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Divalent and Trivalent Gas-Phase Coordination Complexes of Californium: Evaluating the Stability of Cf(II)

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Abstract

The divalent oxidation state is increasingly stable relative to the trivalent state for the later actinide elements, with californium the first actinide to exhibit divalent chemistry under moderate conditions. Although there is evidence for divalent Cf in solution and solid compounds, there are no reports of discrete complexes in which Cf^{II} is coordinated by anionic ligands. Described here is the divalent Cf methanesulfinate coordination complex, $Cf^{II}(CH_3SO_2)_3^-$, prepared in the gas phase by reductive elimination of CH_3SO_2 from $Cf^{III}(CH_3SO_2)_4^-$. Comparison with synthesis of the corresponding Sm and Cm complexes reveals reduction of Cf^{III} and Sm^{III}, and no evidence for reduction of Cm^{III}. This reflects the comparative 3+/2+ reduction potentials: Cf^{3+} (-1.60 V) ≈ Sm^{3+} (-1.55 V) >> Cm^{3+} (-3.7 V). Association of O_2 to the divalent complexes is attributed to formation of superoxides, with recovery of the trivalent oxidation state. The new gas-phase chemistry of californium, now the heaviest element to have been studied in this manner, provide evidence for Cf^{II} coordination complexes and similar chemistry of Cf and Sm.

Introduction

The oxidation state chemistry of the 5f actinide (An) series of elements, thorium through lawrencium, is substantially more diverse than that of the homologous 4f lanthanide (Ln) series, cerium through lutetium, and exhibits completely different trends. The dominant oxidation state of all the lanthanides is trivalent Ln^{III}, though tetravalent and divalent states exist under relatively moderate chemical conditions, notably Ce^{IV}, Sm^{II}, Eu^{II} and Yb^{II}.[1] Divalent and tetravalent oxidation states have been attained for several additional lanthanides under more extreme or exotic conditions. Notably, Evans and co-workers have prepared formally Ln^{II} compounds for all of the lanthanides (except synthetic Pm).[2,3] The first half of the homologous 5f actinide series contrastingly exhibits a wider range of oxidation states under moderate conditions, from trivalent An^{III} to heptavalent An^{VII}.[4] Plutonium, for example, is distinctive among all of the elements in the periodic table in that it can simultaneously exhibit the Pu^{III}, Pu^{IV}, Pu^{V} and Pu^{VI} oxidation states in solution, this being a manifestation of the Pu(VI/V), Pu(V/IV) and Pu(IV/III) reduction potentials, which span the narrow range of 1.01 – 1.04 V.[5] This diverse range of oxidation states reflects the greater ease with which the 5f electrons of the early actinides can be involved in chemical bonding, or removed from the atoms in the case of ion formation. The 4f electrons of the lanthanides are generally lower in energy, which restricts access to higher oxidation states.

Following Pu, the chemistry of Am, Cm and Bk largely resembles that of the lanthanides, with the An^{III} oxidation state being dominant. Another shift in the series begins at Cf, beyond which the divalent oxidation state becomes increasingly stable.[6] Whereas the Cf^{III} dominates the chemistry of californium,[6] there are several known Cf^{II} compounds, notably the dihalides $CfCl_2$,[7] $CfBr_2$,[8] and CfI_2.[9] Although Cf^{2+} is not inherently stable in solution, its existence has been established by radiopolarography in acetonitrile[10] and in aqueous solutions.[11] The known solid state and solution chemistry of Cf, specifically the stability of the divalent oxidation state, closely parallels that of Sm. Beyond Cf the An^{II} oxidation state becomes increasingly stable, such that Cf occupies a pivotal point in the series at which divalent chemistry becomes significant. The disparate stabilities of the divalent oxidation states of lanthanide and actinide elements are evident from Figure 1 where the standard reduction potentials, $E^{o}(3/2)$, for the homologous Ln^{3+} and An^{3+} ions from F. H. David are plotted (several values are estimates).[1] For the first members of the series, to Eu/Am, $E^{o}(3/2)$ for the Ln^{3+} are higher than for the homologous An^{3+}, by >1 V; for the later members of the series, beginning at Tb/Bk, the $E^{o}(3/2)$ for the Ln^{3+} are lower than for the homologous An^{3+}, with the disparity increasing across the series. This key difference between the two series can largely be attributed to an increasing stabilization of the quasi-valence 5f electrons across the actinide series. Among the lanthanides, Sm, Yb and Eu exhibit substantial divalent chemistry. The currently accepted $E^{o}(3/2)$ for Sm^{3+} and Cf^{3+} are similar, -1.55 and -1.60 V, respectively, such that their redox behaviors are predicted to be similar, with Cf at the start of the latter segment of the actinide series for which divalent chemistry is predicted to be significant (and be dominant for No). Furthermore, the ionic radii of Sm^{3+} (0.96 Å) and Cf^{3+} (0.95 Å) are similar;[12] although the ionic radius of Cf^{2+} is not known, it is expected to be comparable to that of Sm^{2+} (1.22 Å). The analogous properties and ionic radii of Cf and Sm are in accord with their similar chemistries and suggest predominantly ionic bonding. Recent results have revealed new chemistry of formally trivalent $\mathrm{Cf^{III}}$ compounds that is a manifestation of the change in redox chemistry at this point in the series, and specifically the metastability of the divalent $\mathrm{Cf^{II}}$ oxidation state.[13,14] Another recently reported feature of Cf chemistry that differentiates it from that of the lanthanides in general, and Sm in particular, is a degree of covalent bonding involving the 5f electrons, which is essentially absent for the homologous 4f electrons.[15] This recent work has renewed interest in the chemistry of Cf in general, and its divalent chemistry in particular.

Although $\mathrm{Cf^{2+}}$ is established in solution and bulk solids, there are no reports of well-characterized discrete $\mathrm{Cf^{II}}$ complexes in which formally $\mathrm{Cf^{2+}}$ is coordinated by neutral or anion donor ligands. Given the difficulty in retaining low metal oxidation states in oxygen-coordination environments, a particularly significant accomplishment was the stabilization of $\mathrm{Cf^{II}}$ at low concentration (1%) in crystalline strontium tetraborate,[16] similarly to the stabilization of $\mathrm{Sm^{II}}$ doped into alkaline-earth feldspars.[17] The scarcity and high radioactivity of the available isotopes of californium have greatly restricted the development of its chemistry, including discovery of discrete molecular coordination compounds or complexes comprising $\mathrm{Cf^{II}}$. In contrast, there are several reports of divalent Sm complexes, such as metallocenes,[18-20] chalcogenates,[21] decaborates,[22] phosphidos,[23] and amides.[24] The stabilization of divalent Sm in oxygen-coordination environments has largely been limited to utilization of aryloxide ligands.[25-27] The dearth of knowledge of $\mathrm{Cf^{II}}$ coordination chemistry leaves a gap in more fully developing and understanding the similarities and differences between the chemistries of the lanthanides and actinides in general, and between $\mathrm{Sm^{II/III}}$ and $\mathrm{Cf^{II/III}}$ in particular. A key issue is whether the possibility of greater covalency of the quasi-valence 5f electrons may substantially affect the redox chemistry of Cf in coordination complexes in general, and whether it is feasible to prepare $\mathrm{Cf^{II}}$ complexes having oxygen-donor coordination, without resorting to the stabilizing effect of a bulk divalent metal ion lattice.[16]

The utility of thermal decomposition by collision induced dissociation (CID) of gas-phase metal complexes to explore fundamental aspects of inorganic and organometallic chemistry is well-established.[28] Among the unimolecular decomposition reactions studied by O'Hair and co-workers was elimination of $\mathrm{SO_2}$ from a copper complex containing a methanesulfinate ligand, $\mathrm{CH_3SO_2}$, to yield an organocuprate complex with a Cu-$\mathrm{CH_3}$ bond.[29] Gas-phase lanthanide complexes with this same ligand, which exhibited different chemistry from that of the copper complexes, were recently demonstrated as an effective approach to evaluate the comparative stabilities of divalent lanthanide oxidation states.[30] These gas-phase experiments resulted in the synthesis of both divalent and trivalent lanthanide coordination complexes having oxygen donor ligands. Because gas-phase ions can be mass-selected and detected with high sensitivity, experiments that employ a quadrupole ion trap mass spectrometer (QIT/MS) as a "complete chemical laboratory"[31] can be performed with very small amounts of metals and are particularly well-suited for exploring the chemistry of scarce and highly radioactive synthetic elements such as Cf. Given that among the lanthanides Sm, along with Eu and Yb, distinctly exhibited divalent chemistry in previous gas-phase experiments,[30] the gas-phase study of Cf is a promising approach to evaluate if analogous coordination and redox chemistry can be achieved for Cf and Sm. Divalent coordination complexes of Sm, Eu and Yb were previously prepared in the gas phase by endothermic elimination of a neutral ligand from the trivalent complexes that comprise the formally anionic methanesulfinate ligand, $CH_3SO_2^-$, reaction 1.[30]

$$[M^{III}(CH_3SO_2)_4]^- \rightarrow [M^{II}(CH_3SO_2)_3]^- + CH_3SO_2 \quad (1)$$

Reduction reaction 1 was not observed for any other lanthanides, in accord with their lower Ln(III/II) reduction potentials; instead, CH_3 elimination to yield $[Ln^{III}(CH_3SO_2)_3(SO_2)]^-$ was observed. It was demonstrated that reaction 1 serves to differentiate lanthanides with Ln(III/II) reduction potentials of Tm^{3+} (-2.3 V) and below from those of Sm^{3+} (-1.55 V) and above, as has been indicated with the horizontal green line at ca. -2 V in Figure 1. If the chemistry of Cf is dominated by its redox properties, it is evident from Figure 1 that it should be possible to prepare divalent coordination complexes via reaction 1 and that the observed chemistry of Cf should be very similar to that of Sm. However, if other factors, such as covalency, perturb the chemistry of Cf, then discrepancies from Sm might appear. In the present work the chemistry of the gas-phase complex $[Cf^{III}(CH_3SO_2)_4]^-$ has been studied for direct comparison with the corresponding Sm^{III} complex to evaluate the chemical correspondence between these two elements, and particularly the stability of Cf^{II} coordination complexes. The $[Cm^{III}(CH_3SO_2)_4]^-$ complex was also studied to provide a basis to enable comparison with a trivalent actinide, Cm^{III}, which is substantially resistant to reduction ($E^o(3/2) \approx -3.7$ V for Cm[1]).

Experimental

Due to the high radioactivity of ^{249}Cf (~10^5 Bq/µg), and the ingestion and inhalation hazards associated with such alpha-decay isotopes, the experiments were performed using only 2.5 µg (10 nmol) of ^{249}Cf. The ^{249}Cf was generated by beta-decay of ^{249}Bk (half-life = 320 d) produced in the High Flux Isotope Reactor at Oak Ridge National Laboratory. The ^{249}Cf isotope has an alpha-decay half-life of 351 y such that at the time of the experiments the sample contained ~5% of daughter ^{245}Cm (0.5 nmol), which enabled simultaneous study of Cf and Cm in the same solution. The following stock solutions were used to prepare the electrospray ionization (ESI) solutions: 0.40 µM ^{249}Cf and ~0.02 µM ^{245}Cm in 100 mM HCl; 10 mM $SmBr_3$ in water; and 15 mM $NaCH_3SO_2$ (Sigma-Aldrich, 98%) in 75% ethanol/25% water. The high concentration of chloride in the Cf/Cm stock solution would have resulted in competition for metal ion complexation during ESI; accordingly, the stock solution was slowly evaporated to reduce the HCl content. The $NaCH_3SO_2$ stock solution was then added to the resulting solid to achieve a Cf concentration of ~100 µM (and ~0.005 µM Cm); the $CH_3SO_2^-$: Cf^{3+} ratio is estimated as ~150:1 ($CH_3SO_2^-$:Cm^{3+} ≈ 3000:1). A large excess of the $CH_3SO_2^-$ ligand was employed to compete with residual Cl^- and produce adequate $[Cf(CH_3SO_2)_4]^-$. The low concentrations of Cf^{3+} and Cm^{3+}, and high concentrations of Na^+, resulted in complex ESI mass spectra with several abundant sodium complexes, and reduced abundances of $[Cf(CH_3SO_2)_4]^-$ and $[Cm(CH_3SO_2)_4]^-$. For ESI of Sm, the stock solutions of $SmBr_3$ and $NaCH_3SO_2$ were mixed to achieve 100 µM of Sm^{3+} and 300 µM of $CH_3SO_2^-$. For both the Cf/Cm and Sm solutions the final ESI solution composition was ~75% ethanol/~25% water. The resulting ESI mass spectra resulted in a greater abundance of $[Sm(CH_3SO_2)_4]^-$ than $[Cf(CH_3SO_2)_4]^-$; the yield of $[Cm(CH_3SO_2)_4]^-$ was even lower. The abundances of all three $[M(CH_3SO_2)_4]^-$ were sufficient to obtain reliable and consistent results.

The ESI mass spectrometry experiments were performed using an Agilent 6340 QIT/MS with MS^n collision induced dissociation (CID) capabilities, as described previously.[30,32,33] Containment of the ESI source in a radiological glove box enables handling of highly radioactive isotopes such as ^{249}Cf.[34] Additionally, ions in the trap can undergo ion-molecule reactions for a fixed time at ~300K. In high resolution mode, the instrument has a detection range of 50 – 2200 m/z and a resolution of ~1700 M/ΔM (~0.3 m/z FWHM at 500 m/z). Mass spectra were acquired using the following instrumental parameters: solution flow rate, 1 µL/min; nebulizer gas pressure, 12 psi; capillary voltage and current, 4100 V, 52.5 nA; end plate voltage offset and current, -500 V, 780 nA; dry gas flow rate, 5 L/min; dry gas temperature, 325 ^{o}C; capillary exit, -192 V; skimmer, -15.0 V; octopole 1 and 2 DC, -12.5 V and 0 V; octopole RF amplitude, 250 V_{pp}; lens 1 and 2, 8.0 V and 100 V; trap drive, 70. High-purity nitrogen gas for nebulization and drying in the ion transfer capillary was supplied from the boil-off of a liquid nitrogen Dewar. As has been discussed elsewhere, the background water pressure in the ion trap is estimated as $\sim10^{-6}$ Torr; reproducibility of hydration rates of $UO_2(OH)^+$ confirms that the background water pressure in the trap varies by less than ±50%.[35] The helium buffer gas pressure in the trap is constant at $\sim10^{-4}$ Torr. The results reported here were obtained at CID energies of about ~0.4 V. It should be noted that the CID energy is an instrumental parameter that only provides an indication of relative ion excitation, not actual ion energetics.

Results and Discussion

The two methanesulfinate solutions that were employed for ESI, as described above, contained (1) ~100 µM $^{249}Cf^{3+}$/~5 µM $^{245}Cm^{3+}$, and (2) 100 µM Sm^{3+}. The large excess of $NaCH_3SO_2$ required to prepare solution (1) resulted in several abundant sodium-containing cluster ions during ESI; sodium clusters were present but less abundant from solution (2). Representative ESI mass spectra of the two solutions are included as Supporting Information (Figure S1). The abundances of $[M^{III}(CH_3SO_2)_4]^-$ were sufficient for M = Cf, Cm and Sm for isolation and CID; for Cm and to a lesser extent Cf, the peaks at m/z corresponding to $[M^{III}(CH_3SO_2)_4]^-$ contained substantial sodium complex impurities; the CID spectra resolved the species of interest from impurity components (Fig. S2). The peak corresponding to the complex containing ^{152}Sm, the most abundant of the seven natural samarium isotopes, was isolated for CID. The computed structures of selected $[Ln^{III}(CH_3SO_2)_4]^-$ were reported previously.[30] The Ln metal center is coordinated in an oxygen bidentate geometry by the four methanesulfinate ligands. This coordination environment was found for the Ln^{3+} having the largest ionic radius (IR),[12] IR[La^{3+}] = 1.03 Å, that having the smallest, IR[Lu^{3+}] = 0.86 Å, as well as for intermediate IR[Yb^{3+}] = 0.87 Å. The same structure is thus expected for the Cm^{3+} (IR = 0.97 Å) and Cf^{3+} (IR = 0.95 Å) complexes. Analogous geometrical structures to those previously computed for the lanthanide complexes are similarly anticipated for the actinide species produced in this work. The computations to obtain accurate structural parameters for the actinide species reported here, which have several 5f electrons and are particularly demanding, are not necessary to understand the empirical observations.

CID of $[M^{III}(CH_3SO_2)_4]^-$

The CID results for the three isolated $[M^{III}(CH_3SO_2)_4]^-$ complexes are shown in Figure 2, with all spectra acquired under the same instrumental conditions. As reported previously,[30] CID of $[Sm^{III}(CH_3SO_2)_4]^-$ resulted primarily in CH_3 elimination to yield $[Sm^{III}(CH_3SO_2)_3(SO_2)]^-$ as shown in reaction 2. The CID process shown in reaction 1 was minor but distinctly apparent for M = Sm. The presence of background oxygen and water in the ion trap[35] resulted in the secondary oxygen addition reaction 3, and a hydrolysis process yielded $[Sm^{III}(CH_3SO_2)_3(OH)]^-$, one possible route to which is given by reaction 4.

$$[M^{III}(CH_3SO_2)_4]^- \rightarrow [M^{III}(CH_3SO_2)_3(SO_2)]^- + CH_3 \quad (2)$$

$$[M^{II}(CH_3SO_2)_3]^- + O_2 \rightarrow [M^{III}(CH_3SO_2)_3(O_2)]^- \quad (3)$$

$$[M^{III}(CH_3SO_2)_4]^- + H_2O \rightarrow [M^{III}(CH_3SO_2)_3(OH)]^- + CH_4 + SO_2 \quad (4)$$

The results for samarium are similar to those previously reported, except for the appearance of minor $[Sm^{III}(CH_3SO_2)_3(OH)]^-$.[30] The dominant CID reaction 2 corresponds to retention of the trivalent oxidation state with an anionic SO_2 anion ligand. Minor CID reaction 1 corresponds to reduction from Sm^{III} to Sm^{II} via loss of a CH_3SO_2 neutral ligand. In the previous study, reduction reaction 1 was observed only for Ln = Sm, Eu and Yb,[30] the three Ln with the highest $E^o(3/2)$ (see Figure 1). The addition of O_2 to oxidize Sm^{II} to Sm^{III} by formation of a superoxide complex with a formally O_2^- ligand was reported previously,[30] and has also been observed in the oxidation of $U^{V}O_2^+$ to $U^{VI}O_2(O_2)^+$.[35,36] The nature of the hydrolysis reaction, possibly reaction 4, is unknown and was not observed previously,[30] suggesting that the partial pressure of water was higher in the present experiments and/or the instrumental parameters were sufficiently different to enable a thermodynamically or kinetically unfavorable hydrolysis process. In contrast to the spontaneous oxygen-addition reaction that is described in detail below, the hydrolysis process occurs only under energetic CID conditions. It is suggested that a trivalent complex is responsible for the hydrolysis because it is also observed for M = Cm, which, as discussed below, does not exhibit reduction to Cm^{II}.

As is evident in Figure 2, the CID behavior of $[Cm^{III}(CH_3SO_2)_4]^-$ differs from that of $[Sm^{III}(CH_3SO_2)_4]^-$ in that neither reduction to $[Cm^{II}(CH_3SO_4)_3]^-$ nor subsequent addition of O_2 to yield $[Cm^{III}(CH_3SO_4)_3(O_2)]^-$ are observed. Rather only CH_3 elimination, reaction 2, and minor hydrolysis are observed. The retention of trivalent Cm is consistent with its low estimated III/II reduction potential (-3.7 V[1]). In previous work,[30] reduction was not observed for any $[Ln^{III}(CH_3SO_4)_4]^-$ complex comprising a Ln with a III/II reduction potential lower than that of Sm (-1.55 V[1]; see Figure 1). The present CID results for the curium complex are in accord with the estimated $Cm^{III/II}$ reduction potential and indicate that, as for the lanthanides, it is the propensity towards reduction that determines the CID fragmentation behavior of $[An^{III}(CH_3SO_2)_4]^-$ complexes.

The primary goal of this work was to assess the redox character of Cf^{3+} and particularly to compare the trivalent/divalent chemistries of Cf and Sm, which have comparable reported III/II reduction potentials. The CID results for $[Cf^{III}(CH_3SO_2)_4]^-$ are included in Figure 2. The similarity to the CID spectrum for $[Sm^{III}(CH_3SO_2)_4]^-$, and the disparity from that for $[Cm^{III}(CH_3SO_2)_4]^-$, is readily apparent. Although CH_3 elimination reaction 2 is dominant, as for the Sm complex, the same divalent chemistry, reaction 1 to yield $[Cf^{II}(CH_3SO_4)_3]^-$ and subsequent oxidation reaction 3 to yield $[Cf^{III}(CH_3SO_4)_3(O_2)]^-$, is apparent. Also evident is the minor hydrolysis product $[Cf^{III}(CH_3SO_2)_3(OH)]^-$.

The comparable CID results for $[Cf^{III}(CH_3SO_2)_4]^-$ and $[Sm^{III}(CH_3SO_2)_4]^-$ indicate that the III/II reduction potentials are indeed similar for Cf and Sm. This result provides strong comparative evidence that for both the actinides and the lanthanides it is the III/II reduction potential that determines whether reduction in gas-phase complexes occurs. That the chemistry of Cf and Sm are essentially the same in this system suggests that there is not a substantial contribution from covalent bonding in the Cf complexes. Although Cf^{III} complexes in which californium is coordinated by oxygen have been reported,[15,37] there are no such reports of a Cf^{II} complex. With the synthesis of a Cf^{II} methanesulfinate in the gas phase and the demonstrated similarity to the chemistry of Sm, it appears that it should be feasible to synthesize condensed phase Cf^{II} complexes having oxygen coordination.

O_2-addition to $[M^{II}(CH_3SO_2)_3]^-$, and replacement of SO_2 by O_2 in $[M^{III}(CH_3SO_2)_3(SO_2)]^-$

Oxygen-addition reaction 3 was observed under CID conditions. To confirm that this is not a high-energy process, the CID products from reaction 1, $[M^{II}(CH_3SO_2)_3]^-$, were isolated and allowed to react with background gases in the ion trap, with the results shown in Figure 3. It is apparent that both $[Cf^{II}(CH_3SO_2)_3]^-$ and $[Sm^{II}(CH_3SO_2)_3]^-$ add O_2 at roughly comparable rates. This phenomenon has been observed for $U^VO_2^+$ and is attributed to formation of a superoxide with oxidation to $U^{VI}O_2(O_2)^+$.[35,36] The U^{VI}/U^V reduction potential, +0.09 V,[4] is ~1.5 V higher than the Cf^{III}/Cf^{II} and Sm^{III}/Sm^{II} reduction potentials[1] such that oxidation of Cf^{II} and Sm^{II} should be more facile than oxidation of U^V. The observed oxidative addition of O_2 to yield $[M^{III}(CH_3SO_2)_3(O_2)]^-$ follows in the same manner as the previous results for uranyl.

The reaction of $[M^{III}(CH_3SO_2)_3(SO_2)]^-$ with O_2 was also studied by isolating the CH_3 elimination products from CID reaction 2 and allowing them to react with background gases in the ion trap. The results, shown in Figure 4, reveal that SO_2 is spontaneously replaced by O_2

according to reaction 5 for all three M = Cf, Sm and Cm, with roughly comparable efficiencies. This replacement phenomenon was previously observed for $[Ln^{III}(CH_3SO_2)_3(SO_2)]^-$ including for Ln = Sm.[30] Given the confidence of a trivalent oxidation state in $[M^{III}(CH_3SO_2)_3(SO_2)]^-$, particularly in $[Cm^{III}(CH_3SO_2)_3(SO_2)]^-$ for which no other oxidation states are reasonably feasible,[4] the substitution reaction provides evidence for a superoxide, $[M^{III}(CH_3SO_2)_2(O_2)]^-$, with no change in oxidation state.

$$[M^{III}(CH_3SO_2)_3(SO_2)]^- + O_2 \rightarrow [M^{III}(CH_3SO_2)_2(O_2)]^- + SO_2 \qquad (5)$$

The electron affinity of O_2, EA[O_2] = 0.4 eV, is substantially lower than that of SO_2, EA[SO_2] = 1.1 eV.[38] If the ligands are essentially anionic O_2^- and SO_2^-, then the ligand with the higher EA should preferentially bind. The result that O_2 replaces SO_2 indicates stronger binding of the former, indicating that the bonding is more than a simple electrostatic interaction between anionic ligands and cationic metals. The stronger binding of O_2 suggests that a partial covalent character which enhances the binding strength may exist in the superoxide complexes.

Summary and Conclusions

Gas-phase chemistry has been employed to further explore the chemistry of californium. Cf is of particular interest as this is the turning point in the actinide series at which divalent chemistry becomes significant. Although divalent Cf chemistry is established, knowledge of this chemistry is very limited due to the experimental challenges in working with this scarce and highly-radioactive synthetic element. Furthermore, the theoretical and computational chemistry of Cf also presents challenges as a result of the number and configuration of the electrons that need to be treated to obtain accurate results at this transition point in the actinide series. In the present work the first complex in which Cf^{II} is coordinated by oxygen-donor ligands was prepared, in the gas-phase by reductive fragmentation of $[Cf^{III}(CH_3SO_2)_4]^-$ to yield $[Cf^{II}(CH_3SO_2)_3]^-$.

Comparison of fragmentation of $[M^{III}(CH_3SO_2)_4]^-$ for M = Cf, Sm and Cm revealed very similar behavior for the Cf and Sm complexes with reduction to the divalent state clearly apparent for both. In contrast, the Cm complex retained the trivalent oxidation state. These results are in accord with the comparable III/II reduction potentials for Cf and Sm, which are much higher than that for Cm. The gas-phase reduction chemistry of Cf is well-predicted from the Cf^{3+} reduction potential, indicating that the bonding in both the lanthanide and actinide methanesulfinate complexes is primarily electrostatic.

The successful production of a Cf^{II} coordination complex in the gas phase under the same conditions as for the corresponding Sm^{II} complex suggests that it should be possible to substantially expand the condensed-phase divalent chemistry of Cf, such as has been achieved for Sm. The reported reduction potential for Es^{3+} is similar to that of Cf^{3+}.[1] Examining gas-phase chemistry for the corresponding Es complexes would establish the validity of the reported $E^o(3/2)$, and the relationship between reduction in solution and that in coordination complexes.

Curium was employed in the present work as an actinide with a particularly low III/II reduction potential. Referring to Figure 1, it is apparent that the chemistry of $[Am^{III}(CH_3SO_2)_4]^-$ would be of special interest because of the substantially higher reduction potential of Am^{III}; this complex was not available for the present study but is a target for future work. Although extending such studies beyond Cf becomes increasingly challenging, gas-phase chemistry would serve as an excellent means to further explore the increasingly divalent nature of the heaviest actinides (Fig. 1). It may not be possible to prepare a trivalent No complex by ESI but it may be feasible to oxidize a No^{II} complex to a No^{III} complex with an adequately effective electron donor ligand such as NO_2.[39]

Supporting Information

ESI mass spectra of the two methanesulfinate solutions, Cf^{3+}/Cm^{3+} and Sm^{3+}. CID mass spectra showing sodium cluster contamination in the peaks corresponding to $[Cm^{III}(CH_3SO_2)_4]^-$ and $[Cf^{III}(CH_3SO_2)_4]^-$.

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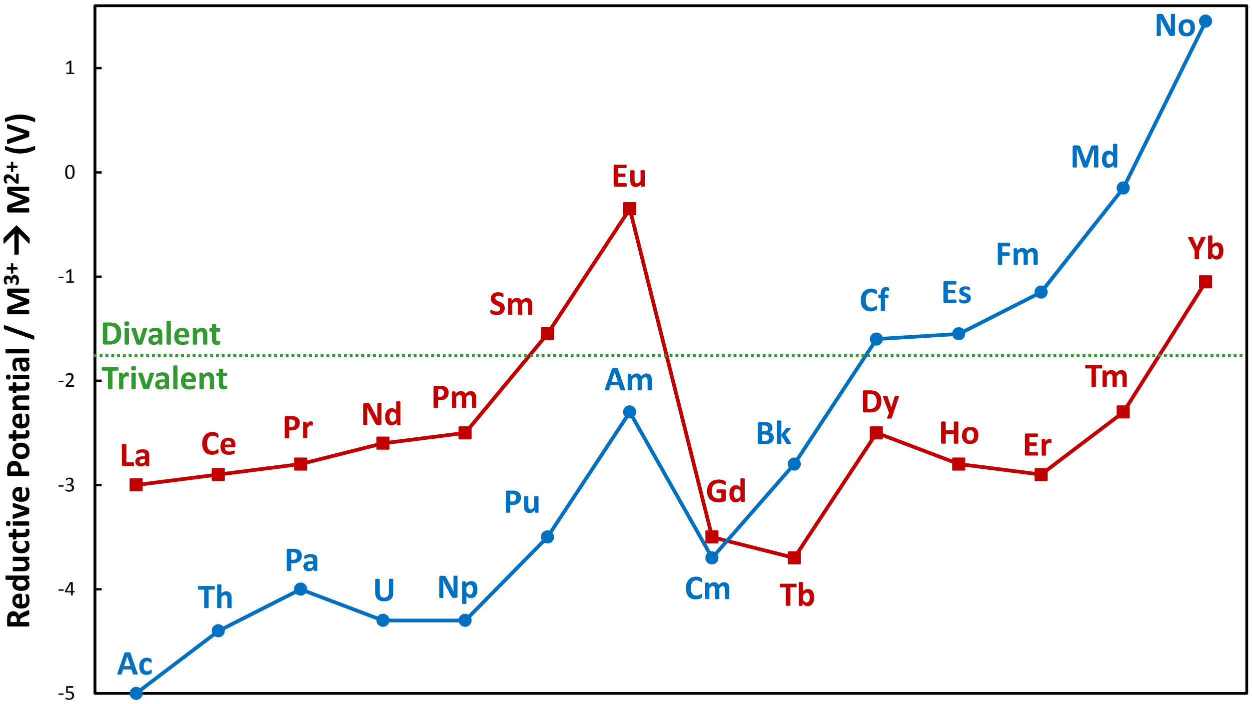


Figure 1. Standard M^{3+}/M^{2+} reduction potentials for the homologous Ln^{3+} (red) and An^{3+} (blue) ions.[1] The horizontal dotted green line indicates the separation between those lanthanides that exhibit divalent chemistry according to reaction 1 from those that retain the trivalent oxidation state.

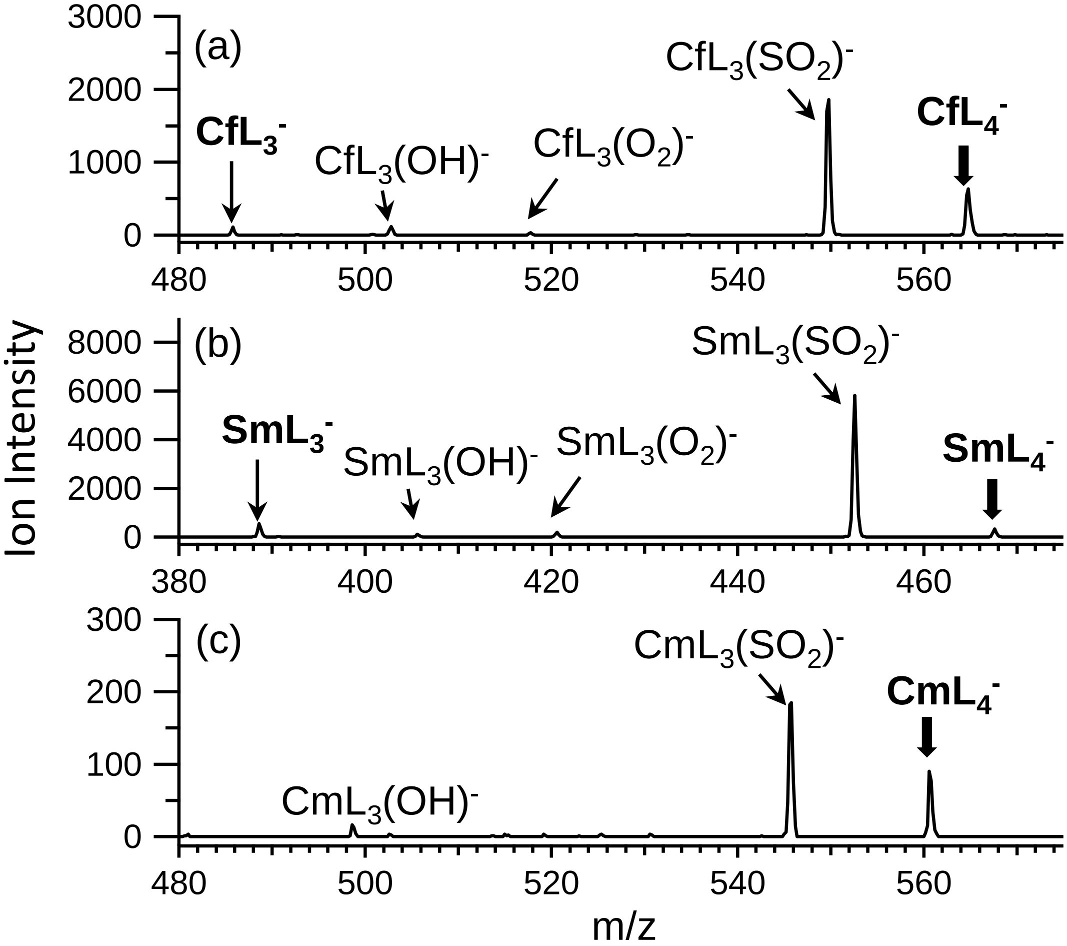


Figure 2. CID mass spectra of $[M^{III}(CH_3SO_2)_4]^-$ for (a) M = Cf; (b) M = Sm; and (c) M = Cm (indicated by red arrows; L = (CH_3SO_2). The identified products are $[M^{III}(CH_3SO_2)_3(SO_2)]^-$; $[M^{II}(CH_3SO_2)_3]^-$; $[M^{III}(CH_3SO_2)_3(OH)]^-$; and $[M^{III}(CH_3SO_2)_3(O_2)]^-$. The peaks at m/z corresponding to CfL_4^-, and more so CmL_4^-, contain substantial sodium complex impurities, as is shown in Fig. S2.

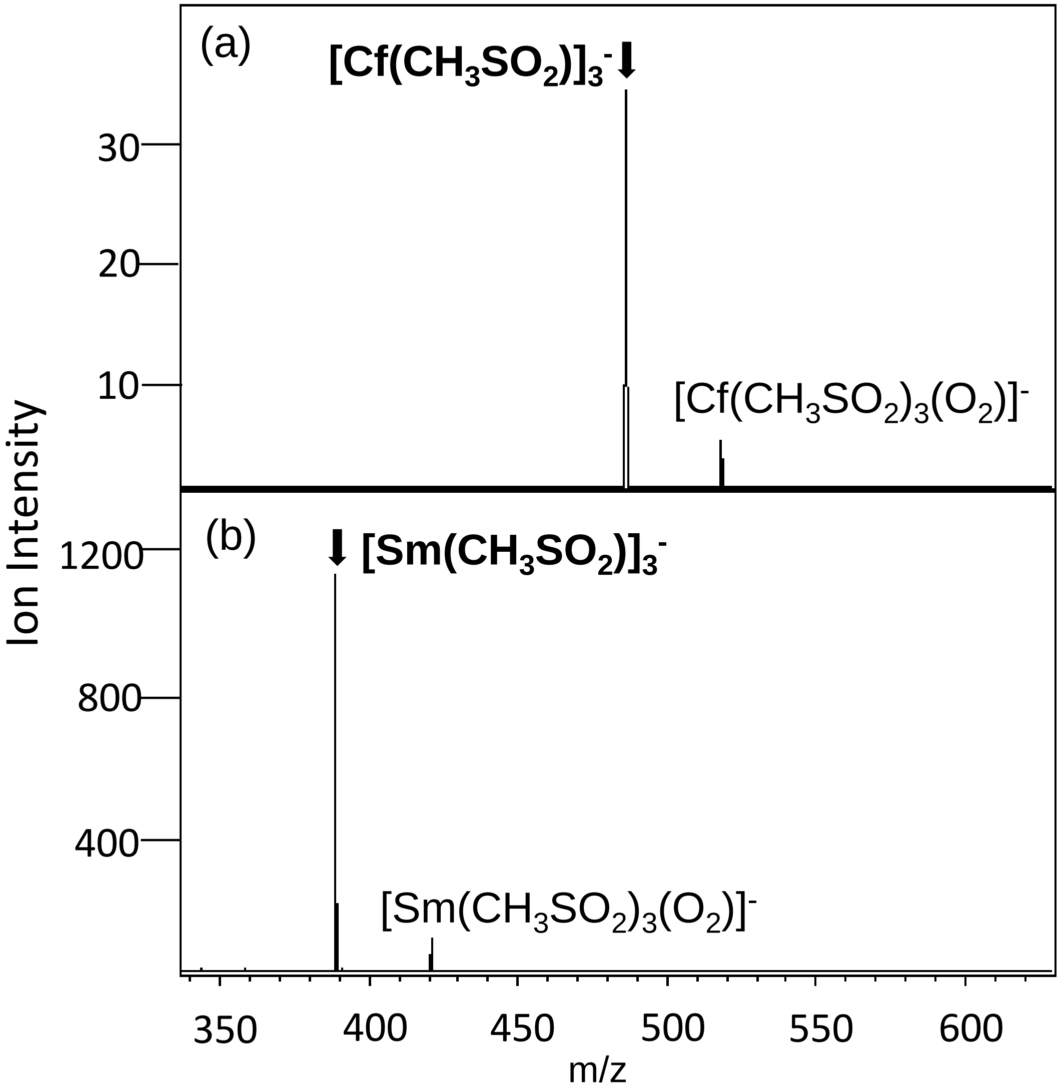


Figure 3. Mass spectra acquired after exposure of isolated (a) $[Cf^{II}(CH_3SO_2)_3]^-$ and (b) $[Sm^{II}(CH_3SO_2)_3]^-$ after exposure to background gases in the ion trap for 50 ms. As is evident from the y-axis scales, the absolute intensity of the $[Cf^{II}(CH_3SO_2)_3]^-$ peak is only ~3% of that of the $[Sm^{II}(CH_3SO_2)_3]^-$ peak.

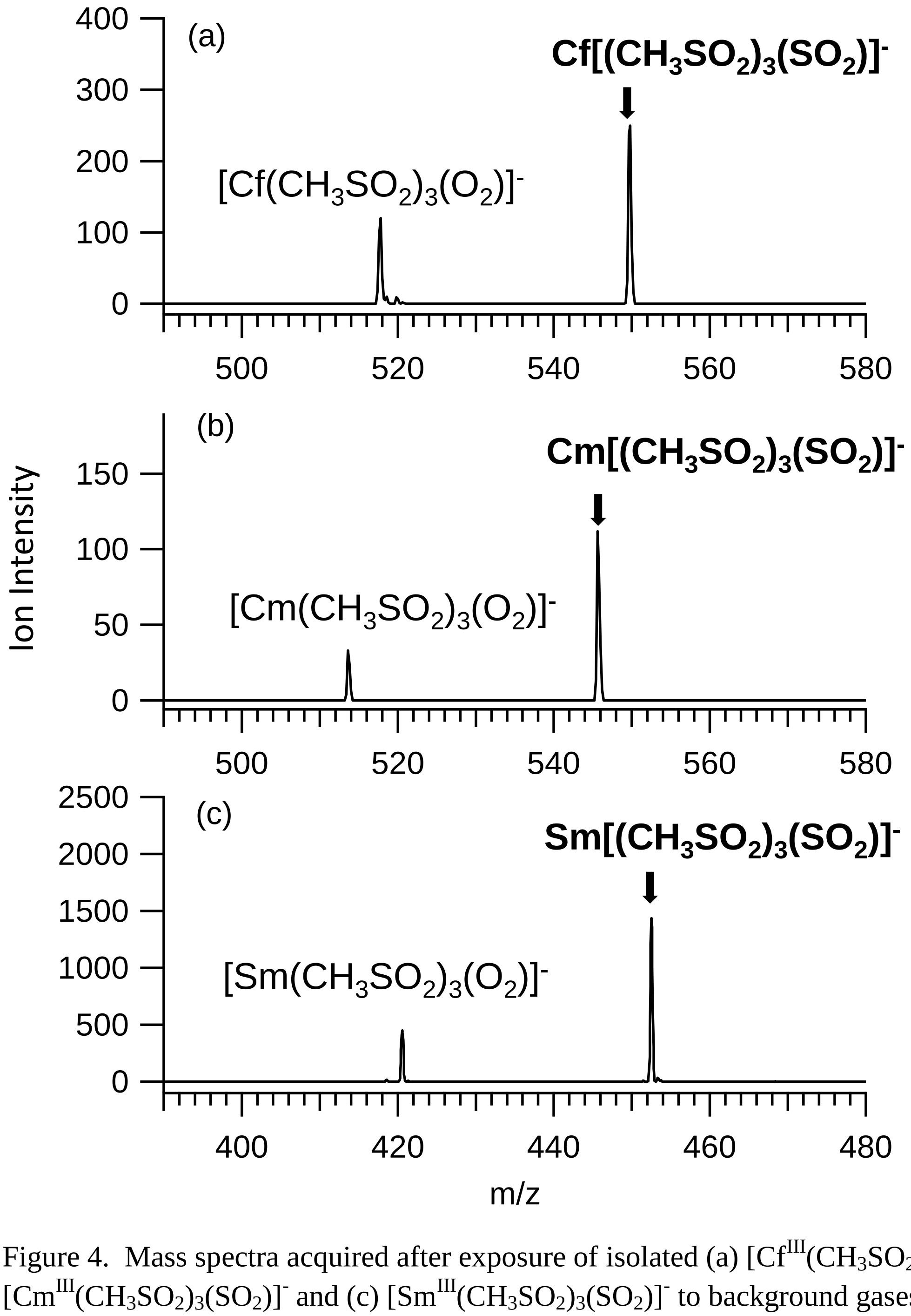
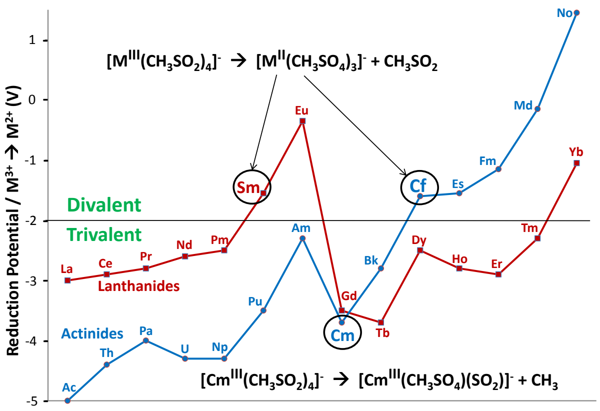


Figure 4. Mass spectra acquired after exposure of isolated (a) $[Cf^{III}(CH_3SO_2)_3(SO_2)]^-$, (b) $[Cm^{III}(CH_3SO_2)_3(SO_2)]^-$ and (c) $[Sm^{III}(CH_3SO_2)_3(SO_2)]^-$ to background gases in the ion trap for 500 ms.

TOC Graphic



Ambivalent Californium: Coordination chemistry of scarce and radioactive Cf, a heavy actinide, is explored in the gas-phase. Discrete Cf coordination complexes reveal both trivalent and divalent chemistry, like samarium among the lanthanides. The results reveal the key position of Cf in the actinide series, at which divalent chemistry becomes significant.