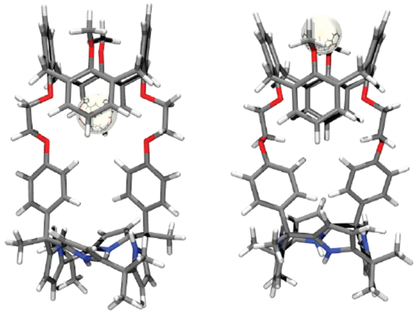


Figure 6. Binding modes of CsF ion pairs stabilized by receptors **1**−**3** and distances between the Cs^+ and F^- ions seen in the complexes as determined by X-ray diffraction analysis. The structures of the CsF complexes of **1** and **3** were reported in references 12 and 10c, respectively.



(a) (b)

Figure 7. (a) Superposition of calculated versus observed (thin black tubes) geometries for the solvated form of (**2**·CsF). (b) Calculated geometry for the encapsulated contact CsF ion pair obtained after solvent is removed.



(a) (b)

Figure 8. Optimized geometries for (2·Cs^+) with the Cs^+ cation located in the internal cavity (a) and external cavity (b).

calix[4]arene cavity. This position, which lacks the extra two oxygen atoms, yields a Cs^+ binding energy of −38.4 kcal/mol. These values can be compared with the value of −38.6 kcal/mol, which is obtained when this model is used to compute the Cs^+ binding energy to the 1,3-alternate conformation of tetramethoxycalix[4]arene. The results confirm that the elongated $Cs^+\cdots O$ distances observed in the X-ray structure represent weak contacts that are worth less than 1 kcal/mol apiece; in other words, the calix[4]arene donor sites account for the majority of Cs^+ binding in the case of **2**.

Taken together, the solid state results obtained for the CsF complexes of compounds **1-3**, leads to the conclusion that the Cs^+ cation complexation is “opportunistic”, with the binding taking place in a way that leads, as expected, to a minimization of the overall energetics. Considered in a different light, the differences seen within this series serve to underscore the fact that the formation of complexes, **1**·CsF, which represents a host-separated ion pair, and **2**·CsF, which represents a solvent-bridged ion pair, allows the unfavorable energetics associated with Cs^+ and F^- charge separation to be overcome. The fact that a solvent-bridged ion pair was observed in the case of (**2**·CsF) led us to consider that the cavity in this receptor might accommodate Cs^+ salts of larger anions, and thus be useful as a cesium cation extractant.

To test whether receptor **2** could be used to effect cesium cation extraction, preliminary extraction studies were carried out using the set up described previously.[24] Specifically, cesium salts were subject to extraction from an aqueous phase into a nitrobenzene layer containing **2** at 10 mM. Measuring the cesium distribution ratios as a function of the cesium salt concentration revealed that CsCl, CsBr, and $CsNO_3$ were extracted as ion pairs in accord with the following thermodynamic equation

$$Cs^+ + X^- + \bar{\mathbf{2}} \overset{K}{\leftrightarrow} \overline{CsX\mathbf{2}}$$

where X^- represents nitrate, chloride, or bromide, and a superscripted line denotes species present in the organic phase. Preliminary thermodynamic modeling of the results is consistent with the presence of dissociated ion pairs at low salt concentration and ion pairing at higher salt concentration, a finding that leads us to suggest that conditions appropriate for crystal growth could stabilize the formation of ion-paired complexes. Further extraction studies are in progress and more complete results, including quantitative analyses, will be presented elsewhere.

The nature of the extracted ion-paired complexes was evaluated with further modeling studies.[22,23] Calculations on CsCl (Figure 9) indicate that the cavity of **2** is too small to contain a water-separated ion pair, but too large for the contact ion pair. When a water molecule is present it binds to the side of the CsCl ion pair with a $Cs\cdots O$ distance of 3.09 Å and a $Cl\cdots H$ distance of 2.14 Å. This microsolvation results in an ion separation of 3.54 Å (Figure 9a). When the water is removed, the separation distance decreases to 3.30 Å as the Cs^+ cation is dragged toward the anion (Figure 9b). Although the effect is not as dramatic as with CsF, where the addition of solvent separates the two ions by 2.54 Å (see Figure 7), the coordination of water to the side of the CsCl contact ion pair

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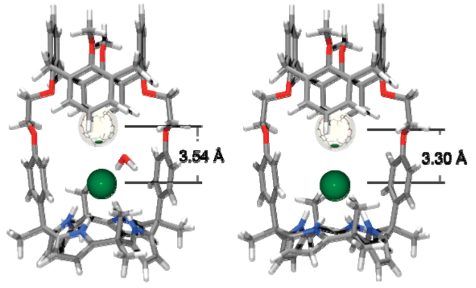
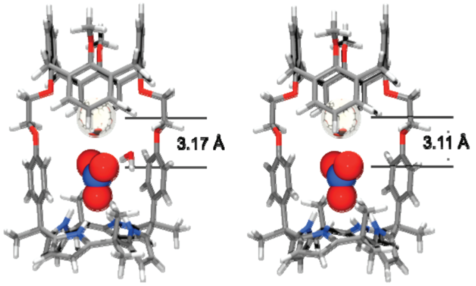
(24) Wintergerst, M. P.; Levitskaia, T. G.; Moyer, B. A.; Sessler, J. L.; Delmau, L. H. *J. Am. Chem. Soc.* **2008**, *130*, 4129–4139.



(a) (b)

Figure 9. (a) Calculated geometry for (**2**·CsCl) with a water molecule coordinated to the ion pair. (b) Calculated geometry for (**2**·CsCl).



(a) (b)

Figure 10. (a) Calculated geometry for (**2**·$CsNO_3$) with a water molecule coordinated to the nitrate anion. (b) Calculated geometry for (**2**·$CsNO_3$).

increases the ion separation by 0.24 Å; this allows a more favorable interaction between the calix[4]arene binding site and the Cs^+ cation. Similar behavior is observed with CsBr (not shown), but given the larger size of this anion, the increase in ion separation on water coordination is smaller, 0.17 Å (Figure S14, Supporting Information).

The largest ion pair, $CsNO_3$, exhibits the best match to the cavity of **2** (Figure 10). Unlike the cesium halide salts where the water interacts with both members of the ion pair, in this case the added water interacts only through hydrogen bonding with the NO_3^- anion (Figure 10a). When the water is removed, the ion separation decreases by only 0.06 Å (Figure 10b), with a drop in Cs···O distance of 3.17−3.11 Å. These calculated values are consistent with Cs···O(nitrate) distances observed in the Cambridge Structural Database (CSD),[25] 3.20 ± 0.09 Å, leading to the prediction that **2** should host $CsNO_3$ as a true contact ion pair.

The solvent extraction and modeling studies provide support for the conclusion that receptor **2** should be able to include cesium salts other than CsF, either as "solvent-loosened" contact ion pairs in the case of CsCl and CsBr or as a true contact ion pair in the case of $CsNO_3$. ^{1}H NMR spectral analyses were carried out in 10% CD_3OD in $CDCl_3$ to test whether **2** would function in this manner. This solvent mixture, dictated by solubility considerations, permitted qualitative studies but, unfortunately, precluded quantitative measurements.

As in the case of CsF, salt-induced spectral shifts were seen in the presence of CsCl, CsBr, and $CsNO_3$, consistent with the formation of ion-pair inclusion complexes with **2** (Figure S9, Supporting Information). It is of particular interest that **2**, unable to complex Lewis basic anions, such as fluoride, in a relatively nonpolar organic solvent system (chloroform), was found to bind a variety of anions (specifically F^-, Cl^-, Br^-, and NO_3^-) in a more polar environment (10% CD_3OD in $CDCl_3$) provided a presumably cobound cesium cation is present; this underscores the fact that under these experimental conditions compound **2** is acting as a *bona fide* ion-pair receptor.

Even though quantitative studies of affinities could not be carried out, it is important to appreciate that small differences in the spectra corresponding to the ion-pair complexes were observed in the case of the various test cesium salts. For instance, treatment with CsCl and CsBr complexes give rise to similar chemical shifts, a reduction of the intensity for the β-pyrrolic protons was seen in the case of CsCl, but not CsBr, as discussed further below. Moreover, in the case of the $CsNO_3$ complex, the various peaks are split further than in the case of the CsCl and CsBr complexes (cf. Figure S9, Supporting Information).

Explanations for these small differences came from solid-state structural analyses. For instance, unlike the 1:1 solvent-bridged CsF complex obtained when receptor **2** is exposed to Cs^+ and F^-, a 2:2 complex is obtained with CsCl ($\mathbf{2}_2$·$(CsCl)_2$), at least in the solid state. Here, a single-crystal X-ray diffraction analysis revealed two different binding modes (Figure 11). One cesium ion is bound within the receptor pocket in analogy to what is seen in the CsF complex. In contrast, the other cesium ion forms a sandwich complex with two cone-shaped calix[4]pyrroles (from different receptors). That is, one CsCl in **2** exists as a "solvent-loosened" contact ion pair within the receptor cavity as predicted by modeling (Figure 9) and the other is spatially separated by the receptor (i.e., host-separated as per Figure 1). The crystal structure of the CsCl complex also shows that the Cs^+ cation within the pocket, labeled as Cs2, is further coordinated by a water molecule with a Cs^+···O distance of 3.17 Å (Figure 11). This cesium cation interacts with the chloride anion labeled as Cl1a, forming the "solvent-loosened" contact ion pair that, in turn, is bound to NH protons of the calix[4]pyrrole *via* hydrogen bonds with distances of 3.32−3.39 Å (N···Cl^- interaction). In contrast, the other cesium cation, labeled as Cs1, is sandwiched between two cone-shaped calix[4]pyrrole *via* π−cation interactions characterized by Cs^+···C(pyrrole) distances of 3.28−3.66 Å. The chloride anion (Cl1), spatially separated from Cs1 by the calix[4]pyrrole skeleton, is also bound to the NH's of the calix[4]pyrrole and an OH of a molecule of methanol *via* hydrogen bonds with distances of 3.24−3.27 Å for the N···Cl^- interaction. Such distances are shorter than those for the interaction between Cl1a and the nitrogen atoms of the calix[4]pyrrole subunit, a finding that is attributable to a stronger interaction of the chloride anion with Cs2. The distances between the Cs^+ cation and the Cl^- anion in $\mathbf{2}_2$·$(CsCl)_2$ are found to be 3.60 Å for the contact ion pair (Cs2···Cl1a interaction) and to be 4.93 Å for the host-separated ion pair (Cs1···Cl interaction), respectively. By contrast, the distance between Cs1 and Cl1a is found to be 6.25 Å, which is interpreted in terms of Cs1 interacting with Cl1 more strongly than with Cl1a.

Further evidence for the proposed interaction between the cesium cation and the calix[4]pyrrole moiety came from the finding that the β-protons of the pyrrole subunits undergo D-for-H exchange in CD_3OD in the presence of CsCl. This is a reaction that has not hitherto been observed in the context of calix[4]pyrrole chemistry. As shown in Figures S9 and S15, Supporting Information, the peaks of the β-pyrrolic

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(25) Allen, F. H.; Kennard, O.; Taylor, R. *Acc. Chem. Res.* **1983**, *16*, 146–153.

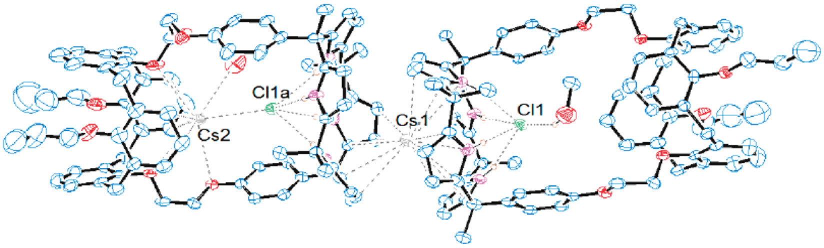

Figure 11. Single-crystal structure of $\mathbf{2}_2\cdot(\mathrm{CsCl})_2\cdot\mathrm{CH_3OH}\cdot\mathrm{H_2O}$. Displacement ellipsoids are scaled to the 30% probability level. Most hydrogen atoms have been removed for clarity.

protons of calix[4]pyrrole subunits are almost absent from the ^{1}H NMR spectra of **2** recorded roughly 10 min after the addition of 5.0 equiv of CsCl in 10% $\mathrm{CD_3OD}$ in $\mathrm{CDCl_3}$ (v/v). In contrast, when the corresponding experiment is run using 10% $\mathrm{CH_3OH}$ (a proton-containing solvent) in $\mathrm{CDCl_3}$ (v/v), the peaks for the β-pyrrolic protons are still observed in the presence CsCl (Figure S15c, Supporting Information). Such observations are completely consistent with the suggestion that the disappearance of the β-pyrrolic proton peak in the presence of $\mathrm{CD_3OD}$ is due to deuterium exchange and that this exchange is abetted by π−metal complexation involving the cesium cation and the four pyrrolic subunits that make up the calix[4]pyrrole core. It important to note that facile D-for-H exchange is not seen in the case of the CsBr or $\mathrm{CsNO_3}$ complexes of **2** (Figure S9, Supporting Information), lending credence to the suggestion that the ion-pair binding mode differs for these two salts.[26]

Considering the extraction studies, modeling results, and the absence of D-for-H exchange seen in 10% $\mathrm{CD_3OD}-\mathrm{CDCl_3}$ (v/v) (*vide supra*), we considered it likely that **2** would bind CsBr and $\mathrm{CsNO_3}$ as contact pairs. Concrete support for this conclusion, at least in the solid state, came from single-crystal diffraction analyses of the latter salt. The structure of the $\mathrm{CsNO_3}$ complex, obtained from crystals grown by slow evaporation of a chloroform/methanol solution of receptor **2** in the presence of $\mathrm{CsClO_4}$ and $\mathrm{TBANO_3}$, is shown in Figure 12. It reveals that the nitrate anion is coordinated to the $\mathrm{Cs^+}$ cation with two oxygen atoms and the third oxygen atom is bound to the calix[4]pyrrole moiety *via* hydrogen-bonding contacts characterized by $\mathrm{N\cdots O^-}$ distances of 2.95−3.04 Å. The distance between the cesium cation and the two oxygen atoms of the nitrate anion (3.12 and 3.17 Å) are in excellent agreement with those predicted by modeling (3.11 Å, Figure 10) and observed in other crystal structures bearing contact $\mathrm{CsNO_3}$ ion pairs (3.20 ± 0.09 Å); confirming that the cesium cation and the nitrate anion exist as a true contact ion pair in this complex.

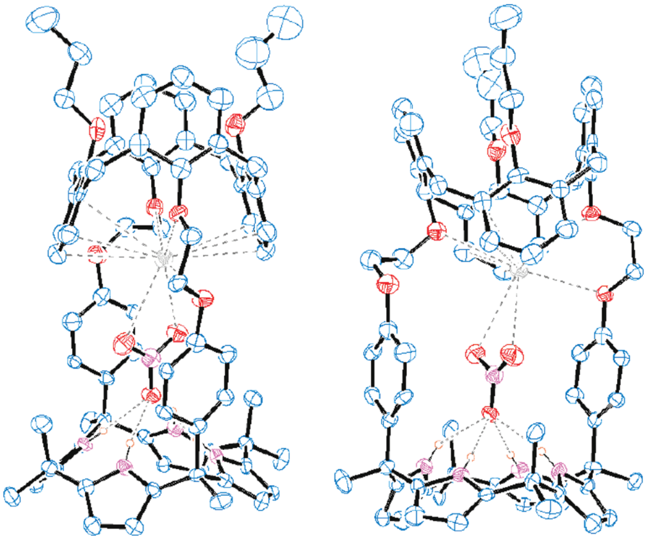

Figure 12. Two different views of the single-crystal structure of $\mathbf{2}\cdot\mathrm{CsNO_3}$. Displacement ellipsoids are scaled to the 30% probability level. Most hydrogen atoms have been removed for clarity.

In conclusion, an ion-pair receptor, **2**, derived by coupling a strong anion-binding site with a weak cation recognition site, has been synthesized and characterized by standard spectroscopic means, as well as through the use of single-crystal X-ray diffraction analysis. Taken in concert, the X-ray crystal structural data and the ^{1}H NMR spectroscopic analyses reveal that in both the solid state and in mixed methanol−chloroform solution, receptor **2** forms a stable 1:1 complex with a solvent-bridged CsF species, but only if both the anion and cation are both present. Such behavior, which follows the terms associated with an *AND* logic gate, stands in marked contrast to what was seen for the earlier system, **1**. This previously reported receptor binds the two constituent ions sequentially, with the $\mathrm{Cs^+}$ cation being bound before the $\mathrm{F^-}$ anion. Receptor **2** was also found to bind other cesium salts in mixed methanol−chloroform solution on the basis of an *AND* logic gate even though it fails to bind the constituent counteranions (as the tetrabutylammonium salts) in pure chloroform. Receptor **2** forms an unprecedented 2:2 complex with CsCl characterized by two different ion-pair binding modes, including one where the anion and cation are separated by the host framework. In contrast, single-crystal X-ray diffraction analyses and ^{1}H NMR spectroscopic studies reveal that **2** forms only a 1:1 complex with $\mathrm{CsNO_3}$, wherein the anion and cation are held together in close proximity as contact ion pairs. These findings reveal receptor **2** to be a versatile ion-pair receptor whose binding behavior can be modulated *via* an appropriate choice of the counteranion.

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[26] The basis for the CsCl-selective deuterium exchange may reflect the favorable cone angle established in this particular anion complex. The cone angle is expected to be larger in the case of the corresponding fluoride complex. This and the existence of more favorable ion-pair binding modes would preclude the presence of substantial quantities of $\mathrm{Cs^+}$ in the calix[4]pyrrole “cup”. Conversely, in the case of the other cesium salts examined, CsBr and $\mathrm{CsNO_3}$, anion complexation will produce structures with smaller cone angles. Thus, even though binding within the cup of calix[4]pyrrole might occur to a certain extent (it is not the dominant mode as noted in the text proper), the resulting complexes would lack an optimal geometry for D-for-H exchange. Further tests of these hypotheses are in progress.

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Supporting Information Available: Synthetic details, NMR spectroscopic data, ITC analyses, Cartesian coordinates for all modeled complexes, and X-ray structural data for **2**·CsF, **2**$_2$·$(CsCl)_2$·CH_3OH·H_2O, and **2**·$CsNO_3$. This material is available free of charge via the Internet at http://pubs.acs.org.

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