Expanding Rare-Earth Oxidation State Chemistry to Molecular Complexes of Holmium(II) and Erbium(II)

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S *Supporting Information*

ABSTRACT: The first molecular complexes of holmium and erbium in the +2 oxidation state have been generated by reducing Cp'_3Ln [$Cp' = C_5H_4SiMe_3$; Ln = Ho (**1**), Er (**2**)] with KC_8 in the presence of 18-crown-6 in Et_2O at −35 °C under argon. Purification and crystallization below −35 °C gave isomorphous [(18-crown-6)K][Cp'_3Ln] [Ln = Ho (**3**), Er (**4**)]. The three Cp' ring centroids define a trigonal-planar geometry around each metal ion that is not perturbed by the location of the potassium crown cation near one ring with K−C(Cp') distances of 3.053(8)−3.078(2) Å. The metrical parameters of the three rings are indistinguishable within the error limits. In contrast to Ln^{2+} complexes of Eu, Yb, Sm, Tm, Dy, and Nd, **3** and **4** have average Ln−(Cp' ring centroid) distances only 0.029 and 0.021 Å longer than those of the Ln^{3+} analogues **1** and **2**, a result similar to that previously reported for the $4d^1$ Y^{2+} complex [(18-crown-6)K][Cp'_3Y] (**5**) and the $5d^1$ La^{2+} complex [K(18-crown-6)(Et_2O)][Cp''_3La] [$Cp'' = 1,3-(Me_3Si)_2C_5H_3$]. Surprisingly, the UV−vis spectra of **3** and **4** are also very similar to that of **5** with two broad absorptions in the visible region, suggesting that **3**−**5** have similar electron configurations. Density functional theory calculations on the Ho^{2+} and Er^{2+} species yielded HOMOs that are largely $5d_{z^2}$ in character and supportive of $4f^{10}5d^1$ and $4f^{11}5d^1$ ground-state configurations, respectively.

Recent developments in rare-earth reductive chemistry have shown that N_2 can be reduced to $(N=N)^{2-}$ and $(N_2)^{3-}$ by combining a Ln^{3+} complex with an alkali metal (Scheme 1).[1] These LnA_3/M and LnA_2A'/M reactions (Ln = Sc, Y, lanthanide; A/A' = monoanionic ligands; M = alkali metal) can provide "LnA_2"-like reactivity even if no Ln^{2+} complexes of the metal are known to exist either as molecular species in

Scheme 1. Reduction of N_2 with Trivalent Rare-Earth Precursors and Alkali Metal
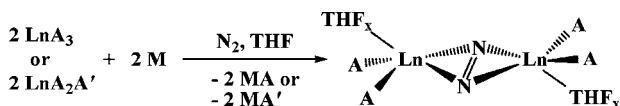
Ln = Sc, Y, La, Ce, Pr, Nd, Gd, Tb, Dy, Ho, Er, Tm, Lu

A = N(SiMe₃)₂, OC₆H₃′Bu₂-2,6, C₅Me₅, C₅Me₄H, C₅H₄SiMe₃, C₅H₂′Bu₃

A' = BPh₄, I, H; M = K, KC₈, Na; x = 0-2

solution or in the solid state. Although this reaction has provided numerous reduced N_2 complexes, mechanistic information on the N_2 reduction has been elusive.

One possible pathway involves formation of transient intermediates in the +2 oxidation state, i.e. "LnA_2" or the ate-salt "$MLnA_3$"[2] (Scheme 2). This is quite reasonable for Tm,

Scheme 2. Possible Pathways for $LnA_3/M/N_2$ and $LnA_2A'/M/N_2$ Reactions
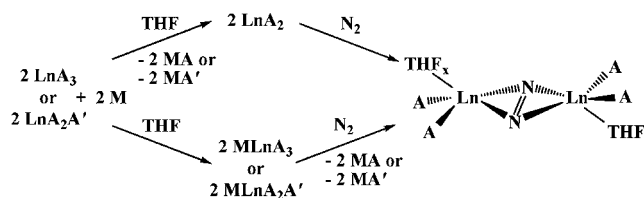
Dy, and Nd since these metals form isolable molecular Ln^{2+} complexes in solution[1h,3] and their solid-state diiodides are best described as $Ln^{2+}(I^-)_2$.[4] This is also reasonable for Y^{2+}, a $4d^1$ ion that reacts with N_2.[1m,n] Molecular divalent complexes of La and Ce are also known,[5] and the $5d^1$ electron configuration of La^{2+} can be rationalized by the argument that the 5d orbitals are close in energy to the 4f orbitals at the beginning of the lanthanide series. However, for Pr, Gd, Tb, Ho, and Er, there is little to no basis to propose the Ln^{2+} reaction pathway since the +2 oxidation state has never been observed in solution and the solid-state diiodides are described as $Ln^{3+}(I^-)_2(e^-)$ materials with a delocalized electron in a conduction band.[4]

The recent isolation of the first molecular Y^{2+} complex, [(18-crown-6)K][Cp'_3Y] (**5**) ($Cp' = C_5H_4SiMe_3$; eq 1)[1n] raised the
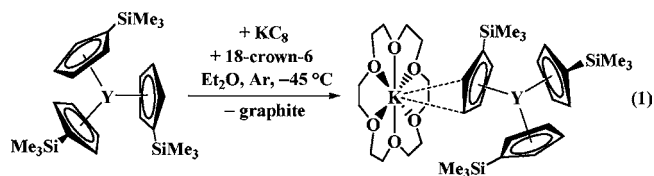
question of the existence of a Ln^{2+} complex of the similarly sized holmium. Since size and charge are so important in rare-earth chemistry, Y^{3+} often behaves like the Ln^{3+} ions of the late lanthanides that have similar sizes. Ever since this Y/late lanthanide connection was recognized in organometallic
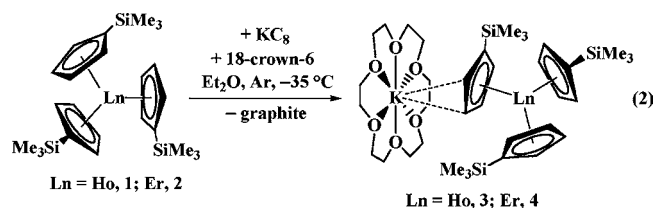
species,[6] examples in which the chemistry of Y is different have been sought. If the availability of d orbitals is critical for stabilizing a +2 oxidation state, then Ho^{2+}, which is expected to be a $4f^{11}$ ion, may not be accessible like Y^{2+}. On the other hand, solid-state reviews have pointed out that Ho is the next most likely lanthanide to have a +2 oxidation state after Tm, Dy, and Nd.[7]

To test these ideas, the synthetic route to [(18-crown-6)K][Cp′$_3$Y] in eq 1 was tested with Ho. This first required the synthesis of Cp′$_3$Ho (**1**) from $HoCl_3$ and KCp′. Although this is not a particularly difficult air-sensitive reaction, the product had to be characterized by X-ray crystallography since Ho^{3+} has a magnetic moment of >10 μ_B, preventing the use of NMR spectroscopy to follow the reaction.

Treatment of yellow Et_2O solutions of **1** with KC_8 in the presence of 18-crown-6 at −45 °C under argon gave a dark maroon-purple solution similar to that observed in the Y reaction. As in the Y reaction, the color of this dark solution faded to orange when the solution was not maintained at low temperature. Attempts to obtain the purple compound as a solid following the protocol of the Y reaction, which involved Schlenk filtration and recrystallization at −45 °C or below, did not give good yields of crystalline products, so new syntheses were pursued. Small amounts of X-ray-quality single crystals were obtained from solutions of **1** placed over a potassium mirror and kept at −35 °C overnight. X-ray crystallography revealed the product to be [(18-crown-6)K][Cp′$_3$Ho] (**3**), the first molecular complex of Ho^{2+} (Figure 1). Subsequently, it
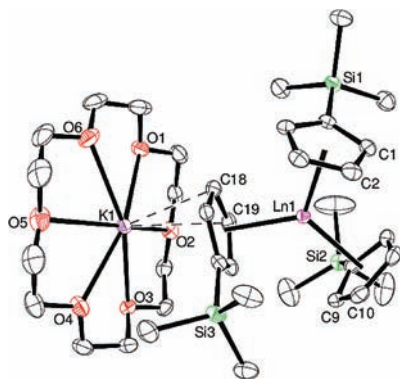

Figure 1. Molecular structure of **3** and **4** with thermal ellipsoids drawn at the 50% probability level and H atoms omitted for clarity.

was found that when all of the components (including the glassware) were prechilled in a −35 °C glovebox freezer, the reaction could be performed much more quickly with KC_8 in a one-step process that consistently gave higher yields. A concentrated solution of **1** and 18-crown-6 in Et_2O was quickly passed through a 1 cm × 10 cm glass column fitted with a filter frit and containing excess KC_8 in the manner of flash chromatography [Figure S1 in the Supporting Information (SI)]. The dark maroon-purple solution emanating from the tip of the column formed dark-purple **3** as a microcrystalline solid within seconds (eq 2). Cooling the solution to −65 °C produced more crystals of **3**.

Encouraged by these results, a similar reaction was tried with erbium, which is of similar size to Ho and Y. It should be noted that while the calculated Ln^{3+}/Ln^{2+} reduction potential for Ho (−2.9 V vs NHE[8]) is the same as the generic reduction potential of K, the calculated potential for Er is −3.1 V vs
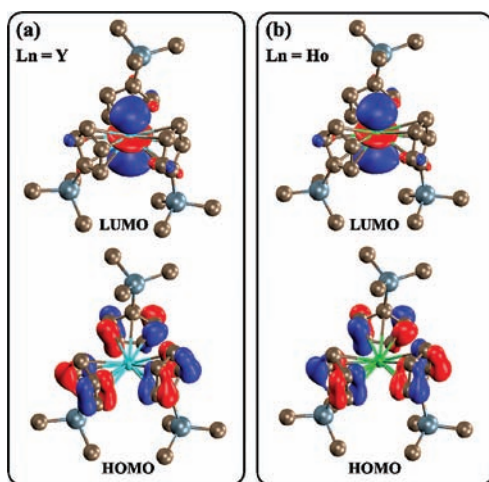

NHE,[8] on which basis a reaction would not be expected. Nonetheless, pale-orange Cp′$_3$Er (**2**) reacted with KC_8 to form the first molecular Er^{2+} complex, [(18-crown-6)K][Cp′$_3$Er] (**4**), as a dark-purple microcrystalline solid (eq 2). Both **3** and **4** decompose in THF, benzene, and toluene and react with N_2, even at −45 °C.

Complexes **3** and **4** (Figure 1) are isomorphous with each other and the Y analogue **5**.[1n] As in **5**, the K^+ ions in **3** and **4** are oriented toward two C atoms of one Cp′ ring, C18 and C19, with K−C distances of 3.053(8)−3.078(2) Å. The analogous distances are 3.079(2) and 3.055(2) Å in **5**. These are significantly shorter than the K−C(η^2-toluene) distances in [K(18-crown-6)(toluene)$_2$]$^+$ complexes (3.357−3.399 Å)[9] but at the long end of the range of K−C distances in KCp′ [2.99(1)−3.04(1) Å].[10] As shown in Table S2 in the SI, the juxtaposition of K^+ affects neither the Ln−C distances, the Ln−(Cp′ ring centroid) distances, nor the C−C distances. All three rings in each complex are bound to the rare-earth ion equivalently within the error limits.

The Ln^{3+} precursors **1** and **2** were crystallographically characterized for comparison with the structures of **3** and **4**. As in the cases of **5** versus Cp′$_3$Y[1n] and [K(18-crown-6)(OEt$_2$)]-[Cp″$_3$La] versus Cp″$_3$La [Cp″ = 1,3-(Me$_3$Si)$_2$C$_5$H$_3$],[5] the average Ln−(Cp′ ring centroid) distances in **3** and **4** are only slightly longer (by 0.021−0.029 Å) than those in **1** and **2**, respectively. This contrasts with the difference in Ln^{3+} versus Ln^{2+} bond distances for Ln = Eu, Yb, Sm, Tm, Dy, and Nd, where the Ln^{2+} distances are typically 0.05−0.2 Å longer than those for the Ln^{3+} ion.[1n,4c,11] It was previously noted[1n] that the smaller Ln^{2+} versus Ln^{3+} differences for La and Y may occur because these Ln^{2+} ions are d^1 and not f^{n+1} species. Bond distances are much less sensitive to the metal oxidation state for transition metals than for lanthanides. The same observation for these Ho and Er complexes is consistent with the density functional theory (DFT) calculations described next.

DFT calculations were carried out on the anions of **3**, **4**, and **5** and also on the neutral trivalent complexes **1**, **2**, and Cp′$_3$Y. Large f-in-core pseudopotentials[12] and the corresponding quasi-relativistic basis sets of Dolg et al.[13] were used for Ho and Er in compounds **1**−**4** to enforce a fixed $4f^n$ configuration for the f core of these metals (n = 10 for Ho and 11 for Er, corresponding to their respective Ln^{3+} configurations). The viability of the f-in-core calculations on **3** and **4** was confirmed by comparison to additional small-core calculations (detailed in the SI) in which the added electron was placed in a 4f orbital rather than a 5d orbital. The results of these calculations also supported a $4f^n5d^1$ occupation, validating the use of the chosen large-core pseudopotentials.

The highest occupied and lowest unoccupied molecular orbitals (HOMO and LUMO) of Cp′$_3$Y are shown in Figure 2a. The HOMO is ligand-based, and the LUMO resembles a $4d_{z^2}$ orbital, which is reasonable since Y is a second-row transition metal. Surprisingly, the HOMOs and LUMOs of the lanthanide complexes **1** and **2** (Figure 2b) are very similar to those of Cp′$_3$Y. Hence, the LUMOs of **1** and **2** resemble $5d_{z^2}$ orbitals,

Figure 2. HOMOs and LUMOs of the neutral complexes Cp'$_3$Ln for (a) Ln = Y and (b) Ln = Ho (**1**). The MO plots for **1** are very similar to those for the Er analogue **2**.

not 4f orbitals. While this was expected for the f-in-core pseudopotentials (in which the f orbitals are necessarily sequestered), the small-core calculations produced analogous results. DFT calculations on **3**–**5** showed a similar situation: the HOMOs of the [Cp'$_3$Ln]$^-$ anions in the Ln^{2+} complexes (Figure 3) are d$_{z^2}$-like orbitals, similar to the LUMOs of the
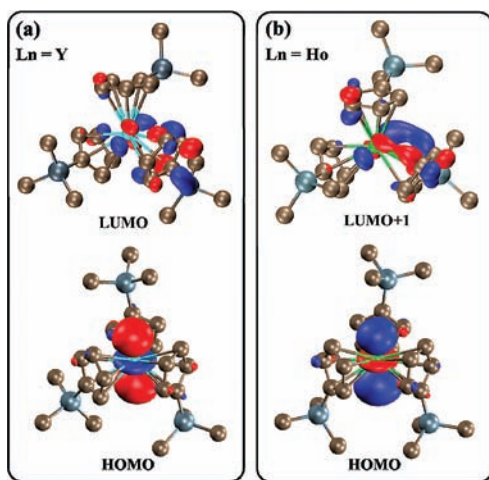

Figure 3. (a) HOMO and LUMO of the [Cp'$_3$Y]$^-$ anion in **5**. (b) HOMO and LUMO+1 of the [Cp'$_3$Ho]$^-$ anion in **3**. The MO plots for **3** are very similar to those for the Er analogue **4**.

neutral Ln^{3+} complexes. A similar set of orbitals was previously calculated for the [Cp''$_3$La]$^-$ anion in the La^{2+} complex [K(18-crown-6)(OEt$_2$)][Cp''$_3$La].[5]

The accessibility of the 5d orbitals in Ln^{2+} ions is supported by atomic spectra,[14] which show that the 4f/5d gap is much smaller in Ln^{2+} than in Ln^{3+}. Recent calculations on solid-state divalent lanthanide halides, chalcogenides, and pnictides consistently show that the 4f and 5d orbitals are similar in energy in the +2 oxidation state.[15] For **3** and **4**, the pseudo-D_{3h} crystal field generated by the three Cp' ligands may split the 4f and 5d orbitals in such a way that singly occupying a 5d orbital is more energetically favorable than forming a spin pair in the 4f manifold. Such splitting would favor the stabilization of the

4f^{n}5d^1 configuration of the metal ion, which is an excited configuration of the free ion.

The UV−vis spectra of **3** and **4** are similar to that of **5** (Figure 4a), which also suggests that **3** and **4** are d^1 species.
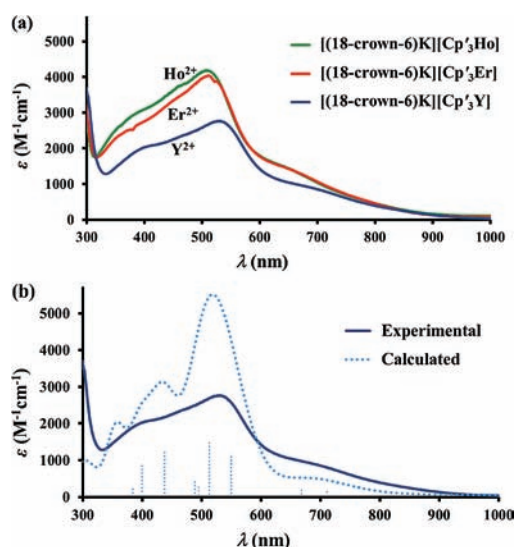

Figure 4. (a) UV−vis spectra of [(18-crown-6)K][Cp'$_3$Ln] [Ln = Ho (**3**), Er (**4**), Y (**5**)] measured at −30 °C in Et$_2$O. (b) Experimental (solid) and calculated (dotted) spectra of **5**.

Previous studies of the bonding and electronic structure of (η^5-C$_5$H$_5$)$_3$M complexes of transition metals,[16] lanthanides,[17] and actinides[17a,18] in which the three (C$_5$H$_5$)$^-$ rings provide a pseudo-D_{3h} coordination environment showed that the d$_{z^2}$ orbital is significantly lower in energy than the other d orbitals. Since the d$_{z^2}$ orbital cannot effectively interact with the π orbitals of the (C$_5$H$_5$)$_3^{3-}$ ligand set, it is not significantly destabilized, if at all, and remains essentially nonbonding with respect to the ligands. Bursten et al.[18a] previously noted for complexes of this type that if the isolated $(n + 1)$d$_{z^2}$ orbital in such D_{3h} structures is low enough in energy, it could potentially compete with the nf orbitals for metal-localized electrons. If **3** and **4**, like **5**, have d^1 configurations, electronic transitions from a ground-state a$_1'$ (d$_{z^2}$) orbital to higher-lying e'' (d$_{xz}$, d$_{yz}$) and e' (d$_{xy}$, d$_{x^2-y^2}$) orbitals in D_{3h} symmetry (or related nondegenerate orbitals in the actual C_1 symmetry) would be expected. As shown in Figure 3, the LUMO of **5** and LUMO+1 of **3** and **4** do show significant d$_{xz}$/d$_{yz}$ character.

Time-dependent DFT (TDDFT) calculations on **5** (see the SI) predicted an absorption maximum at 518 nm and a small shoulder at 665 nm (Figure 4b). These two bands are very close to the experimentally observed maxima for **5** at 530 and 700 nm. Substantial components of these excitations involve transitions from the HOMO to the LUMO, LUMO+2, LUMO+4, and LUMO+5, which Mulliken population analysis (MPA) predicted to have 59, 21, 3, 12, and 14% d character, respectively (Tables S7 and S8). Similarly, for **3** and **4**, excitations with absorption maxima at 476 and 679 nm (**3**) and 494 and 663 nm (**4**) were calculated (Figure S2) and found to comprise transitions from the HOMO to higher-lying LUMOs that also contain significant d character by MPA (Tables S7 and S8). These bands agree well with those experimentally observed at 507 and 650 nm for **3** and 510 and 650 nm for **4**. Both the experimental and theoretical maxima of the absorptions observed for **3** and **4** are slightly blue-shifted with respect to

those for **5**, consistent with stronger splitting for 5d- versus 4d-based orbitals. The extinction coefficients of the absorptions (ε = 900−4150 M^{-1} cm^{-1}) are larger than for pure d → d transitions and suggest significant ligand contributions. MPA also indicated that the orbitals involved in the computed transitions have significant ligand character, as is evident in the selected LUMO plots for **3−5** in Figure 3. The qualitative agreement of the TDDFT excitation spectra with the experimental spectra, in addition to the ground-state structural results, suggest that the 5d orbitals play a more important role in molecular divalent lanthanide chemistry than previously believed.

In summary, it is possible for Ho^{2+} and Er^{2+} to exist in molecular complexes. These new oxidation states require synthesis below −35 °C but do form compounds that are stable at room temperature in the solid state. The existence of these unexpected +2 ions raises the possibility that divalent species could be accessible for all of the lanthanides. In view of the recent reactivity observed for Y^{2+},[1m,n,19] it is likely that these new oxidation states will provide more opportunities for unusual reductive chemistry.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Additional experimental and computational details; crystallographic data collection, structure solution, and refinement; and crystallographic data for **1−4** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org. The crystallographic data for **1−4** have also been deposited with the CCDC (870731−870734).

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Notes
The authors declare no competing financial interest.

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■ NOTE ADDED AFTER ASAP PUBLICATION

Cp″ = 1,3-(Me$_3$Si)$_2$C$_5$Me$_3$ has been corrected to Cp″ = 1,3-(Me$_3$Si)$_2$C$_5$H$_3$, this reposted May 23, 2012.