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High-Resolution X-ray Photoelectron Spectroscopy of Organometallic $(C_5H_4SiMe_3)_3Ln^{III}$ and $[(C_5H_4SiMe_3)_3Ln^{III}]^{1-}$ Complexes (Ln = Sm, Eu, Gd, Tb)

Daniel N. Huh,[†] Jared P. Bruce,[†] Sree Ganesh Balasubramani, Sierra R. Ciccone, Filipp Furche,* John C. Hemminger,* and William J. Evans*



ABSTRACT: The capacity of X-ray photoelectron spectroscopy (XPS) to provide information on the electronic structure of molecular organometallic complexes of Ln(II) ions (Ln = lanthanide) has been examined for the first time. XPS spectra were obtained on the air-sensitive molecular trivalent $4f^n$ Cp'₃Ln^{III} complexes (Ln = Sm, Eu, Gd, Tb; Cp' = C₅H₄SiMe₃) and compared to those of the highly reactive divalent complexes, [K(crypt)]-[Cp'₃Ln^{III}] (crypt = 2.2.2-cryptand), which have either $4f^{n+1}$ (Sm, Eu) or $4f^n$ Sd¹ electron configurations (Gd, Tb). The Ln 4d, Si 2p, and C 1s regions of the Ln(III) and Ln(II) complexes were identified and compared. The metal 4d peaks of these molecular lanthanide complexes were used diagnostically to compare oxidation states. The valence region of the Gd(III) and Gd(II) complexes was also examined with XPS and density function theory/random phase



approximation (DFT/RPA) calculations, and this led to the tentative assignment of a signal from the $5d^1$ electron consistent with a $4f^75d^1$ electron configuration for Gd(II).

INTRODUCTION

One of the recent advances in the chemistry of the lanthanide elements is the discovery that Ln(II) ions are accessible in soluble molecular complexes for not only Eu, Yb, Sm, Tm, Dy, and Nd but also for all the rest of the lanthanides except radioactive Pm.¹⁻⁶ This was surprising since the reduction potentials calculated to convert a 4fⁿ Ln(III) ion to a 4fⁿ⁺¹ Ln(II) ion were predicted to be too negative for the metals other than Eu, Yb, Sm, Tm, Dy, and Nd, to allow formation of isolable complexes that would not react with solvents.⁷⁻⁹ Solid-state data were consistent with this view: LnI₃ + Ln comproportionation reactions under high temperatures (600 °C) gave 4fⁿ⁺¹ Ln(II) products, Ln^{II}I₂, only for the six metals listed above. For all the other metals, the LnI₂ products were identified as Ln^{III}(I)₂(e⁻), i.e., Ln(III) salts with a delocalized electron in the lattice.¹⁰⁻¹²

The new molecular examples of complexes of Ln(II) ions were synthesized by reducing the 4f^a Ln(III) precursors, Cp["]₃Ln (Ln = La, Ce, Pr, Nd; Cp^{''} = $C_5H_3(SiMe_3)_2)^{1,13}$ and Cp[']₃Ln (Cp['] = $C_5H_4SiMe_3$; Ln = La, Ce, Pr, Gd, Tb, Dy, Ho, Er, Lu),^{3,4} using potassium graphite (KC₈) in the presence of a chelating agent 2.2.2-cryptand (crypt) to form [K(crypt)]-[Cp'_3Ln], eq 1, Figure 1.



Figure 1. Ball-and-stick model of single-crystal X-ray structure of $[K(crypt)][(C_5H_4SiMe_3)_3Ln]$, gray = carbon; blue = nitrogen; red = oxygen; green = silicon; pink = potassium; magenta = lanthanide.

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Article





 $\label{eq:R} \begin{array}{ll} \mathsf{R}=\mathsf{H}, & \mathsf{Ln}=\mathsf{La}, \,\mathsf{Ce}, \,\mathsf{Pr}, \,\mathsf{Nd}, \,\mathsf{Sm}, \,\mathsf{Eu}, \,\mathsf{Gd}, \,\mathsf{Tb}, \,\mathsf{Dy}, \,\mathsf{Ho}, \,\mathsf{Er}, \,\mathsf{Tm}, \,\mathsf{Yb}, \,\mathsf{Lu}\\ \mathsf{R}=\mathsf{SiMe}_3, \,\mathsf{Ln}=\mathsf{La}, \,\mathsf{Ce}, \,\mathsf{Pr}, \,\mathsf{Nd} \end{array}$

Additional examples of the new Ln(II) ions were subsequently isolated using various cyclopentadienyl analogs such as $(C_5Me_4H)^{1-,14}$ $[C_5H_2(CMe_3)_3]^{1-,15}$ $[C_5H_4(CMe_3)_2]^{1-,16}$ and $(C_5H_4Me)^{1-17}$ as well as $[N-(SiMe_3)_2]^{1-,18}$ $[OC_6H_2(CMe_3)_2\cdot 2, 6\cdotMe\cdot 4]^{1-,19}$ and tris-(aryloxide)mesitylene, $[(^{Ad,Me}ArO)_3mes]^{1-,20,21}$ For the complexes of all the new Ln(II) ions, structural, spectroscopic, and magnetic data as well as analysis by density functional theory (DFT), indicated that the product of the reduced $4f^{\mu}$ Ln(III) ion was not the expected $4f^{\mu+1}$ Ln(II) of the traditional six but instead a $4f^{\mu}Sd^{1}$ Ln(II) ion.^{3-5,22,23} This result indicated that the reduction potentials previously calculated for $4f^{\mu}$ to $4f^{\mu+1}$ reductions did not apply since a different redox reaction was occurring.^{8,9} The $4f^{\mu}Sd^{1}$ electron configurations of these molecular Ln(II) ions were consistent with the solid-state data on the Ln^{III}I₂(e⁻) compounds which had the electron assigned to a 5d band.¹²

The unusual nature of the $4f'5d^1$ mixed principal quantum number configuration made it a compelling topic for detailed spectroscopic studies. For example, the electronic structure of the $[K(crypt)][Cp'_{3}Ln]$ complexes of Ln = Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu was examined by X-ray absorption near-edge spectroscopy (XANES).²⁴ The L-edge XANES spectra of the $4f^{n+1}$ Ln(II) ions exhibited ~7 eV lower energy than their Ln(III) precursors. However, the $4f^{n}5d^{1}$ Ln(II) ions were only ~ 0.5 eV different from those of the Ln(III) Cp'₃Ln precursors. Initially, there was concern that the samples decomposed during transport to the synchrotron or via beam damage. However, electronic structure calculations revealed that the differences between the $4f^{n+1}$ and $4f^n5d^1$ spectra could be attributed to the greater Coulombic repulsion experienced by the 2p-electrons from 4f-electrons than the 5delectrons.24

A complementary approach to defining electronic structure is X-ray photoelectron spectroscopy (XPS) which provides an evaluation of the core and valence orbitals. However, few molecular organometallic lanthanide complexes have been characterized by XPS. Prior studies of XPS of lanthanides have focused on the metals and metal oxides, chalcogenides, phosphates, and alloys.^{25–31} However, there is a lack of clarity and consistency in much of the reported data often due to insufficient resolution for confident peak assignment or the complicated chemical environment of the element of interest in the solid-state materials which sometimes have surface contamination. Previous studies of molecular lanthanide compounds have been limited to trivalent complexes of a heptadentate tris(aryloxide)tris-imine ligand³² as well as similar species immobilized on carbon electrodes.33 No XPS data on molecular divalent complexes are in the literature to our knowledge.

We present here XPS data on crystalline molecular species of lanthanides in two different oxidation states in complexes with identical ligation so that the data can be directly compared. The electronic structure of the two oxidation states is compared with the assistance of density functional theory (DFT). Specifically, XPS analysis of the trivalent complexes $Cp'_{3}Ln$ and the divalent complexes $[Cp'_{3}Ln]^{1-}$ is presented for Ln = Sm, Eu, Gd, Tb. These metals were selected because Sm(II) and Eu(II) are traditional Ln(II) ions with 4f⁶ and 4f⁷ configurations, respectively, and because Gd(II) and Tb(II) have been assigned the new nontraditional 4f⁷Sd¹ and 4f⁸Sd¹ configurations.⁸ Additionally, these four metals were selected because they are adjacent to each other in the periodic table which ensures that their ionic radii and any charge/radius effects are similar. Since the analysis could be done on-site using an instrument with an appended glovebox using samples crystallized immediately before use, the risk of complications due to decomposition was mitigated.

RESULTS

Sample Preparation and Data Collection. Crystalline samples of $Cp'_{3}Ln$ and $[K(crypt)][Cp'_{3}Ln]$ (Cp' = $[C_5H_4SiMe_3]^{1-}$; Ln = Sm, Eu, Gd, Tb) were prepared according to previously published procedures, eq 1.5 The samples were placed in a Schlenk tube with a Teflon screw cap and then placed on a high-vacuum line (10^{-5} Torr) overnight to remove any residual solvent. The Schlenk tube was then transferred to a N₂ glovebox which is directly attached to the AXIS Supra by a Kratos Analytical XPS instrument. In the glovebox, the lanthanide samples were then mounted on a stainless-steel stub with double-sided copper tape. The stub was then transferred from the glovebox into the XPS instrument for measurement. No changes to the crystal color or size were observed during transfer between gloveboxes, and there was no observable oxidation or hydrolysis of the lanthanide complexes in the photoelectron spectra. Control samples of KCp' and 2.2.2-cryptand were also measured and analyzed by XPS, and the data are in the Supporting Information.

Core Orbitals. Overview of Data. Table 1 shows the Si 2p_{3/2} and C 1s binding energy data, and Table 2 summarizes the Ln 4d data for the main peaks of Cp'₃Ln and $[K(crypt)][Cp'_{3}Ln]$ samples of Ln = Sm, Eu, Gd, Tb. The Si 2p and C 1s regions that provide ligand data will be presented first since there are similarities in all the complexes. These data provide a calibration of the spectra and show the variations that can be observed with analogous complexes. Although the major features can be assigned, there are minor variations that are not understood at this time. In this sense, the data provide spectral fingerprints for the complexes. The Ln 4d data are presented after the Si 2p_{3/2} and C 1s data with sections on each metal since these data proved to be most diagnostic. Data on the N 1s and O 1s regions associated with cryptand and on the K 2p region associated with the K⁺ countercation were also collected and are summarized in the Supporting Information.

Si 2p. Both Si $2p_{3/2}$ and Si $2p_{1/2}$ peaks are modeled in all the silicon spectra, but only the Si $2p_{3/2}$ is discussed here since in every case the accompanying Si $2p_{1/2}$ peak is present with a binding energy 0.6 eV higher in Figure 2.

Each of the $[K(crypt)][Cp'_{3}Ln]$ samples displays a Si $2p_{3/2}$ peak at 101.4–101.5 eV, Table 1, Figure 2. These match the Si $2p_{3/2}$ peaks of KCp' at 101.3 eV (SI). The spectra of the Cp'_{3}Ln complexes, Figure 2, were modeled with primary features that also have similar energies. In addition, the best models for the Cp'_{3}Ln spectra also show a second set of smaller Si 2p peaks with the $2p_{3/2}$ peak at 101.2–101.6 eV. The origin of this second set is unknown at this time. It is possible that this is due to asymmetric exposure of one of the

Table 1. Summary of Si $2p_{3/2}$, C $1s_{ring'}$ and C $1s_{crypt}$ Binding Energies (eV) of Measured Samples of KCp' (Cp' = C₅H₄SiMe₃), Crypt (2.2.2-cryptand), Cp'₃Ln, and [K(crypt)][Cp'₃Ln] (Ln = Sm, Eu, Gd, Tb)^a

	Si 2p _{3/2}	C 1s _{ring}	C 1s _{crypt}
КСр′	101.3	284.6	
2.2.2-cryptand			285.0
Cp′ ₃ Sm	101.3 102.2	285.1	280.1
$[Cp'_3Sm]^{1-}$	101.5	285.9	285.0 287.4
Cp' ₃ Eu	101.3 102.2	285.3	
$[Cp'_3Eu]^{1-}$	101.4	286.0	284.9 287.6
Cp′ ₃ Gd	101.3 102.2	285.1	
$[Cp'_3Gd]^{1-}$	101.4	286.2	285.0 286.2
Cp′ ₃ Tb	101.3 102.6	285.1	
$[Cp'_{3}Tb]^{1-}$	101.4	286.2	285.0 287.8

^{*a*}All values are taken from the fitted curve of the spectra. Spectra were collected with a fixed-analyzer transmission mode; survey scans were collected with a pass energy of 160 eV (see the SI), while high-resolution scans of individual elements were collected with a pass energy of 20 eV.

Table 2. Summary of Ln $4d_{5/2}$, Ln $4d_{3/2}$, and Ln $4d_{shakedown}$ Binding Energies (eV) of Measured Samples Cp'₃Ln and [K(crypt)][Cp'₃Ln] (Ln = Sm, Eu, Gd, Tb)^b

	Ln 4d _{5/2}	Ln 4d _{3/2}	$\Delta E_{\rm SO}$	Ln 4d _{shakedown}
Cp′ ₃ Sm	134.5	138.1	3.6	131.4
[Cp' ₃ Sm] ¹⁻	133.9	137.4	3.5	130.8
Cp′ ₃ Eu	137.6	143.1	5.5	130.7
[Cp' ₃ Eu] ¹⁻	136.7	142.6	5.9	129.4
Cp′ ₃ Gd	145.1 ^a	149.9 ^a	4.8	143.0
$[Cp'_{3}Gd]^{1-}$	144.6 ^a	149.1 ^a	4.5	142.4
Cp′ ₃ Tb	151.0	155.7	4.7	148.3
[Cp' ₃ Tb] ¹⁻	150.9	155.0	4.1	148.2

^{*a*}Previous reports have described peaks that closely resemble a $4d_{3/2}$ peak as ⁷D and $4d_{5/2}$ as ⁹D multiplets.^{25,29,45} ${}^{b}\Delta E_{SO}$ represents the difference in binding energy between Ln $4d_{5/2}$ and Ln $4d_{3/2}$. All values are taken from the fitted curve of the spectra. Spectra were collected with a fixed-analyzer transmission mode; survey scans were collected with a pass energy of 160 eV (see the SI), while high-resolution scans of individual elements were collected with a pass energy of 20 eV.

three Cp' ligands on each complex that is detected in the Cp'₃Ln spectra but not in the $[K(crypt)][Cp'_3Ln]$ spectra. Both complexes have two SiMe₃ groups oriented in one direction and the third SiMe₃ group oriented in an opposite orientation. The difference lies in the excess charge from the supporting $[K(crypt)]^{1+}$ that could influence the third ligand.

C 1s. All of the neutral $Cp'_{3}Ln$ complexes show cyclopentadienyl ring carbon C 1s peaks at 285.1–285.3 eV, Figure 3, which are very close to the 284.6 eV value of the main peak found for the ligand alone in KCp' (SI).

The C 1s spectra of the $[K(crypt)][Cp'_3Ln]$ salts, Figure 3, differ from those of the neutral Cp'_3Ln complexes in that they

have two additional peaks attributed to the carbon atoms in 2.2.2-cryptand: one set in 284.9-285.0 eV and another at 286.1-287.8 eV, Figure 3. These peaks match those at 285.0 and 286.1 eV, for 2.2.2-cryptand alone, and are actually more resolved than in the 2.2.2-cryptand spectrum. The peak arising from the ring carbon atoms of the Cp' ligand is in between the two crypt peaks and can be readily modeled. Shakeup peaks are present in all the spectra but are most prominently observed at 290.2 eV in the Sm and Tb spectra. However, an additional feature is observed \sim 6 eV from the main peak for Sm, Gd, and Tb but not for Eu. This is attributed to a shakeup peak from a π to π^* transition in the aromatic ring. The fact that this is not observed for Eu(II) may be related to the fact that it has a halffilled valence shell 4f⁷ configuration or an increase in metal character in the π^* orbital. Further studies would be needed to determine the nature of this effect.

The relative ratios of each of the carbon species representing the cryptand and ligand display minor changes depending upon the specific lanthanide involved. The exact cause of this is unknown at this time. Adventitious carbon cannot be discounted in playing a role in small changes in intensity.

4d Peaks. The $4d_{5/2}$ and $4d_{3/2}$ peaks are the most diagnostic in this study. These vary depending on the metal and will be discussed in individual sections. Europium and samarium are discussed first since they form more stable Ln(II) ions and have traditional $4f^{n+1}$ electron configurations. Europium also has the best resolved 4d region. Terbium and gadolinium are discussed second since they form more reactive Ln(II) ions and have nontraditional $4f^n$ 5df¹ electron configurations.⁸ All spectra are shown in Figure 4.

Europium. The 4d regions of $Cp'_{3}Eu^{III}$ and [K(crypt)]-[Cp'₃Eu^{II}] in Figure 4 each contain two well-separated Eu $4d_{5/2}$ and Eu $4d_{3/2}$ peaks, Table 1, a shakedown satellite peak, and a Si 2s peak from the Cp' ligand. The binding energies of the Eu $4d_{5/2}$ and Eu $4d_{3/2}$ peaks of the Eu(III) spectrum (4d_{5/2}: 137.6 eV; 4d_{3/2}: 143.1 eV) have higher binding energies than those of the Eu(II) spectrum ($4d_{5/2}$: 136.7 eV; $4d_{3/2}$: 142.6 eV) as expected for the difference in oxidation state. Similar $4d_{5/2}$ and $4d_{3/2}$ assignments have been reported in other XPS studies of Eu(III)-containing materials.^{28,33,42-45,50} For Eu(II), only low-resolution spectra have been reported in the 4d region, and the $4d_{5/2}$ and $4d_{3/2}$ spin orbit split pairs could not be resolved. Often these materials have been reported to contain a mixture of Eu(III)/Eu(II) oxidation states which further complicated spectral interpretation.⁵²⁻⁵⁵ To the best of our knowledge, this is the first example of a well-defined Eu(II) $4d_{5/2}$ and $4d_{3/2}$ spectrum. The 4d spin orbit splitting value of the Cp'₃Eu (5.5 eV) is consistent with previously reported Eu(III) examples,^{33,43,51,55} and the 4d spin orbit splitting value of $[Cp'_{3}Eu]^{1-}$ (5.9 eV) is slightly larger.

A satellite peak is present in both the Eu(III) (129.4 eV) and Eu(II) (130.7 eV) spectra at binding energies lower than the $4d_{5/2}$ peak. These features have been previously reported as "shakedown" satellite peaks due to a reorganization of the 4f subshell.²⁸ The peaks at 153.0 eV for Eu(III) and 152.8 eV for Eu(II) are attributed to the Si 2s peak from the Cp' ligand.⁴⁹

Samarium. The 4d regions of both Cp'_3Sm^{III} and $[K(crypt)][Cp'_3Sm^{II}]$ in Figure 4 were well separated from the Si 2s peaks found at 152.9 eV for both Sm(III) and Sm(II). A peak fit of the Sm(III) spectrum was consistent with three unique traces, shown in red, that could be attributed to $4d_{5/2}$ (134.5 eV), $4d_{3/2}$ (138.1 eV), and a satellite peak (131.4 eV).



Figure 2. Si 2p spectra of $[K(crypt)][Cp'_{3}Ln^{II}]$ (top) and $Cp'_{3}Ln^{III}$ (bottom) for Ln = Sm, Eu, Gd, and Tb. The red peaks represent a single set of model peaks for a Si 2p species in the sample, while the blue is a second feature often observed in Ln(III) species. Each spectrum has a normalized residual for the peak fit against the data and a residual value.

The satellite peak could be a result of a similar shakedown process discussed previously in the Eu 4d section above. In the Sm(II) spectrum, similar features are observed which fit binding energies of $4d_{5/2}$ (133.9 eV), $4d_{3/2}$ (137.4 eV), and a

satellite peak at 130.8 eV. As in the Eu spectra, the Sm(II) binding energies are 0.6–0.7 eV lower than those of Sm(III). A limited number of Sm(III)^{33,42,45,50} and Sm(II)⁵⁶ 4d spectra







Figure 3. C 1s spectra of $[K(crypt)][Cp'_3Ln^{II}]$ (top) and Cp'_3Ln^{III} (bottom) for Ln = Sm, Eu, Gd, and Tb. The red peaks represent a single set of model peaks for the cyclopentadienyl carbon atoms in the sample, while the blue peaks represent a model for the cryptand ligand in the Ln(II) compounds. Each spectrum has a normalized residual for the peak fit against the data and a residual value.

have been reported which in all cases display a similar peak profile.

Terbium. The terbium 4d region in Figure 4 contains four peaks like the europium spectra that can be attributed to $4d_{5/2}$,

 $4d_{3/2}$, a shakedown satellite, and a Si 2s peak. In the terbium case, the Si 2s peaks at 152.7 eV for Tb(III) and 152.6 eV for Tb(II) are in the middle of the 4d peaks. For Tb(III), the $4d_{5/2}$ and $4d_{3/2}$ are assigned to 151.0 and 155.7 eV, respectively,



Figure 4. Ln 4d spectra of $[K(crypt)][Cp'_3Ln^{II}]$ (top) and Cp'_3Ln^{III} (bottom) for Ln = Sm, Eu, Gd, and Tb. The red peaks are modeled for the Ln 4d peaks, while blue peaks are Si 2s peaks that occur in the same region. Each spectrum has a normalized residual for the peak fit against the data and a residual value.

while for Tb(II), these peaks are assigned at 150.9 and 155.0 eV. Again, the Ln(II) peaks are at lower energy as expected for the lower oxidation state. In contrast to the Eu spectra, the spin orbit energy of Tb(III), 4.7 eV, is larger than that of Tb(II),

4.1 eV. As with Eu, Gd, and Sm, a shakedown peak is also present at 148.3 eV for Tb(III) and 148.2 eV for Tb(II). In previous XPS studies of Tb(III) complexes, the 4d peaks could not be discerned and were often very broad.^{45,51,57–61}

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Figure 5. Valence XPS region of Cp'_3Gd^{III} (left) and $[K(crypt)][Cp'_3Gd^{II}]$ (right). The red peaks represent valence orbitals associated with Gd, the blue peaks represent orbitals associated with the Cp' ligand, the gray peak represents the K 2p orbital, and the green peak is assigned to the Gd Sd orbital. The normalized residual standard deviation of the fit with respect to the data is shown above each plot.

Gadolinium. In the 4d region of the Gd(III) and Gd(II) spectra in Figure 4, the Si 2s peaks at 152.8 and 153.2 eV are on the high energy edge of the 4d signals. Two 4d signals and a shakedown peak provide a good model for the data with the Gd(III) $4d_{5/2}$ at 145.1 eV and $4d_{3/2}$ at 149.9 eV. For Gd(II), $4d_{5/2}$ is at 144.6 eV, and $4d_{3/2}$ is at 149.1 eV. Hence, a shift of 0.5–0.8 eV to lower energy is observed going from Gd(III) to Gd(II) which is similar to the 0.5–0.9 eV shift observed for Eu(III) to Eu(II) (vide infra). The Gd spectra are like the Tb spectra in that the spin orbit coupling energy for Gd(III), 4.8 eV, is larger than that of Gd(II), 4.5 eV. The shakedown features have been fitted at 143.0 and 142.4 eV for Gd(III) and Gd(II), respectively. The origin of the broad peaks at 170 eV is unknown.

Valence Orbitals. Analysis of the valence regions of Sm(III), Eu(III), and Tb(III) is complicated by the wide ranging atomic energy levels of the ground states ${}^{6}H_{5/2}$, ${}^{7}F_{0}$, and ${}^{7}F_{6}$, respectively.⁶² However, the isolated ${}^{8}S_{7/2}$ ground state of Gd(III) allows for a more simple assignment of the valence region. As a result, the valence regions of the $4f^{7}$ Gd(III) and $4f^{7}Sd^{1}$ Gd(II) complexes were analyzed. There is significant overlap of peaks in this region, and several samples were analyzed to get the most clearly resolved data. Figure 5 shows the best data obtained to date.

The most intense peaks in both spectra are assigned as the Gd 4f peaks: Gd(III) 4f: 10.5 eV and Gd(II) 4f: 9.9 eV, i.e., a shift of 0.6 eV. The Gd 5p peaks are also observable in both spectra: Gd(III) 5p_{3/2}: 23.3 eV, Gd(III) 5p_{1/2}: 28.3 eV, Gd(II) 5p_{3/2}: 23.2 eV, Gd(II) 5p_{1/2}: 27.4 eV. Peaks associated with Cp' are also identifiable in the valence region and are shown in blue in Figure 5. Measurements on the KCp' control sample (Supporting Information) revealed two Cp' ligand-based peaks at 16.6 and 6.1 eV. Therefore, the valence peaks in the Gd(III) spectrum located at 17.4 eV and the shoulder at 6.9 eV are assigned to the Cp' ligand and are present at 16.3 and 7.4 eV in the Gd(II) valence spectrum. The spectrum of KCp' had a K 3p peak at 18.2 eV which is observed in the Gd(II) valence spectrum at 18.1 eV. There is a shoulder in the Gd(II) spectrum (Figure 5, right, green) located at 6.1 eV that is tentatively assigned as the 5d orbital based on electronic structure calculations discussed in the next section. The assignment must be considered tentative since there are no

precedents in the literature. There is another peak observed at lower binding energy in all spectra around \sim 3 eV. This is likely a contamination from the Cu substrate as the Cu 4d peak is observable at \sim 3 eV.³⁴

Electronic Structure Calculations. The ground state geometries of the neutral $Cp'_{3}Ln$ and the anionic $(Cp'_{3}Ln)^{1-}$ complexes for Ln = Eu and Gd were optimized (computational details are provided in the Supporting Information), starting from the experimental X-ray structures, within density functional theory (DFT). The primary focus is the Gd valence region since Gd offers a more straightforward interpretation of the experimentally observed peak tentatively assigned to the 5d orbital and comparison with DFT calculations due to its spinonly $4f^7$ and $4f^75d^1$ electron configurations.

For the calculations of core and valence ionization potentials, the random phase approximation³⁵ (RPA) occupation number derivatives approach³⁶ was used with the TPSS³⁷ input orbitals and orbital energies. The RPA number derivatives approach has been shown to accurately predict the core and valence ionization potentials of various molecular systems in previous studies^{36,38} and hence is used here. The RPA calculations used the same basis sets as the geometry optimization calculations except for the Gd and Eu atoms, for which larger, polarized triple- ζ valence (def2-TZVPP³⁹) basis sets were used. For performing numerical integration over imaginary frequency, 400 grid points were used. The RPA calculations included implicit solvent effects through the COSMO model within the perturbation theory with a selfconsistent reaction field energy (PTE⁴⁰) scheme that is implemented in TURBOMOLE.⁴¹ The density of states in the valence region of $Cp^\prime{}_3Gd$ and $(Cp^\prime{}_3Gd)^{1-}$ are plotted in Figure 6, and the analogous Eu complexes are plotted in Figure S28 of the Supporting Information. Signals below 9.67 eV for Gd(III) and 8.61 eV for Gd(II) are associated with ligand orbitals with some 4f character with the exception of the 5d Gd(II) signal at 1.76 eV.

The RPA calculations indicate that the electronic state order near the valence band is 4f, 4f+Cp' ligand, finally followed by the 5d peak. The RPA calculations do not generate an exact correlation of the binding energies to the peaks, but this is likely due to a calibration difference between the photoelectron data and the calculations. However, the calculations do predict



Figure 6. Calculated density of states (arbitrary units) in the valence region for the Cp'_3Gd^{II} (bottom) and the $[Cp'_3Gd^{II}]^{1-}$ (top) broadened using Gaussian functions with a half width at half-maximum of 0.5 eV.

the order of frontier orbitals with respect to the binding energy for Gd (and Eu, see the SI) based on the clusters of similar orbital character. The calculations show a change in the formal metal oxidation state of Ln(III) to Ln(II) upon reduction of Cp'₃Gd to [K(crypt)][Cp'₃Gd] via a 1.6 eV shift to the lower binding energy of the Gd 4f. This is higher than the 0.6 eV shift experimentally observed for the same peaks in the photoelectron spectrum. The differences between the Cp' ligand and the Gd 4f peak in the XPS spectra are 3.5 and 2.4 eV for Gd(III) and Gd(II), respectively. This is approximately 1 eV difference between the calculated values of 2.3 and 1.5 eV which could be a consistent deviation that has not been accounted for in the calculation.

DISCUSSION

XPS measurements of $Cp'_{3}Ln$ and $[K(crypt)][Cp'_{3}Ln]$ (Ln = Sm, Eu, Gd, Tb) in the Si 2p and C 1s regions gave similar spectra that could be analyzed by making comparisons with KCp' and 2.2.2-cryptand. The main peak positions varied only slightly from one compound to another and provided baseline information on the ligands present. The differences in the spectra provided a calibration of the variations that can be observed even within a closely related series of complexes.

The Ln 4d and Si 2s regions of the Cp³₃Ln and [K(crypt)][Cp'₃Ln] complexes overlapped, but $4d_{5/2}$ and $4d_{3/2}$ assignments could be made. The 4d binding energies increase with atomic number as expected,⁴⁵ e.g., the $4d_{5/2}$ Cp'₃Ln energies are 134.5, 137.6, 145.1, and 151.0 eV for Sm, Eu, Gd, and Tb. The energies for the Ln(II) compounds are always lower than those of the Ln(III) compounds as expected for the change in oxidation state, but the differences in energies for a specific peak vary from 0.1 to 0.9 eV. The difference in $4d_{5/2}$ peaks of Eu (0.9 eV) is larger than the difference in the $4d_{3/2}$ peaks of Eu (0.5 eV), but the opposite trend is found for Sm (0.7 eV for $4d_{3/2}$ and 0.6 eV for $4d_{5/2}$), Tb (0.7 eV for

 $4d_{3/2}$ and 0.1 for $4d_{5/2}$), and Gd (0.8 eV for $4d_{3/2}$ and 0.5 eV for $4d_{5/2}$). The spin-orbit coupling for the Ln(III) and Ln(II) samples also varies, but the differences depend on the specific metal. For Eu, the spin-orbit coupling in the Ln(II) ion is largest, but for Sm, Tb, and Gd, the opposite is found. It is premature to propose reasons for these differences based on the available data. There is no clear demarcation between Eu and Sm, which add an electron to their 4f orbital upon reduction, compared to Gd and Tb, which add an electron to the 5d orbital. We note that comparison of the XANES spectra of Ln(III) and Ln(II) complexes revealed shifts smaller than expected because of a combination of factors that affected orbital energies.²⁴ No additional features indicating new electron redistribution pathways were observed in any of the Ln(III) or Ln(II) core orbital spectra. This is consistent with the presence of a single molecular species in each of these experiments. This consistency upon reduction suggests that the coordination environment around the lanthanide is preserved when there is a change of oxidation state in this system, 63-65 a situation that is verified by the X-ray structural data on the Cp'₃Ln and [K(crypt)][Cp'₃Ln] complexes.

In addition to the core orbital data that show consistent shifts to lower binding energy with lower oxidation state, the valence region spectra of Gd show a 0.6 eV shift to lower binding energy of the 4f electron in the Gd(II) complex $(Cp'_{3}Gd)^{1-}$. Additionally, a shoulder at 6.1 eV in Figure 5 is assigned to the 5d peak of Gd. XPS studies on d¹ systems have previously been examined on TiO2. Signals resulting from Ti(III) 3d¹ systems have been observed near the Fermi level similar to the 5d feature depicted in the Gd(II) 4f⁷5d¹ valence spectrum in Figure 5.66-69 For example, Hammer and Besenbacher observed the intensity of the Ti(III) 3d peak in reduced TiO₂ steadily decrease upon exposure of oxygen indicating the formation of the stochiometric Ti(IV) TiO₂ species. In the case of the Gd valence spectra in Figure 5, there is a distinct absence of the 5d peak in the Gd(III) and a clear presence of the new 5d peak in the Gd(II) valence region.⁷ Moreover, the experimentally observed differences and order of the orbitals match RPA calculations.

CONCLUSION

For the first time, molecular complexes of Sm(II), Eu(II), Gd(II), and Tb(II) were examined using high-resolution XPS. The electronic structures of the Ln 4d, Si 2p, and C 1s regions were identified for these complexes and compared to Ln(III) analogs with identical coordination environments. These high-resolution spectra have allowed for the identification of Ln 4d shifts between Ln(II) and Ln(III) oxidation states that range from 0.3 to 1.0 eV and correlate with the change in oxidation state. The data demonstrate that XPS can be used diagnostically to identify changes in oxidation states of molecular lanthanide complexes. This important result was achievable even though it was not possible to identify all the features in every spectrum. Since XPS is rarely used to study such complicated molecular systems, more studies will be needed to allow complete assignments.

The study has also revealed the consistent presence of 4d shakedown features in both Ln(III) and Ln(II) 4d spectra. Further examination of other lanthanide complexes outside of Sm, Eu, Gd, and Tb will be required to determine if this feature is general for all lanthanides.

Comparison of the valence regions of the Gd(III) and Gd(II) complexes allowed the tentative assignment of a $5d^1$

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peak consistent with reduction of a $4f^7$ configuration to $4f^7Sd^1$ as previously supported by structural, spectroscopic, magnetic, and DFT analysis. This feature was corroborated by DFT/RPA calculations and suggests that XPS can be used to identify these new electron configurations.

EXPERIMENTAL SECTION

XPS was performed on a Kratos Axis Supra DLD spectrometer (Kratos Analytical Ltd.) with monochromated Al K α radiation (1486.6 eV) at 10-mA emission current and 15 kV anode voltage with a base pressure of 1 imes 10⁻⁹ Torr. One set of experiments was performed with the charge neutralizer with a filament current of 1.8 A and a bias of 3.0 V while the remaining spectra were collected without charge neutralization. No changes in the spectra were observed between charge neutralized and non-neutralized samples. All spectra were charge corrected either to the K 2p peak or to the Si 2p peak. Spectra of $[K(crypt)][Cp'_3Ln^{II}]$ (Ln = Sm, Eu, Gd, Tb) were charge corrected to K 2p of 294 eV, while Cp'₃Ln^{II} was charged corrected to Si 2p or 101.3 eV. This is based on the ligand and cryptand control experiments that were charged corrected to K 2p and subsequently observed a Si 2p peak of 101.3 eV. Spectra were collected with a fixedanalyzer transmission mode, survey scans were collected with a pass energy of 160 eV, while high-resolution scans of individual elements were collected with a pass energy of 20 eV. All samples were mounted on a stainless-steel stub with double-sided copper tape in a nitrogenfilled glovebox attached to the XPS. Samples were fabricated in a different argon-filled glovebox and transported under vacuum in a sealed vial to the glovebox attached to the XPS. Peak fitting was performed with CasaXPS software (Casa Software Ltd.) using a Shirley baseline and 70% Gaussian-30% Lorentzian function for the peaks unless otherwise indicated.⁷¹ All spectra are shown with the Shirley background subtracted from the raw data for clarity. Fitting procedures for all spectra were completed by first fitting the Ln(III) spectrum for each orbital (C 1s, Si 2p, Ln4d, and valence). The model for the Ln(III) spectra was then propagated into the Ln(II) spectra with all variables held constant except for the peak area. The model was then adjusted to fit the appropriate binding energy by loosening restrictions on that variable. Finally, the restrictions on fwhm were loosened by 0.1 eV, beginning with the largest peak in the envelope, until an appropriate fit was achieved. The valence spectra had added complexity as the model from Ln(III) to Ln(II) had additional peaks from the cryptand. These peaks were added to the model based on their parameters from the control spectra shown in the Supporting Information. Special attention was paid to the fit nearest the valence band (0-15 eV) to ensure a quality fit of the data. Spectra were fit until the model reached a convergence with the spectra and the chisquared value no longer changed.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.1c06980.

Additional XPS spectra of $Cp'_{3}Ln^{III}$, [K(crypt)]- $[Cp'_{3}Ln^{II}]$ (Ln = Sm, Eu, Gd, Tb), KCp', and 2.2.2cryptand: O 1s region, N 1s region, K 2p region, Si 2p region, valence region, and survey spectra; computationally optimized structures and calculated binding energies of $Cp'_{3}Ln^{III}$ and $[Cp'_{3}Ln^{II}]^{1-}$ (Ln = Eu, Gd); calculated density of states of $Cp'_{3}Eu^{III}$ and $[Cp'_{3}Eu^{II}]^{1-}$; additional XPS spectra of [K(crypt)]- $[Cp'_{3}Gd^{II}]$ in a different sample location; and calculated atomic ratios from XPS spectra (PDF)

AUTHOR INFORMATION

Corresponding Authors

- Filipp Furche Department of Chemistry, University of California, Irvine, California 92697, United States;
 orcid.org/0000-0001-8520-3971; Email: filipp.furche@ uci.edu
- John C. Hemminger Department of Chemistry, University of California, Irvine, California 92697, United States; orcid.org/0000-0003-2467-6630; Email: jchemmin@ uci.edu

William J. Evans – Department of Chemistry, University of California, Irvine, California 92697, United States;
orcid.org/0000-0002-0651-418X; Email: wevans@uci.edu

Authors

- Daniel N. Huh Department of Chemistry, University of California, Irvine, California 92697, United States; orcid.org/0000-0001-7887-0856
- Jared P. Bruce Department of Chemistry, University of California, Irvine, California 92697, United States; orcid.org/0000-0003-1660-1305
- **Sree Ganesh Balasubramani** Department of Chemistry, University of California, Irvine, California 92697, United States
- Sierra R. Ciccone Department of Chemistry, University of California, Irvine, California 92697, United States

Complete contact information is available at: https://pubs.acs.org/10.1021/jacs.1c06980

Author Contributions

[†]D.N.H. and J.P.B. contributed equally.

Notes

The authors declare no competing financial interest.

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