

# Synthesis of alcohol and tetrahydrofuran complexes of lanthanide(III) ions from hydrated salts

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The aim of this work was the development of a synthetic route for the preparation of anhydrous halide complexes of lanthanide(III) ions with labile organic ligands, employing commercial hydrated salts as starting materials. The desired water-free products are themselves promising precursors of fine chemicals<sup>1</sup>. The methodologies described so far in the literature for these syntheses are intricate, demanding several steps of dehydration or the use of reactants that are difficult to handle<sup>2,3</sup>. In this work, anhydrous compounds were readily prepared by reaction between  $\text{LnCl}_3 \cdot 6\text{H}_2\text{O}$  ( $\text{Ln} = \text{Gd}^{\text{III}}$  or  $\text{Dy}^{\text{III}}$ ) and triethylorthoformate,  $\text{HC}(\text{OC}_2\text{H}_5)_3$ , in the presence of a large excess of propan-2-ol ( $\text{HO}^i\text{Pr}$ ) or tetrahydrofuran (thf). The reaction mixtures [ $1\text{Ln}^{\text{III}}:2.5\text{HC}(\text{OC}_2\text{H}_5)_3$ ] were stirred at room temperature for 30 min, before being dried under vacuum to provide white solids (products **1** and **2** with Gd/isopropanol and Gd/thf, respectively), which were then redissolved in  $\text{HO}^i\text{Pr}$  or thf at room temperature or at 60 °C. Colorless block-like crystals (39% yield of **1** and 61% of **2**) were obtained from these solutions after two days. Results of elemental analysis obtained for **1** were: found (%) C, 23.8 and H, 6.36; required for  $\text{C}_{18}\text{H}_{48}\text{Cl}_6\text{Gd}_2\text{O}_6$  (%): C, 24.4 and H, 5.45. For **2**: found (%) C, 30.5 and H, 6.28; required for  $\text{C}_{28}\text{H}_{56}\text{Cl}_6\text{Gd}_2\text{O}_7$  (%): C, 32.6 and H, 5.47. FTIR analyses of **1** showed a broad band at  $3355\text{ cm}^{-1}$  assigned to  $\nu(\text{O-H})$ , and other absorptions at 1140, 1087 and  $1032\text{ cm}^{-1}$ , attributed to  $\nu(\text{C-O})$  of  $\text{HO}^i\text{Pr}$ , while the single-crystal X-ray diffraction analysis revealed the binuclear structure of  $[\text{Gd}_2\text{Cl}_4(\mu\text{-Cl})_2(\text{HO}^i\text{Pr})_6]$ . For **2**, the FTIR spectrum presented two bands at 922 and  $870\text{ cm}^{-1}$ , assigned to  $\nu_{\text{as}}(\text{COC})_{\text{thf}}$ , and one band at  $670\text{ cm}^{-1}$  due to the  $\nu_{\text{s}}(\text{COC})_{\text{thf}}$  absorption. Also for **2**, X-ray diffractometry revealed the ionic complex  $[\text{trans-GdCl}_2(\text{thf})_5][\text{trans-GdCl}_4(\text{thf})_2]^4$ , with a pentagonal bipyramidal cation and an octahedral anion. Other two products, mononuclear  $[\text{GdCl}_3(\text{thf})_4]$  (complex **3**) and tetranuclear  $[\text{Gd}_4\text{Cl}_6(\text{thf})_{10}]$  (complex **4**), both characterized by single-crystal X-ray diffraction analysis, were obtained respectively by recrystallization of **2** in thf and by reaction of pure **1** with thf at room temperature. For dysprosium(III), in turn, the only tetrahydrofuran-containing complex obtained so far (product **5**) is isostructural with **2**, while the crystalline, isopropanol-containing product **6** is still being characterized. In summary, this work describes an easy synthetic route for anhydrous lanthanide(III) compounds and reveals that the thf-containing complexes of  $\text{Gd}^{\text{III}}$  tend to interconvert in solution. Further solid state and solution characterization of all products by EPR spectroscopy is under way in our laboratory.

<sup>1</sup>Rigamonti, L. *et al. Chem. Eur. J.* **2015**, *21*, 12171; <sup>2</sup>Willey, G.R.; Woodman, T.J., Drew, M.G.B. *Polyhedron* **1997**, *16*, 3385; <sup>3</sup>Niemeyer, M., *Z. Anorg. Allg. Chem.* **2006**, *632*, 1449; <sup>4</sup>Deacon, G.B. *et al. Aust. J. Chem.* **1998**, *51*, 75.