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Electrospray Production and Collisional Dissociation of Lanthanide/Methylsulfonyl Anion Complexes: Sulfur Dioxide Anion as a Ligand

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**Abstract**

Gas-phase lanthanide-SO$_2$ complexes, Ln(CH$_3$SO$_2$)$_3$(SO$_2$)$^-$, were produced by collision induced dissociation (CID) of Ln(CH$_3$SO$_2$)$_4$$^-$ precursors prepared by electrospray ionization. For all lanthanides except Eu, CID of Ln(CH$_3$SO$_2$)$_4$$^-$ resulted in CH$_3$ loss to form Ln(CH$_3$SO$_2$)$_3$(SO$_2$)$^-$, which spontaneously react with O$_2$ to form Ln(CH$_3$SO$_2$)$_3$(O$_2$)$^-$; CID of Eu(CH$_3$SO$_2$)$_4$$^-$ produced only Eu(CH$_3$SO$_2$)$_3$$^-$, with reduction from Eu(III) to Eu(II). For Ln = Yb and Sm, the Ln(CH$_3$SO$_2$)$_4$$^-$ underwent neutral ligand loss to form Ln(CH$_3$SO$_2$)$_3$$^-$, which reacted with O$_2$ to yield Ln(CH$_3$SO$_2$)$_3$(O$_2$)$^-$, recovering the Ln(III) oxidation state. The CID results parallel condensed phase Ln$^{3+}$/Ln$^{2+}$ redox chemistry. Density functional theory (DFT) calculations on Ln(CH$_3$SO$_2$)$_3$(SO$_2$)$^-$ for Ln = La, Yb and Lu reveal that SO$_2$ acts as a bidentate oxygen bound ligand for doublet ground state La(CH$_3$SO$_2$)$_3$(SO$_2$)$^-$ and Lu(CH$_3$SO$_2$)$_3$(SO$_2$)$^-$, while the ground state for Yb(CH$_3$SO$_2$)$_3$(SO$_2$)$^-$ is an open-shell singlet with a monodentate SO$_2$ ligand. Loss of CH$_3$ is computed to be much more favorable than neutral ligand loss for La(CH$_3$SO$_2$)$_4$$^-$ and Lu(CH$_3$SO$_2$)$_4$$, whereas both channels are comparable in energy for Yb(CH$_3$SO$_2$)$_4$, in accord with the experiments. DFT results for fragmentation of Cu(CH$_3$SO$_2$)$_2$ reveal that formation of the organometallic complex, Cu(CH$_3$SO$_2$)(CH$_3$)$^-$, is energetically most favorable, in agreement with contrasting fragmentation pathways of copper and lanthanide complexes.

**Keywords:** collision induced dissociation; lanthanide complexes; methane sulfinate; sulfur dioxide anion; density functional theory; divalent lanthanides
Introduction

The coordination chemistry of SO$_2$ has been well developed in recent years due to interest in weakly coordinated complexes,\(^1\) as well as in materials for SO$_2$ sensors, which require reversible binding of SO$_2$.\(^2,3\) Among the coordination complexes whose structures and properties have been well defined, main group elements and electron rich transition metals have been the primary focus,\(^1,4,5\) while lanthanides have received less attention. Reactions of lanthanides with AsF$_5$ in liquid SO$_2$ results in the formation of polymeric lanthanide-SO$_2$ adducts.\(^6\) Discrete molecular SO$_2$ complexes containing lanthanides were unknown until the recent report of the synthesis of several cone-type lanthanide complexes, in which both oxygen atoms of each of the SO$_2$ moieties are bound to a lanthanide metal center protected by a bulky ligand.\(^7\)

It is possible to form unique coordination complexes in the gas phase by using appropriate precursor ligands that can undergo fragmentation upon low-energy collision induced dissociation (CID).\(^8,9\) Recently, we demonstrated that CID of UO$_2$(CH$_3$SO$_2$)$_2$\(^-\) resulted in CH$_3$ loss to produce UO$_2$(CH$_3$SO$_2$)(SO$_2$)$^-$, in which the SO$_2$ ligand is coordinated to uranium by both oxygen atoms.\(^10\) This is quite different from the fragmentation patterns observed by O’Hair and co-workers during CID of a copper complex having the CH$_3$SO$_2$ ligand: loss of SO$_2$ to form an organocopper complex was observed.\(^11\) Since uranyl is a hard acid,\(^12\) as are the lanthanides, it should be possible to prepare lanthanide-SO$_2$ adducts using the same fragmentation approach applied to UO$_2$(CH$_3$SO$_2$)$_2$\(^-\). In the work reported here, Ln(CH$_3$SO$_2$)$_4$\(^-\) anions for all the lanthanides (except Pm) were prepared by electrospray ionization (ESI) of solutions containing a lanthanide halide and CH$_3$SO$_2$Na. A goal was to discern if CID of these gas-phase complexes reveal essential variations in chemistry across the lanthanide series, particularly differences in the relative stabilities of the trivalent and divalent oxidation states. Density functional theory (DFT) computations were performed on selected complexes to understand the observed chemistry. Fragmentation pathways for complexes of copper with the CH$_3$SO$_2$$^-$ ligand were also computed to illuminate the disparate fragmentation behavior of complexes of the “hard” lanthanides and “soft” late transition metals.

Experimental and Computational Details

All experiments were performed using an Agilent 6340 quadrupole ion trap mass spectrometer (QIT/MS).\(^13\) The Ln(CH$_3$SO$_2$)$_4$\(^-\) anions were produced by ESI of methanol (<5%
water) solutions of CH$_3$SO$_2$Na (Sigma-Aldrich) and LnX$_3$ (X=Cl or Br, 200 μM) (Sigma-Aldrich) with about 4:1 molar excess CH$_3$SO$_2$Na. The MS$^9$ capabilities of the QIT/MS allow isolation of ions with a particular m/z, followed by CID in which ions are excited and undergo multiple low-energy collisions with helium. The reported CID results correspond to an applied voltage of 0.6 V for 40 ms. Experiments employing different CID voltages and/or times resulted in changes in product yields but no discernable changes in fragmentation products; specifically, the distinctive products observed for the Sm, Eu and Yb complexes were not observed for other lanthanides. The consistency of results upon varying the CID conditions indicates that the results are phenomenological, not instrumental, as has been demonstrated in analogous studies by O’Hair and co-workers,$^8$,$^9$,$^{11}$ as well as in previous work performed by our group.$^{10,14-16}$ In the present study the ion intensities were sufficient to perform CID of ions produced by ESI, i.e., MS$^2$, but the fragment ion intensities were insufficient to perform sequential CID, i.e, MS$^3$. The ions isolated inside the trap from the ESI source are at a temperature around 300 K.$^{17}$ In high resolution mode, the instrument has a detection range of m/z 20–2200 with a mass width (FWHM) of m/z ≈ 0.3. The intensity distribution of ions in the mass spectra was highly dependent on instrumental parameters, particularly the RF voltage applied to the ion trap; the parameters were essentially as employed in previous experiments.$^{10}$ The high-purity nitrogen gas for nebulization and drying in the ion transfer capillary was the boil-off from a liquid nitrogen Dewar. As has been discussed elsewhere,$^{18}$,$^{19}$ the background H$_2$O and O$_2$ pressures in the ion trap are estimated to be on the order of 10$^{-6}$ Torr. The helium buffer gas pressure in the trap is constant at ~10$^{-4}$ Torr.

Geometry optimizations and frequency calculations were performed using the PBE functional (exchange and correlation)$^{20}$ together with triple zeta basis sets and the zero-order regular approximation (ZORA), as implemented in the ADF2009.01 package.$^{21,22}$ The frozen core approximation was used for the lanthanide atoms (up to 4d), and for Cu, S, O and C atoms (up to 2p). This level of theory is referred to as PBE-ZORA/TZ2P. Single point computations were performed using the M06-L functional$^{23}$ in combination with the small-core Stuttgart-Dresden pseudopotentials (SDD) for the Ln and Cu atoms,$^{24}$ and 6-311++G(2d,p) basis sets for the rest of the atoms, using the Gaussian09 Rev B.01 program (M06-L/SDD). The M06-L functional has shown good performance in systems containing transition and heavier metals, according to previous reports in literature.$^{25,26}$ Moreover, we have found good performance in the
estimation of LnO and LnO\(^+\) bond dissociation energies for Ln = La, Lu (see Tables S1 and S2 and a brief discussion regarding the choice of the level of theory in Supporting Information). All reported energies (M06-L/SDD//PBE-ZORA/TZ2P) include the zero point vibrational energy corrections at 0 K. Quantum Theory of Atoms in Molecules (QTAIM) analysis was performed on the studied Ln(CH\(_3\)SO\(_2\))\(_3\)(CH\(_3\))\(^+\) ions and, for comparison, on Cu(CH\(_3\)SO\(_2\))(CH\(_3\))\(^-\).\(^{27}\) Wave-function extended files (wfx) were obtained with Gaussian09 at the M06-L/SDD level and analyzed using the AIMAll package.\(^{28}\) The electron density (\(\rho\))BCP\), the Laplacian of electron density (\(\nabla^2\rho\)) and total energy density (\(H\))BCP\) of the Ln-C (and Cu-C) bond critical points are included as Supporting Information (Table S3).

**Results and Discussion**

**ESI and CID Mass Spectra**

The ESI mass spectra of solutions containing LnX\(_3\) and CH\(_3\)SO\(_2\)Na, shown in Figures 1 and 2, revealed a series of peaks over a wide m/z range. In addition to peaks due to Na\(_x\)(CH\(_3\)SO\(_2\))\(_{3x+1}\), which is common in ESI experiments with CH\(_3\)SO\(_2\)Na,\(^{10}\) metal complex peaks such as Ln(CH\(_3\)SO\(_2\))\(_4\) and Ln(CH\(_3\)SO\(_2\))\(_4\)(CH\(_3\)SO\(_2\)Na)\(_x\) dominate the spectra. Since the CH\(_3\)SO\(_2\)\(^-\) anion can be oxidized to CH\(_3\)SO\(_3\),\(^{29}\) weak peaks attributed to species comprising CH\(_3\)SO\(_3\) were also present in the spectra. The Ln(CH\(_3\)SO\(_2\))\(_4\)\(^-\) anions of particular interest were mass selected and subjected to CID. As shown in Figure 3, CID of all the Ln(CH\(_3\)SO\(_2\))\(_4\)\(^-\) complexes (except Ln = Eu) resulted in the appearance of a peak 15 m/z lower than Ln(CH\(_3\)SO\(_2\))\(_4\)\(^-\), which corresponds to CH\(_3\) loss and the formation of Ln(CH\(_3\)SO\(_2\))\(_3\)(SO\(_2\))\(^-\). In contrast, loss of a neutral CH\(_3\)SO\(_2\) ligand to form Eu(CH\(_3\)SO\(_2\))\(_3\)\(^-\) was the only fragmentation channel for Eu(CH\(_3\)SO\(_2\))\(_4\); a secondary product, Eu(CH\(_3\)SO\(_2\))\(_2\)(SO\(_2\))\(^-\), was formed when Eu(CH\(_3\)SO\(_2\))\(_3\)\(^-\) underwent CH\(_3\) loss upon CID. Products arising from neutral ligand loss were also observed for Yb(CH\(_3\)SO\(_2\))\(_4\)\(^-\) and Sm(CH\(_3\)SO\(_2\))\(_4\)\(^-\). While both Yb(CH\(_3\)SO\(_2\))\(_3\)\(^-\) and Yb(CH\(_3\)SO\(_2\))\(_3\)(SO\(_2\))\(^-\) are major fragmentation products upon CID of Yb(CH\(_3\)SO\(_2\))\(_4\), the yield of Sm(CH\(_3\)SO\(_2\))\(_3\)(SO\(_2\))\(^-\) is much lower than that of Sm(CH\(_3\)SO\(_2\))\(_3\)(SO\(_2\))\(^-\). Ligand loss was not detected for other Ln(CH\(_3\)SO\(_2\))\(_4\)\(^-\) complexes.

**Computed Structures of Selected Complexes**

Lanthanide-dependent CID of Ln(CH\(_3\)SO\(_2\))\(_4\)\(^-\) reveals the influence of the metal centers on gas-phase fragmentation chemistry. To get further insights into the fragmentation reactions, DFT calculations were carried out on the structures and dissociation reaction thermodynamics of Ln(CH\(_3\)SO\(_2\))\(_4\)\(^-\) for La, Yb, and Lu. We selected La and Lu as representative of the lanthanide ions
that favor trivalency and have, respectively, the largest and smallest Ln\(^{3+}\) ionic radii, and Yb as a representative lanthanide with a greater propensity towards divalent chemistry. Comprehensive computations for all of the Ln complexes, were beyond the scope of this effort; the DFT results for these representative cases provide insights into the overall experimental results. For comparison, and specifically to understand the differing chemistries of Ln and Cu, the same dissociation reactions were analyzed by DFT for Cu(CH\(_3\)SO\(_2\))\(_2\)^-\(\). The optimized geometrical parameters of the initial complexes and dissociation products are shown in Figure 4. More information regarding geometrical parameters and electronic states of the ground-state structures and of some relevant higher-energy lanthanide isomers, as well as copper complexes, are included as Supporting Information (Figures S2 to S5). Both La(CH\(_3\)SO\(_2\))\(_4\) and Lu(CH\(_3\)SO\(_2\))\(_4\)\(^-\) have singlet ground spin states with all the CH\(_3\)SO\(_2\)\(^-\) ligands having bidentate coordination to the metal center via oxygen atoms. A similar geometry was obtained for the Yb(CH\(_3\)SO\(_2\))\(_4\)\(^-\) doublet ground spin state. For the CH\(_3\)-loss product, isomers very close in energy and differing only in the coordination mode of SO\(_2\) (bidentate vs. monodentate) were located. The La(CH\(_3\)SO\(_2\))\(_3\)(SO\(_2\))\(^-\) doublet spin GS structure is characterized by a bidentate SO\(_2\) ligand, whereas the lowest-energy SO\(_2\) monodentate isomer is only 17 kJ.mol\(^{-1}\) higher in energy. The Lu(CH\(_3\)SO\(_2\))\(_3\)(SO\(_2\))\(^-\) doublet spin GS isomer also has a bidentate SO\(_2\) ligand and is almost degenerate in energy (within 7 kJ.mol\(^{-1}\)) with the monodentate SO\(_2\) isomer. In the case of Yb(CH\(_3\)SO\(_2\))\(_3\)(SO\(_2\))\(^-\) a number of singlet and triplet spin state mono- and bidentate isomers were located within a range of 70 kJ.mol\(^{-1}\). At the level of theory used here, the lowest-energy structure corresponds to a singlet open-shell structure with a monodentate SO\(_2\) ligand. The spin density corresponding to an unpaired electron was found to be delocalized on the SO\(_2\) moiety in all the Ln(CH\(_3\)SO\(_2\))\(_3\)(SO\(_2\))\(^-\) isomers. Moreover, the S-O bond distances in the SO\(_2\) ligands of La(CH\(_3\)SO\(_2\))\(_3\)(SO\(_2\))\(^-\) and Lu(CH\(_3\)SO\(_2\))\(_3\)(SO\(_2\))\(^-\) (Figures S2 and S4) are ca. 0.02 Å and 0.09 Å longer than those computed for isolated SO\(_2\)\(^-\) (1.524 Å at the present level of theory) and SO\(_2\) (1.459 Å), respectively. Hence, both the La(CH\(_3\)SO\(_2\))\(_3\)(SO\(_2\))\(^-\) and Lu(CH\(_3\)SO\(_2\))\(_3\)(SO\(_2\))\(^-\) complexes are considered as a trivalent lanthanide cation coordinated by three CH\(_3\)SO\(_2\)\(^-\) ligands and one SO\(_2\)\(^-\) ligand, similar to the UO\(_2\)(CH\(_3\)SO\(_2\))(SO\(_2\))\(^-\) complex.\(^10\) Although the two S-O bond lengths of SO\(_2\) in Yb(CH\(_3\)SO\(_2\))\(_3\)(SO\(_2\))\(^-\) differ more than those in La(CH\(_3\)SO\(_2\))\(_3\)(SO\(_2\))\(^-\) and Lu(CH\(_3\)SO\(_2\))\(_3\)(SO\(_2\))\(^-\) due to the monodentate character of SO\(_2\) in the Yb complex, it is reasonable to consider the SO\(_2\) ligand
in \( \text{Yb(\text{CH}_3\text{SO}_2)_3(SO}_2^- \) as SO\(_2^-\) based on comparison with the bond lengths of neutral and anionic SO\(_2^-\) and on the spin density distribution.

*Computed Fragmentation Energies of Selected Complexes*

To understand the metal-dependence of the fragmentation patterns, computations were carried out for both CH\(_3\) loss (reaction 1) and ligand loss (reactions 2 and 3) for La(\text{CH}_3\text{SO}_2)_4^-, Yb(\text{CH}_3\text{SO}_2)_4^- and Lu(\text{CH}_3\text{SO}_2)_4^-.

Experimental results from O’Hair and co-workers indicate that CID of anionic Cu complexes favor the formation of the organometallic products, in striking contrast to the Ln homologues; for the Cu(\text{CH}_3\text{CO}_2)(\text{CH}_3\text{SO}_2)^- complex, CID reaction (4) was observed.\(^{11}\) Similarly, our experimental results for CID of Cu(\text{CH}_3\text{SO}_2)_2^- revealed the formation of Cu(\text{CH}_3\text{SO}_2)(\text{CH}_3)^-, in striking contrast to the homologous Ln complexes. Although the instrumental conditions may be somewhat different between the different experiments, this result demonstrates that the CID conditions employed here are such that the present results can be compared with those from O’Hair and co-workers. To obtain insight into the origin of the contrasting behavior of Ln and Cu we have computed possible CID reactions for Cu(\text{CH}_3\text{SO}_2)_2^- (Figure S5, Supporting Information).

\[
\begin{align*}
\text{Ln(\text{CH}_3\text{SO}_2)_4^-} & \rightarrow \text{Ln(\text{CH}_3\text{SO}_2)_3(SO}_2^-) + \text{CH}_3 \quad (1) \\
\text{Ln(\text{CH}_3\text{SO}_2)_4^-} & \rightarrow \text{Ln(\text{CH}_3\text{SO}_2)_3}^- + \text{CH}_3\text{OSO} \quad (2) \\
\text{Ln(\text{CH}_3\text{SO}_2)_4^-} & \rightarrow \text{Ln(\text{CH}_3\text{SO}_2)_3} + \text{CH}_3\text{SO}_2^- \quad (3) \\
\text{Cu(\text{CH}_3\text{CO}_2)(\text{CH}_3\text{SO}_2)^-} & \rightarrow \text{Cu(\text{CH}_3\text{CO}_2)(\text{CH}_3)^-} + \text{SO}_2 \quad (4)
\end{align*}
\]

As reported in Table 1, loss of CH\(_3\) is always less endothermic than both neutral and anionic CH\(_3\)SO\(_2\) ligand loss. Our computations indicate that the neutral methoxysulfanyl cis-CH\(_3\)OSO radical is 13 kJ.mol\(^{-1}\) more stable than the methysulfonyl CH\(_3\)SO\(_2\) isomer, which is in agreement with previous DFT (B3LYP/aug-cc-pVTZ,\(^{30}\) B3P86/aug-cc-pVTZ,\(^{30}\) B3LYP/6-311++G(d,p)\(^{31}\)) and ab-initio (G2(MP2)\(^{32}\), MP2/6-311++G(d,p)\(^{31}\), PMP4SDTQ/6-311G(d,p)/MP2/6-31G(d,p)\(^{33}\) and CCSD(T)/6-311++G(d,p)\(^{31}\) and CCSD(T)/Aug-cc-pV(Q+d)Z//CCSD(T)/6-311++G(2df,p)\(^{34}\)) computational results, which in all cases indicate the methoxysulfanyl isomer is the ground-state structure. Therefore, CH\(_3\)OSO is considered as the fragmentation product in reaction 2. Previous computational calculations have estimated the energy for rearrangement from CH\(_3\)SO\(_2\) to CH\(_3\)OSO to be between 98 and 222 kJ.mol\(^{-1}\),
depending on the level of theory.\textsuperscript{31,32} It is unlikely that such a rearrangement would occur under the present experimental conditions. However, in view of the small energy difference between the two isomers, interpretation of the results is not affected by consideration of the (slightly) lower-energy rearrangement isomer. The energies required for loss of CH$_3$SO$_2^-$ are 222-243 kJ.mol$^{-1}$ for the three computed Ln complexes, which are higher in energy than those for the CH$_3$-loss reaction. It is much more endothermic for La(CH$_3$SO$_2$)$_4^-$ and Lu(CH$_3$SO$_2$)$_4^-$ to lose a neutral CH$_3$OSO ligand, processes computed to be endothermic by more than 400 kJ.mol$^{-1}$. In contrast, neutral ligand loss for Yb(CH$_3$SO$_2$)$_4^-$ is endothermic by only 203 kJ.mol$^{-1}$, 20 kJ.mol$^{-1}$ lower in energy than the loss of anionic CH$_3$SO$_2^-$. As shown in reactions 2 and 3, neutral CH$_3$OSO loss results in the formation of Ln(CH$_3$SO$_2$)$_3^-$ with a divalent Ln(II), whereas neutral Ln(CH$_3$SO$_2$)$_3^-$ with a trivalent Ln(III) is formed upon CH$_3$SO$_2^-$ loss. For lanthanides, the oxidation state Ln(III) is accessible in all cases, while the oxidation state Ln(II) is most commonly observed for Ln = Eu, Yb and Sm.\textsuperscript{35} As the CID results reveal, it is more favorable to form complexes retaining the Ln(III) oxidation state for most of the lanthanides, with the exceptions of Eu, Yb and Sm. Our computed energetics for ligand loss reactions are in accord with this trend. Since loss of CH$_3$OSO to form Yb(CH$_3$SO$_2$)$_3^-$ is endothermic by only 203 kJ.mol$^{-1}$, this fragmentation channel becomes competitive with CH$_3$ loss, resulting in the experimental observation of both Yb(CH$_3$SO$_2$)$_3^-$ and Yb(CH$_3$SO$_2$)$_3$(SO$_2$). Based on the experimental results, it can be assumed that neutral CH$_3$OSO loss should be least endothermic for Eu(CH$_3$SO$_2$)$_3^-$, followed by Yb(CH$_3$SO$_2$)$_3^-$ and then Sm(CH$_3$SO$_2$)$_3^-$, in accord with the decreasing (more negative) reduction potentials from Eu$^{3+}$/Eu$^{2+}$ to Yb$^{3+}$/Yb$^{2+}$ to Sm$^{3+}$/Sm$^{2+}$.\textsuperscript{35} According to our computational results, loss of CH$_3$SO$_2^-$ is a possible fragmentation pathway; however, the low-mass cutoff of the QIT/MS in CID mode precludes its detection. Although it is hypothetically feasible to infer the formation of CH$_3$SO$_2^-$ based on a diminishment in the total ion intensity, this approach was not practical in the present work due to a substantial reduction in ion intensity upon CID as a result of ion loss from the trap not due to fragmentation; such substantial ion loss upon any type of ion manipulation is routinely observed in our instrument.

The fragmentation patterns of Ln(CH$_3$SO$_2$)$_4^-$ are quite different from those observed for copper complexes comprising the CH$_3$SO$_2^-$ ligand, for which loss of SO$_2$ is predominant.\textsuperscript{11} Our computations indicate that the thermodynamically most favorable fragmentation reaction for Cu(CH$_3$SO$_2$)$_2^-$ is loss of SO$_2$ with formation of Cu(CH$_3$SO$_2$)(CH$_3$)$_3^-$ (Table 1). This result is in
accord with results from O’Hair and co-workers,¹¹ and indicates that whereas the oxophilic lanthanides induce elimination of CH₃ to produce complexes with the SO₂⁻ ligand, copper contrastingly induces elimination of SO₂ to yield organocopper complexes. QTAIM bond analysis was performed on all the Ln(CH₃SO₂)(CH₃)⁺ (Ln = La, Yb and Lu) complexes and on Cu(CH₃SO₂)(CH₃)⁺ (Supporting Information, Table S3). The Ln-C bond critical point (bcp) has the characteristics of an ionic bond, with electron densities at the bond critical points (ρₐ) lower than 0.075 au., positive laplacians of the electron density at the BCPs (∇²ρₐ), and total electronic energy densities (Hₐ) that are very small and negative (between -0.0173 and -0.0025 au.). The delocalization indexes (DI) indicate that in all cases the number of electrons shared by the metal and oxygen atoms is very low (< 0.60 e⁻). The Cu-C bond characteristics are also mainly ionic in nature; however, the charge density at the bcp roughly doubles the La-C value and is almost three times higher than the Yb-C value. The delocalization number is also notably higher than the same value for the Ln-C bonds (i.e. DI (Cu,C) = 0.958). The negative partial (QTAIM) charge on the C atom involved in the Ln-C bond is significantly higher (ca. -0.50 e⁻) than the same quantity for the Cu-C bond (-0.15 e⁻).

The computations indicate that there are two isomers for the SO₂ loss products, as shown in reactions 5 and 6.

\[
\text{Ln(CH}_3\text{SO}_2\text{)}_4^- \rightarrow \text{Ln(CH}_3\text{SO}_2\text{)}_3(\text{CH}_3)^+ + \text{SO}_2 \quad (5)
\]

\[
\text{Ln(CH}_3\text{SO}_2\text{)}_4^- \rightarrow \text{Ln(CH}_3\text{SO}_2\text{)}_2(\text{CH}_3\text{SO})(\text{OCH}_3)^+ + \text{SO}_2 \quad (6)
\]

The Ln(CH₃SO₂)₂(CH₃SO)(OCH₃)⁺ isomers (Ln = La, Yb, Lu) are computed to be ca. 80-100 kJ.mol⁻¹ more stable than the Ln(CH₃SO₂)₃(CH₃) isomers, and reaction 6 is thus the most thermodynamically favorable among the five reactions considered. Although SO₂ loss was not observed, the barrier for the rearrangement of the hypothetical products of reactions 5 and 6 were computed. This evaluation provides a prototypical example of the role of kinetics in determining experimentally observed fragmentation pathways. Formation of the more stable Ln(CH₃SO₂)(CH₃SO)(OCH₃) isomer would involve a significant reorganization of the ligands, which results in substantial energy barriers (Figure 5). The transition state for the transformation between the two isomers, Ln(CH₃SO₂)₃(CH₃)⁺ → Ln(CH₃SO₂)₂(CH₃SO)(OCH₃)⁺, involve significant reaction barriers, between 187 and 203 kJ.mol⁻¹ (Figure 5). These barriers explain
why low-energy SO₂ elimination (reaction 6) was not observed. In contrast, CH₃ loss (reaction 1) is most likely barrierless, resulting in the appearance of SO₂ adducts despite the greater endothermicity of this process. Although the reaction pathways for the elimination of SO₂ were not analyzed in detail, the initial step for reaction 6 was studied for Ln = La, Lu. This process involves the transfer of the CH₃⁻ moiety from one of the ligands to an adjacent ligand, which consequently becomes monodentate. It was found that this process gives rise to significant energy barriers, i.e. the TS relative energies with respect to the Ln(CH₃SO₂)₄⁻ initial complex are higher than 300 kJ.mol⁻¹ (Supporting Information, figure S6). Despite that we have not studied the reaction barriers involved in a direct transfer of the CH₃ moiety to the Ln cation, we anticipate higher barriers than those reported in Figure S6 considering the higher endothermicity (i.e. between 75 and 101 kJ.mol⁻¹) involved in the formation of the lanthanide organometallic products (Table 1).

**Reactions with Background O₂**

When Ln(CH₃SO₂)₃(SO₂)⁻ was mass selected and allowed to react with background gases in the ion trap, a peak on the low m/z side of Ln(CH₃SO₂)₃(SO₂)⁻ (Ln = La-Lu, except Eu) appeared; the examples of Ln = Sm and Tm are shown in Figure 6. The difference of 32 m/z indicates that the new species is Ln(CH₃SO₂)₃(O₂)⁻, where the SO₂ ligand has been replaced by background O₂ in the ion trap. This process also results in the appearance of weak peaks (labeled D in Figure 3) during CID of Ln(CH₃SO₂)₄⁻. The yield of Ln(CH₃SO₂)₃(O₂)⁻ increases substantially when Ln(CH₃SO₂)₃(SO₂)⁻ is isolated and a reaction time of 0.3 s is applied (Figure 6), confirming the spontaneous formation of dioxygen complexes. Since Ln(III) is the most common oxidation state for all the lanthanides that form Ln(CH₃SO₂)₃(O₂)⁻, it is reasonable to assume that the O₂ ligand in this complex is a superoxide. Although the oxidation state IV is common for Ce, the rather high reduction potential for Ce(IV)/Ce(III) (1.72 V)⁴ makes it unlikely that Ce(CH₃SO₂)₃(O₂)⁻ is a Ce(IV) peroxo complex. Our recent investigations of the structure and reactivity of UO₂(CH₃SO₂)(SO₂)⁻ similarly revealed the formation of UO₂(CH₃SO₂)(O₂)⁻ during the reaction of O₂ with UO₂(CH₃SO₂)(SO₂)⁻.¹⁰ The O₂ ligand in this complex was characterized as peroxide on the basis of its bond length and vibrational frequency. In contrast to Ce, the very low reduction potential for U⁶⁺O₂²⁻/U⁵⁺O₂²⁻ (0.062V)³⁴ makes it relatively facile for U⁵⁺O₂²⁻ to be oxidized to U⁶⁺O₂²⁻ to yield a peroxide complex.
As shown in Figure 3, the CID behavior of Yb(CH$_3$SO$_2$)$_4^-$, Sm(CH$_3$SO$_2$)$_4^-$, and especially Eu(CH$_3$SO$_2$)$_4^-$, is quite different from the rest of the lanthanide analogs. While CID of Eu(CH$_3$SO$_2$)$_4^-$ resulted exclusively in Eu(CH$_3$SO$_2$)$_3^-$, the yields of Yb(CH$_3$SO$_2$)$_3^-$ and Sm(CH$_3$SO$_2$)$_3^-$ are lower. These three lanthanide complexes exhibit the oxidation state Ln(II), which might be oxidized to Ln(III) upon reaction with O$_2$. It has been demonstrated that U$^\text{VI}$O$_2^+$ is spontaneously oxidized to the superoxide U$^\text{V}$O$_2$(O$_2$)$^+$ by O$_2$ addition.$^{19}$ Given that the reduction potentials of the Ln$^{3+}$ ions are all below that of U$^\text{VI}$O$_2^+$,$^{35}$ it is predicted that spontaneous O$_2$ addition should similarly oxidize Ln(II) to Ln(III). The Eu(CH$_3$SO$_2$)$_3^-$ and Yb(CH$_3$SO$_2$)$_3^-$ complexes were mass selected to assess their reactivity towards O$_2$. The Eu(CH$_3$SO$_2$)$_3$(O$_2$)$^-$ and Yb(CH$_3$SO$_2$)$_3$(O$_2$)$^-$ complexes were apparent in the mass spectra after a reaction time of 0.5 s (Figure 7), but the yield of Eu(CH$_3$SO$_2$)$_3$(O$_2$)$^-$ was lower than that of Yb(CH$_3$SO$_2$)$_3$(O$_2$)$^-$.

No O$_2$ adduct was observed without applying a reaction delay; the intensities of the precursor reactant ions were too low to obtain meaningful time-dependent reaction kinetics. The apparently lower reactivity of the Eu(II) complex is consistent with the fact that the Eu$^{3+}$/Eu$^{2+}$ reduction potential is about 0.7 V higher than that of Yb$^{3+}$/Yb$^{2+}$,$^{35}$ though it should be noted that after CID thermalization may not be effective such that the observed relative reaction efficiencies could be attributable to differences in internal energy that result in differences in adduct stabilization, rather than intrinsic reactivities. It was not possible to mass select Sm(CH$_3$SO$_2$)$_3^-$ due to the low yield and multiple isotopes. However, based on the lower reduction potential of Sm$^{3+}$/Sm$^{2+}$, it should be more favorable for Sm(CH$_3$SO$_2$)$_3^-$ to undergo oxidation and form Sm(CH$_3$SO$_2$)$_3$(O$_2$)$^-$, which results in the peak labeled D in Figure 3 during CID of Sm(CH$_3$SO$_2$)$_4^+$. In view of the high O-atom affinity of most lanthanides there should be an energetic propensity for the formation of Ln=O bonds. Addition of O$_2$ to Ln(CH$_3$SO$_2$)$_3^-$ could hypothetically proceed via O-O bond cleavage to yield O=Ln(CH$_3$SO$_2$)$_2$(CH$_3$SO$_2$)$^-$, where CH$_3$SO$_2^-$ is a mesylate anion ligand. However, the oxidation state in this product would be Ln(IV), which is inaccessible for most lanthanides, particularly for Eu, Yb and Sm.$^{35}$

**Conclusions**

ESI of solutions containing lanthanide halides and CH$_3$SO$_2$Na resulted in the formation of Ln(CH$_3$SO$_2$)$_4^-$ in the gas phase. Subsequent CID of these complexes gave rise to Ln(CH$_3$SO$_2$)$_3$(SO$_2$)$^-$ via loss of CH$_3$ with the sole exception of Eu(CH$_3$SO$_2$)$_4^+$. DFT calculations
indicate that SO₂ acts as a bidentate ligand in La(CH₃SO₂)₃(SO₂)⁻ and Lu(CH₃SO₂)₃(SO₂)⁺, with doublet ground spin states; SO₂ monodentate isomers are close in energy (within 14kJ.mol⁻¹). The open-shell singlet Yb(CH₃SO₂)₃(SO₂)⁻ ground state has a monodentate SO₂ ligand. Based on the optimized geometrical parameters and the distribution of the spin density, it is concluded that the SO₂ ligand in these complexes is negatively charged, indicating that Ln(CH₃SO₂)₃(SO₂)⁻ should be considered as Ln(III) complexes. All of the Ln(CH₃SO₂)₃(SO₂)⁻ complexes spontaneously react with O₂ to form Ln(CH₃SO₂)₃(O₂)⁺, presumably Ln(III) superoxo complexes. CID of Eu(CH₃SO₂)₄⁻ distinctively resulted in only Eu(CH₃SO₂)₃⁺, with reduction from Eu(III) to Eu(II). Reduction was also observed upon CID of Yb(CH₃SO₂)₄⁻ and Sm(CH₃SO₂)₄⁻; the resulting Yb(CH₃SO₂)₃⁻ and Sm(CH₃SO₂)₃⁻ complexes exhibited O₂-addition to produce Yb(CH₃SO₂)₃(O₂)⁺ and Sm(CH₃SO₂)₃(O₂)⁺, in which the Ln(III) oxidation state is recovered. Computed energetics reveal that loss of CH₃ is much more favorable than reduction via neutral ligand loss for La(CH₃SO₂)₄⁻ and Lu(CH₃SO₂)₄⁻, whereas both channels are close in energy for Yb(CH₃SO₂)₄⁻, consistent with the experimental observations. Unobserved loss of SO₂ to form Ln(CH₃SO₂)₃(CH₃)⁺, or the lower-energy Ln(CH₃SO₂)₂(CH₃SO)(OCH₃)⁻ isomer, were also analyzed computationally. Despite that it is the least endothermic fragmentation channel, high energy barriers to yield Ln(CH₃SO₂)₂(CH₃SO)(OCH₃)⁻ render it inaccessible upon CID.

The results for the lanthanide complexes reflect the relative stabilities of the Ln(II) oxidation states, as indicated by the Ln³⁺/Ln²⁺ reduction potentials. The greatest propensity towards reduction was exhibited by Eu(III), with lesser reduction of Yb(III) and Sm(III), and no reduction of the other Ln(III). The computed energetics for reactions of La(III), Lu(III) and Yb(III) complexes are also in accord with the higher (less negative) Yb³⁺/Yb²⁺ reduction potential. The computed energetics for Cu(CH₃SO₂)₂⁻ are in accord with the formation of organocopper complexes. The chemistry of the Ln(CH₃SO₂)₄⁻ complexes, which do not form organolanthanides, reflects the “hard” oxophilic character of the lanthanides, in contrast to “softer” transition metals such as copper.

Changes in oxidation state of gas-phase complexes can be evaluated based on reduction potentials or ionization energies. In the present work we have considered the relative stabilities of the Ln(III) and Ln(II) oxidation states as indicated by the Ln³⁺/Ln²⁺ reduction potentials. Alternatively, comparisons can be made by considering the Ln²⁺→Ln³⁺ ionization energies (IE3), which generally correlate with the Ln³⁺/Ln²⁺ reduction potentials.³⁷,³⁸ Although usually a higher
IE3 predicts a higher Ln$^{3+}$/Ln$^{2+}$ reduction potential, there are deviations from this correlation. In particular, IE3[Yb] is ca. 0.1 V higher than IE3[Eu], whereas the Yb$^{3+}$/Yb$^{2+}$ reduction potential is ca. 0.7 V lower than the Eu$^{3+}$/Eu$^{2+}$ reduction potential. The present results suggest that it is the condensed phase redox behavior, i.e. the Ln$^{3+}$/Ln$^{2+}$ reduction potentials, rather than the gas-phase atomic ionization energies, which better predict behavior in gas-phase coordination complexes. This is consistent with the retention of chemical bonding, as opposed to electron removal by ionization, in coordination complexes, regardless of whether they are in gas or condensed phase.

Supporting Information
Computational details regarding the choice of level of theory; comparison between the computed and experimental LnO and LnO$^+$ bond dissociation energies for La, Yb and Lu; QTAIM analysis of Ln(CH$_3$SO$_2$)$_3$(CH$_3$)$^-$ (Ln = La, Yb, Lu) and the Cu(CH$_3$SO$_2$)(CH$_3$)$^-$ ground-state structures; $<S^2>$ and $<S^2>_A$ values for Yb species; ESI mass spectra of solutions of LnX$_3$ (X=Br for La, Ce, Pr, Nd, Sm and Gd; X=Cl for Eu) and CH$_3$SO$_2$Na; CID spectra of Ln(CH$_3$SO$_2$)$_4^-$ (Ln=Pr, Nd, Ho and Er); optimized structures of Ln(CH$_3$SO$_2$)$_4^-$ and their possible dissociation products for Ln = La, Yb and Lu; optimized structure of Cu(CH$_3$SO$_2$)$_2^-$ and its possible dissociation products; optimized xyz coordinates of all the reported structures.

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Table 1. Ln(CH$_3$SO$_2$)$_4^-$ and Cu(CH$_3$SO$_2$)$_2^-$ computed dissociation energies.$^a$

<table>
<thead>
<tr>
<th></th>
<th>CH$_3$ loss (reaction 1)</th>
<th>CH$_3$SO$_2$ loss (reaction 2)</th>
<th>CH$_3$SO$_2^-$ loss (reaction 3)</th>
<th>SO$_2$ loss with formation of Ln-CH$_3$ (reaction 5)</th>
<th>SO$_2$ loss with formation of Ln-OCH$_3$ (reaction 6)</th>
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<td>La(CH$_3$SO$_2$)$_4^-$</td>
<td>193</td>
<td>410</td>
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<td>Lu(CH$_3$SO$_2$)$_4^-$</td>
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<td>Cu(CH$_3$SO$_2$)$_2^-$</td>
<td>179</td>
<td>341</td>
<td>259</td>
<td>108</td>
<td>129</td>
</tr>
</tbody>
</table>

$^a$ Ln = La, Yb, Lu. Energies in kJ.mol$^{-1}$. M06-L/SDD single point calculations were performed on PBE-ZORA/TZ2P optimized structures (M06-L/SDD// PBE-ZORA/TZ2P).
Figure 1. ESI mass spectra for mixtures of LnX₃ (X=Br for La, Ce, Pr, Nd, Sm and Gd; X=Cl for Eu) and CH₃SO₂Na. A: CH₃SO₂(CH₃SO₂Na)ₓ (x=0-6); B: Ln(CH₃SO₂)₄(CH₃SO₂Na)ᵧ (y=0-2).
Figure 2. ESI mass spectra of mixtures of LnCl₃ (Ln=Tb-Lu) and CH₃SO₂Na. A: CH₃SO₂⁻(CH₃SO₂Na)ₙ (n=0-3); B: Ln(CH₃SO₂)₄(CH₃SO₂Na)ₙ⁻ (n=0-2).
Figure 3. CID mass spectra of selected Ln(CH$_3$SO$_2$)$_4^-$ (CID conditions: 0.6 V applied for 40 ms). A: Ln(CH$_3$SO$_2$)$_4$; B: Ln(CH$_3$SO$_2$)$_3$ (SO$_2$)$_2$; C: Ln(CH$_3$SO$_2$)$_3$; D: Ln(CH$_3$SO$_2$)$_3$(O$_2$)$_2^-$. The asterisked peak is due to Eu(CH$_3$SO$_2$)$_2$(SO$_2$)$_2^-$.
Figure 4. Selected geometrical parameters of Ln(CH$_3$SO$_2$)$_4^-$ and its dissociation products for Ln = La (bold), Yb, and Lu (italics). Distances are in angstroms.
Figure 5. (a) \( \text{Ln(CH}_3\text{SO}_2)_3(\text{CH}_3)^- \) and \( \text{Ln(CH}_3\text{SO}_2)_2(\text{OCH}_3)(\text{CH}_3\text{SO})^- \) isomers, and the connecting transition states at the M06-L/SDD/PBE-ZORA/TZ2P level of theory. TS imaginary frequencies are: 482i cm\(^{-1}\)(La), 517i cm\(^{-1}\)(Yb), and 503i cm\(^{-1}\)(Lu). Distances are in angstroms (La in bold and Lu in italics). (b) \( \text{Ln(CH}_3\text{SO}_2)_3(\text{CH}_3)^- \), \( \text{Ln(CH}_3\text{SO}_2)_2(\text{OCH}_3)(\text{CH}_3\text{SO})^- \) and TS relative energies—La in red, Yb in blue and Lu in green — with respect to the \( \text{Ln(CH}_3\text{SO}_2)_4^- \) initial complex.
Figure 6. Mass spectra of isolated Sm(\(\text{CH}_3\text{SO}_2\))_3(\text{SO}_2)^- (a) and Tm(\(\text{CH}_3\text{SO}_2\))_3(\text{SO}_2)^- (c). Spectra (b) and (d) were obtained after reactions of Sm(\(\text{CH}_3\text{SO}_2\))_3(\text{SO}_2)^- and Tm(\(\text{CH}_3\text{SO}_2\))_3(\text{SO}_2)^- with background O_2 in the ion trap for 0.3 s.
Figure 7. Mass spectra obtained after reactions of isolated Eu(CH$_3$SO$_2$)$_3^-$ and Yb(CH$_3$SO$_2$)$_3^-$ with background O$_2$ in the ion trap for 0.5 s.