

“Impossible” Divalent Lanthanide Complexes

Tiffany Diane Hopper

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For many years, the lanthanides did not generate much interest, as it was believed that their chemistry was limited, owing to the restricted availability of oxidation states other than that of Ln^{3+} . In fact, for the better part of a century, Eu^{2+} , Yb^{2+} , Sm^{2+} , and Ce^{4+} were the only non-trivalent lanthanide ions thought achievable in molecular complexes.¹ The reduction potentials for the $\text{Ln}^{3+} + e^- \rightarrow \text{Ln}^{2+}$ process (Figure 1) make it clear why Ln^{2+} ions are commonly seen only for a few lanthanides: the majority of the Ln^{3+} ions have reduction potentials of -2.3 V or greater.² In the latter half of the twentieth century, a flurry of solid state syntheses led to lattice-bound divalent lanthanides which were, as a rule, produced under extreme conditions (for example, by reacting lanthanide metal with lanthanide trihalides in a welded tantalum crucible at 600-1000 °C).³ Despite the discovery of these divalent lanthanide ions, their utilization in molecular chemistry was not reported, and the assumption that Eu^{2+} , Yb^{2+} , and Sm^{2+} were the only divalent lanthanides available for reduction chemistry persisted. It was not until 1997, when the first report of a crystallographically-characterized molecular complex of divalent thulium appeared,⁴ that the perception of available lanthanide oxidation states began to change.

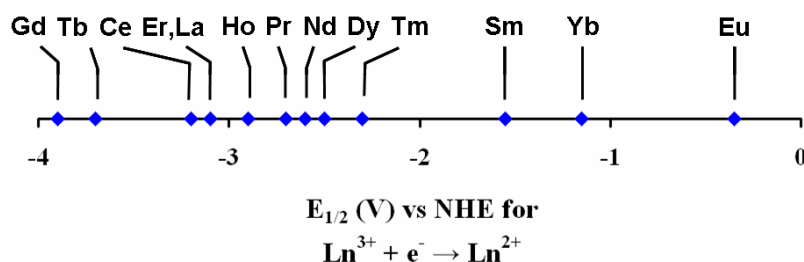
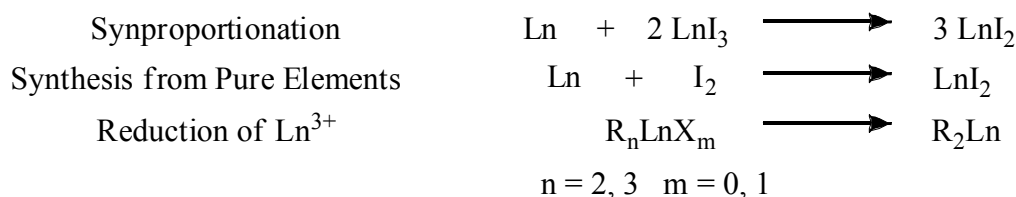


Figure 1. Reduction potentials for the $\text{Ln}^{3+} + e^- \rightarrow \text{Ln}^{2+}$ process.

The discovery of a molecular complex of divalent thulium, which was synthesized by reduction of TmI_3 by Tm metal in refluxing 1,2-dimethoxyethane (DME),⁴ quickly led to the discovery of synthetic routes to other divalent lanthanides.⁵⁻⁹ The three primary methods for obtaining divalent lanthanides are shown in Scheme 1. The first is a synproportionation reaction, in which the trivalent triiodide is reduced by the lanthanide metal.⁴ A second method is synthesis directly from the pure metal and iodine.⁵⁻⁷ Finally, the third approach is reduction of a trivalent lanthanide, R_nLnX_m (where R is an anionic organic ligand, X is a halide, $n = 2$ or 3 , and $m = 0$ or 1).^{8,9} The following reports of “new” divalent lanthanides (those other than Sm, Eu, and Yb) are organized based on the synthetic approach used to make them: synproportionation, synthesis from the pure elements, and reduction of R_nLnX_m .



Scheme 1. Synthetic methods for obtaining divalent lanthanides other than Sm^{2+} , Eu^{2+} , and Yb^{2+} .

The first “new” divalent lanthanide obtained by the synproportionation reaction was also the first non-Sm, Eu, Yb divalent lanthanide molecular complex, the divalent thulium complex, $\text{TmI}_2(\text{DME})_3$ **1**.⁴ This molecule adopts a pentagonal bipyramidal geometry (Figure 2) that has also been observed in the related samarium diiodide complexes $\text{SmI}_2(\text{THF})_5$ **2**, $\text{SmI}_2(\text{DME})(\text{THF})_3$ **3**, and $\text{SmI}_2(\text{DME})_2(\text{THF})$ **4**. The average Tm – I distance of 3.16(2) Å in **1** is about 0.1 Å less than the Sm – I distances in **3** and **4** (3.231(1) – 3.246(1) Å), which is consistent with the 0.13 Å difference in ionic radii between Tm and Sm. Other bond distances in **1** and **3-4**, as well as in Tm^{3+} complexes, support the presence of Tm^{2+} in **1**. Additionally, the measured effective magnetic moment of **1**, 4.53 μ_B (293 K), is in agreement with the calculated value for a $4f^{13}$ electron configuration of 4.5 μ_B , and is significantly different from typical values measured for Tm^{3+} , which fall in the range of 7.1 – 7.5 μ_B .⁴ Taken together, this information confirms the divalent nature of the thulium center in **1**.

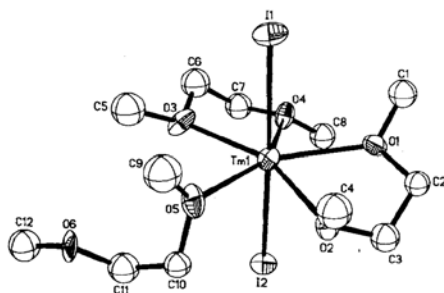


Figure 2. Crystal structure of $\text{TmI}_2(\text{DME})_3$ (thermal ellipsoid plot, with ellipsoids drawn at the 50% probability level). Figure from reference 4.

The second synthetic method for achieving “new” divalent lanthanides, synthesis from the pure elements, has found great success. Use of this method led to the first molecular complexes of divalent neodymium and dysprosium in 1999.⁵ Briefly, dysprosium or neodymium metal shavings were combined with iodine in a sealed glass tube, and heated under static vacuum to ~200 °C. The mixture reacts violently to yield the divalent lanthanide diiodide as a black solid, which can be crushed with a mortar and pestle and subsequently dissolved in DME or THF to yield colored solutions of the solvated lanthanide diiodide ($\text{NdI}_2(\text{THF})_5$, $\text{NdI}_2(\text{DME})_3$, $\text{DyI}_2(\text{THF})_5$, $\text{DyI}_2(\text{THF})_3$, and $\text{DyI}_2(\text{DME})_3$, **5 – 9** respectively). The divalent nature of these complexes was supported by the measured effective magnetic moment (Nd only), elemental analysis, UV-Vis, IR, and qualitatively by solution and/or crystal color. Whereas Bochkarev et al. described the first synthesis and solvation of NdI_2 and DyI_2 , Evans et al. reported the first crystal structure of $\text{DyI}_2(\text{DME})_3$, produced a year later by the same method.⁶ Through an analysis similar to that applied to the crystal structure of $\text{TmI}_2(\text{DME})_3$, as well as through energy dispersive absorption X-ray spectroscopy (EDAX) studies of the crystal, Evans et al. unambiguously established the divalency of dysprosium in **9**. Two years after the initial report of divalent neodymium and dysprosium complexes, Bochkarev et al. published the first crystal structure of a divalent neodymium molecular complex, $\text{NdI}_2(\text{THF})_5$, also synthesized by the method originally reported.⁷ Comparison of the crystal structure parameters (bond lengths and angles) of **5** with other divalent lanthanide complexes further verified that the neodymium was in the 2+ oxidation state (in addition to the measured magnetic moment⁵ reported previously).

Utilization of the third approach, reduction of a trivalent organolanthanide to yield the divalent organolanthanide, supplied the first divalent lanthanum molecular complex, $[\text{K}([\text{18}]\text{crown-6})(\eta^2\text{-C}_6\text{H}_6)_2][(\text{La}(\eta^5\text{-C}_5\text{H}_3(\text{CMe}_3)_2\text{-1,3})_2(\mu\text{-}\eta^6\text{:}\eta^6\text{-C}_6\text{H}_6))]^8$. The divalency of this complex was established by comparison of the bond lengths with those of similar trivalent La complexes. This method has also yielded organodysprosium(II) complexes, $[(\text{Cp}^{\text{ttt}})_2\text{Dy}(\mu\text{-X})\text{K}([\text{18}]\text{crown-6})]$, where X = BH_4 , Br, or I.⁹

In addition to serving as precursors to other divalent lanthanide complexes, several of the lanthanide diiodides have been applied to organic reactions. Early work indicated that reagents such as $\text{TmI}_2(\text{DME})_3$ may be too reducing to be useful in organic syntheses.¹⁰ However, later reports by Evans et al. and Bochkarev et al. established that the reductive reactivity of TmI_2 , DyI_2 , and NdI_2 is intermediate between that of $\text{Sm}(\text{II})$ complexes and Birch reducing agents, offering more reducing power than $\text{Sm}(\text{II})$ while maintaining greater functional group selectivity than Birch reducing agents.^{6,11-13} DyI_2 and NdI_2 can reduce naphthalene to 1,4-dihydronaphthalene,^{6,11} while all three LnI_2 compounds (Ln = Tm, Nd, Dy) reduce azobenzene to 1,2-diphenylhydrazine.¹² Additionally, these three LnI_2 compounds have shown improved activity over analogous SmI_2 complexes in the coupling of alkyl halides with ketones^{6,11,13} and aldehydes,¹¹ while avoiding the use of carcinogenic HMPA. Recently, DyI_2 was found to initiate silyl-radical catalyzed cyclotrimerization of terminal alkynes and polymerization of methyl methacrylate with higher chemoselectivity and under milder conditions than the previous system, which utilized expensive Si_2Cl_6 .¹⁴

Over the past decade, the number of molecular divalent lanthanide complexes accessible in solution has more than doubled. This fact is surprising, considering that the stable oxidation states of the lanthanides were considered to be well established prior to these discoveries. Use of these new divalent lanthanide complexes in synthetic organic applications is still in the early developmental stages, and, thus, their potential as one electron reductants is largely unexplored.

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