Lanthanum(II) Compounds

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Lanthanum Does Form Stable Molecular Compounds in the +2 Oxidation State**

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Dedicated to Professor William J. Evans on the occasion of his 60th birthday

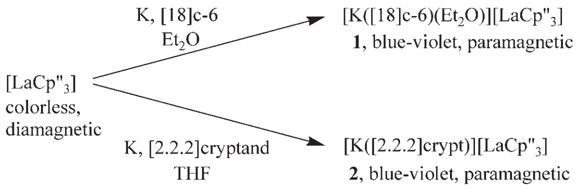
The continuing quest for molecular complexes of low-oxidation-state lanthanides (other than the well-known samarium(II), europium(II), and ytterbium(II)) has produced significant achievements.[1] The majority of such compounds are derivatives of neodymium, dysprosium, and thulium,[2] obtained from the corresponding molecular iodides (often prepared in situ): $[NdI_2(thf)_5]$,[2a] $[DyI_2(dme)_3]$[2b,c] (dme = dimethoxyethane), and $[TmI_2(dme)_3]$,[2c,d] or by the reduction of an appropriate Ln^{III} derivative.[2e,f] The present state of lanthanum, cerium, praseodymium, and gadolinium redox chemistry was described by S. A. Cotton: "None of these metals exhibits a stable +2 state in any of its compounds and … they are unlikely to form stable compounds in this state."[3] Thus, the isolation of room-temperature-stable solid La^{II} compounds is a very unexpected and significant breakthrough in the chemistry of lanthanides.

Related to the subject of this study is a large group of inorganic materials: reduced or metal-rich rare-earth-metal halides,[4] including LaI_2 (featuring an extended structure with La $5d^1$ electrons delocalized on a conduction band), in which a lanthanum atom can be considered as being in the +2 oxidation state.[4b] These compounds are better treated in a materials science context, where the metal valence[5,6] rather than the oxidation state is of primary importance.

Previously we have observed unstable La^{II}-containing intermediates in solution by EPR spectroscopy. However, such solutions produced only La^{III} alkoxides or $[C_6H_6]^{2-}$ derivatives as solids.[7] La, Ce, and Nd dinuclear complexes of the general formula $[K([18]crown\text{-}6)(\eta^2\text{-arene})_2][(LnCp^x_2)_2(\mu\text{-}\eta^6{:}\eta^6\text{-arene})]$ (arene = C_6H_6 or PhMe; $Cp^x = \eta^5\text{-}1,3\text{-}(SiMe_3)_2C_5H_3 = Cp''$ or $\eta^5\text{-}1,3\text{-}tBu_2C_5H_3 = Cp^{tt}$] were isolated as crystalline solids.[8] The latter featured redox ambiguity, which was also found in cerocene[9] and bis(pentalene)cerium,[10] in which a metal-bound ligand had readily accessible adjacent oxidation states. For the binuclear arene-bridged complexes, three different metal–ligand formal charge distributions are possible: $Ln^{2+}/Ln^{2+}/[arene]^-$, $Ln^{2+}/Ln^{3+}/[arene]^{2-}$, or $Ln^{3+}/Ln^{3+}/[arene]^{3-}$; however, the presence of a triply reduced benzene or toluene moiety is very unlikely.[11]

Now we have obtained stable mononuclear La^{II} compounds, in which the lanthanum oxidation state is confirmed by structural, spectroscopic, magnetic, and computational studies.

Reaction of the colorless diamagnetic La^{III} compound $[LaCp''_3]$ with a potassium mirror and [18]crown-6 in Et_2O or [2.2.2]cryptand in THF produced the crystalline complexes $[K([18]c\text{-}6)(OEt_2)][LaCp''_3]$ (**1**) and $[K([2.2.2]crypt)][LaCp''_3]$ (**2**), respectively (Scheme 1). Reduction with K and [18]crown-6 did not proceed cleanly, and the product was contaminated with a small amount of $K([18]c\text{-}6)(Cp'')$. In contrast, compound **2** was readily purified (the somewhat low carbon analysis is often observed for organolanthanide compounds with a high silicon content). Compounds **1** and **2** were both isolated as very dark, blue-violet, paramagnetic crystals easily soluble in THF and sparingly so in Et_2O; addition of aromatic solvents to crystalline **1** led to immediate decomposition with the formation of a green precipitate apparently analogous to the previously reported complexes with a bridging arene moiety.[8] Recrystallized complexes **1** and **2** showed remarkable stability both in the solid state and in Et_2O solution (THF solutions decolorized slowly): **1** was recovered from its Et_2O solution after storing at 10 °C for one year.



Scheme 1.

X-ray crystallography has shown that complexes **1** and **2** contain well-separated encapsulated potassium cations and $[LaCp''_3]^-$ anions (illustrated for **2** in Figure 1). The geometric

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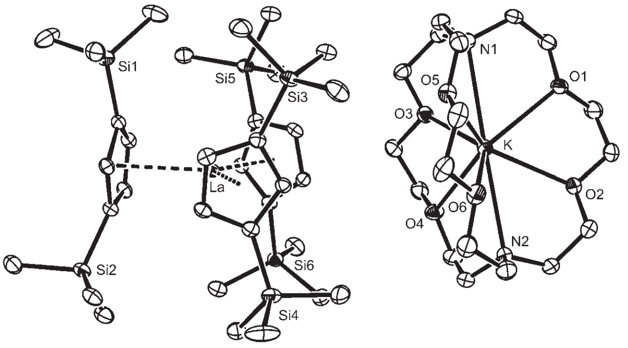

Figure 1. Thermal ellipsoid plot of **2** drawn at the 30% probability level. Hydrogen atoms are omitted for clarity.

parameters of the $[\mathrm{K}([18]\mathrm{c}\text{-}6)(\mathrm{OEt}_2)]^+$ and $[\mathrm{K}([2.2.2]\mathrm{crypt})]^+$ ions in **1** and **2** are very similar to those of the numerous crystallographically characterized salts containing such cations. An alternative formulation of **1** and **2** as electrides with cocrystallized neutral $[\mathrm{LaCp}''_3]^0$ moieties, that is, $[\mathrm{K}([18]\mathrm{c}\text{-}6)(\mathrm{OEt}_2)][\mathrm{e}^-]\cdot[\mathrm{LaCp}''_3]$ or $[\mathrm{K}([2.2.2]\mathrm{crypt})][\mathrm{e}^-]\cdot[\mathrm{LaCp}''_3]$, is very unlikely, because the thermal stability of electrides with oxygen-containing ligands is insufficient to allow their isolation and handling at room temperature.[12]

The geometric parameters of the anion are almost identical for both complexes. The anion has a nearly planar trigonal arrangement, with the La atom 0.019 or 0.016 Å out of the plane determined by the centroids of the three Cp″ ligands (M1, M2, and M3) for **1** and **2**, respectively. The average La–M distances are 2.632 (**1**) and 2.620 Å (**2**), which are slightly longer than the corresponding distance in the $\mathrm{La^{III}}$ precursor (2.600 Å).[13] The average La–C(Cp″) bond lengths, at 2.893 (**1**) and 2.884 Å (**2**), are also slightly greater than those in $[\mathrm{LaCp}''_3]$ (2.852 Å). These data show small but systematic increases of La–C and La–M distances in **1** and **2** as compared to those in neutral $[\mathrm{LaCp}''_3]$.

Recently, a prediction was made that the ionic radii of $\mathrm{La^{2+}}$ and $\mathrm{Ce^{2+}}$ will approach 1.25 and 1.23 Å, respectively, or 0.22 Å longer than the values for the six-coordinate $\mathrm{La^{3+}}$ and $\mathrm{Ce^{3+}}$ ions.[14] This prediction was based on the ionic-radius increase upon reduction of $\mathrm{Eu^{3+}}$ to $\mathrm{Eu^{2+}}$ that implies an increase in the number of electrons of the inner 4f shell (i.e. $4\mathrm{f}^6$ to $4\mathrm{f}^7$); similar considerations are applicable to all six lanthanides (Nd, Sm, Eu, Dy, Tm, Yb) previously known to form stable compounds in the +2 oxidation state. The nature of the electronic configuration change in the case of La is different: $4\mathrm{f}^0 5\mathrm{d}^0 \rightarrow 4\mathrm{f}^0 5\mathrm{d}^1$ for $\mathrm{La^{3+}}$ to $\mathrm{La^{2+}}$ reduction (increasing the number of electrons in the outer 5d shell). The $4\mathrm{f}^0 5\mathrm{d}^1$ electronic configuration was found by low-temperature EPR spectroscopy for $\mathrm{La^{2+}}$ ions incorporated in $\mathrm{CaF_2}$ lattice;[15a,b] its stability has been confirmed by DFT computations.[16] The most closely related situation was observed for the $\mathrm{Zr^{4+}}$ to $\mathrm{Zr^{3+}}$ reduction ($4\mathrm{d}^0 \rightarrow 4\mathrm{d}^1$).[17] Indeed, $\mathrm{Zr^{III}}$–C(Cp) distances ($\mathrm{Cp} = \mathrm{C_5H_5}$) in $[\mathrm{ZrCp_3}]$[17a] or $[\mathrm{ZrCp^{tt}_2Cl}]$[17b] were considered essentially the same as in their $\mathrm{Zr^{IV}}$ precursors, while in $[\mathrm{ZrCp^{tt}_2I}]$ they were significantly shorter (by 0.05 Å) than in $[\mathrm{ZrCp^{tt}_2I_2}]$.[17c] Thus, taking into account that in the given examples of $\mathrm{Zr^{4+}}$ to $\mathrm{Zr^{3+}}$ reduction, the metal coordination number (C.N.) decreased and in the reduction of $[\mathrm{LaCp}''_3]$ to complexes **1** or **2** C.N. did not change, the La–C and La–M distances in the latter compounds are expected to be the same or slightly longer than those in $[\mathrm{LaCp}''_3]$.

Preliminary computational study at the DFT level using small-core effective core potentials (ECPs; explicit treatment of the f electrons) on the neutral $[\mathrm{LaCp}''_3]$ molecule and the $[\mathrm{LaCp}''_3]^-$ ion revealed their La–M distances to be 2.595 and 2.637 Å, respectively; these values are in excellent agreement with the experimental data. The analysis of the spin density in the anionic complex clearly indicates that the electron is mainly located at the lanthanide center. This result is further confirmed by a natural bond orbital (NBO) analysis, since the natural electronic configuration of the lanthanide center is 6s(0.37) 5d(0.52). As expected, the singly occupied molecular orbital (SOMO) of the anionic complex is located on the metal (clearly a d_{z^2} orbital) and also corresponds to the lowest unoccupied MO of the neutral complex (see Figure 6S in the Supporting Information).

In general, the electronic configuration of the La atoms in **1** and **2** can be described as $[\mathrm{Xe}]4\mathrm{f}^0 5\mathrm{d}^1$ and the lanthanum oxidation state as +2. In $\mathrm{LaI_2}$, the La atom has the same electronic configuration, but considerations of d-electron delocalization on a conduction band led to the conclusion that in this material lanthanum is actually trivalent.[2b,4] Such considerations are completely inapplicable to organometallic molecular compounds, in which metal centers are isolated from each other by bulky ligands.

The most prominent feature of complexes **1** and **2** is their paramagnetism, which clearly distinguishes them from the vast majority of diamagnetic lanthanum compounds. The solid-state EPR spectra showed very broad asymmetric singlets (line width 660 and 760 G for **1** and **2**, respectively) with a partly resolved hyperfine structure for **1**. Diluted solutions of **1** or **2** in $\mathrm{Et_2O}$ (the two spectra were almost identical) showed a well-resolved octuplet with $g_{\mathrm{av}} = 1.990$ and a hyperfine coupling constant $a(^{139}\mathrm{La})_{\mathrm{av}} = 133.5$ G, thus confirming that **1** and **2** produced the same EPR-active species in solution, namely $[\mathrm{LaCp}''_3]^-$ ions, with the unpaired electron located on the $^{139}\mathrm{La}$ nucleus.

Any other formal charge distribution is not consistent with the EPR data presented above. If unpaired electrons were in ligand-based orbitals (the lanthanum oxidation state remains unchanged), the EPR spectra would show a narrow signal with a g value close to the free-electron value and hyperfine coupling to protons and other magnetically active nuclei of the ligand ($^{13}\mathrm{C}$, $^{29}\mathrm{Si}$), while $a(^{139}\mathrm{La})$ would be significantly smaller (e.g. in $[\mathrm{La(bipy)_2I_2(thf)_2}]$ $a(^{139}\mathrm{La}) = 5.9$ G[18]). And if the extra electrons were trapped in the cavities formed by closely packed encapsulated $\mathrm{K^+}$ cations and neutral $[\mathrm{LaCp}''_3]$ molecules in a manner similar to electrides, narrow signals with the free-electron g value would be observed.[12]

The paramagnetic properties were confirmed by temperature-dependent susceptibility measurements by the SQUID technique. The magnetic behavior of **2** (Figure 2) in the temperature range 16–300 K follows the Curie–Weiss law ($\chi_{\mathrm{m}} - \chi_0 = C(T-\theta)^{-1}$ with $C = 0.245$, $\theta = 1.5$ K, $\chi_0 = -0.73 \times 10^{-3}$ emu mol^{-1}). The calculated magnetic moment of $1.40\,\mu_{\mathrm{B}}$

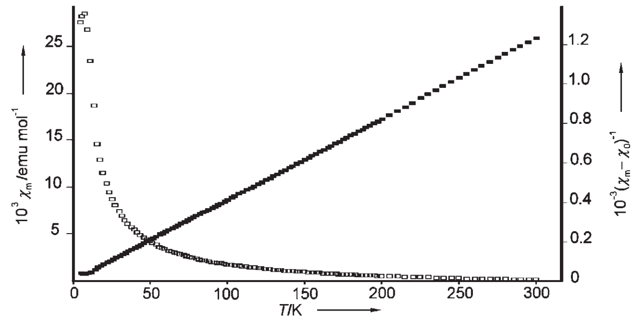

Figure 2. The temperature dependence of the molar magnetic susceptibility χ_m (□) and the reciprocal magnetic susceptibility $(\chi_m-\chi_0)^{-1}$ (■), corrected for the diamagnetic contribution of the sample and sample holder.

($1.17\,\mu_B$ for **1**) is slightly lower than the value corresponding to an isolated spin. These data show that the observed paramagnetism is the intrinsic property of complexes **1** or **2** rather than that of some reactive intermediates or impurities.

Attempted reduction of [CeCp″$_3$] with a K mirror and [18]crown-6 in Et$_2$O resulted in a mixture of products (the ^{1}H NMR spectrum was consistent with the presence of at least two paramagnetic Cp″-containing products in an approximate 1:1 ratio). When excess [CeCp″$_3$] was used, the resulting deep violet solution was more stable, allowing crystallization of the cocrystals [K(18[c]-6)(OEt$_2$)$_2$][CeCp″$_3$]·[CeCp″$_3$] (**3**). X-ray crystallography identified the [K([18]c-6)(OEt$_2$)$_2$]$^+$ ion and two alternating [CeCp″$_3$] moieties, one of which had very similar geometric parameters to those of the Ce^{III} precursor,[13b] while the second moiety, assigned as the [CeCp″$_3$]$^-$ ion, had Ce−M separations elongated by 0.03 Å. Such remarkable analogy with the La^{II} compounds **1** and **2** suggests that cerium is also able to form Ce^{II} compounds having a 4f^{1}5d^1 electronic configuration (albeit less stable than corresponding lanthanum complexes).

Earlier computational study of [CeCp″$_3$] showed that all the ligand-based unoccupied molecular orbitals are much higher in energy than the MOs with predominant metal character.[19] Thus, upon reduction, an additional electron will occupy one of these metal-based orbitals, hence yielding a [CeCp″$_3$]$^-$ ion with the Ce atom in the +2 oxidation state.

In conclusion, use of the bulky cyclopentadienyl ligand [η^5-1,3-(SiMe$_3$)$_2$C$_5$H$_3$]$^-$ and the reduction system K and [18]crown-6 or [2.2.2]cryptand has led to the isolation of the stable lanthanum(II) complexes **1** and **2**. The synthesis of these compounds opens a new area of organometallic chemistry of lanthanides as d elements. The study of d^1 lanthanide inorganic compounds has already produced exciting results for materials science[4d] and now can be extended to molecular organolanthanide complexes.

Experimental Section

All manipulations were carried out in an atmosphere of dry argon (N$_2$ can react with Ln complexes under reducing conditions) or under vacuum in a sealed all-glass apparatus.

2: A solution of [2.2.2]cryptand (4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane, 0.096 g, 0.25 mmol) and [LaCp″$_3$] (0.216 g, 0.28 mmol) in THF (10 mL) was added to an ampoule containing a K mirror (0.010 g, 0.26 mmol) and a glass-coated magnetic stirring bar. After stirring at room temperature overnight, the mixture was filtered, and the filtrate was concentrated, layered with hexane, and stored at −27 °C for three days, yielding black crystals. Washing with cold Et$_2$O/pentane produced complex **2** (0.185 g, 0.16 mmol, 63 %), m.p. 122–125 °C (decomp.). Elemental analysis (%) calcd for $C_{51}H_{99}KLaN_2O_6Si_6$: C 51.8, H 8.44, N 2.37; found: C 50.8, H 8.62, N 2.48.

Further experimental details, including synthesis of **1** and **3**, EPR spectra, magnetic data, X-ray crystallography, and computational details, are given in the Supporting Information.

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