Lanthanide compounds are presently used in several fields of fundamental and applied chemistry, such as organic synthesis and catalysis. Moreover, they have played a relevant role in the development of new technologies, being used, for instance, in superconductors and magnetic materials, luminescent sensors, contrast reagents, and shift reagents in NMR spectroscopy. Therefore, the availability of convenient lanthanide precursors to prepare new materials is currently an important target of modern research.

We have found that lanthanides can be conveniently extracted as \(N,N\)-dibutylcarbamato complexes from aqueous solutions of their chlorides into heptane solutions of dibutylamine saturated with \(\text{CO}_2\). This method allowed the extraction of \(
\text{La(III), Ce(III), Nd(III), Sm(III), Eu(III), Tb(III) and, recently, Tm(III) carbamato derivatives. Complexes of formula [\text{Ln} (\text{O}_2 \text{CNBu}_2)_3\], [\text{NH}_2 \text{Bu}_2]_2[\text{Ln}_6 (\text{CO}_3)(\text{O}_2 \text{CNBu}_2)]_2\text{] and [\text{Ln}_4 (\text{CO}_3)(\text{O}_2 \text{CNBu}_2)]_10\text{] have been obtained and characterized. Interestingly, starting from aqueous solutions containing two or more lanthanide chlorides in a well-defined molar ratio, the preparation of mixed carbamato complexes is possible where the lanthanides molar ratio can be controlled. For example, when the procedure of extraction was carried out starting from an aqueous solution containing \(\text{Eu}^{3+}, \text{Tb}^{3+}\) and \(\text{Tm}^{3+}\) ions (Eu:Tb:Tm molar ratio 1:1:1), complex \([\text{NH}_2 \text{Bu}_2]_2[\text{Ln}_4 (\text{CO}_3)(\text{O}_2 \text{CNBu}_2)]_2\text{] formed, with \(\text{Ln}_4 = \text{Eu}_{1.33} \text{Tb}_{1.33} \text{Tm}_{1.33}\). Metal carbamato complexes, [\text{M} (\text{O}_2 \text{CNR}_2)_n]\text{, react with protic agents LH, with evolution of CO}_2\text{ and R}_2\text{NH and formation of the corresponding [Ln(L)]}_n\text{] (eq 1). This reaction has been conveniently used for the preparation of pentafluorophenolate and dibenzoylmethane complexes of Tb(III) and Nd(III) starting from the appropriate [\text{Ln} (\text{O}_2 \text{CNBu}_2)_3]\text{. The products so obtained can easily add other ligands, because of the usually high coordination numbers shown by lanthanide metal centers. This way, ligands showing a strong “antenna effect” can be introduced into the coordination sphere of the metal, leading to photoluminescent complexes. Moreover, a solid support containing Brønsted’s acid sites on the surface can be used as protic agent (eq 1). When this procedure was carried out with silica, it was possible to graft the metals on the support surface. The following further derivatization of the obtained material with “antenna” ligands afforded luminescent silica based samples. The photoluminescence properties of all the complexes prepared as well as those of the silica samples obtained after grafting of lanthanides on its surface, are currently under investigation.

\[
\text{Ln} (\text{O}_2 \text{CNBu}_2)_3 + \text{LH} + \text{R}_2\text{NH} \rightarrow \text{Ln} (\text{O}_2 \text{CNBu}_2)_3 \text{L} + \text{CO}_2 + \text{R}_2\text{NH}
\]

(eq 1)

\#

represent the molecular fragment A or the support surface.

The reactivity of carbamato complexes towards protic agents has been further exploited with LH = \(\text{H}_2\text{O}\). In this case, a controlled hydrolysis of lanthanide carbamato precursors was carried out, leading to carbonato intermediates that were converted, upon a suitable thermal treatment, into the corresponding oxides. For...
example, when \([\text{Ce}((\text{CNBu}_2)_3])\) was hydrolyzed, nanocrystalline cerium(III) carbonates or hydroxocarbonate (characterized by IR, XRD and metal content) were obtained, in dependence of the experimental conditions. Thermal treatment of these products at relatively low temperatures (200 °C) yielded \(\text{CeO}_2\) in the form of a light yellow powder. The structure and morphology of the samples were studied by transmission electron microscopy (TEM), field emission scanning electron microscopy (FESEM), specific surface area determinations (BET) and X ray diffraction (XRD) studies. The medium crystallite dimensions, calculated according to the Scherrer’s equation and checked by TEM, appear to be of a few nanometers.

The use of carbamato complexes as precursors of oxides appears to be convenient for the preparation of mixed species: if the hydrolysis procedure is carried out on a mixture of metal carbamates where the molar ratio between metals is accurately chosen, the composition of the final oxide can be controlled. A similar hydrolysis/calcination procedure has been carried out on a mixture of \([\text{Cu}(\text{O}_2\text{CNBu}_2)_2(\text{Py}^*)_2]\) and \([\text{La}_4(\text{CO}_3)(\text{O}_2\text{CNBu}_2)_{10}]\) (\(\text{Py}^* = 4\text{-dimethylaminopyridine, [La]/[Cu] molar ratio = 2.06}\)), leading to the mixed oxide \(\text{La}_2\text{CuO}_4\) that was characterized by XRD. The approach is particularly attractive for the controlled preparation of many mixed oxides.

Key words: lanthanides, carbamato complexes, photoluminescence, grafting, silica, oxides

Publications:

1. Daniela Belli Dell’Amico, Luca Labella, Fabio Marchetti, Simona Samaritani
   A convenient route to dinuclear chloro-bridged platinum(II) derivatives via nitrile complexes

2. Daniela Belli Dell’Amico, Claudio Broglia, Luca Labella, Fabio Marchetti, Daniele Mendola, Simona Samaritani
   Platinum(II) complexes containing unsaturated ligands. Nucleophilic substitution versus nucleophilic attack to ligand: a stereochemistry driven outcome

3. Daniela Belli Dell’Amico, Luca Labella, Fabio Marchetti, Piero Mastrorilli, Simona Samaritani, Stefano Todisco
   Oxidation by dioxygen of manganese(II) and iron(II) complexes

4. Daniela Belli Dell’Amico, Luca Labella, Fabio Marchetti, Simona Samaritani
   The reactivity of the dinuclear halo-bridged cycloplatinated complex \([\text{Pt}(\mu-\text{Cl})(k^2-P,C)\text{P}(\text{OC}_6\text{H}_4)(\text{OPh})_2)]_2\)
towards neutral ligands

5. Lidia Armelao, Daniela Belli Dell’Amico, Paolo Biagini, Gregorio Bottaro, Stefano Chiaberge, Paola Falvo, Luca Labella, Fabio Marchetti, Simona Samaritani
   Preparation of N,N-dialkylcarbamato lanthanide complexes by extraction of lanthanide ions from aqueous solution into hydrocarbons

6. Lidia Armelao, Daniela Belli Dell’Amico, Gregorio Bottaro, Paola Falvo, Luca Labella, Fabio Marchetti, Daniela Parisi, Simona Samaritani
   From lanthanide chlorides to lanthanide pentafluorophenolates via lanthanide N,N-dialkylcarbamates
   Polyhedron 2015, 85, 770.

7. S. Dolci, D. Belli Dell’Amico, A. Pasini, L. Torre, G. Pace, D. Valentini
   Platinum Catalysts Development for 98% Hydrogen Peroxide Decomposition in Pulsed Monopropellant Thrusters

8. Daniela Belli Dell’Amico, Massimo De Sanctis, Randa Ishak, Sara Dolci, Luca Labella, Marco Lezzerini, Fabio Marchetti
   Cerium(III) N,N-dibutylcarbamate as precursor to nanocrystalline cerium dioxide
   Cat. Today, submitted.
SUPPLEMENTARY MATERIAL

Position of the components of the Research Groups

<table>
<thead>
<tr>
<th>Name</th>
<th>Surname</th>
<th>Position *</th>
<th>Affiliation</th>
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<tbody>
<tr>
<td>Daniela</td>
<td>Belli Dell’ Amico</td>
<td>PO</td>
<td>University of Pisa</td>
</tr>
<tr>
<td>Luca</td>
<td>Labella</td>
<td>PA</td>
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</tr>
<tr>
<td>Fabio</td>
<td>Marchetti Sr</td>
<td>PA</td>
<td>University of Pisa</td>
</tr>
<tr>
<td>Simona</td>
<td>Samaritani</td>
<td>RU</td>
<td>University of Pisa</td>
</tr>
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*: PO = Full professor; PA = Associate professor; RU = University researcher; CO = contract; PoD = Postdoctoral fellows; RC = CNR staff or other Institutions Research; T = technician, VR = visiting researcher, S = student

Equipment

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<td>FTIR spectrometer Spectrum 100 with extended range (7800-225 cm⁻¹)</td>
<td>PerkinElmer</td>
<td>2009</td>
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<tr>
<td>Stirred.high pressure reactor 300 mL with temperature control</td>
<td>Parr Instrument Company</td>
<td>2009</td>
</tr>
<tr>
<td>Microscope SteREO Discovery.V8 supplied with photo-camera</td>
<td>Zeiss</td>
<td>2008</td>
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Technical skills
- Synthesis and characterization of organometallic and coordination compounds.
- Study of the reactivity of organometallic and coordination compounds.