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Study on mass spectrometric behavior of samarium di-iodide in tetrahydrofuran solution

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Abstract

The mass spectrometric behavior of the SmI_2 in tetrahydrofuran (THF) solution was studied by ESI-Q-MS/MS and ESI-TOF-MS. Results obtained show that the trivalent samarium ions were the dominating species observed, which could be explained by the electron donor nature of the Sm^{II}. The rich coordination chemistry around Sm^{II} and Sm^{III} centers were also discussed. Besides, the fast ligand exchange of the THF-solvated samarium complexes with hexamethylphosphoramide (HMPA) was monitored by on-line ESI-Q-MS, which demonstrated the strong coordination of HMPA to samarium.

Keywords: Samarium complex; Mass spectrometry

1. Introduction

Samarium di-iodide is a powerful one-electron reducing reagent in synthetic organic laboratories [1–4]. Since introduced by Kagan and co-workers in the late 1970, it has steadily developed into a successful reagent for promoting a multitude of synthetic organic transformations [5–10]. There is a rich coordination chemistry around Sm^{II} and Sm^{III} centers, which give rise to various types of selectivities. The reactivity of the SmI_2 can be increased and tuned by introduction of various additives and cosolvents such as HMPA, H_2O and Fe^{III} salts. Some rationalizations have been attempted by the combined use of electrochemistry [11,12] and X-ray crystallographic data [13–18], but more are confused and waiting for research.

Recently, electrospray ionisation [19] has provided many opportunities to analyze the chemistry of metal complexes and organometallic systems in solution [20–22]. However to our knowledge, the ESI-MS literature for samarium especially solvated samarium remains few. Kebarle and coworkers investigated the gas phase ion chemistry of $M(H_2O)^{3+}$ which involve the Sm^{III} for the first time [23]; Horlick and Stewart successfully examined the existing of bare lanthanides ions (Ln^+ or Ln^{2+}) and molecular ions (LnO^+) by changing the solvent, declustering conditions and instrumental design characteristics of ICPMS [24]; Chan and coworkers studied the trivalent lanthanide sandwich complexes by FT-ICR-MS [25]. These studies are very significant because they provide the fundamental reports on lanthanide complexes identified by mass spectrometry.

In this study, the solvated samarium di-iodide are examined by ESI-Q-MS/MS and ESI-TOF-MS. As first example, the mass spectrometric behavior of SmI_2 in THF was presented. Results show that the trivalent samarium ions were dominating species in the spectrum, which could be explained by the electron donor nature of the Sm^{II}. The rich coordination chemistry around Sm^{II} and Sm^{III} centers were also observed and discussed. Besides, this the dynamic ligand exchange of the THF-solvated samarium complexes with hexamethylphosphoramide (HMPA) was monitored by on-line ESI-Q-MS, which demonstrated the strong coordination of HMPA to samarium.

2. Materials and methods

2.1. Materials and sample preparation

SmI_2 was prepared by stirring Sm metal and 1,2-diiodoethane in THF under inert atmosphere at room temperature, until the

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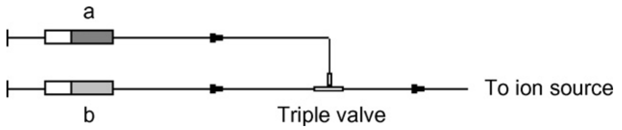


Scheme 1. Strategy designed to monitor the dynamic ligand exchange of samarium complexes. (“a” was THF-solvated SmI_2 solution; “b” was HMPA solution.)

characteristic color (blue–green) of Sm^{2+} appeared. The tetrahydrofuran and methanol were HPLC-grade solvents from Merck (Merck Co., Darmstadt, Germany) and were carefully distilled for being anhydrous and deoxygenated under nitrogen before using intraday [33]. Before the ESI-MS spectra acquisition, the PEEK tube was flushed with the worked THF, then SmI_2 solution (0.040 mol/L) was diluted with THF or combination of THF and CH_3OH (V_{THF}:V_{CH_3OH} = 100:1), fixing the final sample concentration at about 10^{-4} M.

2.2. Instruments

MS experiments were performed on a Finnigan TSQ (Thermo Finnigan, Quantum Access™) triple quadrupole mass spectrometer equipped with a standard ESI ion source and an Applied Biosystems Mariner time-of-flight mass spectrometer with a microspray ion source, respectively. Mass spectra are recorded in the positive ion mode. The following conditions are used in the ESI-Q-MS experiments: ionized voltage, 3800 V, capillary offset, 37 V and capillary temperature, 300 °C, spectra were collected from *m/z* 400 to 1000. The following conditions are used in the ESI-TOF-MS experiments: spray tip potential, 3800 V; nozzle potential, 80 V and nozzle temperature, 140 °C; the detector voltage is 2000 V, spectra were collected from *m/z* 400 to 1000 at an acquisition rate of 2 s per scan.

Collision-induced dissociation (CID, collision gas helium) was performed in a Finnigan TSQ (Thermo Finnigan, Quantum Access™) triple quadrupole mass spectrometer equipped with a standard ESI ion source. The collision energy ranged from 1 to 10 eV, depending on the dissociation liability of the precursor ion. Data acquisition and analysis were done with the Xcalibur (version 2.0, Thermoquest Finnigan) software package.

The on-line strategy for monitoring the ligand exchange was shown in Scheme 1. The two different solutions could be delivered independently to the triple valve by two infusion syringe pumps, they were mixed while delivered to the ESI ion source, so the substitution reaction occurred in the sprayer [31,32]. The mix and reaction time can be adjusted by the length of the PEEK tube and the flow rate.

3. Results and discussion

3.1. Observed spectra in positive modes by ESI-Q-MS

At the beginning of the study, the solution of SmI_2 was diluted with THF; we failed to get satisfactory intensity until the capillary temperature was increased to 370 °C. One typical spectrum is shown in Fig. 1. For better intensity, the mixed solvents should be used. Considering methanol is often used as additive in the reaction of SmI_2 in organic chemistry, the mixed dilution of THF and CH_3OH (V_{THF}:V_{CH_3OH} = 100:1) was tried and the signal was improved (Fig. 2). This indicates that it is effective to investigate the mass spectrometric behavior of SmI_2 solution in the positive ion mode. These two spectra displayed the same dominated signal: the largest peak was observed at *m/z* 694, which was assigned to $[Sm^{III}I_2(THF)_4]^+$ based on the characteristic isotopic distribution and the CID experiment. Most of observed peaks were consisted of samarium with several THF, H_2O or CH_3OH molecules, and all the samarium species could be confirmed as Table 1 displays.

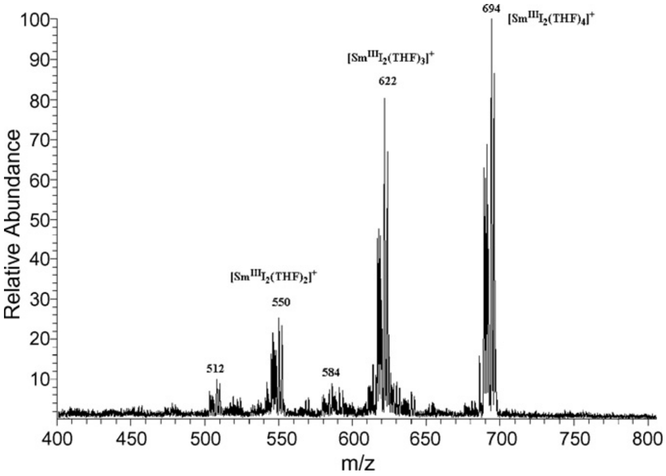


Fig. 1. The ESI mass spectrum for the solution of the SmI_2 in THF by ESI-Q-MS (diluted by THF).

From these, we found that the dominated samarium species detected were trivalent samarium. It could be explained by the nature of the SmI_2: SmI_2 is a powerful electron donor ($E^0(Sm^{3+}/Sm^{2+}) = -1.55$ V) [3], which tends to lose electrons in the earlier stage of many reactions [1–4]. So, when the solution of SmI_2 entered the electrospray source, which could be described as “an electrolytic cell” [26–27], the electrochemical oxidation occurred and the trivalent samarium species could be formed (Scheme 2).

In addition to the existence of $[Sm^{III}I_2(THF)_n]^+$, another two kind of Sm^{III} species exist is the forms of

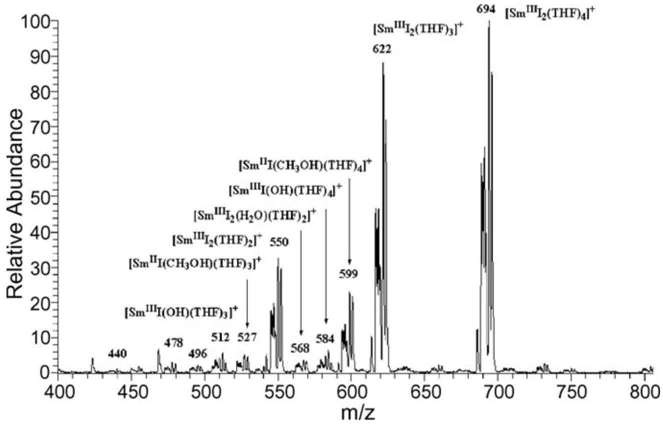


Fig. 2. The ESI mass spectrum for the solution of the SmI_2 in THF by ESI-Q-MS (diluted by combination of THF and CH_3OH).

Table 1
Assignment of ions detected in the ESI mass spectra of SmI_2 in THF

m/*z*	Complex ions
694	$[Sm^{III}I_2(THF)_4]^+$
622	$[Sm^{III}I_2(THF)_3]^+$
599	$[Sm^{II}I(CH_3OH)(THF)_4]^+$
584	$[Sm^{III}I(OH)(THF)_4]^+$
568	$[Sm^{III}I_2(H_2O)(THF)_2]^+$
550	$[Sm^{III}I_2(THF)_2]^+$
527	$[Sm^{II}I(CH_3OH)(THF)_3]^+$
512	$[Sm^{III}I(OH)(THF)_3]^+$
496	$[Sm^{III}I_2(H_2O)(THF)]^+$
478	$[Sm^{III}I_2(THF)]^+$
440	$[Sm^{III}I(OH)(THF)_2]^+$

$$Sm^{II}I_2L_n \xrightarrow[\text{At the electrospray needle}]{-e} Sm^{III}I_2L_n^+$$

Scheme 2. The electrochemical oxidation process for divalent samarium complexes (L stands for ligand and $n = 1$–4).

$[Sm^{III}I_2(H_2O)(THF)_n]^+$ and $[Sm^{III}I(OH)(THF)_n]^+$. It could be seen that the dominated species were $[Sm^{III}I_2(THF)_n]^+$ ($n = 4$–2) and the signal of $[Sm^{III}I_2(THF)_4]^+$ was the base peak. The signal of $[Sm^{III}I_2(H_2O)(THF)_n]^+$, which is small in the spectra, were formed by substitution of THF with the trace H_2O which inevitably exist in the sampling and introducing process through PEEK tube. The signal of $[Sm^{III}I(OH)(THF)_n]^+$, which is also small in the spectra, maybe originated from the ion-molecule reaction of $[Sm^{III}I_2(H_2O)(THF)_2]^+$ with the nebulize gas to lose HI. The losing of neutral molecule is normal in the in source-CID [28,29], and this kind of process could be further confirmed by CID experiments of $[Sm^{III}I_2(H_2O)(THF)_2]^+$.

Besides, in the spectrum, the divalent samarium ions could only be seen as the form of $[Sm^{II}I(CH_3OH)(THF)_n]^+$($n = 4$–3). It seems that the oxidation ability of $SmI_2(CH_3OH)(THF)_n$ is weaker than that of the $SmI_2(THF)_n$, so the signal of $[Sm^{II}I(CH_3OH)(THF)_n]^+$ were observed instead of $[Sm^{III}I_2(CH_3OH)(THF)_n]^+$, and the signal of $[Sm^{II}I(THF)_n]^+$ were not observed while the signal of $[Sm^{III}I_2(THF)_n]^+$ were dominant in the spectrum. It could be inferred that the divalent samarium may partly stabilized by the replacement of THF by CH_3OH (Scheme 3).

In summary, we found the THF-solvated SmI_2 mainly tends to lose one-electron to form Sm^{III} ions other than the conventional situation of dissociating one halogen anion to form positive ions for most metal halide [30]. We consider that it could be explained by the nature of the SmI_2, a powerful one-electron donor, and the redox process occurred in ESI because of the high positive voltage applied to the ESI tip (in this case +3.8 kV). Because of the strong oxygen affinity for SmI_2, it is easy to form samarium complexes even if little amount of H_2O or CH_3OH exists.

$$Sm^{II}I_2(THF)_n \xrightarrow{-e} [Sm^{III}I_2(THF)_n]^+$$

$$Sm^{II}I_2(H_2O)(THF)_n \xrightarrow{-e} [Sm^{III}I_2(H_2O)(THF)_n]^+$$

$$Sm^{II}I_2(CH_3OH)(THF)_n \xrightarrow{-I^-} [Sm^{II}I(CH_3OH)(THF)_n]^+$$

Scheme 3. The different ionization approaches observed for samarium complexes.

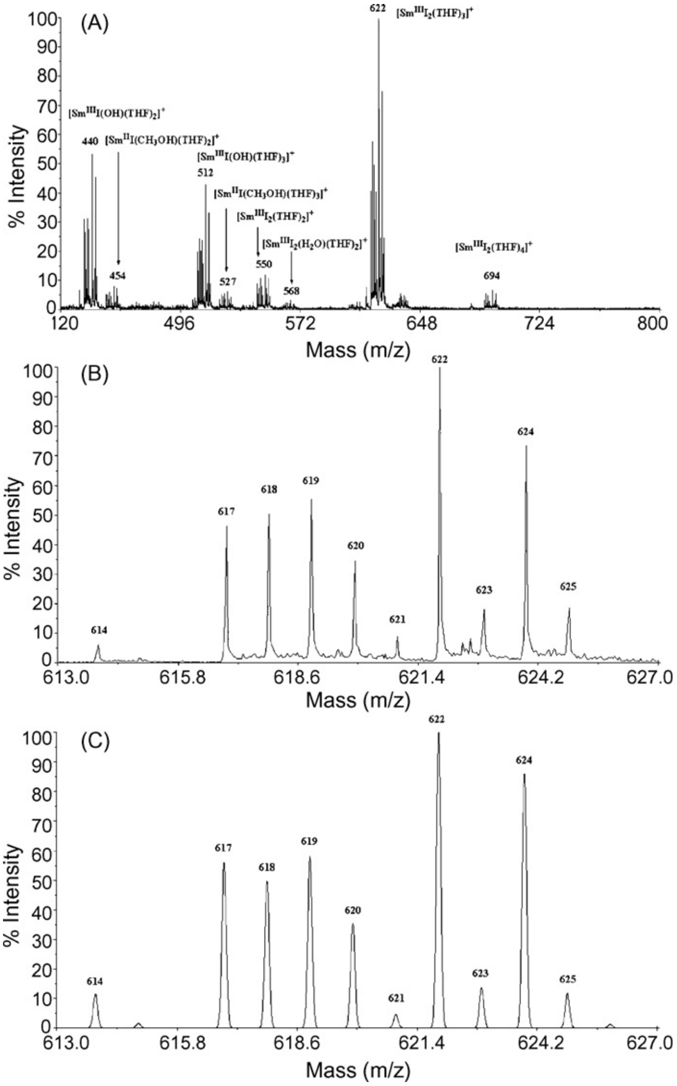


Fig. 3. The ESI mass spectrum for the solution of the SmI_2 in THF by ESI-TOF-MS: (A) the full scan; (B) the experimental isotopic distribution for *m*/*z* 622; (C) the theoretical isotopic distribution for $SmI_2C_{12}H_{24}O_3^+$ simulated by Mariner Data Explorer 4.0.0.1 software.

3.2. Comparison with ESI-TOF-MS spectra

We also investigated the behavior of SmI_2 in THF by ESI-TOF-MS and got typical spectra as Fig. 3 shown. The composition of this spectrum is similar to the spectrum got by ESI-Q-MS, but the relative intensity was different. First, the base peak was *m*/*z* 622 standing for $[Sm^{III}I_2(THF)_3]^+$, not *m*/*z* 694 standing for $[Sm^{III}I_2(THF)_4]^+$. Second, the intensity of *m*/*z* 440 and 512 has increased a lot, and the former (*m*/*z* 440) is higher than the latter (*m*/*z* 512). Because high spray potential and nozzle potential was applied for satisfied intensity, it is reasonable

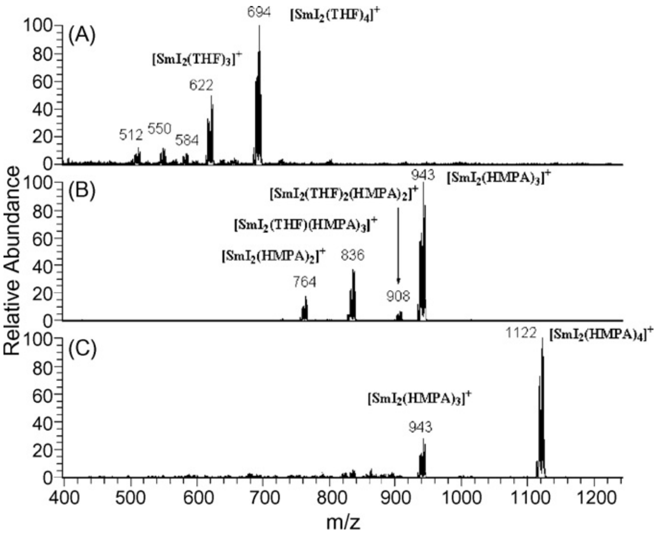


Fig. 4. The ESI spectra of (A) the SmI_2 dissolved in THF; (B) the SmI_2 dissolved in THF and HMPA ($n_{SmI_2}:n_{HMPA} = 10:1$); (C) the SmI_2 dissolved in THF and HMPA ($n_{SmI_2}:n_{HMPA} = 1:1$).

that the fragment of $[\mathrm{Sm^{III}I_2(THF)_4}]^+$ was increased and the intensity of $[\mathrm{Sm^{III}I_2(THF)_3}]^+$ was enhanced.

3.3. The ligand exchange of the samarium complexes in THF solution monitored by on-line ESI-Q-MS

Although hexamethylphosphoramide (HMPA) is often used as additive for increasing the redox potential of SmI_2, there are few mass spectrometric data about this powerful and useful complexation. This time, the fast ligand exchange of the samarium complexes was monitored by ESI-Q-MS. The on-line strategy was designed so that SmI_2 solution and HMPA solution were delivered independently to the ESI ion source by two infusion syringe pumps, and mixed at a triple valve, and then the substitution reaction occurred in the sprayer [31,32]. After mixing and reaction for 1 s, the spectra were shown in Fig. 4.

From Fig. 4A and B, it is observed clearly that two to four THF groups were substituted by the added HMPA to form new species. When the amount of HMPA increased (form n_{SmI_2}: $n_{HMPA} = 10:1$ to $n_{SmI_2}:n_{HMPA} = 1:1$), all THF groups were substituted by the HMPA and no THF coordinated species could be observed. This result demonstrated even few HMPA exist the samarium would be coordinated with HMPA firstly. This indicated the strong coordination capacity of HMPA to samarium, and it is consistent with the known data based on other experiments [15]. It could be inferred that the HMPA coordinated species were dominated in the samarium catalyzed reaction when HMPA was used as additive (normally, n_{SmI_2}: n_{HMPA} is smaller then 1:1), and it is also consistent with the known information [34].

3.4. Structural identification for the observed samarium complexes

The CID spectrum with Ar collision gas in Q2 for samarium species are shown in Figs. 5–8. For complex ions $[\mathrm{SmI_2(THF)}_n]^+$, successive loss of THF was observed in Fig. 5. The collision energy ranged from 1 to 5 eV, which indicated the THF ligand was easy to dissociate from samarium center.

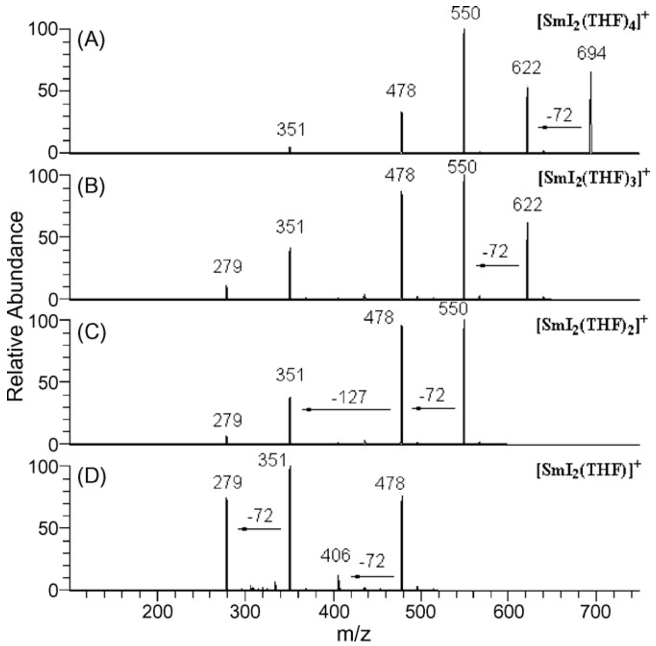


Fig. 5. MS/MS for samarium complexes $[\mathrm{SmI_2(THF)}_n]^+$: (A) $n = 4$; (B) $n = 3$; (C) $n = 2$; (D) $n = 1$.

In Fig. 6, the ligand dissociation of H_2O and THF could be seen for $[\mathrm{SmI(H_2O)(THF)}_n]^+$, and the signals at m/z 550 and 478 are dominant which show the loss of H_2O is main pathway for this kind of samarium complexes. In addition, the elimination of HI to yield $[\mathrm{SmI(OH)(THF)}_n]^+$ ($n = 2$, m/z 440; $n = 1$, m/z 368) were observed, which could confirm the origin of signal at m/z 440 and 368 in the full scan. In Fig. 7, besides the similar successive loss of THF, the β elimination of HI for $[\mathrm{SmI(OH)(THF)}_n]^+$ to yield $[\mathrm{Sm{=}O(THF)}]^+$ (m/z 240) were observed.

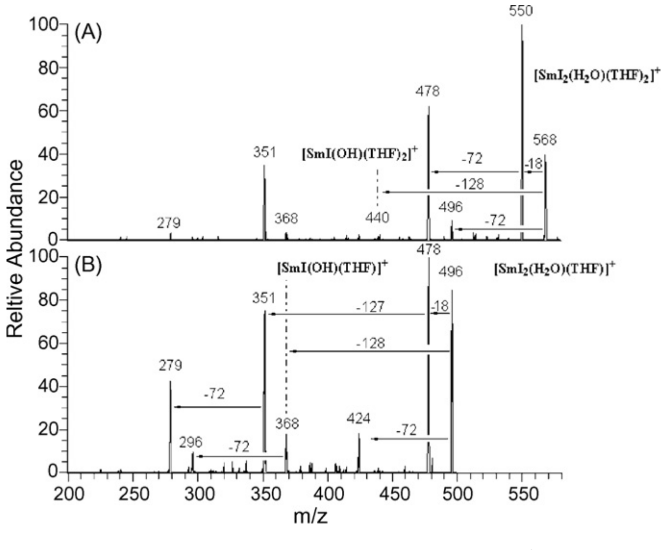


Fig. 6. MS/MS for samarium complexes $[\mathrm{SmI(H_2O)(THF)}_n]^+$: (A) $n = 2$; (B) $n = 1$.

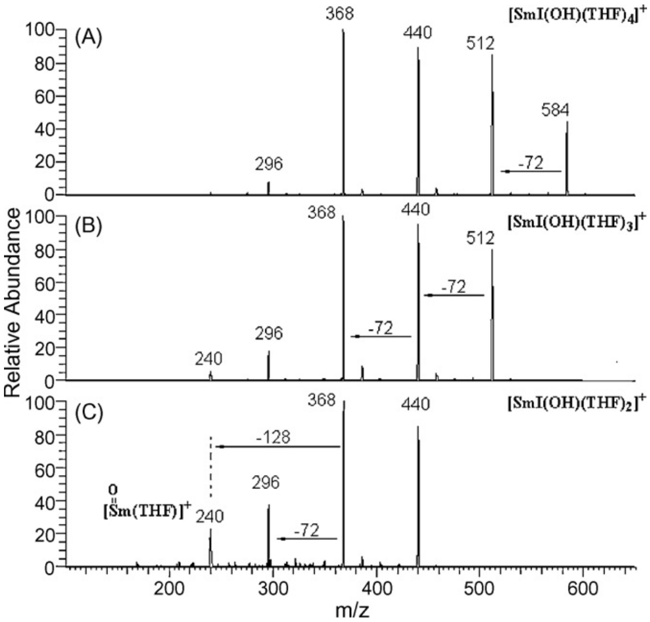


Fig. 7. MS/MS for samarium complexes $[SmI(OH)(THF)_n]^+$: (A) $n=4$; (B) $n=3$; (C) $n=2$.

For the fragmentation of complex ions $[SmI(HMPA)_n]^+$, the collision energy ranged from 5 to 10 eV, which indicted the HMPA ligand was relatively harder to dissociate from samarium center compared with THF ligand. So it is reasonable that the loss of THF is the main pathway for fragmentation of complex ions $[SmI(THF)_m(HMPA)_n]^+$ in Fig. 8C and D. As far as we know, it is the first report describing the detailed fragmentation for the samarium species (Schemes 4 and 5).

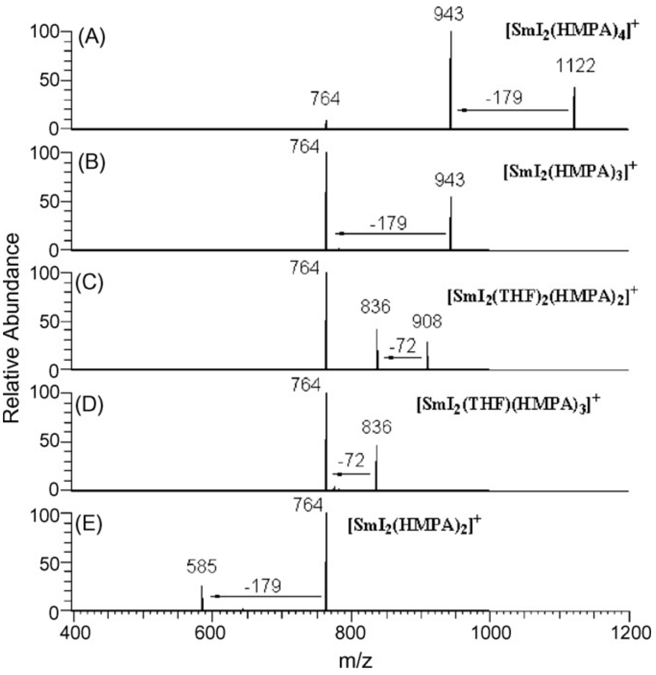
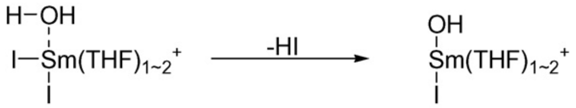
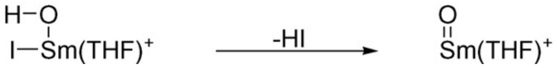


Fig. 8. MS/MS for samarium complexes $[SmI(THF)_m(HMPA)_n]^+$: (A) $m=0$, $n=4$; (B) $m=0$, $n=3$; (C) $m=2$, $n=2$; (D) $m=1$, $n=3$; (E) $m=0$, $n=2$.



Scheme 4. The origination of $[SmI(OH)(THF)_{1-2}]^+$ in the full spectrum: the elimination of HI observed for samarium complexes $[SmI(H_2O)(THF)_{1-2}]^+$ in the MS/MS spectra.



Scheme 5. The β elimination of HI observed for samarium complexes $[SmI(OH)(THF)]^+$ in the MS/MS spectrum.

4. Conclusions

ESI-Q-MS/MS and ESI-TOF-MS have been applied to the study SmI_2 in THF. This is first research to appoint the mass spectrometric behavior of the solvated samarium. Results obtained show that $[Sm^{III}I_2(THF)_n]^+$ ions can be mainly observed because of the electron donor nature of the SmI_2 and the redox process occurred in ESI. From the spectra, the rich coordination chemistry around Sm^{II} and Sm^{III} centers could be observed and discussed. Based on the study, more about the samarium complexes could be studied and further experiments are under way in our laboratory.

Acknowledgements

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