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# 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<sub>2</sub><sup>-</sup>) and hexafluorophosphate (PF<sub>6</sub><sup>-</sup>) 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<sub>2</sub><sup>-</sup> and PF<sub>6</sub><sup>-</sup> with Cs<sup>+</sup> were explored in this work. The results of DFT calculation indicated that both Cs<sup>+</sup> and Cs(18C6)<sup>+</sup> prefer to interact with two NTf<sub>2</sub> or PF<sub>6</sub><sup>-</sup> anions in gas phase, where 18C6 is 18-crown-6. The complex of Cs(NTf<sub>2</sub>)<sup>-</sup><sub>2</sub> was observed in electrospray ionization mass spectrometry (ESI-MS), and the complexes of [Cs(18C6)NTf<sub>2</sub>]<sub>2</sub> and [Cs(18C6)PF<sub>6</sub>]<sub>2</sub> were crystallized in which Cs(18C6)<sup>+</sup> interacted with two anions. The interactions of NTf<sub>2</sub><sup>-</sup> with cesium resulted in a synergistic effect between dicyclohexano-18-crown-6 (DCH18C6) and NTf<sub>2</sub><sup>-</sup> in the extraction of Cs<sup>+</sup> using *n*-octanol as diluent. However, DFT calculation revealed that the complex Cs(DCH18C6)<sup>+</sup> interacted with one NTf<sub>2</sub><sup>-</sup> anion was more thermodynamically stable than that with two anions in organic phase, different from that in gas phase.

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# 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<sub>2</sub>) and hexa-fluorophosphate (PF<sub>6</sub>) are very common which can construct hydrophobic ILs in combination with organic cations such as the imidazolium cations 1-butyl-3-methylimidazolium ( $C_4$ mim<sup>+</sup>).

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Hydrophobic ILs have been considered as promising solvents for separation processes in the advanced nuclear fuel cycle [7]. The radioactive isotope <sup>137</sup>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 <sup>137</sup>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<sup>+</sup> has attracted much atten[9e16]

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<sup>+</sup> with ILs, the pure IL C<sub>4</sub>mimNTf<sub>2</sub> or C<sub>4</sub>mimPF<sub>6</sub> can extract Cs<sup>+</sup> 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<sup>+</sup> is exchanged with the C₄mim<sup>+</sup> cation into the IL phase [18]. It is very likely that  $NTf_2$  and  $PF_6$  can coordinate with Cs<sup>+</sup>, but investigations on the coordinating behavior are very limited. We reported a ternary complex of Cs<sup>+</sup> with bis(2propyloxy)calix [4]crown-6 (BPC6) and NTf<sub>2</sub>, in which Cs<sup>+</sup> is coordinated with BPC6 by the six oxygen atoms of the crown and the cation  $-\pi$  interactions, and also with the anion NTf<sub>2</sub> 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<sup>+</sup>, 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<sub>2</sub> and Cs(BPC6)NTf<sub>2</sub> by density functional theory (DFT) calculation [16], and the calculated structure of Cs(BPC6)NTf<sub>2</sub> was similar with our crystal structure [19]. To obtain more information about the interactions between Cs<sup>+</sup> and NTf<sub>2</sub><sup>-</sup>, more complexes of Cs<sup>+</sup> and NTf<sub>2</sub><sup>-</sup> 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<sup>+</sup> 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<sup>+</sup> 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<sup>+</sup> with 18C6 containing  $NTf_2^-$  or  $PF_6^-$ . We hope that our work will facilitate the underphase. 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:

$$E_{\text{int}} = E_{\text{CP}}(\text{AB}) - E_{\text{min}}(\text{A}) - E_{\text{min}}(\text{B}) + \Delta \text{ZPVE}$$
(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<sup>+</sup> 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<sup>+</sup> with NTf<sub>2</sub><sup>-</sup>, 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<sub>2</sub>, the two  $-CF_3$  fragments of NTf<sub>2</sub> are cis to each other, identical to that in the literature [16], allowing three oxygen atoms coordinating to Cs<sup>+</sup> 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<sup>+</sup> and the two oxygen atoms of each NTf<sub>2</sub><sup>-</sup> are 3.156 and 3.160 Å, respectively. The calculated  $E_{int}$  of Cs<sup>+</sup> with one, two, and three  $NTf_2^-$  are -317.8, -399.7 and -269.4 kJ/mol, respectively, indicating that Cs<sup>+</sup> is most likely stabilized by two  $NTf_2^-$  anions. In the structure of  $NTf_2^-$  coordinating with two  $Cs^+$ , each Cs<sup>+</sup> 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<sub>6</sub>, Cs(PF<sub>6</sub>)<sup>2</sup> and Cs(PF<sub>6</sub>)<sup>2</sup><sup>-</sup> (Fig. 1), all PF<sub>6</sub> anions coordinate with Cs<sup>+</sup> via three fluorine atoms, and the point group of these three complexes are C<sub>3v</sub>, C<sub>3</sub> and C<sub>1</sub>. 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<sub>6</sub> coordinates with cesium ions. The calculated  $E_{int}$  values reveal that Cs<sup>+</sup> with two PF<sub>6</sub> anions is the most stable structure with an  $E_{int}$  value of -475.0 kJ/mol, while the interaction energies for Cs<sup>+</sup> with one and three PF<sub>6</sub> anions are -344.1 and -225.6 kJ/mol, respectively. As compared with NTf<sub>2</sub>, PF<sub>6</sub> shows slightly lower binding energies when coordinating with Cs<sup>+</sup>. The conformer of Cs<sub>2</sub>PF<sub>6</sub><sup>+</sup> belongs D<sub>3d</sub> point group, and each Cs<sup>+</sup> cation interacts with PF<sub>6</sub><sup>-</sup> 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  $Cs^{\scriptscriptstyle +}$  and  $Cs(18C6)^{\scriptscriptstyle +}$  with  $NTf_2^-$  and  $PF_6^-.$ 

	Bond length (Å)		
	Cs-O (NTf <sub>2</sub> )	Cs–O (Crown)	
CsNTf <sub>2</sub>	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 <sub>2</sub>	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 <sub>6</sub>	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 <sub>6</sub>	3.055, 3.067, 3.144	3.136-3.296	
Cs(18C6)(PF <sub>6</sub> ) <sub>2</sub>	3.163, 3.163, 3.214, 3.214	3.319-3.597	

The higher interaction energies in the complexes of  $Cs(NTf_2)_3^{-1}$ 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<sub>2</sub><sup>-</sup> in Cs(NTf<sub>2</sub>)<sup>3</sup><sub>2</sub><sup>-</sup>. In Cs(PF<sub>6</sub>)<sup>3</sup><sub>2</sub><sup>-</sup>, no penetration of ESP was not observed, meaning that the electrostatic repulsion between PF<sub>6</sub><sup>-</sup> 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<sup>+</sup>. The crown ethers have been demonstrated to be qualified [11–13]. After Cs<sup>+</sup> is complexed by the macrocyclic compounds, whether NTf<sub>2</sub><sup>-</sup> or PF<sub>6</sub><sup>-</sup> coordinates with the deficient complexes is very interesting. We reported previously the crystal structure of Cs(BPC6)NTf<sub>2</sub> [19], suggesting the coordination of NTf<sub>2</sub><sup>-</sup> with the deficient Cs(BPC6)<sup>+</sup> complexes. We herein employed the most frequently used macrocyclic compound 18C6 to theoretically calculate the interactions of both NTf<sub>2</sub><sup>-</sup> and PF<sub>6</sub><sup>-</sup> with the complex Cs(18C6)<sup>+</sup> as well as to synthesize the complexes of Cs<sup>+</sup> and 18C6 with NTf<sub>2</sub><sup>-</sup> and PF<sub>6</sub>.

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<sup>+</sup> the opportunity to interact with other ligands. In the complex of Cs(18C6)NTf<sub>2</sub>, the two  $-CF_3$  fragments of NTf<sub>2</sub> are trans to each other, affording two oxygen atoms from different sulfonyl groups to coordinate with Cs<sup>+</sup>. In the complexes of Cs(18C6)(NTf<sub>2</sub>)<sub>2</sub>, one NTf<sub>2</sub> 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<sup>+</sup>, 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<sub>6</sub> anions interact with Cs<sup>+</sup>. The steric effect should be also responsible for this difference.

The calculated  $E_{int}$  between Cs(18C6)<sup>+</sup> with one and two NTf<sub>2</sub><sup>-</sup> anions are -225.6 and -233.5 kJ/mol, respectively, while those between Cs(18C6)<sup>+</sup> with one and two PF<sub>6</sub><sup>-</sup> anions are -263.6 and -311.5 kJ/mol, respectively. The results of interaction energy suggest that Cs(18C6)<sup>+</sup> prefer to interact with two NTf<sub>2</sub><sup>-</sup> or PF<sub>6</sub><sup>-</sup> anions. A summary of the bond length in the complexes of Cs(18C6)<sup>+</sup> with NTf<sub>2</sub><sup>-</sup> and PF<sub>6</sub><sup>-</sup> is presented in Table 2. One can see that the Cs-O (Crown) distances are lengthened by the interaction of NTf<sub>2</sub><sup>-</sup> or PF<sub>6</sub><sup>-</sup> with Cs<sup>+</sup>.

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)<sup>+</sup> moieties via coordinating to cesium ions. The two  $-CF_3$  fragments of the  $NTf_2^-$  anion are trans to each other in [Cs(18C6)NTf2]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<sub>2</sub>. Each NTf<sub>2</sub> 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<sub>2</sub>, 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,

and each PF<sub>6</sub><sup>-</sup> 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<sub>2</sub>]<sub>2</sub>. In the DFT calculations, the binding energies between Cs(18C6)<sup>+</sup> and PF<sub>6</sub><sup>-</sup> are a little lower than those between Cs(18C6)<sup>+</sup> and NTf<sub>2</sub><sup>-</sup>, suggesting the stronger interaction between Cs(18C6)<sup>+</sup> and PF<sub>6</sub><sup>-</sup>. The Cs–O (Crown) distances in [Cs(18C6)PF<sub>6</sub>]<sub>2</sub> are a little longer than those in [Cs(18C6) NTf<sub>2</sub>]<sub>2</sub> due to the stronger coordination of PF<sub>6</sub><sup>-</sup> with Cs<sup>+</sup>. The coordination of PF<sub>6</sub><sup>-</sup> with Cs<sup>+</sup> weakens the complexation of 18C6 toward Cs<sup>+</sup>, 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)<sup>+</sup> is generally consistent in the crystal structures and the calculated structures, that is, it is definitely demonstrated that the deficient complex Cs(18C6)<sup>+</sup> 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<sub>2</sub> as reported in the literature [33]. In K(18C6)NTf<sub>2</sub>, two K(18C6)<sup>+</sup> moieties are connected by only one NTf<sub>2</sub><sup>-</sup>. Different from Cs<sup>+</sup> residing out of the six



**Fig. 5.** Crystal structure of Cs(18C6)NTf<sub>2</sub> and Cs(18C6)PF<sub>6</sub> 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 <sub>2</sub> ] <sub>2</sub>		[Cs(18C6)PF <sub>6</sub> ] <sub>2</sub>	[Cs(18C6)PF <sub>6</sub> ] <sub>2</sub>	
Cs-01	3.049(3)	Cs-F1	3.213(11)	
Cs-02	3.105(3)	Cs-F2	3.528(16)	
Cs-03′	3.174(3)	Cs-F3′	3.144(6)	
Cs-05	3.087(3)	Cs-01	3.064(4)	
Cs-06	3.193(3)	Cs-O2	3.264(4)	
Cs-07	3.061(3)	Cs-03	3.095(4)	
Cs-08	3.184(3)	Cs-O4	3.224(5)	
Cs-09	3.028(3)	Cs-O5	3.104(4)	
Cs-010	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<sub>2</sub>.

## 3.3. Coordination effect on extraction

The DFT calculations and the experimental results demonstrated

the coordination of NTf<sub>2</sub> and PF<sub>6</sub> with Cs<sup>+</sup> and Cs(18C6)<sup>+</sup>. The coordination of NTf<sub>2</sub> and PF<sub>6</sub> with Cs<sup>+</sup> should be the crucial one of the reasons why the pure ILs such as C<sub>4</sub>mimNTf<sub>2</sub> and C<sub>4</sub>mimPF<sub>6</sub> can extract Cs<sup>+</sup> from aqueous solution in the absence of extractants as aforementioned. In the presence of extractants such as crown ethers or calixcrown ethers, whether NTf<sub>2</sub> or PF<sub>6</sub> in ILs coordinates the deficient Cs<sup>+</sup> 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<sub>4</sub>mimNTf<sub>2</sub> were added into the organic phase, to investigate the synergistic effect between DCH18C6 and NTf<sub>2</sub> during the extraction of Cs<sup>+</sup>.

The variation of the distribution ratios of  $Cs^+$  is shown in Fig. 6. In the given extraction condition, DCH18C6 shows no extraction toward Cs<sup>+</sup>, while C<sub>4</sub>mimNTf<sub>2</sub> can somewhat extract Cs<sup>+</sup>. For example, 0.02 mol/L C4mimNTf2 in n-octanol achieves a distribution ratio of 0.015. The extraction of Cs<sup>+</sup> by C<sub>4</sub>mimNTf<sub>2</sub> in *n*-octanol should be attributed to the coordination of NTf<sub>2</sub><sup>-</sup> with Cs<sup>+</sup> and the exchange of C<sub>4</sub>mim<sup>+</sup> into aqueous phase. The difference between  $D_{\text{mix}}$  and  $(D_{\text{A}} + D_{\text{B}})$  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<sub>2</sub> is very obvious. Synergistic effect usually suggests a formation of ternary complex during extraction. so one can infer that  $NTf_{\overline{2}}$  coordinate with the complex of  $Cs(DCH18C6)^+$  during the extraction with *n*-octanol. As to the extraction of Cs<sup>+</sup> 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<sup>+</sup> cation was included in the optimization of  $Cs(DCH18C6)^+$  with two  $NTf_2^-$  anions. This is consistent with our extraction experiment as  $C_4$ mim $NTf_2$  and DCH18C6 were both added into *n*-octanol as extractants. The optimized structure of  $Cs(DCH18C6)NTf_2$  and





complexes of Cs(DCH18C6)NTf2 and Fig. 7. Optimized structure of the Cs(DCH18C6)(NTf<sub>2</sub>)·(C<sub>4</sub>mim) in n-octanol.

 $Cs(DCH18C6)(NTf_2)_2 \cdot (C_4 mim)$  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)<sup>+</sup> in *n*-octanol prefer to interact with only one  $NTf_2^-$  anions, which is different from that in gas phase.

# Cs(DCH18C6)NTf<sub>2</sub>

$$+ C_4 \operatorname{mim} NTf_2 \leftrightarrow Cs(DCH18C6)(NTf_2)_2 \cdot (C_4 \operatorname{mim})$$
(2)

### 4. Conclusion

DFT calculation, ESI-MS and crystallization demonstrated that both NTf<sub>2</sub> and PF<sub>6</sub> coordinate with Cs<sup>+</sup> or Cs(18C6)<sup>+</sup> complex forming 2:1 complexes in gas phase. The binding energies in DFT calculation suggested a stronger interaction between PF<sub>6</sub> and Cs<sup>+</sup>

than that between  $NTf_2^-$  and  $Cs^+$ . The coordination of  $NTf_2^-$  with  $Cs^+$ induced the synergistic effect in the extraction of Cs<sup>+</sup> by DCH18C6 and C<sub>4</sub>mimNTf<sub>2</sub> 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<sup>+</sup> by using ILs as solvents.

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# 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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