

XAFS studies and computational simulation of calixcrowns–caesium complexes in solution

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Caesium L_{3-} edge XANES (X-ray absorption near-edge structure) and EXAFS (extended X-ray absorption fine structure) have been evaluated as means of probing the local structure and the interaction of caesium ions with BPC6 {1,3-alternate bis(2-propyloxy)calix[4]arene-crown-6}, BOC6 {1,3-alternate bis(octyloxy)calix[4]arene-crown-6} and BisC6 (1,3-alternate calix[4]arene bis-crown-6) in NPME (*o*-nitrophenyl methyl ether) or OA (*n*-octyl alcohol). The XANES results indicate that the molecular symmetry is enhanced as the caesium ions are embedded. The EXAFS spectra demonstrate that the coordination numbers (N) and average distances (R) from the central caesium ion to the O atoms are: for BPC6, $N = 7.0$, $R = 3.22 \text{ \AA}$ (in NPME), and $N = 7.0$, $R = 3.23 \text{ \AA}$ (in OA); for BOC6, $N = 6.8$, $R = 3.28 \text{ \AA}$ (in NPME), and $N = 6.9$, $R = 3.27 \text{ \AA}$ (in OA); for BisC6, $N = 6.9$, $R = 3.21 \text{ \AA}$ (in NPME). Density functional theory at the triple- ζ adding polarization basis set level was used to simulate the BPC6, BOC6 and BisC6 coordination with the caesium ions. Data show that the seven-oxygen-configuration average distances from the central caesium ion to the O atoms are $R = 3.38$ for BPC6, $R = 3.40$ for BisC6 and $R = 3.39$ for BOC6.

1. Introduction

The safe treatment and disposal of high-level liquid waste has been the subject of intense research (Zhu & Jiao, 1994; Vandegrift *et al.*, 1994; Cuillardier *et al.*, 1991). Along with ⁹⁰Sr, ¹³⁷Cs constitutes a major source of heat in these wastes (Tong, 2000). Its removal would therefore greatly simplify handling, storage and ultimate disposal.

To date, besides X-ray diffraction, there is no good method of determining a complex structure directly. However, single crystals cannot be easily obtained for all complexes for X-ray diffraction. Moreover, it is a problem as to whether or not the solid-state structure is a rational explanation of its complex performance in solution. Caesium has the least exothermic enthalpy and highest entropy of hydration known for a metal ion (Schulz & Bray, 1987). The free energy of a caesium complex is insufficient to completely dehydrate the cation. In solution, the charge density of caesium is low and the complex ability is weak (Bard & Parsons, 1985). The caesium ion coordination chemistry has thus been defied analysis by standard techniques.

It is important to determine the complex structure in solution in the study of caesium ion coordination chemistry. Introducing the XAFS (EXAFS and XANES) method and computational simulation to the caesium ion structural determination in solution is essential. Antonio *et al.* (1997) have studied the caesium complex with dibenzo-crown ethers in tri-*n*-butyl phosphate, and Kemner *et al.* (1995) have studied CsBr in dibenzo-18-crown-6 ether solution using the EXAFS method. In the last decades, Alfieri *et al.* (1983), Hill *et al.* (1994), Asfari, Bressot *et al.* (1995) and Asfari, Wenger & Vicens (1995) have studied calixcrowns for the high Cs⁺/Na⁺ selectivity in caesium separation from nuclear waste solution. In INNET, the synthesis costs of calixcrowns has reduced to about USD 3 g⁻¹. It is obviously possible that calixcrowns might be used for nuclear waste disposal. However, studies on the preparation and characterization of the complexes of caesium with calixcrowns in NPME (or OA) by XAFS and the Amsterdam Density Functional (ADF) computation simulation have not yet been reported. In this paper we have processed the L_{3-} edge XAFS data of the caesium ion coordination chemistry with BPC6, BOC6 and BisC6. For theo-

retical analysis purposes, we have applied ADF computations. The computational data agreed well with the XAFS experiments.

2. Experiment

2.1. Reagents

NPME and OA were obtained from the Shanghai First Reagent Plant and Beijing Chemical Plant, respectively, and used as received. Calixcrowns were synthesized (Casnati *et al.*, 1995; Gao *et al.*, 2003) in our laboratory and characterized by ^1H NMR, ^{13}C NMR, mass spectroscopy, FT-IR, element analysis and X-ray diffraction.

2.2. XAFS sample preparation

0.1218 g of CsNO_3 was dissolved in 25 ml of 1 mol l^{-1} HNO_3 , and then a 0.1 mol l^{-1} CsNO_3 solution was prepared. Extraction experiments were performed using the following method: an aqueous solution of freshly prepared calixcrowns/NPME (or calixcrowns/OA) was pre-equilibrated *via* three contacts ($V_{\text{aq}} = V_{\text{org}}$) with 1 mol l^{-1} HNO_3 aqueous solution by stirring magnetically for 10 min at 298 K. Then the pre-equilibrated calixcrowns/NPME (or calixcrowns/OA) was added to an equal volume of freshly prepared CsNO_3 solution using a vortex mixer for 10 min (298 K). The mixed phases were then centrifuged until complete phase separation was achieved. The organic phase was sampled and collected as the extraction complex of Cs for XAFS.

2.3. Experiment conditions

X-ray absorption spectra at the L_3 -edge were collected at the Beijing Synchrotron Radiation Facility (BSRF) on wiggler beamline 4W1B under dedicated ring conditions (2.2 GeV, 50–100 mA) using a Si(111) double-crystal monochromator. Detuning the crystals in the monochromator rejected the higher-order harmonic content of the beam so that the incident flux was reduced to about 30% of its maximum at the end of the scan energy. The energy range for the measurements was fixed between 5000 and 5600 eV. The vertical slit width was 0.5 mm, which reduced the effects of beam instabilities and monochromator glitches while providing high photon flux. Spectra were collected in transmission mode using an Ar-filled ionization chamber at ambient temperature as detector. The path length of the cell was realised as 0.1 cm.

2.4. Sample cell

The primary sample cell consisted of a polyethylene body with two Mylar film windows and one radial injection hole ($r = 0.1\text{ cm}$). About 1 ml of Cs extraction complex solution was injected into the primary cell through the injection hole using a syringe.

Three XAFS scans were collected three times and averaged to improve the statistics. The data were treated using the program WINXAS (Version 2.3) (Ressler, 1997). The EXAFS oscillations were isolated using standard procedures for pre-

edge subtraction, data normalization and spline removal. A four-region spline function was used to fit the background over the EXAFS region, which extended out to $k = 9.0\text{ \AA}^{-1}$. Four transforms or the k^3 -weighted data were calculated over the range $k = 2.0\text{--}9.0\text{ \AA}^{-1}$ with a Gaussian window function of 0.2 \AA half-width. Back transforms were carried out from $R = 2.0$ to 4.0 \AA using a Gaussian window function. Curve fitting was performed on those Fourier-filtered EXAFS data over the range $k = 2.0\text{--}9.0\text{ \AA}^{-1}$. For each fit, only the bond lengths (R) and coordination numbers (N) were allowed to vary. The coordination of caesium in the $\text{CsNO}_3\text{--H}_2\text{O}$ system is known: there are six nearest water molecules at an average distance of 3.25 \AA , and two at 4.00 \AA (Krestov *et al.*, 1994).

In the system the cation is Cs^+ . Although BPC6, BOC6 and BisC6 are different, the XAFS absorption spectra of BPC6/ Cs^+ , BOC6/ Cs^+ and BisC6/ Cs^+ are very similar before data processing. The absorption spectrum of BisC6/ Cs^+ is shown in Fig. 1 as a representative example.

2.5. EXAFS data processing

Data processing of the EXAFS at the Cs L_3 -edge for the samples followed standard procedures for pre-edge background subtraction and EXAFS background removal. The EXAFS (χ) is defined as (Lytle *et al.*, 1975)

$$\chi(E) = [\mu(E) - \mu_0(E)]/\mu_0(E),$$

where $\mu(E)$ and $\mu_0(E)$ are the X-ray absorption coefficients for the sample and the isolated atom, respectively. The normalized EXAFS data were converted to a wavevector (k) space using

$$k = [2m(E - E_0)/\hbar^2]^{1/2},$$

where E_0 is the maximum of the first derivative of the spectroscopy, m is the mass of an electron, E is the photon energy and \hbar is the Planck constant divided by 2π .

The resulting oscillations were weighted with k^3 and Fourier-transformed, giving the radial structure function of the edge. The main peak was inverse-Fourier-transformed into k space again, and was curve-fitted by the non-linear least-

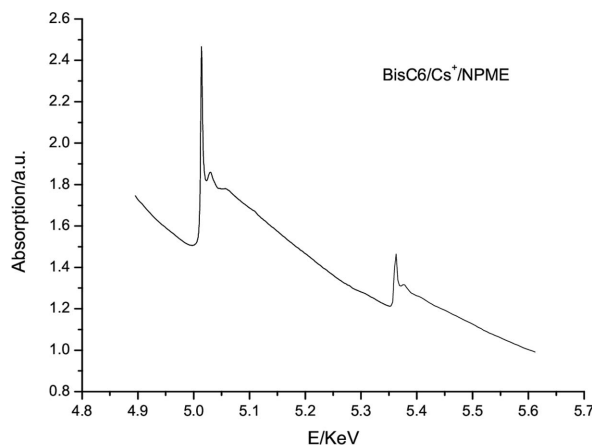


Figure 1
XAFS absorption spectrum of BisC6/ Cs^+ .

squares curve-fitting method using the following EXAFS formula,

$$\chi(k) = \sum (N_j S / k r_j^2) f_j(k) \exp(-2\sigma_j^2 k^2) \sin[2kr_j + \varphi_j(k)],$$

where j is the ordinal number of the shell, $f_j(k)$ is the back-scattering amplitude function and $\varphi_j(k)$ is the total phase-shift function derived from a reference sample of CsNO₃ aqueous solution. N_j is the number of atoms in the j shell at an average distance r_j , *i.e.* the true coordination number of photoelectron scatterers at distance r_j . S is the damping factor, which was fixed and evaluated also from the coordination number of the CsNO₃ aqueous solution reference sample, and σ_j^2 , the Debye–Waller factor, represents the variance at the distance r_j . The Debye–Waller factor contains contributions from both static disorder and thermally induced vibration displacements within a shell of neighbors.

3. Results and discussion

3.1. XANES at the Cs L₃-edge

The XANES results at the Cs L₃-edge in CsNO₃/calixcrowns/NPME and CsNO₃/calixcrowns/OA are shown in Figs. 2, 3 and 4. Double peaks appeared in the XANES of the

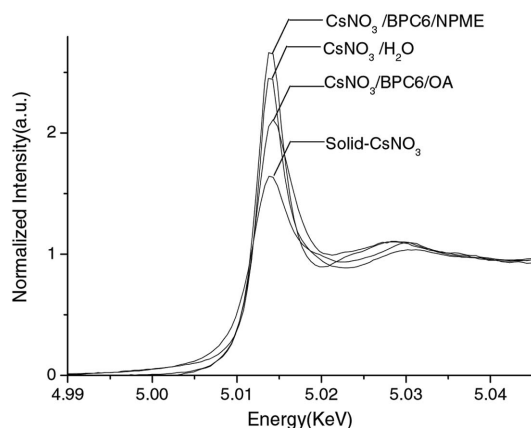


Figure 2 XANES at the Cs L₃-edge (Cs⁺/BPC6).

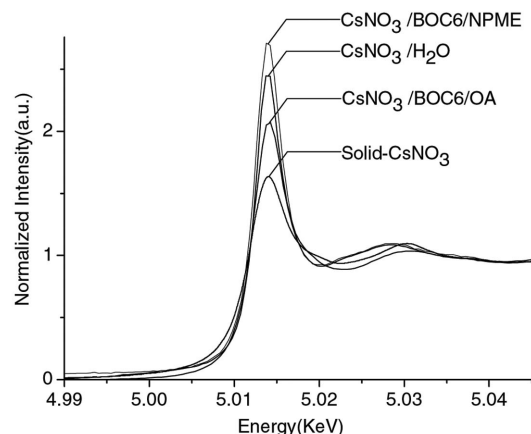


Figure 3 XANES at the Cs L₃-edge (Cs⁺/BOC6).

sample at the Cs L₃-edge. The L₃-edge sharp peak of Cs in calixcrowns/NPME is much higher and sharper than the others, a common trend in Figs. 2, 3 and 4. In fact, the L₃-edge sharp resonance is very sensitive to the changes of molecular geometry and can even couple with nuclear motion (Bonnelle & Mandel, 1982). This might mean that the coordinate symmetry in NPME is much higher than that in OA or in aqueous solution as the caesium ions are embedded. This agrees well with the NMR results (Gao, 2004). These observations clearly suggest that in this class of ionophores the preferred solvent to bind caesium is NPME. Additionally, XANES spectroscopy indicates that the solvent effect causes the disorder increase since the first trough appears slightly earlier than in solid CsNO₃. The solubility of BisC6 is insufficient to complex caesium ions in OA, so the curve is omitted in Fig. 4.

3.2. EXAFS at the Cs L₃-edge

The energy levels of the Cs L₃- and L₂-edges are 5012 eV and 5359 eV, respectively. The energy range is not very wide (Fig. 1) and the signal-to-noise ratio is influenced by the L₂-edge during the collection of L₃-edge data. We attempted to increase the caesium concentration of the initial aqueous phase and the result was improved. Although the k -range of the Cs L₃-edge EXAFS was limited to $\Delta k = 9.5 \text{ \AA}^{-1}$ by the onset of the L₂-edge, the Cs–O and the Cs–C peaks are clearly resolved (see Fig. 7*b*). The Cs–O distance is slightly shorter (Gao, 2004) than the Cs–C distance; the assignment of peaks in the Fourier transforms indicate that the first two peaks in Fig. 7*b*) can be attributed to Cs–O and the third to Cs–C interactions. The isolated and k^3 -weighted EXAFS oscillations are shown in Figs. 5, 6 and 7. The coordination numbers are approximately integer 7 (Table 1). In the data evaluation procedure, considering that the error range and coordination number are usually integers, these have been normalized so that the coordination number is 7.

Here the coordination number N is derived from the Cs–O peak. The EXAFS results indicate that the Cs atoms are seven-coordinated by O atoms. From the results, it could be deduced that the caesium ion coordinates towards six O atoms

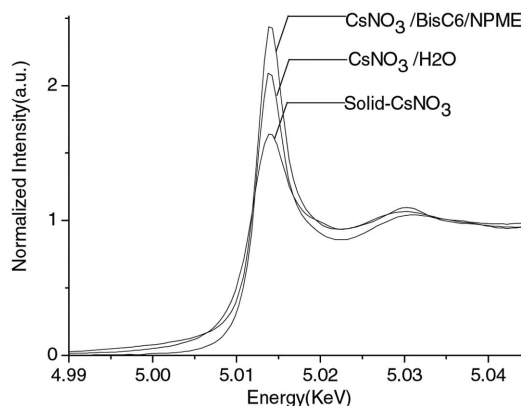


Figure 4 XANES at the Cs L₃-edge (Cs⁺/BisC6).

Table 1

Average Cs—O distance (R) and the coordination number (N) obtained from the curve fitting of the Cs L_3 -edge EXAFS.

σ^2 is the Debye–Waller factor. Errors in distances (0.015 Å) and coordination numbers ($\pm 15\%$) are estimated from the deviation between the fitting results from models of known structure and their true values.

Molecule	N	R (Å)	σ^2 (Å ²)
BPC6/NPME	7.0	3.22	0.015
BPC6/OA	7.0	3.23	0.023
BOC6/NPME	6.8	3.28	0.004
BOC6/OA	6.9	3.27	0.014
BisC6/NPME	6.9	3.21	0.010

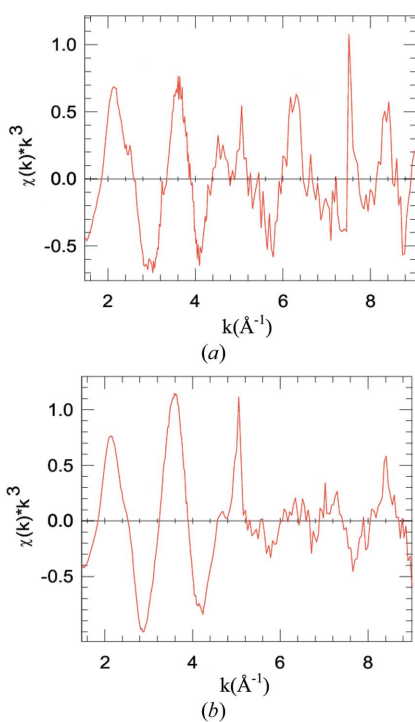


Figure 5
Cs L_3 -edge EXAFS $k^3\chi(k)$ spectra for CsNO₃. (a) BPC6/NPME. (b) BPC6/OA.

from the crown ether chain. The extra O atom might come from H₂O or NO₃[−] according to ESI-MS spectroscopy (Gao, 2004). Ungaro *et al.* (1994) found that the caesium ion appeared to be coordinated by eight O atoms (six from the calixcrown, two from the picrate ion) in the 1,3-dialkoxy-calix[4]arene-crowns-6/Cs⁺Pic[−]/CD₃CN system. Thuéry *et al.* (2000) obtained the crystal structures of [(Cs⁺)₂(ReO₄[−])-BisC6](ReO₄[−])·H₂O and [(Cs⁺)₂(ReO₄[−])-BisC6](ReO₄[−])-(H₂O)_{0.5} in acidic medium. Varnek & Wipff (1996) reported the extensive molecular dynamics (MD) and free energy perturbation simulation on conformationally locked 1,3-alternate calix-bis-crown host molecules in the free state and complexed by alkali cations. They predicted a polarization effect of the solvent in the extraction process. In calixcrowns complexes, one to two MeOH, MeCN or H₂O molecules are coordinated. Lamare *et al.* (1998) determined the crystal structure compared with the MD results of calix[4]dibenzo-crown-6. One or half a molecule of water is observed in these

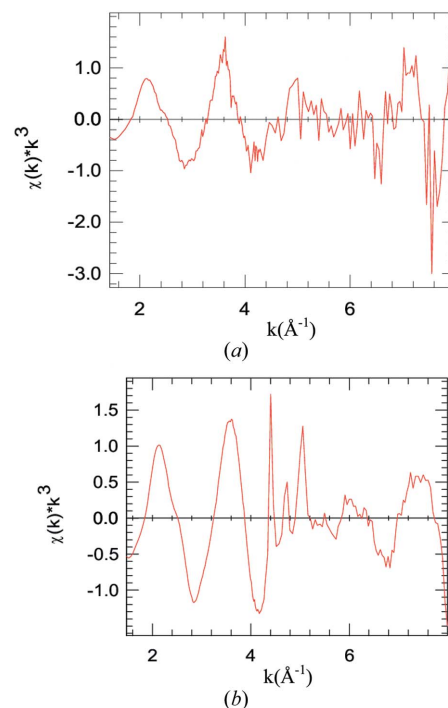


Figure 6
Cs L_3 -edge EXAFS $k^3\chi(k)$ spectra for CsNO₃. (a) BOC6/NPME. (b) BOC6/OA.

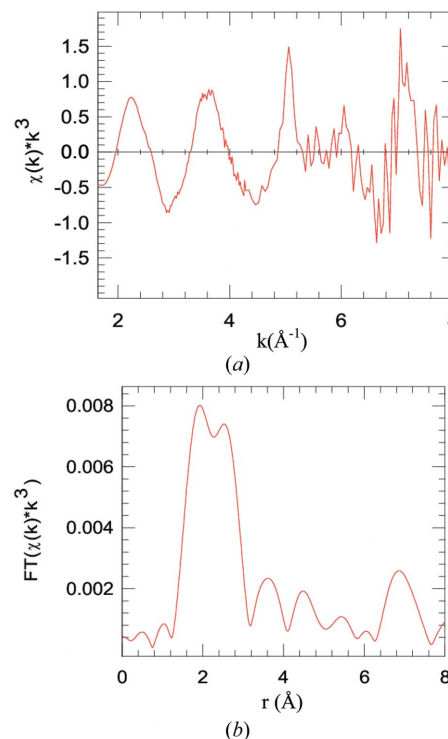


Figure 7
(a) Cs L_3 -edge EXAFS $k^3\chi(k)$ spectra for CsNO₃ in BisC6/NPME. (b) Fourier transform spectra of Cs L_3 -edge EXAFS $k^3\chi(k)$ spectra in BisC6/NPME.

early reports in the solid state or in solution. The EXAFS seven-oxygen-coordinated structure result agrees well with these early reports, *i.e.* six O atoms coordinated by the crown

ether, plus, in some cases, extra coordination to the oxygen of water or a counterion. Here we do not agree that the extra oxygen comes from a solvent. This is because the sterically hindered solvents such as NPME, NPOE, NPHE or OA hinder the solvent oxygen coordinate to the caesium ion. In the periodic table of elements, the outer-electron configuration of the caesium ion is [4*f*, 5*d*, 6*s*]. The 4*f* orbit energy is normally lower than that of the 5*d* and 6*s*. It would be filled first by the lone-pair electron of the O atom. The 4*f* orbit contains seven sub-electronic shells; the caesium ion first shell might be reasonable for seven-coordination. Wipff & Lauterbach (1995) presented the MD and free-energy calculations of calixcrowns in the gas phase and in water. They found that the conformation of the calixcrowns intrinsically affects the coordination. Asfari *et al.* (1996) studied the crystal structures of free BisC6 and three of its mononuclear and binuclear caesium complexes by X-ray diffraction on single crystals. They investigated the complexing properties of BisC6 towards the caesium ion by ¹³³Cs and ¹H NMR spectroscopy. These structures show that the ligand is preorganized for caesium ion complexation.

The average Cs–O bond distance is between 3.21 and 3.28 (Table 1). These values compare well with those reported (Casnati *et al.*, 1995; Thuéry *et al.*, 2000; Lamare *et al.*, 1998) for systems in which Cs–O interactions have been documented. The large caesium ion radius matches well with the 1,3-alternater conformer. The Cs–O interatomic distances for calixcrowns suggest that cavities can accommodate the caesium, as expected from comparison with the diameter of the crown ether.

4. Computational methods

The geometries of BPC6, BOC6 and BisC6 were optimized with no restrictions using the ADF program package (Amsterdam Density Functional, 2003). The local density approximation with local exchange and correlation potentials made use of the Vosko, Wilk and Nusair correlation functional (Vosko *et al.*, 1998). Becke's (1988) non-local exchange correction and Perdew's (1986) non-local correlation correction were added in each SCF (self-consistent field) consistent cycle. We adopted the TZP (triple- ζ polarization) basis sets in ADF, which contained triple- ζ basis sets for all atoms and a polarization function from the H to Ar atoms. The frozen-core approximation for the inner-core electrons was used and the orbits up to 4*p* for the Cs atom, and up to 1*s* for C and O atoms, were kept frozen. The numerical integration procedure applied for the calculations was the polyhedron method developed by Velde and co-workers (Boerrigter *et al.*, 1988; Velde & Baelends, 1992). The BFGS (Broyden–Fletcher–Goldfarb–Shanno) (Broyden, 1970; Fletcher, 1970; Goldfarb, 1970; Shanno, 1970) procedure was used for Hessian updating in the geometry optimizations.

The coordination numbers and the distances of caesium to the O atom are shown in Table 2. The total atom numbers of {Cs·BPC6·H₂O}⁺, {Cs·BisC6·H₂O}⁺ and {Cs·BOC6·H₂O}⁺ are 110, 139 and 140, respectively. We attempted to simulate

Table 2

Computational data for BPC6, BisC6 and BOC6: distance of caesium to the O atom.

	<i>R</i> (Å)		
	BPC6	BOC6	BisC6
Cs ⁺ –O ₁	3.31	3.31	3.20
Cs ⁺ –O ₂	3.31	3.32	3.18
Cs ⁺ –O ₃	3.50	3.58	3.26
Cs ⁺ –O ₄	3.54	3.52	3.62
Cs ⁺ –O ₅	3.56	3.59	3.30
winCs ⁺ –O ₆	3.51	3.49	3.53
Cs ⁺ –O _{H₂O}	2.91	2.91	3.70
Total	23.64	23.72	23.79
Average	3.38	3.39	3.40

{Cs⁺·calixcrowns·NO₃[−]} after simulating {Cs·calixcrowns·H₂O}⁺; however, NO₃[−] is a stereo-structure and H₂O is a plane structure. The replacement caused the computation to increase 100-fold. The computation was not fulfilled at eight parallel machines (a cluster of 24 CPUs) for the capacity was inadequate in the Quantum Chemistry Computation Group of Peking University. Moreover, molecular modeling shows that mononuclear species, associated with one molecule of water, are the most stable (Wipff & Lauterbach, 1995). This paper gave the {Cs·calixcrowns·H₂O}⁺ structure only.

5. Conclusions

The coordination environments of Cs–calixcrown complexes in solution have been investigated by XAFS. XANES results suggested that the molecular symmetry was increased as the caesium ions are embedded. The EXAFS results show that the extraction complexes of BPC6, BOC6 and BisC6 with Cs have the same coordination structure with seven-oxygen-coordinated configurations; six O atoms coordinated by the crown ether, plus, in some cases, an extra oxygen from water or a counterion. In the configuration, the Cs–O distance is between 3.21 and 3.28 Å. The ADF optimized data show that the Cs–O distance is between 3.38 and 3.40 Å. Considering the error range of a supermolecule, the EXAFS structural data agreed quite well with the computational simulation. The periodic table of elements shows that the seven-oxygen-coordinated configuration is reasonable.

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