The activity of this research group concerns:

i) Synthesis of lanthanide complexes for the preparation of highly luminescent materials;

ii) Synthesis of lanthanide and transition metal carbamato complexes for the preparation of mixed oxides;

iii) Synthesis of platinum complexes with antiproliferative properties.

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 $CO_2$. This method allowed the extraction of La(III), Ce(III), Nd(III), Sm(III), Eu(III), Tb(III) and, recently, Tm(III) carbamato derivatives. Complexes of formula $[Ln(O_2CNBu_2)_3]$, $[NH_2Bu_2]_2[Ln_4(CO_3)(O_2CNBu_2)]_{12}$ and $[Ln_4(CO_3)(O_2CNBu_2)]_{10}$ 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 $Eu^{3+}$, $Tb^{3+}$ and $Tm^{3+}$ ions ($Eu:Tb:Tm$ molar ratio 1:1:1), complex $[NH_2Bu_2]_2[Ln_4(CO_3)(O_2CNBu_2)]_{12}$ formed, with $Ln_4 = Eu_{1.33}Tb_{1.33}Tm_{1.33}$. Metal carbamato complexes, $[M(O_2CNR_2)_3]$, react with protic agents LH, with evolution of $CO_2$ and $R_2NH$ and formation of the corresponding $[Ln(L)_3]_n$ (eq 1).

$$3LH + [Ln(O_2CNR_2)_3] \rightarrow [Ln(L)_3]_n + CO_2 + NHR_2$$ (1)

This reaction has been conveniently used for the preparation of pentafluorophenolato, dibenzyolmethanato and hexafluoroacetylacetonato complexes of Tb(III) and Nd(III) starting from the appropriate $[Ln(O_2CNBu_2)_3]$ precursor. 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. Complexes $[Ln(L)_3]_n$ were then successfully reacted with divergent bidentate ligands and afforded highly luminescent 1D-zig-zag coordination chains. Moreover, a solid support containing Brønsted’s acid sites on the surface can be used as protic agent (Scheme). 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.
ii) The reactivity of carbamato complexes towards protic agents has been further exploited with LH = H$_2$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 [Ce(O$_2$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 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 [Cu(O$_2$CNBu$_2$)$_2$(Py$^*$)$_2$] and [La$_4$(CO$_3$)(O$_2$CNBu$_2$)$_{10}$] (Py$^*$ = 4-dimethylaminopyridine, [La]/[Cu] molar ratio = 2.06), leading to the mixed oxide La$_2$CuO$_4$, that was characterized by XRD. The approach is particularly attractive for the controlled preparation of many mixed oxides.

iii) New neutral and ionic platinum complexes were prepared starting from cis-[PtCl$_2$(PPh$_3$)(NCMe)] or trans-[Pt$_2$Cl$_4$(PPh$_3$)$_2$] (Figure 1). The antiproliferative properties of some of the complexes were tested in vitro towards cancer cell lines HeLa, H460, A549, MSTO-211H, A2780 and A2780cis. Complexes bearing N-coordinated ligands trans to PPh$_3$ showed the highest activity, being in some cases able to overcome cisplatin resistance.

Figure 1. New platinum(II) complexes prepared. a) L = DMSO, N-benzo[thiazole, pyrazine, pyridine, HN=C(Me)N=Et, CO, R(R')C=N=N(0H); b)L' = ArCH$_2$NH(Bu), pyridine, R(R')C=N=N(0H); c) N—N = pyrazine, 4,4'-bipyridyl, piperazine, 1,4-phenylenediamine; d) N—N = 2,2'-bipyridyl, 1,10-phenanthroline.

Studies are in progress to prepare analogous platinum(IV) derivatives.
External collaborations:

- Università di Padova;
- CNR ICMATE and INSTM, Dipartimento di Scienze Chimiche, Università di Padova
- Istituto di Scienze e Tecnologie Molecolari, ISTM-CNR, Milano
- Centro Ricerche per le Energie Rinnovabili e l’Ambiente. Istituto Donegani, ENI S.p.A
- Università di Cagliari

Key words: lanthanides, carbamato complexes, photoluminescence, grafting, silica, oxides, platinum, antiproliferative properties.

Publications:

1. 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

2. 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

   Platinum Catalysts Development for 98% Hydrogen Peroxide Decomposition in Pulsed Monopropellant Thrusters

4. 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

   Interaction of cisplatin and two potential antitumoral platinum(II) complexes with a model lipid membrane: a combined NMR and MD study

6. Daniela Belli Dell’Amico, Paolo Biagini, Stefano Chiaberge, Lorenzo Falchi, Luca Labella, Marco Lezzerini, Fabio Marchetti, Simona Samaritani
   Partial and exhaustive hydrolysis of lanthanide N,N-dialkylcarbamato complexes. A viable access to lanthanide mixed oxides

7. 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

8. Daniela Belli Dell’Amico, Lisa Dalla Via, Aida Nelly Garcia-Argaez, Luca Labella, Fabio Marchetti, Simona Samaritani
   Antiproliferative activity of platinum(II) complexes containing triphenylphosphine: Correlation between structure and biological activity

9. Lisa Dalla Via, Aida Nelly Garcia-Argáez, Enzo Agostinelli, Daniela Belli Dell’Amico, Luca Labella, Simona Samaritani
   New trans dichloro (triphenylphosphine)platinum(II) complexes containing N-(butyl),N-(aryl methyl)amino ligands: Synthesis, cytotoxicity and mechanism of action
10. Lidia Armelao, Daniela Belli Dell’Amico, Luca Bellucci, Gregorio Bottaro, Luca Labella, Fabio Marchetti, Simona Samaritani
Smart Grafting of Lanthanides onto Silica via N,N-Dialkylcarbamato Complexes

11. Lidia Armelao, Daniela Belli Dell’Amico, Luca Bellucci, Gregorio Bottaro, Luca Labella, Fabio Marchetti, Simona Samaritani
A convenient synthesis of highly luminescent lanthanide 1D-zigzag coordination chains based only on 4,4’-bipyridine as connector

12. Daniela Belli Dell’ Amico, Luca Labella, Fabio Marchetti, Simona Samaritani, Gustavo Alejandro Hernández-Fuentes, Aida Nelly García-Argáez, Lisa Dalla Via
Synthesis and antiproliferative activity of ionic platinum(II) triphenylphosphino complexes
Polyhedron 2016, 119, 396.

13. Daniela Belli Dell’ Amico, Luca Bellucci, Luca Labella, Fabio Marchetti, Simona Samaritani
Reactivity of platinum(II) triphenylphosphino complexes with nitrogen donor divergent ligands
Polyhedron 2016, 119, 403.

14. Daniela Belli Dell'Amico, Alessio Di Giacomo, Lorenzo Falchi, Luca Labella, Marcello Marelli, Claudio Evangelisti, Marco Lezzerini, Fabio Marchetti, Simona Samaritani
A convenient preparation of La4CuO4 from molecular precursors
Polyhedron 2017, 123, 33.

SUPPLEMENTARY MATERIAL

Position of the components of the Research Groups

<table>
<thead>
<tr>
<th>Name</th>
<th>Surname</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>
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<td>PA</td>
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<tr>
<td>Fabio</td>
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</tr>
<tr>
<td>Simona</td>
<td>Samaritani</td>
<td>RU</td>
<td>University of Pisa</td>
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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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<tr>
<td>FTIR spectrometer Spectrum 100 with extended range (7800-</td>
<td>PerkinElmer</td>
<td>2009</td>
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Technical skills
• Synthesis and characterization of organometallic and coordination compounds.
• Study of the reactivity of organometallic and coordination compounds.