Note

Crystallization of cesium complex containing bis(2-propyloxy)calix[4]crown-6 and bis[(trifluoromethyl)sulfonyl]imide

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ABSTRACT

A complex of Cs^+ with the calixcrown bis(2-propyloxy)calix[4]crown-6 (BPC6) and bis[(trifluoromethyl)sulfonyl]imide (NTf_2^-), an anion of ionic liquid (IL), was crystallized in the interface region between n-octanol and water. The compound was characterized by single crystal X-ray diffraction, ESI-MS, FT-IR, TGA and PXRD. Cs^+ is coordinated with BPC6 by both the six oxygen atoms of the crown and the cation–π interactions, and with the anion NTf_2^- via one oxygen atom of the sulfonyl group. This single crystal explains the good extraction ability of BPC6 to Cs^+ and reflects a coordinating interaction of NTf_2^- with the deficient complex $[Cs·BPC6]^+$ during the extraction with an IL as diluent.

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1. Introduction

Room-temperature ionic liquids (ILs) have been considered as alternative solvents for synthetic, catalytic, electrochemical and separation sciences because of their unique properties such as low vapor pressure, solvating properties and thermal stability [1–5]. Especially, they have become potential replacements of volatile organic compounds (VOCs) in the extraction of metal ions, in particular, in the reprocessing of spent nuclear waste [6–11]. ^{137}Cs, as a major radioactive fission product in spent nuclear waste, contributes a large part of the heat load and radiation in high level liquid waste (HLLW). Removal of ^{137}Cs from HLLW will reduce waste volume and subsurface storage time, and facilitate handling and transportation. The calixcrown–ILs systems have been regarded as a potential method to extract ^{137}Cs from HLLW [10,12]. For instance, using a calixcrown bis(2-propyloxy)calix[4]crown-6 (BPC6, Fig. 1) as extractant in the ILs 1-alkyl-3-methylimidazolium bis[(trifluoromethyl)sulfonyl]imide ($C_nmimNTf_2$), we found that Cs^+ was efficiently extracted into the IL phase as a complex of $[Cs·BPC6]^+$ [10]. Besides, we also found that $C_nmimNTf_2$ themselves could extract Cs^+ with a considerable distribution ratio in the absence of extractants [10], meaning that the function of $C_nmimNTf_2$ is both as diluent and as extractant, that is, NTf_2^- is able to coordinate with Cs^+.

The coordinating ability of NTf_2^- has been realized and several complexes were reported in recent years. NTf_2^- can coordinate with lanthanides or alkaline earth metal ions through an oxygen atom of each sulfonyl group without the additional coordination of other molecules [13–15] and also can stabilize deficient transition metal or uranyl complexes via distinct modes [16,17]. Temperature elevation is usually necessary in these syntheses. Recently, the complexes $[Ba(18-crown-6)][NTf_2]_2$ and $[K(18-crown-6)][NTf_2]$ were crystallized by Yan et al. at the interface of $C_2mimNTf_2$ and water, in which an imidazolium based acid was used as a precursor [18].

The coordinating ability of NTf_2^- leads to an interesting question in the extraction of metal ions with an IL as diluent, that is, is there an interaction between NTf_2^- and the deficient metal-extractant complex? Using extended X-ray fine structure (EXAFS), Dietz and co-workers found that water molecules rather than NTf_2^- interacted with $[Sr·DCH18C6]^{2+}$ during the extraction, where DCH18C6 is dicyclohexano-18-crown-6 [19]. This is due to the fact that Sr^{2+} has very high hydration energy [20]. The hydration energy of Cs^+ is low [20] so that the anion NTf_2^- probably coordinates with the deficient Cs-extractant complex. The crystallization method can demonstrate the coordinating ability of NTf_2^- and provide a way to answer the question mentioned above. Without rising temperature or using other precursors, however, no crystallization was found during the extraction of Cs^+ by BPC6-$C_nmimNTf_2$ systems [10]. If the interaction between NTf_2^- and $[Cs·BPC6]^+$ does exist, non-ionic circumstance instead of ionic circumstance (IL phase) will facilitate the crystallization. In this paper, a new complex, $[Cs·BPC6]^+NTf_2^-$ was synthesized in the interface region between n-octanol and water, and characterized by single crystal X-ray diffraction, ESI-MS, FT-IR, TGA and PXRD.

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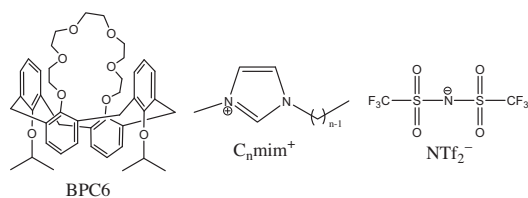E-mail address: xshen@pku.edu.cn (X. Shen).

Fig. 1. Structures of BPC6 and the cation $C_n mim^+$, the anion NTf_2^- of ILs.

2. Experimental

2.1. Materials and methods

The ILs 1-alkyl-3-methylimidazolium bis[(trifluoromethyl)sulfonyl]imide ($C_n mimNTf_2$) were synthesized via a metathetical reaction as previously reported [10]. BPC6 (>95%) was obtained from INET, Tsinghua University, PR China, and was used as received. n-Octanol of analytical grade was purchased from Beijing Yili Fine Chemical Co., Ltd. and used without further purification.

2.2. Crystallization of [Cs·BPC6]$^+$NTf$_2^-$

A 0.5 mL of n-octanol solution containing BPC6 (15 mmol dm^{-3}) and $C_n mimNTf_2$ (15 mmol dm^{-3}, n = 2, 4, 6, 8 and 10) was added slowly to a 0.5 mL of the aqueous solution of CsCl (50 mmol dm^{-3}). Standing for 3 days gave thin plate like crystals in the interface region between n-octanol and water. Anal. Calc. for $C_{46}H_{54}NO_{12}S_2F_6Cs$: C, 49.15; N, 1.25; H, 4.85. Found: C, 49.23; N, 1.33; H, 4.89%.

2.3. X-ray crystallography

The crystallographic data for the single crystal were collected at room temperature on a Nonius Kappa CCD diffractometer with a

Table 1
Crystallographic data for the complex.

	[Cs·BPC6]$^+$NTf$_2^-$
Chemical formula	$C_{46}H_{54}CsF_6NO_{12}S_2$
Formula weight	1123.93
T (K)	293(2)
Crystal system	triclinic
Space group	$P\bar{1}$
a (Å)	10.6429(2)
b (Å)	13.5876(3)
c (Å)	17.5651(4)
α (°)	86.2114(8)
β (°)	87.9841(7)
γ (°)	89.4630(10)
V (Å^3)	2532.93(9)
Z	2
ρ_{calcd} (g cm^{-3})	1.474
λ (Mo Kα) (mm^{-1})	0.71073
Crystal size (mm)	$0.22 \times 0.15 \times 0.07$
T_{min}, T_{max}	0.877, 0.942
θ_{min}, θ_{max} (°)	3.395, 25.028
Total reflections	19201
Unique reflections (R_{int})	0.0558
Observed reflections ($I \geqslant 2\sigma(I)$)	5142
Parameters	642
R_1[a], wR_2[b] ($I \geqslant 2\sigma(I)$)	0.0476, 0.1121
R_1[a], wR_2[b] (all data)	0.1034, 0.1263
Goodness-of-fit (GOF)	0.960
$\Delta\rho$[c] (e Å^{-3})	0.497, −0.417
Maximum and mean[d] Δ/σ	0.001, 0.000

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.
[b] $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.
[c] Maximum and minimum residual electron density.
[d] Maximum and mean sigma/shift.

Table 2
Selected bond lengths (Å) and angles (°).

	[Cs·BPC6]$^+$NTf$_2^-$
Cs(1)–O(1)	3.130(3)
Cs(1)–O(2)	3.206(4)
Cs(1)–O(3)	3.279(4)
Cs(1)–O(4)	3.185(4)
Cs(1)–O(5)	3.152(4)
Cs(1)–O(6)	3.223(3)
Cs(1)–O(9)	3.507(8)
O(1)–Cs(1)–O(2)	52.84(9)
O(2)–Cs(1)–O(3)	52.56(12)
O(4)–Cs(1)–O(3)	52.65(12)
O(5)–Cs(1)–O(4)	53.74(11)
O(5)–Cs(1)–O(6)	52.61(9)
O(1)–Cs(1)–O(6)	105.56(7)
O(1)–Cs(1)–O(9)	92.02(16)
O(2)–Cs(1)–O(9)	71.42(14)
O(3)–Cs(1)–O(9)	76.94(14)
O(4)–Cs(1)–O(9)	70.08(17)
O(5)–Cs(1)–O(9)	94.10(16)
O(6)–Cs(1)–O(9)	135.05(12)
O(9)–S(1)–N(1)	143.1(7)
O(9)–S(1)–N(2)	90.2(5)
O(11)–S(2)–O(12)	115.9(11)
O(13)–S(2)–O(14)	119.8(17)
S(1)–N(1)–S(2)	120.4(8)
S(2)–N(2)–S(1)	131.6(8)

2.0 kW sealed anode source using graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) [21,22]. The structure was solved by direct methods and refined by full-matrix least-squares on F^2 using the SHELX program [23]. The hydrogen atoms were added according to the ideal geometry, and were not refined for good refinement convergence. NTf$_2^-$ showed disorder thus treated in two orientations. The details of data collection, data reduction, and crystallographic data are summarized in Table 1. Selected bonds and angles are given in Table 2.

2.4. Other characterizations

Electrospray ionization mass spectra (ESI-MS) of the crystals dissolved in acetonitrile were acquired in both positive-ion and negative-ion mode with a Bruker Apex IV FTMS. FT-IR spectrum was measured on a Thermo-Fischer Nicolet iN10 MX spectrometer between 600 and 4000 cm^{-1}. Thermogravimetric analysis (TGA) was performed on a Q600 SDT thermoanalyzer under N$_2$ atmosphere with the temperature ranging from 25 to 1000 °C at a heating rate of 5 °C min^{-1}. Powder X-ray diffraction (PXRD) data were measured on a DMAX-2400 diffractometer using Cu Kα radiation ($\lambda = 1.5406$ Å).

3. Results and discussion

To simulate the extraction procedure, n-octanol containing $C_n mimNTf_2$ (n = 2, 4, 6, 8 and 10) and BPC6 was used to contact with the aqueous solution of CsCl. All the samples with different ILs could form colorless crystals at the interface and they are the same phase (see later). The crystal synthesized by $C_8 mimNTf_2$ was subjected in the structure determination and other characterizations.

The molecular structure of [Cs·BPC6]$^+$NTf$_2^-$ is shown in Fig. 2. The host molecule BPC6 has its calix[4]arene part in the 1,3-alternate conformation, with the crown ether and two phenyl groups on the same side. The cesium ion locates at the center of the crown, coordinated by the six ether oxygen atoms, with the Cs–O distances in range from 3.129 to 3.280 Å, comparable to those in other Cs-calixcrown complexes [24,25]. The cation–π interaction is observed between Cs$^+$ and the two upper phenyls. The short Cs$\cdots$C contacts between Cs$^+$ and the upper-rim C atoms of the two
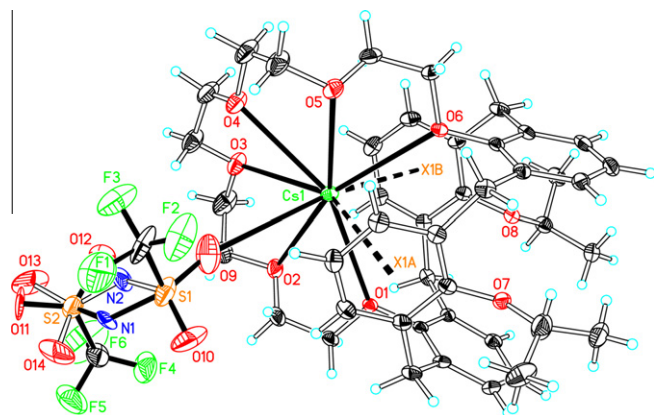
Fig. 2. The structure of [Cs·BPC6]$^+$NTf$_2^-$ in 20% thermal ellipsoids. C atoms are not labeled. X1A and X1B are the centeroids of the two phenyl rings, and the distances (dashed bonds) between the Cs and the two centeroids are 3.572 (X1A) and 3.540 (X1B) Å, respectively.

phenyls are 3.445 to 3.677 Å, the two distances of Cs$^+$ to the centeroids of the two phenyl rings are 3.572 and 3.540 Å, and the Cs$^+$ ion is 3.404 and 3.406 Å above the phenyl planes. These are indicative of the existence of Cs$^+$–π interaction [26–28]. The NTf$_2^-$ anion compensates the positive charge of [Cs·BPC6]$^+$ moiety, and one oxygen atom of a SO$_2$ group further coordinates with Cs$^+$ ion, with a long Cs–O distance of 3.507 Å. In the structure the anion shows disorder, with the N and the non-coordinated SO$_2$ group in two orientations (N1/N2 40:60). In the lattice (Fig. 3), the column like molecules are arranged head-to-end along the *b* direction, and further arrange in a nearly hexagonal closest packing extending along *a* and *c* directions.
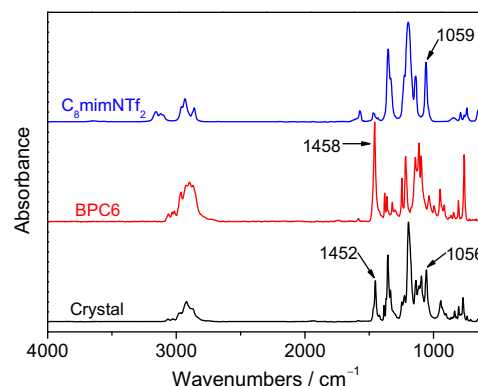
Fig. 4 shows the ESI-MS of the crystal in acetonitrile. A peak in positive mode is displayed at m/z = 843.3 that is attributed to [Cs·BPC6]$^+$. In negative mode, a peak at m/z = 280.1 corresponding to NTf$_2^-$ is observed. It was reported that ion parings were observed at high concentrations and naked ions in the positive or
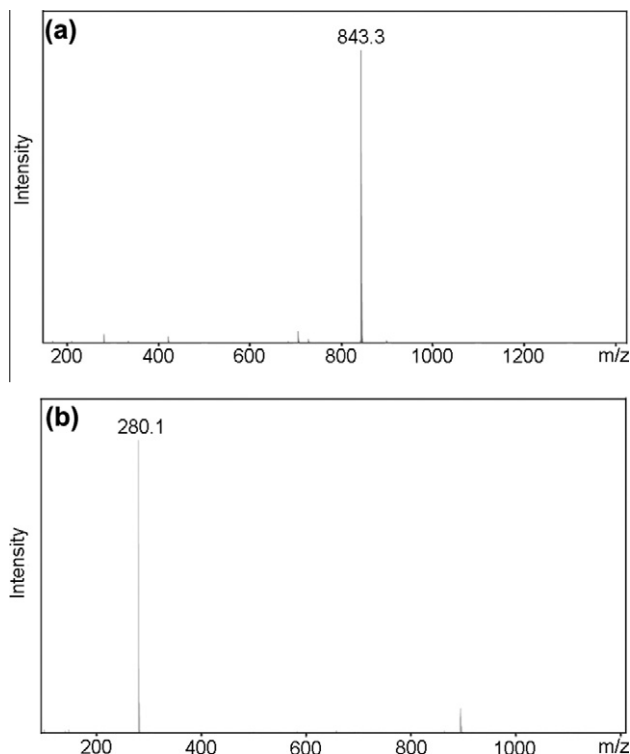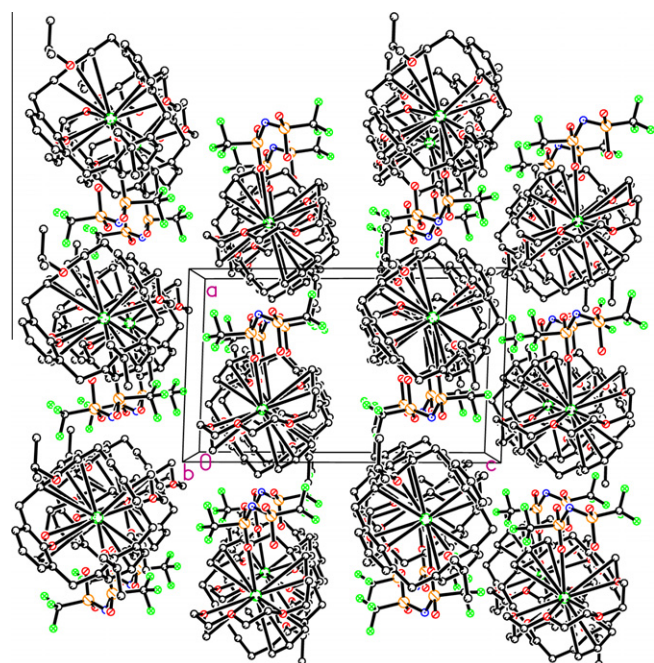

Fig. 4. ESI-MS of the single crystal in positive mode (a) and in negative mode (b).

negative mode were observed in highly diluted conditions. A peak of alkyltrifluoroborate anion with two [K(18-crown-6)]$^+$ in ESI-MS was observed in the literature [29]. However, no ion pairings were observed in our experiments even at high concentrations, owing to the steric hindrance. In the FT-IR spectrum of the single crystal (Fig. 5), the absorption peak of 1056 cm^{-1} is assigned as the stretching vibration of S=O. Comparing with the value of 1059 cm^{-1} in C$_8$mimNTf$_2$, it shifts to lower frequency because of the coordination between the sulfonyl group and cesium ion. The stretching vibration of C=C group of the phenyl ring in BPC6 shifts from 1458 to 1452 cm^{-1} after it trapping Cs$^+$.

The thermal stability of the single crystal after grinding was examined by TGA under N$_2$ atmosphere from 25 to 1000 °C (Fig. 6). The complex was decomposed in two continuing degradation steps within the temperature range from 315 to 465 °C and then further slowly lost weight with increasing temperature. The first step from 315 to 425 °C with a weight loss of 39.5% corresponds to the decomposition of BPC6. From 425 to 465 °C the weight loss of 18.3% is the decomposition of NTf$_2^-$ anion. Comparing the TGA curve of the single crystal with that of BPC6, one can

Fig. 3. Packing of [Cs·BPC6]$^+$NTf$_2^-$ molecules in the crystal structure, viewed along *b* direction.

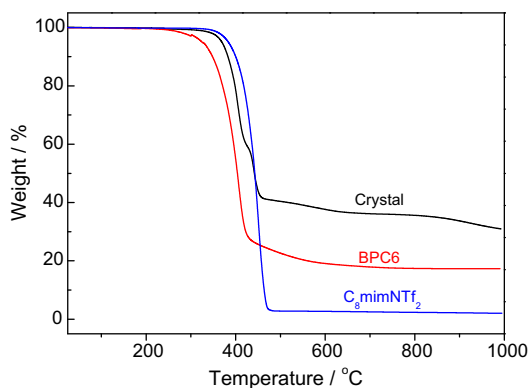**Fig. 5.** FT-IR spectra of the single crystal, BPC6 and C$_8$mimNTf$_2$.

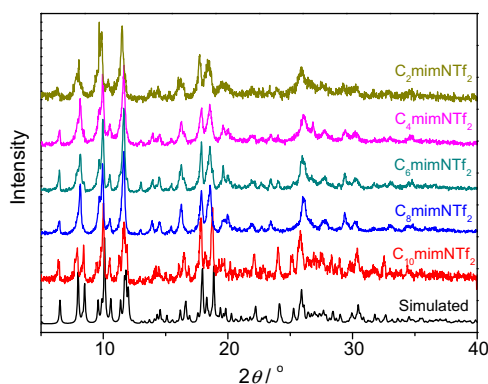**Fig. 6.** TGA curves of the single crystal, BPC6 and $C_8mimNTf_2$.

Fig. 7. Experimental PXRD of single crystals synthesized with different ILs, compared with the simulated result.

find that the thermal stability of BPC6 is enhanced after it trapping cesium ion.

The crystals synthesized using different ILs $C_nmimNTf_2$ ($n = 2, 4, 6, 8$ and 10) were investigated by powder X-ray diffraction (Fig. 7). The main peaks of $2\theta = 8.5°, 10.1°, 11.8°, 16.6°, 18.0°, 18.9°, 25.9°$ and $30.4°$ in the PXRD patterns for ILs with different alkyl chains agree well with the simulated one based on the structure of $[Cs\cdot BPC6]^+NTf_2^-$ and the alkyl chain of the imidazolium cation did not influence the crystal structure.

We subsequently tried to crystallize BPC6 and NTf_2^- with Na^+ and K^+, according to the literature [30,31]. However, no crystallization was found in the interface region between *n*-octanol and water. This may be due to the large cavity of BPC6 compared with the ionic radius of Na^+, K^+ and the weak coordinating ability of NTf_2^- to Na^+ and K^+. Crystallization of metal ions with BPC6 and NTf_2^- is influenced both by the match of the cavity of BPC6 with the ionic radius of metal ions and by the coordinating ability of NTf_2^- to metal ions.

4. Conclusion

A new complex of Cs^+ containing BPC6 and NTf_2^- was crystallized in the interface region between *n*-octanol and water. BPC6

combines the cesium ion with both the six oxygen atoms of the crown and the cation–π interactions, explaining its good extraction ability to Cs^+. The coordinating interaction of NTf_2^- with the deficient complex $[Cs\cdot BPC6]^+$ provides an insight into the extraction mechanism of Cs^+ with BPC6 in ILs.

Acknowledgments

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.ica.2012.04.005.

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