Divalent Lanthanides

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Superbulky Ligands and Trapped Electrons: New Perspectives in Divalent Lanthanide Chemistry**

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electron localization · lanthanides · lanthanum · samarium · superbulky ligands

Halides of the rare-earth elements in the oxidation state +2 have been known since the early decades of the 20th century. $EuCl_2$, $SmCl_2$, and $YbCl_2$ were the first to be reported.[1,2] For the elements europium, samarium, and ytterbium all twelve MX_2 halides are known. This is not the case for the elements thulium, dysprosium, and neodymium for which only the halides of the triad chlorine, bromine, and iodine have been synthesized and crystallographically characterized. They structurally bear close resemblance to the respective alkaline-earth metal halides.[3,4] The electronic configurations of the M^{2+} ions of these six elements are $6s^0 5d^0 4f^n$ with $n=4$ (Nd), 6 (Sm), 7 (Eu), 10 (Dy), 13 (Tm), and 14 (Yb).

These halides are produced as solids either by comproportionation reactions ($2\,MX_3$ + M)[4] or by Wöhler's metallothermic reduction from the trihalides with alkali metals.[4c] The reduction potentials for the reactions $M^{3+} + e^- \rightarrow M^{2+}$ range between -0.35 V (M = Eu) and -2.6 V (Nd),[5] the highest values being similar to that of the half cell K/K^+ (-2.92 V).[6] With the proper choice of ligand, it should be possible to produce these six lanthanides in solution in the oxidation state +2 by alkali metal (potassium) reduction from trivalent precursors.

There were two major discoveries in the outgoing 20th century that boosted the solution chemistry of divalent lanthanides: First, the synthesis of $[Sm(C_5Me_5)_2]$[7] and the discovery that it reduces molecular nitrogen to form the dimeric $[Sm_2(C_5Me_5)_4N_2]$.[8] Second, the discovery that THF or DME would not be reduced by divalent thulium.[9] $[TmI_2(dme)_3]$[10] followed by $[DyI_2(dme)_3]$[11] and $[NdI_2(thf)_5]$[12] were the first molecular complexes of divalent thulium, dysprosium, and neodymium that could be handled in solution under argon (!) and crystallized. Although these latter three complexes were not organometallic compounds, their existence has stimulated vigorous research with organic ligands and, meanwhile, there are organometallic examples for all of these six lanthanides in the oxidation state +2.[13]

Two strategies have proved successful: 1) The ligands should preferably be (super)bulky organic ligands. 2) The formation of an anionic complex in combination with a bulky cation enhances the stability by its gain in lattice energy. Two examples for the use of superbulky ligands alone were first reported in lectures at a conference on rare-earth metals ("Tage der Seltenen Erden 2007") in Bonn. The first is $[Sm(Cp^{BIG})_2]$, which was synthesized by spontaneous reduction of the Sm^{III} species $[Sm_3(2\text{-}Me_2N\text{-benzyl})]$ with $Cp^{BIG}H$ $[Cp^{BIG}H = (4\text{-}n\text{BuC}_6H_4)_5C_5H)]$.[15] The dark brown crystals consist of molecules with parallel ligands of opposite chirality (Figure 1). The second is the Yb^{II} compound $[Yb(CpPh_5)_2]$ produced in different ways from Yb^{II} precursors (Figure 2).[16]

The spontaneous reduction of $[Sm^{III}(2\text{-}Me_2N\text{-benzyl})_3]$ with $Cp^{BIG}H$ to give $[Sm(Cp^{BIG})_2]$ is another beautiful example of the application of the sterically induced reduction

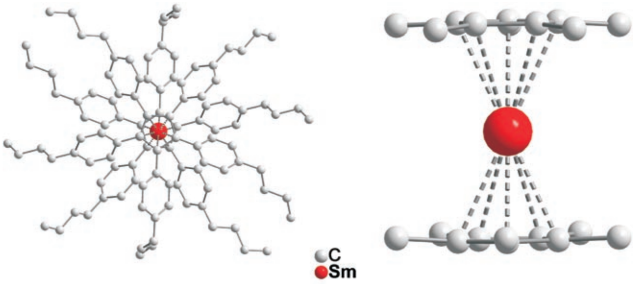

Figure 1. The molecular structure of $[Sm(Cp^{BIG})_2]$ in the solid state as viewed from the top and from the side. The Sm–Cp_{center} distance is 250.50(8) pm; for the analogous compound $[Yb(Cp^{BIG})_2]$, Yb–Cp_{center} is 238.2(1) pm.

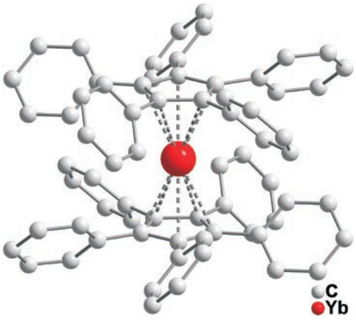

Figure 2. The molecular structure of $[Yb(CpPh_5)_2]$ in the solid state, d(Yb–Cp_{center}) = 237.1 pm.

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(SIR) concept, which was introduced by Evans[17] to explain, for example, why [SmCp*$_3$] (Cp* = C_5Me_5) may act as a reductant. The sterically overcrowded environment of Sm^{III} is thought to be responsible for the high reactivity of [SmCp*$_3$], which is either reduced by the (Cp*)$^-$ ligand to a Sm^{II} species that then transfers one electron to a reactant, or one only loosely bound ligand reduces directly (the (Cp*)$^•$ radicals dimerize in any case) leaving a Sm^{II} species behind.

The chemistry of the six divalent lanthanides, whose compounds mimic the (divalent) alkaline-earth elements structurally and electronically in a sense that there are only 4f states occupied, is now well under way, although by no means fully explored. However, there are ten more rare-earth elements that deserve consideration. Four of these elements are known to form diiodides (LaI_2, CeI_2, PrI_2, and GdI_2); hence the metal atoms adopt the oxidation state +2.[3] LaI_2 behaves like a two-dimensional 5d metal.[18] CeI_2 shows antiferromagnetic order at $T_N = 10$ K.[19] PrI_2 has at least five modifications that exhibit the full range between metallic, semi-metallic, and insulating behavior; one modification features a tetrahedral cluster.[20] GdI_2 is a ferromagnet below 290 K and displays giant negative magnetoresistance.[21] Scandium "diiodide" is in fact $Sc_{0.9}I_2$.[22] It behaves as a (two-dimensional) metal above about 100 K and an insulator below this temperature. The phase transition is associated with an electronic transition from a 3d^1 band at high temperatures to a localized 3d^1 state at low temperatures. Thus, at low temperatures the electrons are trapped at the scandium core, hence scandium is then "truly" divalent. PrI_2-IV appears to behave analogously at low temperatures. Therefore, we cannot only state that praseodymium has the oxidation state +2 (this is the case in all modifications of PrI_2), it is also divalent in the sense that "Pr^{2+}" has the electronic configuration 6s^{0}5d^{1}4f^2.[20b] The important difference to the above-mentioned six pseudo-alkaline-earth lanthanides is that a "configuration crossover" has taken place. One electron is now in a 5d state as opposed to the six pseudo-alkaline-earth lanthanides, in which all electrons are localized in 4f states!

Attempts to get solid LaI_2 in solution in a controlled manner have not been successful. The above-mentioned concepts (superbulky ligands, formation of a salt) have recently been applied to isolate [K([2.2.2]crypt)][LaCp″$_3$] (Cp″ = 1,3-$(SiMe_3)_2C_5H_3$), [2.2.2]crypt = 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane) as a blue-violet paramagnetic solid from the colorless precursor [LaCp″$_3$] by potassium reduction in THF in the presence of [2.2.2]crypt (Figure 3).[23] The anion [LaCp″$_3$]$^-$ is nearly trigonal planar, the average La-Cp″$_{center}$ distance is 262.0 pm, slightly larger than the corresponding distance in the La^{III} precursor [LaCp″$_3$] (260.0 pm).[24]

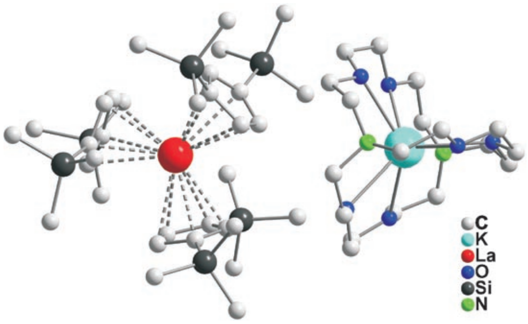

Figure 3. The molecular structures of the cation and anion of [K([2.2.2]crypt)][LaCp″$_3$] in the solid state.

Magnetic susceptibility measurements reveal one unpaired electron in [K([2.2.2]crypt)][LaCp″$_3$]. Solid-state and especially solution EPR spectra show that this unpaired electron is located ("trapped") at the ^{139}La nucleus and not at one of the three ligands which would then have to be dinegatively charged. Thus, divalent lanthanum is present. In principle, the electronic configuration for lanthanum(II) could be 6s^{0}5d^{1}4f^0 or 6s^{0}5d^{0}4f^1. The latter configuration would mean that the attraction between La^{2+} and the three (Cp″)$^-$ ligands would only be strictly ionic, the former could involve three-center–one-electron bonding orbitals. Indeed, computational studies at the DFT level show that the singly occupied molecular orbital (SOMO) of the anionic complex is located on the lanthanum atom (Figure 4), which supports the configuration 6s^{0}5d^{1}4f^0.

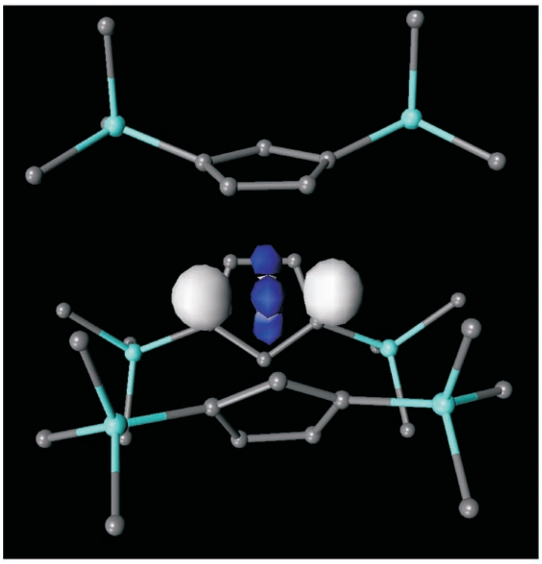

Figure 4. The SOMO in the anion [LaCp″$_3$]$^-$; cyan Si, gray C. Reproduced with permission from Prof. M. Lappert (University of Sussex).

The first observation of lanthanum(II) centers in the salts [K([2.2.2]crypt)][LaCp″$_3$] and [K([18]crown-6)(Et_2O)][LaCp″$_3$] as well as of cerium(II) centers in the co-crystals [K([18]crown-6)(Et_2O)][CeCp″$_3$]·[CeCp″$_3$][23] is not only spectacular in its own right but it opens up a completely new area of research in reduced rare-earth element chemistry. The race is now on to complete the series of divalent complexes for the remainder of the rare-earth elements (Y, Tb, Ho, Er, Lu). Furthermore, in connection with the recently established Mg^I compounds, RMg–MgR (R = $(2,6\text{-}i\text{Pr}_2C_6H_3N)_2CN\,i\text{Pr}_2$),[25] it appears possible to establish σ-bonded dinuclear scandium or lanthanide compounds using the synthetic strategies now well established. Furthermore, as lanthanum(I) is known in the solid state in LaI,[26] why should it not be possible to realize molecular lanthanum(I) compounds in solution? And, with the above-mentioned cerium(II) compound as well as cerium's well-established oxidation state +4 in mind, two-electron reduction processes, which are so important in transition-metal chemistry, are perhaps in reach.

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[6] All these values are referenced for aqueous solutions against NHE (normal hydrogen electrode). In other solvents they may be reduced dramatically. Cyclic voltammetric measurements of the Sm^{3+} to Sm^{2+} reduction exhibit values of −1.51 V in THF and −0.22 V in the ionic liquid (mppyr)(Tf_2N) [1-methyl-1-propyl-pyrrolidinium bis(trifluoromethanesulfonyl)amide]. A.-V. Mudring, personal communication, **2008**.

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[13] The term valence is used here although there is no unanimous definition for it. Pauling's definition that the term "…valence…determines the number of other atoms with which an atom of the element can combine."[14] is strictly only useful for molecular compounds. The oxidation number of an atom in a compound is straightforwardly defined as the "number which represents the electrical charge which the atom would have if the electrons in a compound were assigned to the atoms" for which there are clear rules.[14] The electronic configuration of the respective atoms is often not considered in detail although it is the only physical reality.

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