Inorganica Chimica Acta 390 (2012) 8-11

Contents lists available at SciVerse ScienceDirect

## Inorganica Chimica Acta

journal homepage: www.elsevier.com/locate/ica

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

## Taoxiang Sun, Zheming Wang, Xinghai Shen\*

Beijing National Laboratory for Molecular Sciences (BNLMS), College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, PR China Radiochemistry and Radiation Chemistry Key Laboratory of Fundamental Science, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, PR China

#### ARTICLE INFO

Article history: Received 29 June 2011 Received in revised form 16 January 2012 Accepted 2 April 2012 Available online 17 April 2012

Keywords: lonic liquids Single crystal X-ray crystallography Extraction Cs<sup>+</sup>

#### 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 <sup>137</sup>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 <sup>137</sup>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<sub>n</sub>mimNTf<sub>2</sub>), we found that Cs<sup>+</sup> was efficiently extracted into the IL phase as a complex of [Cs·BPC6]<sup>+</sup> [10]. Besides, we also found that C<sub>n</sub>mimNTf<sub>2</sub> themselves could extract Cs<sup>+</sup> with a considerable distribution ratio in the absence of extractants [10], meaning that the function of  $C_n$  mimNTf<sub>2</sub> 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

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

#### ABSTRACT

A complex of Cs<sup>+</sup> with the calixcrown bis(2-propyloxy)calix[4]crown-6 (BPC6) and bis[(trifluoromethyl)sulfonyl]imide (NTf<sub>2</sub><sup>-</sup>), 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<sup>+</sup> is coordinated with BPC6 by both the six oxygen atoms of the crown and the cation– $\pi$  interactions, and with the anion NTf<sub>2</sub><sup>-</sup> via one oxygen atom of the sulfonyl group. This single crystal explains the good extraction ability of BPC6 to Cs<sup>+</sup> and reflects a coordinating interaction of NTf<sub>2</sub><sup>-</sup> with the deficient complex [Cs-BPC6]<sup>+</sup> during the extraction with an IL as diluent.

© 2012 Elsevier B.V. All rights reserved.

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<sub>2</sub>]<sub>2</sub> and [K(18-crown-6)][NTf<sub>2</sub>] were crystallized by Yan et al. at the interface of C<sub>2</sub>mimNTf<sub>2</sub> and water, in which an imidazolium based acid was used as a precursor [18].

The coordinating ability of NTf<sub>2</sub><sup>-</sup> leads to an interesting question in the extraction of metal ions with an IL as diluent, that is, is there an interaction between NTf2<sup>-</sup> and the deficient metalextractant complex? Using extended X-ray fine structure (EXAFS), Dietz and co-workers found that water molecules rather than  $NTf_2^-$  interacted with  $[Sr \cdot DCH18C6]^{2+}$  during the extraction, where DCH18C6 is dicyclohexano-18-crown-6 [19]. This is due to the fact that Sr<sup>2+</sup> has very high hydration energy [20]. The hydration energy of Cs<sup>+</sup> is low [20] so that the anion NTf<sub>2</sub><sup>-</sup> probably coordinates with the deficient Cs-extractant complex. The crystallization method can demonstrate the coordinating ability of NTf<sub>2</sub><sup>-</sup> 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<sup>+</sup> by BPC6-C<sub>n</sub>mimNTf<sub>2</sub> systems [10]. If the interaction between  $NTf_2^-$  and  $[Cs \cdot BPC6]^+$  does exist, non-ionic circumstance instead of ionic circumstance (IL phase) will facilitate the crystallization. In this paper, a new complex, [Cs·BPC6]<sup>+</sup>NTf<sub>2</sub><sup>-</sup> 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.





<sup>\*</sup> Corresponding author. Tel.: +86 10 62765915.

<sup>0020-1693/\$ -</sup> see front matter  $\odot$  2012 Elsevier B.V. All rights reserved. http://dx.doi.org/10.1016/j.ica.2012.04.005



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<sub>2</sub>) 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]<sup>+</sup>NTf<sub>2</sub><sup>-</sup>

A 0.5 mL of *n*-octanol solution containing BPC6 (15 mmol dm<sup>-3</sup>) and  $C_n \text{mimNTf}_2$  (15 mmol dm<sup>-3</sup>, *n* = 2, 4, 6, 8 and 10) was added slowly to a 0.5 mL of the aqueous solution of CsCl (50 mmol dm<sup>-3</sup>). Standing for 3 days gave thin plate like crystals in the interface region between *n*-octanol and water. *Anal.* Calc. for  $C_{46}H_{54}NO_{12}S_2$  F<sub>6</sub>Cs: 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] <sup>+</sup> NTf <sub>2</sub> <sup>-</sup>
Chemical formula	$C_{46}H_{54}CsF_6NO_{12}S_2$
Formula weight	1123.93
Т (К)	293(2)
Crystal system	triclinic
Space group	ΡĪ
a (Å)	10.6429(2)
b (Å)	13.5876(3)
<i>c</i> (Å)	17.5651(4)
α (°)	86.2114(8)
β (°)	87.9841(7)
γ (°)	89.4630(10)
V (Å <sup>3</sup> )	2532.93(9)
Ζ	2
$\rho_{\rm calcd} ({\rm g}{\rm cm}^{-3})$	1.474
$\lambda$ (Mo K $\alpha$ ) (mm <sup>-1</sup> )	0.71073
Crystal size (mm)	$0.22 \times 0.15 \times 0.07$
T <sub>min</sub> , T <sub>max</sub>	0.877, 0.942
$\theta_{\min}, \theta_{\max}$ (°)	3.395, 25.028
Total reflections	19201
Unique reflections $(R_{int})$	0.0558
Observed reflections $(I \ge 2\sigma(I))$	5142
Parameters	642
$R_1^{a}, wR_2^{b} (I \ge 2\sigma(I))$	0.0476, 0.1121
$R_1^{a}$ , $wR_2^{b}$ (all data)	0.1034, 0.1263
Goodness-of-fit (GOF)	0.960
$\Delta \rho^{c} (e A^{-3})$	0.497, -0.417
Maximum and mean <sup>a</sup> $\Delta/\sigma$	0.001, 0.000

<sup>a</sup>  $R_1 = \Sigma ||F_0| - |F_c|| / \Sigma |F_0|.$ 

<sup>b</sup>  $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^2)^2]^{1/2}.$ 

<sup>c</sup> Maximum and minimum residual electron density.

<sup>d</sup> Maximum and mean sigma/shift.

#### Table 2

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

	[Cs·BPC6] <sup>+</sup> NTf <sub>2</sub> <sup>-</sup>
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 K $\alpha$  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<sub>2</sub><sup>-</sup> 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<sup>-1</sup>. Thermogravimetric analysis (TGA) was performed on a Q600 SDT thermoanalyzer under N<sub>2</sub> atmosphere with the temperature ranging from 25 to 1000 °C at a heating rate of 5 °C min<sup>-1</sup>. Powder X-ray diffraction (PXRD) data were measured on a DMAX-2400 diffractometer using Cu K $\alpha$  radiation ( $\lambda = 1.5406$  Å).

#### 3. Results and discussion

To simulate the extraction procedure, *n*-octanol containing  $C_n \min NTf_2$  (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  $C_8 \min NTf_2$  was subjected in the structure determination and other characterizations.

The molecular structure of  $[Cs \cdot BPC6]^+ NTf_2^-$  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– $\pi$  interaction is observed between Cs<sup>+</sup> and the two upper phenyls. The short Cs···C contacts between Cs<sup>+</sup> and the upper-rim C atoms of the two phenyls are 3.445 to 3.677 Å, the two distances of Cs<sup>+</sup> to the centeroids of the two phenyl rings are 3.572 and 3.540 Å, and the Cs<sup>+</sup> ion is 3.404 and 3.406 Å above the phenyl planes. These are indicative of the existence of Cs<sup>+</sup>- $\pi$  interaction [26–28]. The NTf<sub>2</sub><sup>-</sup> anion compensates the positive charge of [Cs·BPC6]<sup>+</sup> moiety, and one oxygen atom of a SO<sub>2</sub> group further coordinates with Cs<sup>+</sup> 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<sub>2</sub> 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  $[Cs\cdotBPC6]^+$ . 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

negative mode were observed in highly diluted conditions. A peak of alkyltrifluoroborate anion with two [K(18-crown-6)]<sup>+</sup> 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<sup>-1</sup> is assigned as the stretching vibration of S=O. Comparing with the value of 1059 cm<sup>-1</sup> in C<sub>8</sub>mimNTf<sub>2</sub>, 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<sup>-1</sup> after it trapping Cs<sup>+</sup>.

The thermal stability of the single crystal after grinding was examined by TGA under N<sub>2</sub> 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<sub>2</sub><sup>-</sup> anion. Comparing the TGA curve of the single crystal with that of BPC6, one can

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

The crystals synthesized using different ILs  $C_n \text{mimNTf}_2$  (n = 2, 4, 6, 8 and 10) were investigated by powder X-ray diffraction (Fig. 7). The main peaks of  $2\theta = 8.5^{\circ}$ ,  $10.1^{\circ}$ ,  $11.8^{\circ}$ ,  $16.6^{\circ}$ ,  $18.0^{\circ}$ ,  $18.9^{\circ}$ ,  $25.9^{\circ}$  and  $30.4^{\circ}$  in the PXRD patterns for ILs with different alkyl chains agree well with the simulated one based on the structure of  $[\text{Cs}\cdot\text{BPC6}]^+\text{NTf}_2^-$  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<sup>+</sup> and K<sup>+</sup>, 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<sup>+</sup>, K<sup>+</sup> and the weak coordinating ability of