DFT calculation and experimental validation on the interactions of bis(trifluoromethylsulfonyl)imide and hexafluorophosphate with cesium

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ABSTRACT

Bis(trifluoromethylsulfonyl)imide (NTf_2^-) and hexafluorophosphate (PF_6^-) are the most frequently used anions for hydrophobic ionic liquids (ILs) which have been considered as promising solvents in the extraction of cesium ions. The interactions of NTf_2^- and PF_6^- with Cs^+ were explored in this work. The results of DFT calculation indicated that both Cs^+ and $Cs(18C6)^+$ prefer to interact with two NTf_2^- or PF_6^- anions in gas phase, where 18C6 is 18-crown-6. The complex of $Cs(NTf_2)_2^-$ was observed in electrospray ionization mass spectrometry (ESI-MS), and the complexes of $[Cs(18C6)NTf_2]_2$ and $[Cs(18C6)PF_6]_2$ were crystallized in which $Cs(18C6)^+$ interacted with two anions. The interactions of NTf_2^- with cesium resulted in a synergistic effect between dicyclohexano-18-crown-6 (DCH18C6) and NTf_2^- in the extraction of Cs^+ using n-octanol as diluent. However, DFT calculation revealed that the complex $Cs(DCH18C6)^+$ interacted with one NTf_2^- anion was more thermodynamically stable than that with two anions in organic phase, different from that in gas phase.

1. Introduction

Room-temperature ionic liquids (ILs) are composed entirely of organic cations and organic or inorganic anions, and have been applied in many fields including synthesis, catalysis, energy and separation sciences [1—4]. There are a large amount of ILs with different cations and anions [5], and the functionalization of the cations and anions can lead to more task specific ILs [6]. Among the anions of ILs, bis(trifluoromethylsulfonyl)imide (NTf_2^-) and hexafluorophosphate (PF_6^-) are very common which can construct hydrophobic ILs in combination with organic cations such as the imidazolium cations 1-butyl-3-methylimidazolium (C_4mim^+).

Hydrophobic ILs have been considered as promising solvents for separation processes in the advanced nuclear fuel cycle [7]. The radioactive isotope ^{137}Cs is one of the most troublesome isotopes in the treatment of high level liquid waste (HLLW) due to its heat-emitting property. It is of great importance to remove ^{137}Cs prior to the waste vitrification, for not only reducing the waste volume but also minimizing the long-term hazards [8]. The extraction of Cs^+ has attracted much attention using crown ethers or calix crown ethers as extractants in combination with ILs based on NTf_2^- or PF_6^- [9—16].

Choosing an appropriate solvent is extremely important for a separation process, as the properties of the solvent significantly affect the extraction performance. The extraction mechanism in the extraction of cesium ions using ILs as solvents is usually cation exchange [17], different from the neutral complex extraction mechanism by using traditional organic solvents. In the cation exchange mechanism, cationic moieties (cesium ions or complexes of cesium ions) are transferred into the IL phase and the IL cations are simultaneously exchanged into the aqueous phase. In this

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context, an interesting question is whether the IL anions can coordinate with the cesium cations or deficient complexes of cesium ions, facilitating the extraction process. Some phenomena indeed reflected the interactions of NTf_2^- and PF_6^- with cesium. In the extraction of Cs^+ with ILs, the pure IL $C_4mimNTf_2$ or C_4mimPF_6 can extract Cs^+ with unneglectable distribution ratios in the absence of other extractants [11,13], whilst most of other metal ions can hardly be extracted by pure ILs. Cs^+ is exchanged with the C_4mim^+ cation into the IL phase [18]. It is very likely that NTf_2^- and PF_6^- can coordinate with Cs^+, but investigations on the coordinating behavior are very limited. We reported a ternary complex of Cs^+ with bis(2-propyloxy)calix [4]crown-6 (BPC6) and NTf_2^-, in which Cs^+ is coordinated with BPC6 by the six oxygen atoms of the crown and the cation$-\pi$ interactions, and also with the anion NTf_2^- via one oxygen atom of the sulfonyl group [19]. A crystal structure containing cesium and PF_6^- was reported by Salorinne et al., in which PF_6^- coordinated with the deficient Cs^+ complex [20].

The coordination of NTf_2^- or PF_6^- with cesium is very important for understanding the mechanism in the extraction of Cs^+, but the characterization method is very limited. Theoretical calculation is a useful approach to investigate the coordinating interactions. Ali et al. optimized the structures of the complexes of $CsNTf_2$ and $Cs(BPC6)NTf_2$ by density functional theory (DFT) calculation [16], and the calculated structure of $Cs(BPC6)NTf_2$ was similar with our crystal structure [19]. To obtain more information about the interactions between Cs^+ and NTf_2^-, more complexes of Cs^+ and NTf_2^- should be calculated. Furthermore, to the best of our knowledge, there has been no theoretical calculation dealing with the interaction between Cs^+ and PF_6^-. Crystallization, as mentioned above, is another powerful means to illustrate the interactions between Cs^+ and NTf_2^- or PF_6^-. Particularly, using the same ligands in the synthesis of ternary complexes will facilitate the comparison of these two anions in the interaction with deficient Cs^+ complexes. In this work, we calculated the interactions of NTf_2^- and PF_6^- with Cs^+ as well as with the deficient complex $Cs(18C6)^+$ (18C6 is 18-crown-6), and synthesized the ternary complex of Cs^+ with 18C6 containing NTf_2^- or PF_6^-. We hope that our work will facilitate the understanding of the extraction using ILs as solvents.

2. Experimental

2.1. Materials and methods

$HNTf_2$ (95%), HPF_6 (~55%wt in H_2O) and CsOH (50 wt.% in H_2O, 99.9% trace metals basis) were purchased from Aldrich. The crown ether 18-crown-6 (18C6, $\geq$99.5%) was purchased from Fluka, and dicyclohexano-18-crown-6 (DCH18C6) was synthesized in INET. $CsNTf_2$ and $CsPF_6$ were prepared by the reaction of CsOH in aqueous solution with equal mole of $HNTf_2$ and HPF_6, respectively, followed by evaporation of water. All other reagents were of analytical grade and used without further purification.

2.2. Electrospray ionization mass spectra

Electrospray ionization mass spectra (ESI-MS) were acquired in both positive and negative modes with a Bruker Apex IV FTMS. 20 μL of an aqueous solution of $CsNTf_2$ (0.08 mol/L) was diluted 20 times by methanol and then injected into the equipment.

2.3. Synthesis of [Cs(18C6)NTf₂]₂

1 mL of chloroform solution containing 18C6 (10.5 mg) was added into a flask containing $CsNTf_2$ (30 mg). The mixture was stirred for over 24 h and the supernatant was transferred to a beaker. After evaporating for 2 days, colorless bulk crystals were

found at the bottom of the beaker. The solid was removed, washed with water, and then taken for further characterization. ESI-MS (m/z): positive mode: 397.06328 $[Cs(18C6)]^+$, negative mode: 279.91657 NTf_2^-; 692.74113 $Cs(NTf_2)_2^-$.

2.4. Synthesis of [Cs(18C6)PF₆]₂

1 mL of dichloromethane solution containing 18C6 (13.2 mg) was added into a flask containing $CsPF_6$ (30 mg). The mixture was stirred for over 48 h, the supernatant was transferred to a beaker, and 0.2 mL of *n*-heptane was added. After evaporating very slowly for 7 days, colorless bulk crystals were found at the bottom of the beaker. The solid was removed, washed with water, and then taken for further characterization. ESI-MS (m/z): positive mode: 397.06293 $[Cs(18C6)]^+$; 939.11347, $[Cs(18C6)]_2PF_6^+$, negative mode: 422.83164 $Cs(PF_6)_2^-$.

2.5. X-ray crystal structure determination

The crystallographic data were collected on an Image Plate X-Ray Diffractometer. Using Olex2, the structure was solved with the Superflip structure solution program using Charge Flipping and refined with the XL refinement package using Least Squares minimization [21–23]. The details of data collection, data reduction, and crystallographic data are summarized in Table 1.

2.6. Extraction experiments

1 mL of *n*-octanol containing single or mixtures of DCH18C6 and $C_4mimNTf_2$ with total concentration of 0.02 mol/L and 1 mL of aqueous solution containing 0.002 mol/L of $CsNO_3$ and trace amount of ^{137}Cs were added into a plastic tube, followed by vibrating for 2 h at 298.2 K. Then the mixture was centrifuged and phase separated, and ^{137}Cs both in the organic phase and in the aqueous phase were measured by ultra-low level liquid scintillation QUANTULUS 1220 with Ultima Gold™ AB as the scintillation solution (0.1 mL sample and 10 mL scintillation solution). The distribution ratio of Cs^+ (D) was defined as the ratio of the radioactivity of ^{137}Cs in the organic phase to that in the aqueous

Table 1
Crystallographic data for the complexes of $[Cs(18C6)NTf_2]_2$ and $[Cs(18C6)PF_6]_2$.

	$[Cs(18C6)NTf_2]_2$	$[Cs(18C6)PF_6]_2$
Chemical formula	$C_{28}H_{48}Cs_2F_{12}N_2O_{20}S_4$	$C_{24}H_{48}Cs_2F_{12}O_{12}P_2$
Formula weight	1354.74	1084.38
Temperature (K)	180.0(1)	298(2)
Crystal system	monoclinic	monoclinic
Space group	$C2/c$	$C2/c$
a (Å)	24.9730(10)	25.2084(17)
b (Å)	9.0296(3)	8.5402(6)
c (Å)	23.5008(9)	21.4061(14)
α (°)	90.00	90
β (°)	109.240(5)	117.576(2)
γ (°)	90.00	90
V (Å³)	5003.4(3)	4084.9(5)
Z	4	4
ρ_{calcd} (g·cm⁻³)	1.798	1.763
F(000)	2688	2144
μ (mm⁻¹)	1.739	1.968
θ_{min}, θ_{max} (°)	3.33, 26.02	2.553, 27.568
Total reflections	9520	51751
Unique reflections (R_{int})	0.0329	0.0306
Data/Restraints/Parameters	4903/0/307	4684/0/235
R1, w$R2$ [I ≥ 2σ(I)]	0.0371, 0.0871	0.0510, 0.1548
R1, w$R2$ (all data)	0.0474, 0.0934	0.0584, 0.1637
Δρ (eÅ⁻³)	0.63, −1.16	1.005, −1.260
Goodness of fit (GOF)	1.057	1.120

phase. Each experiment was performed at least twice and the results agreed within an error of 3%.

2.7. Computation methods

All theoretical calculations were performed using the Gaussian 09 software package [24]. The structures of the complexes were fully optimized by DFT using the hybrid B3LYP exchange correlation functional [25,26] in conjunction with the Stuttgart-Dresden relativistic effective core potential (RECP) basis set for cesium and 6-31G(d,p) for other atoms. All the optimized structures are confirmed to be global minima structures on the potential energy hypersurface by vibrational frequency analysis at the same level of theory. The binding energies (E_{int}) were corrected with the basis set superposition error (BSSE) using the Boys-Bernardi counterpoise technique [27]. The final expression for the E_{int} was as follows:

$$E_{int} = E_{CP}(AB) - E_{min}(A) - E_{min}(B) + \Delta ZPVE \qquad (1)$$

where E_{CP} is the counterpoise corrected electronic energy, E_{min} is the electronic energy in the minimum-energy geometry, and ZPVE is the zero-point vibrational energy. Calculations taking into account solvation effects were carried out by using integral equation formalism version of the polarizable continuum model (IEFPCM) [28–31], where the dielectric constant used for n-octanol was 10.34.

3. Results and discussion

3.1. Interactions of NTf_2^- and PF_6^- with Cs^+

Fig. 1 shows the structures of the complexes of Cs^+ with one, two and three NTf_2^- or PF_6^- as well as one NTf_2^- or PF_6^- with two Cs^+ optimized by DFT calculation. In the complexes of Cs^+ with NTf_2^-, only the oxygen atoms from the sulfonyl group of NTf_2^- coordinate to the cesium ion, and the Cs—O distances are listed in Table 2. For the conformer of $CsNTf_2$, the two $-CF_3$ fragments of NTf_2^- are cis to each other, identical to that in the literature [16], allowing three oxygen atoms coordinating to Cs^+ with Cs—O distances of 2.947, 3.130 and 3.135 Å, respectively. The conformer of $Cs(NTf_2)_2^-$ belongs to C_2 symmetry with the two $-CF_3$ fragments of both NTf_2^- trans to each other. Each NTf_2^- binds to Cs^+ through two oxygen atoms, and the Cs—O distances are 3.024 and 3.047 Å, respectively. In the conformer of $Cs(NTf_2)_3^{2-}$, the structure belongs to C_3 symmetry, and the distances between Cs^+ and the two oxygen atoms of each NTf_2^- are 3.156 and 3.160 Å, respectively. The calculated E_{int} of Cs^+ with one, two, and three NTf_2^- are −317.8, −399.7 and −269.4 kJ/mol, respectively, indicating that Cs^+ is most likely stabilized by two NTf_2^- anions. In the structure of NTf_2^- coordinating with two Cs^+, each Cs^+ interacts with the two oxygen atoms from one sulfonyl group and the Cs—O distances are 3.088 and 3.144 Å, respectively.

In the complexes of $CsPF_6$, $Cs(PF_6)_2^-$ and $Cs(PF_6)_3^{2-}$ (Fig. 1), all PF_6^- anions coordinate with Cs^+ via three fluorine atoms, and the point group of these three complexes are C_{3v}, C_3 and C_1. The Cs—F distances in these complexes are listed in Table 2, and their average values for the three complexes are 2.935, 3.083 and 3.254 Å, increasing gradually as more PF_6^- coordinates with cesium ions. The calculated E_{int} values reveal that Cs^+ with two PF_6^- anions is the most stable structure with an E_{int} value of −475.0 kJ/mol, while the interaction energies for Cs^+ with one and three PF_6^- anions are −344.1 and −225.6 kJ/mol, respectively. As compared with NTf_2^-, PF_6^- shows slightly lower binding energies when coordinating with Cs^+. The conformer of $Cs_2PF_6^+$ belongs D_{3d} point group, and each Cs^+ cation interacts with PF_6^- via coordinating with three fluorine atoms with a Cs—F distance of 3.087 Å.
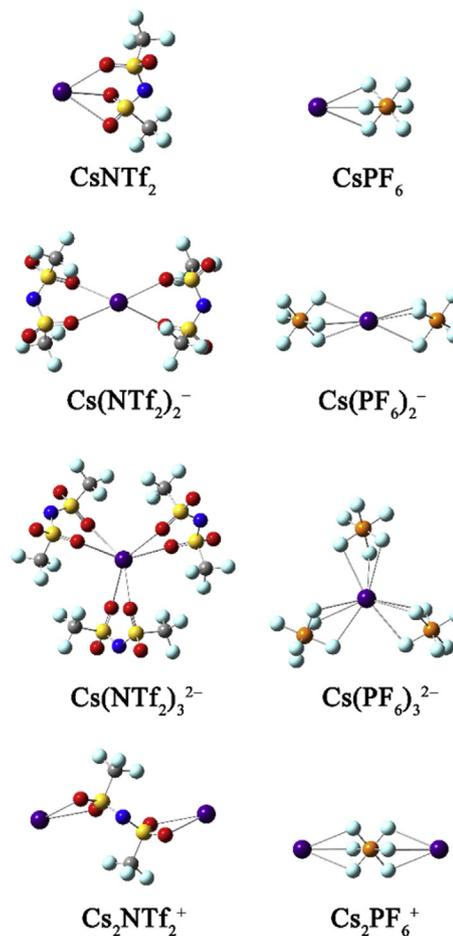

Fig. 1. Optimized structure of the complexes of Cs^+ with NTf_2^- and PF_6^-.

Table 2
Values of bond length in the calculated structures of Cs^+ and $Cs(18C6)^+$ with NTf_2^- and PF_6^-.

	Bond length (Å)	
	Cs—O (NTf_2^-)	Cs—O (Crown)
$CsNTf_2$	2.947, 3.130, 3.135	
$Cs(NTf_2)_2^-$	3.024, 3.047	
$Cs(NTf_2)_3^{2-}$	3.156, 3.160	
$Cs_2NTf_2^+$	3.088, 3.144	
$Cs(18C6)NTf_2$	3.020, 3.057	3.115–3.283
$Cs(18C6)(NTf_2)_2^-$	3.174, 3.192, 3.210, 3.494	3.240–3.513
	Cs—F (PF_6^-)	Cs—O (Crown)
$CsPF_6$	2.935	
$Cs(PF_6)_2^-$	3.083	
$Cs(PF_6)_3^{2-}$	3.207–3.280	
$Cs_2PF_6^+$	3.087	
$Cs(18C6)PF_6$	3.055, 3.067, 3.144	3.136–3.296
$Cs(18C6)(PF_6)_2^-$	3.163, 3.163, 3.214, 3.214	3.319–3.597

The higher interaction energies in the complexes of $Cs(NTf_2)_3^{2-}$ and $Cs(PF_6)_3^{2-}$ as compared with those in the complexes of $Cs(NTf_2)_2^-$ and $Cs(PF_6)_2^-$ can be explained by electrostatic repulsion. Fig. 2 shows the electrostatic potential (ESP) of each NTf_2^- in $Cs(NTf_2)_3^{2-}$ and PF_6^- in $Cs(PF_6)_3^{2-}$. The blue color over oxygen atoms in NTf_2^- indicates the electronegative nature, and the red color over the $-CF_3$ group indicates the electropositive nature. It can be seen that mutual penetration occurs at the sites of the $-CF_3$ group
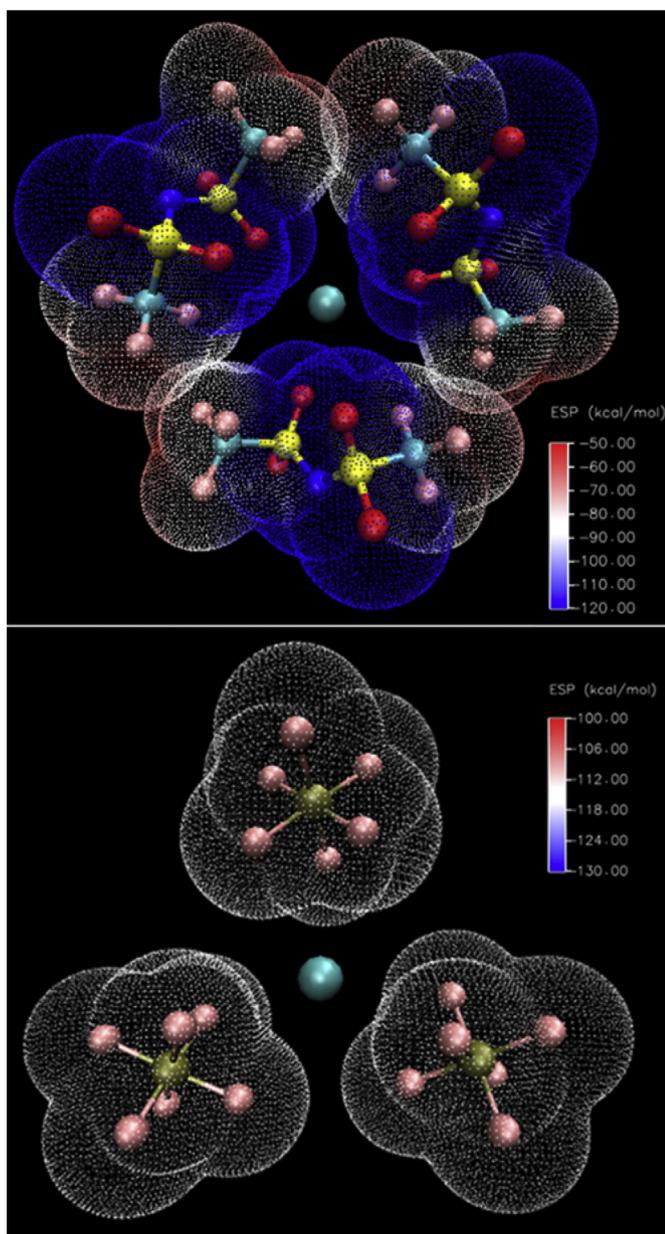
Fig. 2. ESP of NTf_2^- in $Cs(NTf_2)_3^{2-}$ and PF_6^- in $Cs(PF_6)_3^{2-}$.

between the ESP of NTf_2^- in $Cs(NTf_2)_3^{2-}$. In $Cs(PF_6)_3^{2-}$, no penetration of ESP was not observed, meaning that the electrostatic repulsion between PF_6^- is smaller.

Some of the calculated results were validated by the electrospray ionization mass spectrometry (ESI-MS), as shown in Fig. 3. The peaks at 545.73360 in the positive mode belonged to $Cs_2NTf_2^+$ and 692.73862 in the negative mode belonged to $Cs(NTf_2)_2^-$ were observed in the ESI-MS spectra. Interestingly, a peak at 958.56466 belonged to $Cs_3(NTf_2)_2^+$ was also detected. We also tried to verify the calculation of the interactions between Cs^+ and PF_6^- by ESI-MS. Unfortunately, due to the poor solubility of $CsPF_6$, we did not observe the peaks belonged to $Cs(PF_6)_2^-$ or $Cs_2PF_6^+$ in ESI-MS.

3.2. Interactions of NTf_2^- and PF_6^- with $Cs(18C6)^+$

The above results demonstrate that NTf_2^- and PF_6^- can coordinate with Cs^+ in the absence of other ligands. In the extraction,

extractants are usually added in ILs to achieve a high distribution ratio and good extraction selectivity toward Cs^+. The crown ethers have been demonstrated to be qualified [11–13]. After Cs^+ is complexed by the macrocyclic compounds, whether NTf_2^- or PF_6^- coordinates with the deficient complexes is very interesting. We reported previously the crystal structure of $Cs(BPC6)NTf_2$ [19], suggesting the coordination of NTf_2^- with the deficient $Cs(BPC6)^+$ complexes. We herein employed the most frequently used macrocyclic compound 18C6 to theoretically calculate the interactions of both NTf_2^- and PF_6^- with the complex $Cs(18C6)^+$ as well as to synthesize the complexes of Cs^+ and 18C6 with NTf_2^- and PF_6^-.

The optimized structures of the complexes of $Cs(18C6)^+$ with NTf_2^- and PF_6^- are illustrated in Fig. 4. One can see that the cesium atom is located out of the plane of the six oxygen atoms of 18C6 due to its larger ionic radii as compared with the ring size of 18C6, affording Cs^+ the opportunity to interact with other ligands. In the complex of $Cs(18C6)NTf_2$, the two $-CF_3$ fragments of NTf_2^- are trans to each other, affording two oxygen atoms from different sulfonyl groups to coordinate with Cs^+. In the complexes of $Cs(18C6)(NTf_2)_2^-$, one NTf_2^- anion keeps the similar coordinating behavior as that in $Cs(18C6)NTf_2$, while the other one coordinates with Cs^+ via two oxygen atoms from one sulfonyl group, which should be explained by the steric effect. In the structure of $Cs(18C6)PF_6$, there are three fluorine atoms interacting with Cs^+, consisting with the optimized structure of Cs^+ with PF_6^-. In the structure of $Cs(18C6)(PF_6)_2^-$, differently, only two fluorine atoms from each PF_6^- anions interact with Cs^+. The steric effect should be also responsible for this difference.

The calculated E_{int} between $Cs(18C6)^+$ with one and two NTf_2^- anions are -225.6 and -233.5 kJ/mol, respectively, while those between $Cs(18C6)^+$ with one and two PF_6^- anions are -263.6 and -311.5 kJ/mol, respectively. The results of interaction energy suggest that $Cs(18C6)^+$ prefer to interact with two NTf_2^- or PF_6^- anions. A summary of the bond length in the complexes of $Cs(18C6)^+$ with NTf_2^- and PF_6^- is presented in Table 2. One can see that the Cs–O (Crown) distances are lengthened by the interaction of NTf_2^- or PF_6^- with Cs^+.

The calculated results of the interactions between $Cs(18C6)^+$ and NTf_2^- or PF_6^- were validated by the corresponding crystal structure. The crystallization of Cs^+ and 18C6 with NTf_2^- and PF_6^- gives the complexes of $[Cs(18C6)NTf_2]_2$ and $[Cs(18C6)PF_6]_2$, respectively, which are both dimers with bridging the anions, as shown in Fig. 5. Select bond lengths are listed in Table 3.

In the crystal structure of $[Cs(18C6)NTf_2]_2$, two NTf_2^- anions connect two $Cs(18C6)^+$ moieties via coordinating to cesium ions. The two $-CF_3$ fragments of the NTf_2^- anion are trans to each other in $[Cs(18C6)NTf_2]_2$. Each cesium is nine-coordinate, different from that in the calculated structure of $Cs(18C6)(NTf_2)_2^-$, and the coordination sphere is formed by the six oxygen atoms of the crown ether and three oxygen atoms from NTf_2^-. Each NTf_2^- coordinates to one cesium via one oxygen atom in each sulfonyl group and to the other cesium ion via one oxygen atom only from one sulfonyl group. The Cs–O distances between the oxygen atoms in the crown moiety and the cesium ion range from 3.028(3) to 3.235(3) Å, comparable to those in other Cs-crown ether complexes [32]. Besides, these values are slightly longer than those of the Cs–O distances between the cesium ion and the oxygen atoms in NTf_2^-, which are ranging from 3.049(3) to 3.174(3) Å. The Cs–O distances between the cesium ion and the oxygen atoms in NTf_2^- in $[Cs(18C6)NTf_2]_2$ are much shorter than that in the complex of $Cs(BPC6)NTf_2$ [19]. This should be due to the fact that the cesium ion is deeply located in the cavity of BPC6 in $Cs(BPC6)NTf_2$, which weakens the interaction of NTf_2^- with cesium ion.

In the crystal structure of $[Cs(18C6)PF_6]_2$, similarly, two PF_6^- connect two $Cs(18C6)^+$ moieties via coordinating to cesium ions,
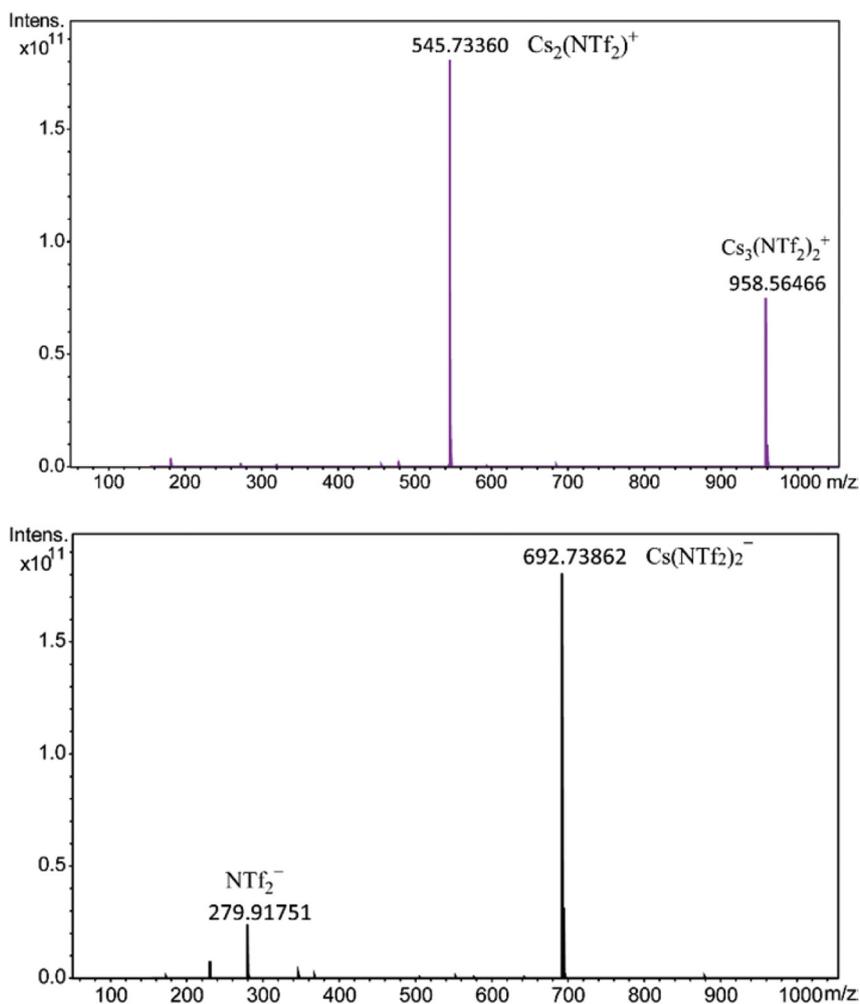
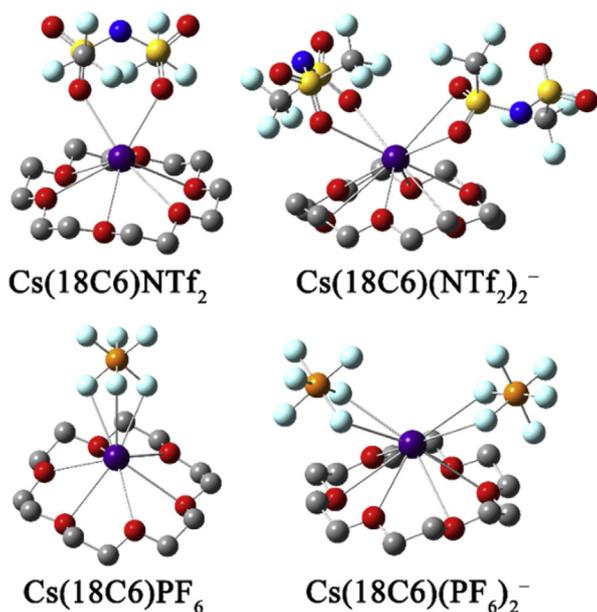**Fig. 3.** Positive and negative mode of the ESI-MS of CsNTf$_2$ solution.

Fig. 4. Optimized structure of the complexes of Cs(18C6)$^+$ with NTf$_2^-$ and PF$_6^-$. Hydrogen atoms are omitted for clarity.

and each PF$_6^-$ coordinates to one cesium ion via two fluorine atoms and to the other cesium ion via one fluorine atom, thus cesium is also nine-coordinate. The Cs–F distances are ranged from 3.143 to 3.528 Å. The Cs–O (Crown) distances are from 3.064 to 3.263 Å, a little longer than those in [Cs(18C6)NTf$_2$]$_2$. In the DFT calculations, the binding energies between Cs(18C6)$^+$ and PF$_6^-$ are a little lower than those between Cs(18C6)$^+$ and NTf$_2^-$, suggesting the stronger interaction between Cs(18C6)$^+$ and PF$_6^-$. The Cs–O (Crown) distances in [Cs(18C6)PF$_6$]$_2$ are a little longer than those in [Cs(18C6) NTf$_2$]$_2$ due to the stronger coordination of PF$_6^-$ with Cs$^+$. The coordination of PF$_6^-$ with Cs$^+$ weakens the complexation of 18C6 toward Cs$^+$, thus the Cs–O (Crown) distances are lengthened.

After comparing the crystal structures of [Cs(18C6)NTf$_2$]$_2$ and [Cs(18C6)PF$_6$]$_2$ with their corresponding calculating results, one can find some differences such as the bond lengths and the coordination number. Nevertheless, the coordinating behavior of NTf$_2^-$ or PF$_6^-$ with Cs(18C6)$^+$ is generally consistent in the crystal structures and the calculated structures, that is, it is definitely demonstrated that the deficient complex Cs(18C6)$^+$ interact with two anions of NTf$_2^-$ or PF$_6^-$, forming 1:2 complexes.

It is worthwhile mentioning that the structure of [Cs(18C6) NTf$_2$]$_2$ is different from that of K(18C6)NTf$_2$ as reported in the literature [33]. In K(18C6)NTf$_2$, two K(18C6)$^+$ moieties are connected by only one NTf$_2^-$. Different from Cs$^+$ residing out of the six crown oxygen atoms, K$^+$ is located in the plane of the six crown oxygen atoms, thus NTf$_2^-$ coordinates to K$^+$ from two sides of the
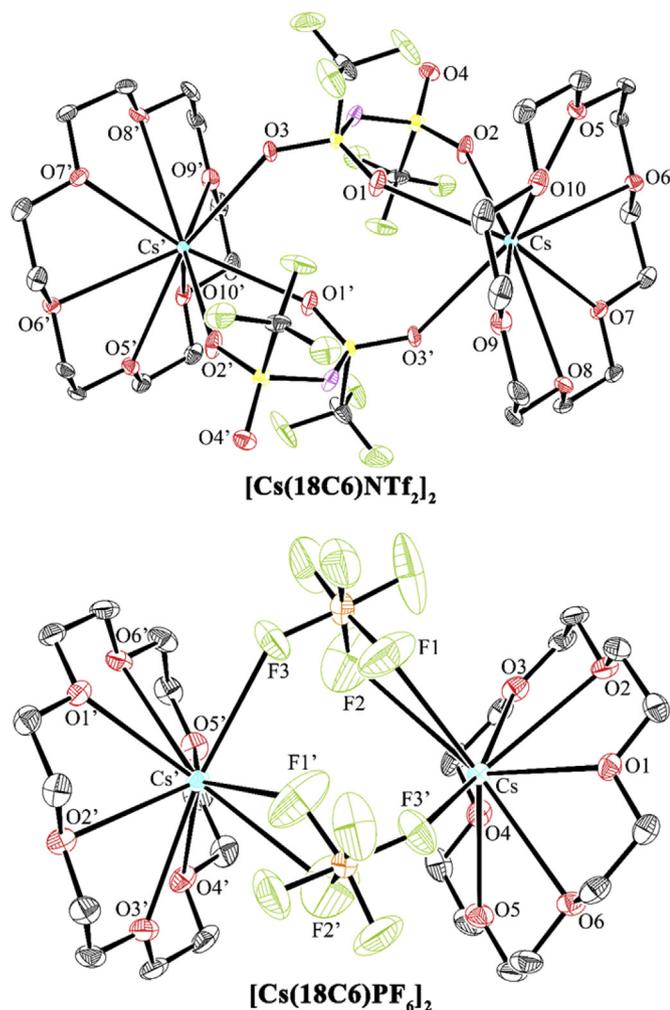
Fig. 5. Crystal structure of Cs(18C6)NTf$_2$ and Cs(18C6)PF$_6$ in 20% thermal ellipsoids. Hydrogen atoms are not showed and C atoms are not labeled for clarity.

Table 3
Selected bond length (Å) for the crystal structures of [Cs(18C6)NTf$_2$]$_2$ and [Cs(18C6)PF$_6$]$_2$.

[Cs(18C6)NTf$_2$]$_2$		[Cs(18C6)PF$_6$]$_2$	
Cs—O1	3.049(3)	Cs—F1	3.213(11)
Cs—O2	3.105(3)	Cs—F2	3.528(16)
Cs—O3′	3.174(3)	Cs—F3′	3.144(6)
Cs—O5	3.087(3)	Cs—O1	3.064(4)
Cs—O6	3.193(3)	Cs—O2	3.264(4)
Cs—O7	3.061(3)	Cs—O3	3.095(4)
Cs—O8	3.184(3)	Cs—O4	3.224(5)
Cs—O9	3.028(3)	Cs—O5	3.104(4)
Cs—O10	3.235(3)	Cs—O6	3.226(4)

K(18C6)$^+$ moiety and the complex forms as a coordination polymer. In the lattice of [Cs(18C6)NTf$_2$]$_2$ (Fig. S1), the column like dimers are arranged head-to-end, and are further arranged in a nearly hexagonal closest packing. The match of the cation radius and the ring size of 18C6 should be one of the critical factors to crystallize the complexes of the alkali metal ions with 18C6 and NTf$_2^-$.

3.3. Coordination effect on extraction

The DFT calculations and the experimental results demonstrated

the coordination of NTf$_2^-$ and PF$_6^-$ with Cs$^+$ and Cs(18C6)$^+$. The coordination of NTf$_2^-$ and PF$_6^-$ with Cs$^+$ should be the crucial one of the reasons why the pure ILs such as C$_4$mimNTf$_2$ and C$_4$mimPF$_6$ can extract Cs$^+$ from aqueous solution in the absence of extractants as aforementioned. In the presence of extractants such as crown ethers or calixcrown ethers, whether NTf$_2^-$ or PF$_6^-$ in ILs coordinates the deficient Cs$^+$ complexes and then contributes to the extraction is hard to be revealed because related methods and techniques are very limited. Nevertheless, we herein studied the coordination effect on the extraction using the traditional organic solvent *n*-octanol, in which both the crown ethers DCH18C6 (18C6 was not used because of its high aqueous solubility) and C$_4$mimNTf$_2$ were added into the organic phase, to investigate the synergistic effect between DCH18C6 and NTf$_2^-$ during the extraction of Cs$^+$.

The variation of the distribution ratios of Cs$^+$ is shown in Fig. 6. In the given extraction condition, DCH18C6 shows no extraction toward Cs$^+$, while C$_4$mimNTf$_2$ can somewhat extract Cs$^+$. For example, 0.02 mol/L C$_4$mimNTf$_2$ in *n*-octanol achieves a distribution ratio of 0.015. The extraction of Cs$^+$ by C$_4$mimNTf$_2$ in *n*-octanol should be attributed to the coordination of NTf$_2^-$ with Cs$^+$ and the exchange of C$_4$mim$^+$ into aqueous phase. The difference between D_{mix} and $(D_A + D_B)$ representing the increase of D after mixing extractants can intuitively reflect the synergistic effect in the extraction system. One can see that the values of D_{mix} are much larger than those of $(D_A + D_B)$ in Fig. 6, thus the synergistic effect between DCH18C6 and NTf$_2^-$ is very obvious. Synergistic effect usually suggests a formation of ternary complex during extraction, so one can infer that NTf$_2^-$ coordinate with the complex of Cs(DCH18C6)$^+$ during the extraction with *n*-octanol. As to the extraction of Cs$^+$ using ILs as solvents, it is hard to perform the same extraction experiment because the ILs act both solvents and extractants.

The above calculated results indicated that Cs$^+$ or Cs(18C6)$^+$ prefer to interact with two NTf$_2^-$ anions in gas phase. However, structures in organic phase cannot be definitely identical to those in gas phase due to the solvation effect. Thus we optimized the structures of Cs(DCH18C6)$^+$ with one and two NTf$_2^-$ anions in *n*-octanol. To maintain charge neutrality, a C$_4$mim$^+$ cation was included in the optimization of Cs(DCH18C6)$^+$ with two NTf$_2^-$ anions. This is consistent with our extraction experiment as C$_4$mimNTf$_2$ and DCH18C6 were both added into *n*-octanol as extractants. The optimized structure of Cs(DCH18C6)NTf$_2$ and
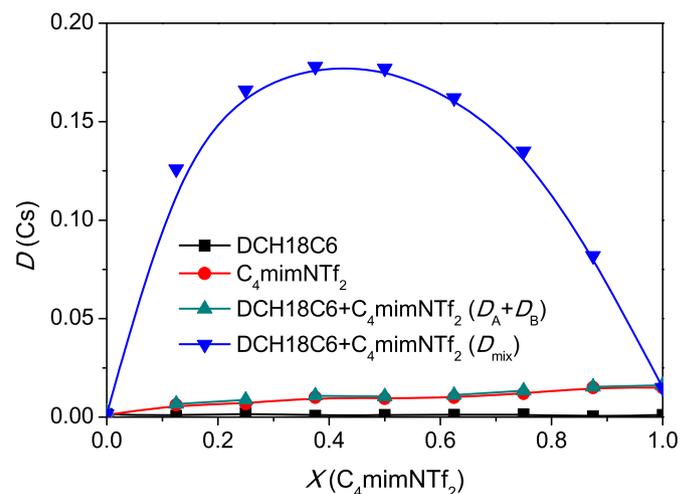

Fig. 6. Extraction of Cs$^+$ with single and mixtures of DCH18C6 and C$_4$mimNTf$_2$ in *n*-octanol. Aqueous phase: C(Cs$^+$) = 0.002 mol/L; Organic phase: C(DCH18C6) + C(C$_4$mimNTf$_2$) = 0.02 mol/L.
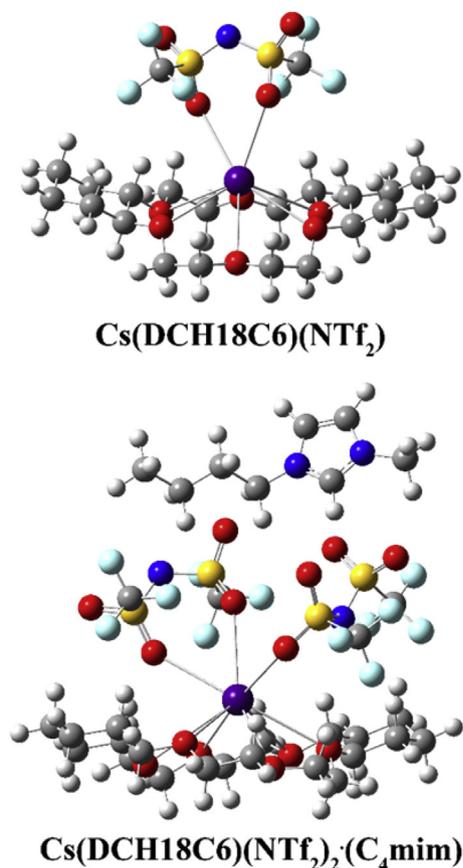
Cs(DCH18C6)(NTf$_2$)

Cs(DCH18C6)(NTf$_2$)$_2$·(C$_4$mim)

Fig. 7. Optimized structure of the complexes of Cs(DCH18C6)NTf$_2$ and Cs(DCH18C6)(NTf$_2$)·(C$_4$mim) in *n*-octanol.

Cs(DCH18C6)(NTf$_2$)$_2$·(C$_4$mim) were shown in Fig. 7, and the interaction of NTf$_2^-$ with cesium is similar to that in the complexes of Cs(18C6)$^+$ with NTf$_2^-$ in gas phase (Fig. 4). The Gibbs free energy for the reaction (2) as shown below in *n*-octanol were calculated to be 78.4 kJ/mol, indicating that Cs(DCH18C6)$^+$ in *n*-octanol prefer to interact with only one NTf$_2^-$ anions, which is different from that in gas phase.

Cs(DCH18C6)NTf$_2$

+ C$_4$mimNTf$_2$ ↔ Cs(DCH18C6)(NTf$_2$)$_2$·(C$_4$mim) (2)

4. Conclusion

DFT calculation, ESI-MS and crystallization demonstrated that both NTf$_2^-$ and PF$_6^-$ coordinate with Cs$^+$ or Cs(18C6)$^+$ complex forming 2:1 complexes in gas phase. The binding energies in DFT calculation suggested a stronger interaction between PF$_6^-$ and Cs$^+$

than that between NTf$_2^-$ and Cs$^+$. The coordination of NTf$_2^-$ with Cs$^+$ induced the synergistic effect in the extraction of Cs$^+$ by DCH18C6 and C$_4$mimNTf$_2$ in *n*-octanol. However, DFT calculation indicated that Cs(DCH18C6)$^+$ in *n*-octanol prefer to interact with only one NTf$_2^-$ anion. This study provides some useful information for the extraction of Cs$^+$ by using ILs as solvents.

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.molstruc.2017.07.048.

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