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Unraveling Cooperative Interactions between Complexed Ions in Dual-Host Strategy for Cesium Salt Separation

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Abstract

The dual-host strategy offers a straightforward approach to ion separation, yet the nature of cooperative interactions between receptor-complexed cations and anions remains poorly understood. In this study, we utilize [18] crown-6 ether as a cation receptor and a tripodal hexaurea receptor **L** as an anion receptor to extract cesium salts (chloride, nitrate, carbonate, sulfate, and phosphate) from the solid phase into chloroform. Remarkably, Cs_3PO_4 exhibits the highest extraction efficiency, driven by strong cooperative interactions involving ion-dipole coordination between Cs^+ and carbonyl (C=O) groups, as well as direct ion-pairing interactions between [18] crown-6-complexed Cs^+ and hexaurea-bound PO_4^{3-}. Single-crystal structural analysis corroborates these interactions, shedding light on the underlying mechanisms and

providing valuable guidance for the rational design of advanced dual-host systems for selective ion separation.

Keywords

Introduction

Ion-pair interaction, defined as the electrostatic attraction between a positively charged cation and a negatively charged anion, is prevalent across various disciplines including biology, chemistry, materials science, and ion batteries [1-3]. Fundamental understanding of ion-pairing can help to regulate their roles and relevant applications in chemical catalysis, battery performance, and ion binding, transport and separation [4-8]. Building on the extensive research into anion and cation receptors within the realm of supramolecular chemistry [9-12], numerous heteroditopic ion-pair receptors have been elaborately developed [13-15]. These receptors, consisting of binding sites for both anions and cations within a single molecule, have facilitated advancements in ion-pair recognition. This progress has led to the development of ion separation utilizing ion-pair receptors [16-20], which eliminate the need for auxiliary reagents to balance overall charges compared to the use of individual anion or cation receptors [21]. An alternative approach for ion separation involves the combination of an anion receptor and a cation receptor, known as the dual-host strategy [22-24]. Unlike ion-pair receptors, this strategy avoids the intricate, multi-step synthesis required for designing and making new receptors, thereby saving considerable time. However, the selectivity of ion separation achieved through the dual-host strategy may not match that of ion-

pair receptors, possibly due to less defined interactions between the receptor-complexed anions and cations.
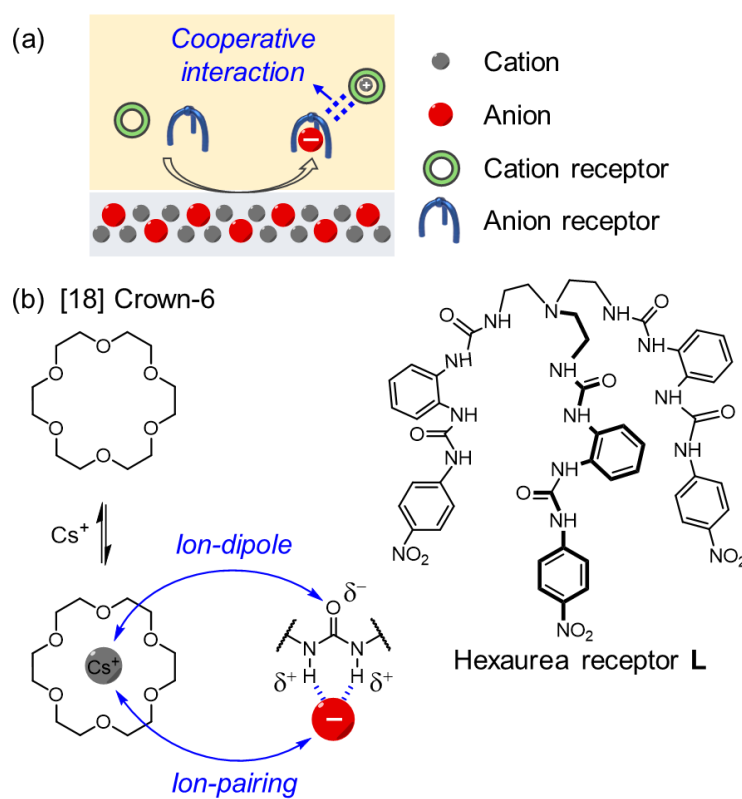
Figure 1: (a) Schematic illustration of dual-host strategy for ion pair extraction vis solid-liquid method, showing the cooperative interaction between complexed anion and complexed cation. (b) Molecular structures of [18] crown-6 ether (for Cs^+ binding) and tripodal hexaurea receptor **L** (for anion binding), where cooperative interactions od ion-dipole and ion-pairing are shown.

Early studies employing the dual-host strategy were aimed at separating alkali metal halide salts from aqueous solutions into organic phases, including KCl, CsCl, and $CsNO_3$ [23-29]. In these studies, [18] crown-6 ether was commonly utilized, and various anion receptors were selected to achieve tailored anion binding. Compared to the use of individual anion or cation receptors, the dual-host strategy can significantly enhance the efficiency of ion-pair extraction. However, the driving forces and cooperative interactions of the complexed ions remain poorly understood (Figure 1a).

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To the best of our knowledge, only two examples provide clear evidence of cooperative interactions based on single crystal structures [28-29], where the [18] crown-6 complexed K^+ cation forms ion-dipole interactions with the carbonyl (C=O) or nitro (NO_2) groups of the anion-bound receptors (KF and K_2CO_3).

Recently, we demonstrated that a tripodal hexaurea receptor **L** (Figure 1b) could selectively and reversibly extract sulfate and phosphate anions from water into organic phase (under pH control) [30-33]. Single crystal structures of receptor-K_2SO_4 complex in the presence of [18] crown-6 clearly displayed ion-dipole interactions between K^+ and C=O moiety [31], similar to these seen in the single crystal structures of KF and K_2CO_3 complexes. These provide a promising opportunity that can used to identify the cooperative interaction underpinning complexed ions in dual-host strategy-based extraction. To do this, the hexaurea receptor, [18] crown-6 and Cs^+ cation are selected as model system, with the counter anion being varied from chloride, nitrate, carbonate, sulfate to phosphate. Solid-liquid extraction experiments and single-crystal structures demonstrated that the cooperative interactions (ion-dipole and ion-pairing) could be enhanced along with the charge of anion and its binding affinity with **L** (from Cl^- to CO_3^{2-}, and PO_4^{3-}). Notably, for the first time, direct ion-pairing between receptor complexed phosphate and [18] crown-6 complexed cesium is observed in single crystal structure, facilitating highly efficient Cs_3PO_4 extraction.

Results and Discussion

The tripodal hexaurea receptor **L** is comprised of a central tren (tris(2-aminoethyl)amine) core and three arms of *ortho*-phenylene bis(urea) unit, which can fold inward to encapsulate anion inside the cavity through up to 12 hydrogen bonds [30]. According to our previous results, the binding affinity of **L** with chloride, sulfate

and phosphate is determined to be 2.2×10^2 M^{-1}, 9.9×10^4 M^{-1}, and 3.8×10^6 M^{-1}, respectively (in DMSO) [31]. Such strong anion binding affinity has led to selective extraction of sulfate and phosphate from basic aqueous solution into chloroform and controllable release into acidic solution [32]. Very recently, it was found that the receptor **L** alone can further extract solid Li_2SO_4 into DMSO solution [33], where sulfate binding is sufficiently strong to drive the solid-liquid extraction. DFT calculations suggest that ion-dipole interaction of Li$^+$ cation and carbonyl groups also contribute to the extraction. The negative electrostatic potential (δ^-) of O=C is attributed to a high dipole moment of urea unit (mono(urea): 3.95 D, bis(urea): 7.55 D) [34-36], which has been demonstrated to be capable of binding Na$^+$ and K$^+$ by oligourea foldamers and macrocycles [37-39]. However, in the solid-liquid extraction of Li_2SO_4 in DMSO, addition of crown ether did not help to increase the extraction efficiency. This is because ion-dipole interaction is negligible in high polar solvent, and Li$^+$ binding is weak [40-42]. Therefore, to further understand how the ion-dipole interactions regulate ion-pair separation, Cs$^+$ is selected as of its relatively strong binding with [18] crown-6 ether, $> 10^4$ M^{-1} in CH_3CN, $\sim 10^3$ M^{-1} in DMSO [40, 43]. Solid-liquid extraction is studied in chloroform as the ion-pairing interaction in nonpolar solvent could be stronger than that in polar solvent [44-47].

The ion-dipole interaction between complexed Cs$^+$ cation and receptor-sulfate complex was first identified by single crystal structure. The overall stoichiometry of **L**, [18] crown-6, Cs$^+$, and SO_4^{2-} is 4:5:4:2 in the crystalized structure. Like the structure of K_2SO_4 complexes [31], one Cs$^+$ cation is encapsulated by [18] crown-6 and further stabilized by one ion-dipole interaction with the O=C unit of hexaurea receptor. The Cs-O distance is measured at 3.2 Å. The other two Cs$^+$ cations are found to be co-stabilized by three [18] crown ether macrocycles.
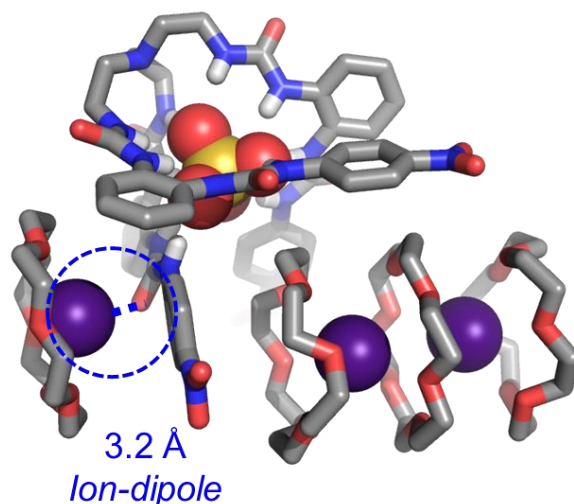
Figure 2: Single crystal structures of complexed Cs_2SO_4 with [18] crown-6 ether and tripodal receptor **L** (CCDC: 2411573). One sulfate anion is encapsulated inside the hexaurea cavity through 12 × N-H···O hydrogen bonds. One Cs^+ cation is co-stabilized by electrostatic interaction with one [18] crown-6 ether and ion-dipole interaction with O=C unit. Two Cs^+ cations are complexed by two 18-crown-6 ether showing no interaction with anion receptor. The overall stoichiometry of Cs^+, SO_4^{2-}, [18] crown-6 ether and anion receptor is 4:2:5:2. Nonpolar hydrogen atoms, solvent molecules are omitted for clarity.

Next, a solid-liquid extraction experiment was first conducted for Cs_2SO_4 salts. A solution of hexaurea receptor **L** and two equivalents of [18] crown-6 in $CHCl_3$ was prepared, and solids of Cs_2SO_4 were added into the solution. Under stirring at 60°C for 5 hours, all the solids were dissolved indicating the completion of solid-liquid extraction of Cs_2SO_4. In contrast, by changing the solvent from chloroform to acetonitrile, the Cs_2SO_4 solids were barely dissolved, consistent with weaken Cs^+ binding affinity with [18] crown-6 ether and negligible cooperative interaction between complexed ions in polar solvent of acetonitrile.

Table 1: Summary of extraction efficiency and anion binding affinity. [a]

	Cation host only	Anion host only	Dual host	Anion binding affinity [b] M^{-1}	Anion hydration [c] $kJ\ mol^{-1}$
CsCl	68%	10%	82%	2.2×10^2	-344
CsNO$_3$	31%	13%	36%	3.3×10^3	-286
Cs$_2$CO$_3$	39%	10%	61%	8.4×10^3	-1324
Cs$_2$SO$_4$	16%	4%	41%	9.9×10^4	-975
Cs$_3$PO$_4$	59%	5%	100%	3.8×10^6	-2753

[a] solid-liquid extraction condition: 30°C, 0.5 h, stirring rate: 1500 r/min, one equivalent of anion receptor versus corresponding anion and one equivalent of 18-crown-6 ether versus Cs$^+$ were used, respectively. The extraction efficiency is defined as the extracted Cs$^+$ over initial (total) Cs$^+$ as determined by ion chromatography analysis. [b] Anion binding affinities are determined by ^{1}H NMR titrations in DMSO-d_6. Chloride, sulfate and phosphate binding affinities were reported in previous studies. [c] Gibbs energies of anion hydration at 25 °C. For Cs$^+$, the hydration energy is -266 kJ mol^{-1}.

Solid-liquid extraction of other cesium salts including CsCl, CsNO$_3$, Cs$_2$CO$_3$, and Cs$_3$PO$_4$ were further studied in the presence of one equivalent of hexaurea receptor versus anion and one equivalent of [18] crown-6 versus Cs$^+$ cation. The best extraction efficiency was observed for Cs$_3$PO$_4$, where all the solids could be dissolved in CHCl$_3$ in 0.5 hour at 30 °C. Therefore, the extraction experiments were done at the same condition (30 °C, 0.5 h, stirring rate: 1500 r/min), and the extraction results were summarized in Table 1. Specifically, the determined extraction efficiency (extracted Cs$^+$ versus the initial amount, concentrations were recorded by ion chromatography) of CsCl, CsNO$_3$, CS$_2$CO$_3$, Cs$_2$SO$_4$ and Cs$_3$PO$_4$ are 82%, 36%, 61%, 41%, and 100%, respectively. In contrast, by using individual [18] crown-6 ether or hexaurea receptor, a clear enhancement of extraction efficiency was seen for the dual-host strategy. Additionally, use of [18] crown-6 ether alone displays better extraction efficiency than

that of hexaurea receptor (Table 1), which is attributed to relatively poor solubility of hexaurea receptor in $CHCl_3$.

For cesium slats with various oxyanions, the extraction efficiency follows the order of $PO_4^{3-} > CO_3^{2-} > SO_4^{2-} > NO_3^-$, consistent with the order of negative charges as well as anion's hydration energies (Table 1) [48-49]. This *anti*-Hofmeister selectivity of phosphate over other studied oxyanions is normally seen in liquid-liquid and solid-liquid anion extractions, likely due to relatively strong phosphate binding with hexaurea receptor (3.8×10^6 M^{-1}). In comparison, the binding affinity of hexaurea receptor with nitrate and carbonate was calculated to be 3.3×10^3 M^{-1} and 8.4×10^3 M^{-1}, respectively (*vide infra*), as determined by ^1H NMR titrations in DMSO.

The resulting complexes after solid-liquid extraction were also characterized by ^1H NMR spectroscopy (Figure 3), showing consistent anion binding profiles. By comparing with free hexaurea receptor **L**, chemical shift of urea units N-H from obtained complexes are observed to downfield shifted indicative of anion binding. The relative peak positions of N-H (8.5 – 13.5 ppm, Figure 3) are consistent with their anion binding affinity and solid-liquid extraction efficiency, $PO_4^{3-} > CO_3^{2-} > SO_4^{2-}$. In addition, the chemical shift of [18] crown-6 ether (3.4 – 3.6 ppm) is observed to slightly upfield shifted by comparing to that of free crown ether, indicating Cs^+ binding and consistent with their extraction efficiency. The relatively upfield shifted chemical shift for Cs_3PO_4 complex may indicate strong cooperative interaction upon solid-liquid extraction.
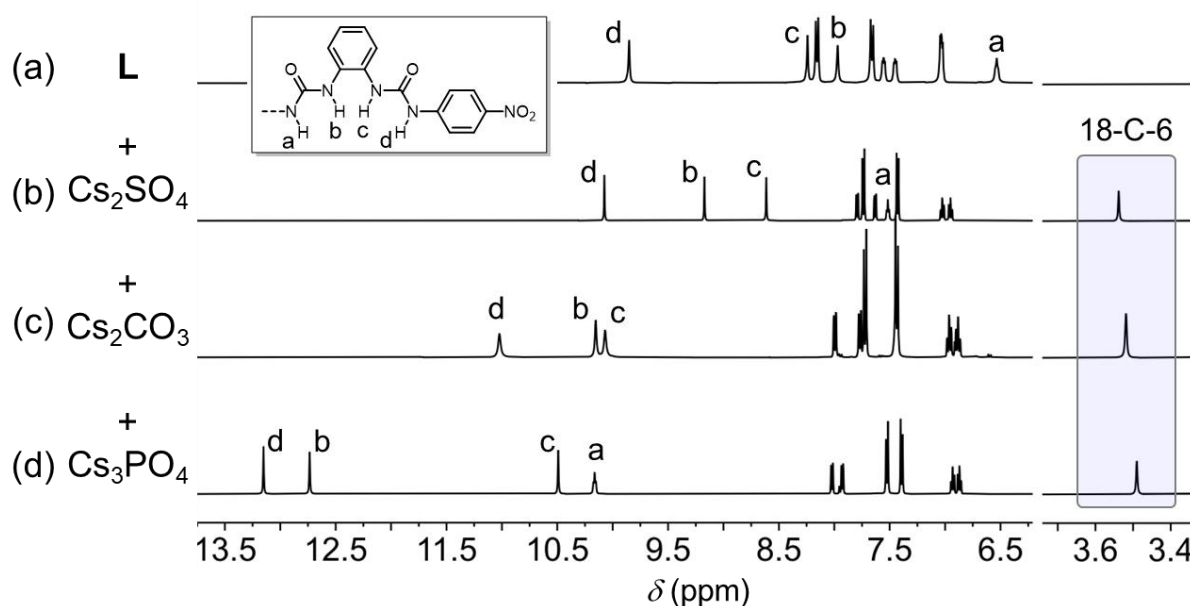
Figure 3: Stacked ^{1}H NMR spectra of (a) free anion receptor **L** and its complexes with one equivalent of (b) Cs_2SO_4, (c) Cs_2CO_3, and (d) Cs_3PO_4 in the presence of [18] crown-6 ether. (DMSO-d_6, 1 mM, 400 MHz, 298 K)

To understand cooperative interactions between complexed ions, we tried to grow crystal structure of studied salts. Fortunately, single crystals of Cs_2CO_3 and Cs_3PO_4 complexes were obtained by slow vapor diffusion from acetonitrile and diethyl ether. Notably, clearly stronger ion-dipole interactions of complexed carbonate and complexed phosphate are illustrated than those as seen in the single crystal structure of Cs_2SO_4 complex. To our surprise, direct ion-pairing between receptor complexed phosphate and [18] crown-6 ether complexed cesium is observed for the first time in single crystal structure (*vide infra*).
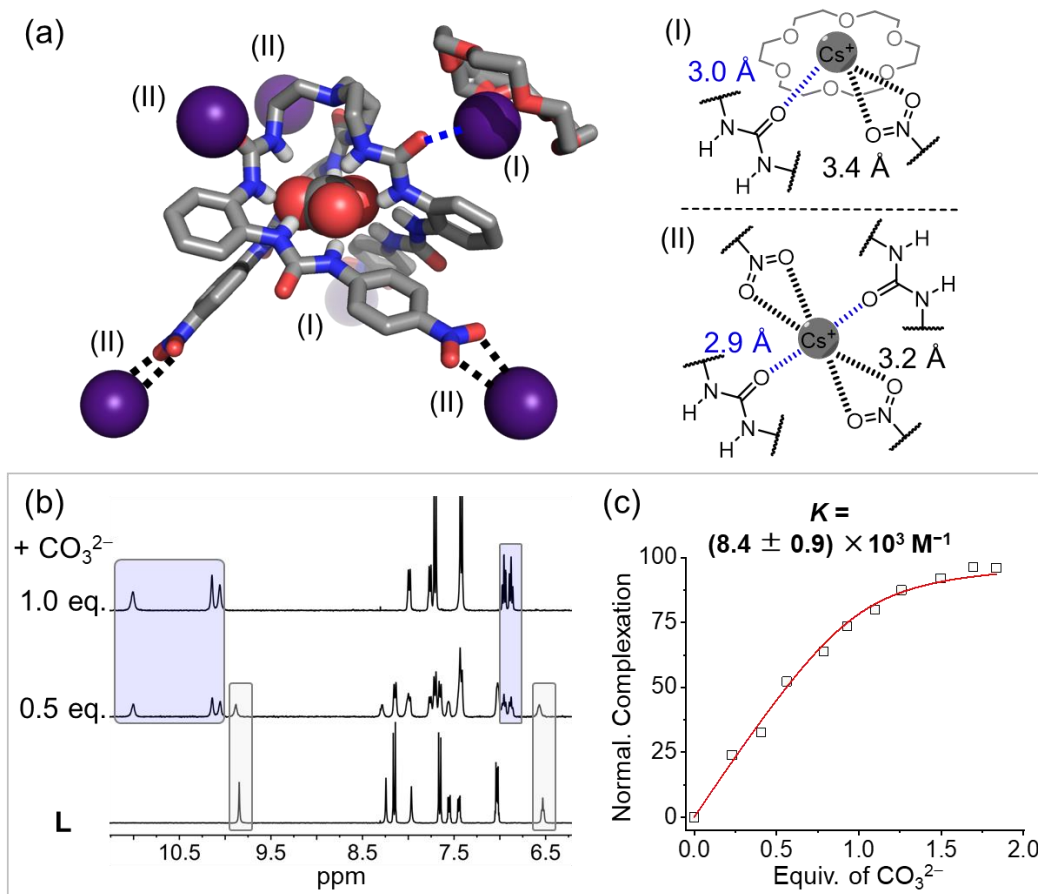
Figure 4: Single crystal structures of complexed Cs_2CO_3 (CCDC: 2411574) with [18] crown-6 ether and tripodal receptor **L**. Carbonate anion is encapsulated inside the hexaurea cavity and stabilized by 12 × N-H$\cdots$O hydrogen bonds. Two types of Cs^+ complexations are observed, (I) one [18] crown-6 ether complexed Cs^+ interacts with carbonyl (O=C) and nitro (-NO_2) groups through three ion-dipole interactions, (II) the other Cs^+ is stabilized by six ion-dipole interactions from carbonyl (O=C) and nitro (-NO_2) groups. The overall stoichiometry of Cs^+, CO_3^{2-}, [18] crown-6 ether and anion receptor is 2:1:1:1. Nonpolar hydrogen atoms, solvent molecules are omitted for clarity. (b) Stacked ^1H NMR spectra of free anion receptor **L** by adding carbonate (in the form of 18-crown-6 ether complexed Na_2CO_3) showing slow-exchange of NMR signals (DMSO-d_6, [**1**] = [salts] = 1 mM, 400 MHz, 298 K). (c) Simulated binding curve of carbonate complexation with receptor **L** as derived from NMR titration.

For the crystal of Cs_2CO_3 with [18] crown-6 ether and receptor **L** (Figure 4), an overall stoichiometry of one hexaurea receptor, one [18] crown-6 ether, one carbonate and two cesium cations are obtained. Firstly, carbonate is encapsulated inside the folded cavity of hexaurea receptor through twelve hydrogen bonds. The average distance of N···O is measured at 2.85 ± 0.08 Å, which is comparable to those that are seen in the single crystal structure of Cs_2SO_4 (average distance is 2.9 ± 0.07 Å). Based on an NMR titration of hexaurea receptor L by adding CO_3^{2-}, slow exchange of NMR signals is displayed (Figure 4b), which is similar to that of sulfate anion titration results and indicative of strong carbonate binding affinity. The carbonate binding constant is determined to be 8.4 ± 0.9 $\times10^3$ M^{-1} in DMSO-d_6 (Figure 4c), which is weaker than sulfate binding (9.9 $\times10^4$ M^{-1}). This is because that carbonate displays higher hydration energy than that of sulfate, and the tetrahedral shape of sulfate anion matches the pseudo-tetrahedral cavity of folded hexaurea receptor [30].

Secondly, for Cs^+ cations, two types of Cs^+ binding are shown in solid state. Two type-(I) cesium cations are found to be stabilized by the binding with [18] crown-6 ether and three ion-dipole interactions with O=C (urea unit) and O-N (terminal nitro group). Distances of Cs-O are measured at 3.0 Å and 3.4 Å. Regarding type-(II) cesium binding, four cesium cations are observed to interact with two urea units and two nitro groups through six Cs-O ion-dipole interactions (2.9 Å and 3.2 Å). These intermolecular interactions of Cs^+ cations with [18] crown-6 ether and hexaurea receptors help to form 3D framework in solid state, which may reinforce cooperative interactions between complexed Cs^+ and complexed CO_3^{2-} for solid-liquid extraction. In contrast, only one ion-dipole interaction (3.2 Å) is observed in the single crystal structure of Cs_2SO_4 complex. The enhanced ion-dipole interactions of complexed Cs_2CO_3 corresponds to relatively higher extraction efficiency (61%) than that of Cs_2SO_4 (41%).
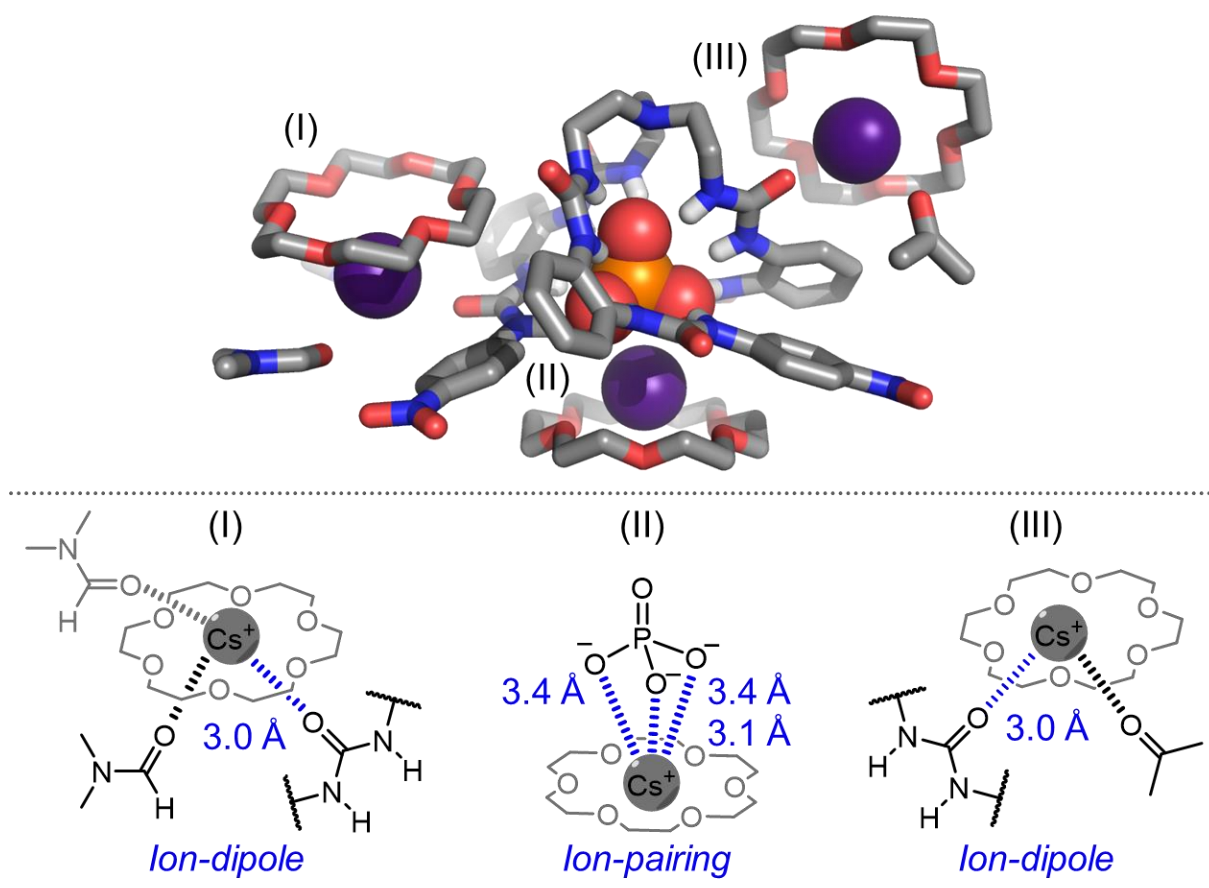
Figure 5: Single crystal structures of complexed Cs_3PO_4 with [18] crown-6 ether and tripodal receptor (CCDC: 2411575). Phosphate anion is encapsulated inside the hexaurea cavity and stabilized by 12 × N-H⋯O hydrogen bonds. Three types of Cs^+ complexations are observed. All Cs^+ are seen to be complexed with [18] crown-6 ether and further stabilized by (I) ion-dipole interactions with DMF and carbonyl (O=C) group, (II) ion-pairing with receptor-complexed phosphate anion, and (III) ion-dipole interactions with acetone and carbonyl (O=C) group.

The cooperative interaction of complexed Cs^+ with complexed phosphate is illustrated in single crystal structure. Like other anions, phosphate is also complexed inside the cavity of hexaurea receptor through twelve hydrogen bonds. The average N⋯O distance is 2.79 ± 0.03 Å, corresponding to strong phosphate binding (3.8 ×10⁶ M^{-1} in DMSO) [32]. All three Cs^+ cations are encapsulated by [18] crown-6 ether yet

further stabilized by different secondary interactions. Specifically, the type-(I) and type-(III) Cs^+ cations form three and two ion-dipole interactions with O=C (urea unit, DMF, or acetone molecules), respectively. For the type-(II) Cs^+ cation, direct ion-pairing interaction with complexed phosphate anion is clearly illustrated, where average P⋯O distance is 3.3 ± 0.2 Å. To the best of our knowledge, this is the first time that receptor-complexed anion and complexed Cs+ form ion-pairing as verified by single crystal structure. These ion-pairings combined with multiple ion-dipole interactions support highly efficient solid-liquid extraction of Cs_3PO_4 over other cesium salts.

Conclusion

In summary, by using a model system of [18] crown-6 ether and tripodal hexaurea anion receptor **L** for the solid-liquid extraction of cesium salts (with various conteranion, chloride, nitrate, carbonate, sulfate and phosphate) into chloroform, we demonstrate efficient extraction of Cs_3PO_4 solids. The extraction efficiency follows the order of Cs_3PO_4 > CsCl > Cs_2CO_3 > Cs_2SO_4 > $CsNO_3$, reflecting the hydration energies and binding affinities of the corresponding anions. Notably, single-crystal structural analysis reveals that the extraction performance correlates with cooperative interactions between [18] crown-6-complexed Cs^+ and hexaurea-bound anions. For the Cs_3PO_4 complex, direct ion-pairing interactions are identified for the first time. These findings highlight the accessibility of the dual-host strategy and suggest that cooperative interactions between receptor-complexed ions can be fine-tuned for selective ion separation. Ongoing work aims to explore diverse combinations of anion and cation receptors for targeted ion separation applications.

Supporting Information

Nuclear magnetic resonance (NMR), Mass and X-ray diffraction data are included in the Supporting Information document. Deposition numbers 2411573 (CS_2SO_4 complex), 2411574 (CS_2CO_3 complex), and 2411575 (CS_3PO_4 complex) contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallo-graphic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service via https://www.ccdc.cam.ac.uk/.

Acknowledgements

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