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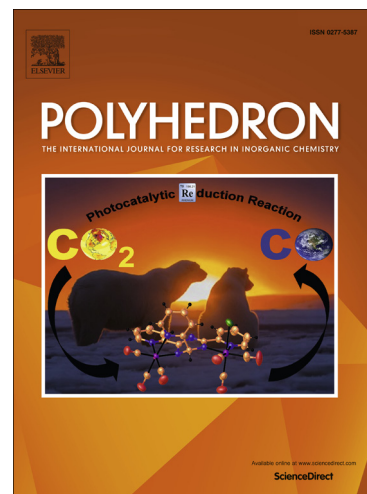
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Partial and exhaustive hydrolysis of lanthanide *N,N*-dialkylcarbamato complexes. A viable access to lanthanide mixed oxides.

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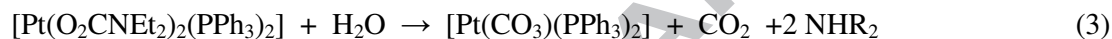
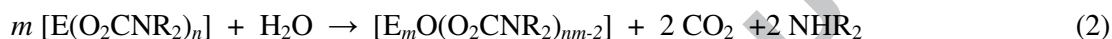
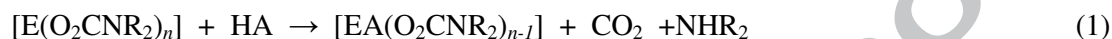
ABSTRACT

Partial hydrolysis ($\text{H}_2\text{O}/\text{Ln}$ molar ratio = $\frac{1}{4}$) of lanthanum di-*iso*-propylcarbamato complex, $[\text{La}(\text{O}_2\text{CN}^i\text{Pr}_2)_3]$, **1**, afforded the tetranuclear μ -oxo derivative $[\text{La}_4\text{O}(\text{O}_2\text{CN}^i\text{Pr}_2)_{10}]$, **2**, which was structurally characterized by single crystal X-Ray diffraction studies. The carbonato-carbamato derivative of lanthanum, $[\text{La}_4(\text{CO}_3)(\text{O}_2\text{CNBu}_2)_{10}]$, **3**, was prepared by extraction of lanthanum ions from aqueous solution into heptane by the $\text{NHBu}_2/\text{CO}_2$ system. Partial hydrolysis ($\text{H}_2\text{O}/\text{Ln}$ molar ratio = $\frac{1}{2}$) of *N,N*-di-*iso*-propylcarbamato complexes of neodymium, europium, gadolinium and terbium, $[\text{Ln}(\text{O}_2\text{CN}^i\text{Pr}_2)_3]$, yielded the derivatives $[\text{Ln}_2(\text{CO}_3)(\text{O}_2\text{CN}^i\text{Pr}_2)_4]$ ($\text{Ln} = \text{Nd}$, **4**, Eu , **5**, Gd , **6**). Exhaustive hydrolysis of $[\text{Ln}(\text{O}_2\text{CNR}_2)_3]$ ($\text{Ln} = \text{Nd}$, Tb , $\text{R} = \text{Bu}$; $\text{Ln} = \text{Eu}$, Gd , $\text{R} = ^i\text{Pr}$, Bu) produced hydrated lanthanide carbonates, $\text{Ln}_2(\text{CO}_3)_3 \cdot n \text{H}_2\text{O}$. For sake of comparison with a block d metal, the exhaustive hydrolysis of two copper(II) carbamato complexes, $[\text{Cu}(\text{O}_2\text{CNEt}_2)_2(\text{NH}_2\text{Et})_2]$ and $[\text{Cu}(\text{O}_2\text{CN}^i\text{Pr}_2)_2]$, was carried out with formation in both cases of the hydrated basic carbonate $\text{Cu}_2(\text{OH})_2(\text{CO}_3) \cdot n \text{H}_2\text{O}$. The exhaustive hydrolysis of mixtures of cerium and lanthanum or cerium and terbium *N,N*-dibutylcarbamato complexes allowed the preparation of mixed oxides containing the two metals in the desired molar ratio, via the intermediate formation of the corresponding mixed carbonates.

1. Introduction

N,N-dialkylcarbamato complexes, $[E(O_2CNR_2)_n]$ and $[E(O_2CNR_2)_nL_m]$, containing the anionic ligand $R_2NCO_2^-$, are a family of compounds where E can be an element of all the blocks of the periodic table (s, p, d and f), for instance Na, Mg, B, Al, Si; Sn, Ti, Fe, Mo, Pd, Au, Nd, Lu, U, to cite only a part of them [1]. These derivatives readily react with protic agents, HA, with evolution of CO_2 and substitution of the carbamato ligand (Eq 1).

Their partial hydrolysis yields μ -oxo derivatives, as sketched in eq 2 [2]. In a few cases the formation of carbonato complexes is observed (Eq 3) [3].



The first μ -oxo derivative of this class of compounds, $[U_4(\mu_3-O)_2(O_2CNEt_2)_{12}]$, was obtained serendipitously, in low yields, in the course of the synthesis of $[U(O_2CNEt_2)_4]$ [2a]. The formation of the uranium(IV) μ -oxo tetranuclear compound in good yields by reaction of the homoleptic precursor with the stoichiometric amount of water was subsequently demonstrated. Several μ_n -oxo-carbamato complexes ($n = 2, 3, 4$) of various nuclearity (3, 4, 8, 10), as obtained by partial hydrolysis of the homoleptic precursors, have been structurally characterized (Table 1) [2].

Among the examples of evolution of the hydrolysis towards carbonato species (Table 2), beyond the platinum complex reported in eq 3 [3a], a mononuclear derivative of ruthenium(II) [3b] was structurally characterized. Furthermore, polynuclear carbonato-carbamato derivatives of magnesium [4] and of some lanthanides (Sm, Eu, Tb) [5] were obtained in the course of syntheses of metal carbamato complexes carried out without complete exclusion of water.

It is interesting that μ -oxo-carbamato- instead of expected carbonato-carbamato derivatives are often obtained also for low valent metal centres, reasonably associated with rather basic oxides. For instance, in the case of magnesium(II), μ -oxo- or μ -carbonato-carbamato species (Tables 1 and 2) were obtained in the course of the carbonation of the metal amide $[Mg(N^iPr_2)_2]$ in dependence of the reaction conditions. According to the authors [4b], crystals

of the partial hydrolysis product $[\text{Mg}_6(\mu_4\text{-O})(\text{O}_2\text{CN}^i\text{Pr}_2)_{10}]$, in place of the expected $[\text{Mg}(\text{O}_2\text{CN}^i\text{Pr}_2)_2]$, were obtained after having bubbled CO_2 into a $\text{Mg}(\text{N}^i\text{Pr}_2)_2$ solution for 5 min. Any attempts of carbonation of $[\text{Mg}_6(\mu_4\text{-O})(\text{O}_2\text{CN}^i\text{Pr}_2)_{10}]$ in THF failed. On the other hand, when CO_2 was bubbled into the $[\text{Mg}(\text{N}^i\text{Pr}_2)_2]$ solution for 30 min and the product was then recrystallized from HMPA/ toluene, crystals of $[\text{Mg}_5(\mu_5\text{-CO}_3)(\text{O}_2\text{CN}^i\text{Pr}_2)_8(\text{HMPA})_2]$ separated out. The formation of the oxo- or carbonato complex from the same precursor is interesting and can be a useful example that shows as the outcome of the process may depend on apparently negligible differences of the reaction conditions.

Table 1. Structurally characterized oxo-dialkylcarbamato derivatives obtained by hydrolysis of metal *N,N*-dialkylcarbamato complexes

<i>Metal ion</i>	<i>formula</i>	<i>R</i>	<i>Ref</i>
U(IV)	$[\text{U}_4(\mu_3\text{-O})_2(\text{O}_2\text{CNR}_2)_{12}]$	Et	[2a]
Cu(II)	$[\text{Cu}_8(\mu_4\text{-O})_2(\text{O}_2\text{CNR}_2)_{12}]$	ⁱ Pr	[2b]
Zn(II)Ni(II)	$[\text{Zn}_2\text{Ni}_6(\mu_4\text{-O})_2(\text{O}_2\text{CNR}_2)_{12}]$	ⁱ Pr	[2c]
Cr(III)	$\text{Cr}_3(\mu_3\text{-O})(\text{O}_2\text{CNR}_2)_6\text{Cl}(\text{NHR}_2)$	Et	[2d]
Fe(II)	$[\text{Fe}_8(\mu_4\text{-O})_2(\text{O}_2\text{CNR}_2)_{12}]$	ⁱ Pr	[2e]
Mg(II)	$[\text{Mg}_6(\mu_4\text{-O})(\text{O}_2\text{CNR}_2)_{10}]$	ⁱ Pr	[4b]
Al(III)	$[\text{Al}_4(\mu_3\text{-O})_2(\text{O}_2\text{CNR}_2)_8]$	ⁱ Pr	[2f]
Fe(III)	$\text{Fe}_4(\mu_3\text{-O})(\text{O}_2\text{CNR}_2)_9\text{Cl}$	^s Bu	[2g]
Fe(III)	$\text{Fe}_{10}(\mu_3\text{-O})_3(\mu_4\text{-O})_3(\text{O}_2\text{CNR}_2)_{17}\text{Cl}$	Et	[2g]
Mn(II), Co(II), Ni(II)	$[\text{M}_8(\mu_4\text{-O})_2(\text{O}_2\text{CNR}_2)_{12}]$	ⁱ Pr	[2k]
Zn(II)	$[\text{Zn}_4(\mu_4\text{-O})(\text{O}_2\text{CNR}_2)_6]$	Me, Bu	[2i]
Ti(IV)	$[\text{Ti}_8(\mu_2\text{-O})_8(\text{O}_2\text{CNR}_2)_{16}]$	Et	[2l]

Table 2. Structurally characterized carbonato derivatives obtained by hydrolysis of metal *N,N*-dialkylcarbamato complexes

<i>Metal ion</i>	<i>formula</i>	<i>Notes about CO₃ group</i>	<i>R</i>	<i>Ref</i>
Pt(II)	$\text{Pt}(\text{CO}_3)(\text{PPh}_3)_2$	Terminal, bidentate	Et	[3a]
Ru(II)	$\text{Ru}(\text{CO}_3)(\text{CO})_2(\text{PPh}_3)_2$	Terminal, bidentate	ⁱ Pr	[3b]
Mg(II)	$[\text{R}_2\text{NH}_2]_3[\text{Mg}_8(\mu_6\text{-CO}_3)_2(\text{O}_2\text{CNR}_2)_{15}]$		Me	[4a]
Mg(II)	$[\text{Mg}_5(\mu_5\text{-CO}_3)(\text{O}_2\text{CNR}_2)_8(\text{HMPA})_2]$		ⁱ Pr	[4b]
Sm(III)	$[\text{NH}_2\text{R}_2]_2[\mu_3\text{-Sm}_4(\text{CO}_3)(\text{O}_2\text{CNR}_2)_{12}]$		Bu	[5]
Eu(III)	$[\text{NH}_2\text{R}_2]_2[\mu_3\text{-Eu}_4(\text{CO}_3)(\text{O}_2\text{CNR}_2)_{12}]$		Bu	[5]
Tb(III)	$[\text{NH}_2\text{R}_2]_2[\mu_3\text{-Tb}_4(\text{CO}_3)(\text{O}_2\text{CNR}_2)_{12}]$		Bu	[5]
Ag(I)	Ag_2CO_3		ⁱ Pr	[6]

Hydrolysis of molecular complexes is an attractive approach to finely divided oxides [7], especially when the precursors can be easily prepared.

Exhaustive hydrolysis of carbamato complexes was reported for silicon and aluminum with production of dialkylammonium silicates $[\text{NH}_2\text{R}_2]_2\text{Si}_n\text{O}_{2n+1}$ or aluminates $[\text{NH}_2\text{R}_2]\text{Al}_n\text{O}_{(3n+1)/2}$ [8]. Moreover the complete hydrolysis of titanium(IV) *N,N*-dialkylcarbamato complexes yielded dialkylammonium titanates [9]. Furthermore, starting from cerium(III) *N,N*-dibutylcarbamate, the hydrated metal carbonates, $\text{Ce}_2(\text{CO}_3)_3 \cdot n\text{H}_2\text{O}$ were obtained when the hydrolysis was carried out at room temperature [10] and they were readily converted to CeO_2 by treatment at 200 °C in air. Indeed ceria based materials find a lot of applications in several

fields of chemistry and technology [11,12],[13] and the development of efficient methods for the preparation of pure or doped ceria is a theme of considerable interest [14].

As a part of a project aimed at studying the *N,N*-dialkylcarbamato metal complexes, $[M(O_2CNR_2)_n]$, as precursors of oxo- or carbonato derivatives we have examined the partial and exhaustive hydrolysis of some lanthanide complexes. In this paper the hydrolysis of lanthanide *N,N*-dialkylcarbamates, with production of oxo-carbamato or carbonato-carbamato complexes and of lanthanide hydrated carbonates is reported.

In the final part of this paper we describe the preparation of mixed Ce/Ln cerium oxides starting from solutions containing *N,N*-dibutylcarbamato complexes of cerium(III) and a second lanthanide (La or Tb) in a specific molar ratio. Mixed lanthanide oxides have been obtained showing the lanthanide molar ratio used in the parent solution.

2. Experimental

2.1. Materials and instrumentation

Commercial lanthanum and terbium oxides (La_2O_3 , Aldrich, 99.9 %; Tb_4O_7 , Strem Chemicals, 99.9 %, Nd_2O_3 , Aldrich, 99.9 %); Gd_2O_3 (Koch Light Laboratories LTD, 99.9 %); Eu_2O_3 (Strem Chemicals, 99.99 %) and cerium chloride heptahydrate ($CeCl_3 \cdot 7H_2O$, Carlo Erba) were used without further purification. $NHEt_2$, NH^iPr_2 and $NHBU_2$ were freshly distilled under N_2 according to the conventional methods. In the extraction processes commercial $NHBU_2$ was used without purification. Aqueous solutions of the lanthanum and terbium chlorides were prepared by dissolving the appropriate metal oxide in diluted hydrochloric acid. The solution was then evaporated to dryness and the solid residue was dissolved in water. $[LaCl_3(DME)]$ was prepared according to the literature [15]. $[Ln(O_2CN^iPr_2)_3]$, $[Ln(O_2CNBU_2)_3]$ ($Ln = Nd, Eu, Gd$) [16], $[Ce(O_2CNBU_2)_3]$ [10] and $[Tb(O_2CNBU_2)_3]$ [5] were prepared according to the literature.

All manipulations except extractions were performed under a dinitrogen atmosphere unless otherwise noted. FTIR spectra in the solid state were recorded with a Perkin-Elmer "Spectrum One" spectrometer, with ATR technique. The lanthanide content of the products was determined according to this procedure: each sample was treated in a platinum crucible with diluted HNO_3 and the mixture gently warmed; the resulting solution was then evaporated to dryness. After calcination, the weight of the solid residue [corresponding to the lanthanide oxide] was determined. The copper content was determined by EDTA titration. The carbon dioxide content of metal carbamates was measured by gas-volumetry of the CO_2 content upon

decomposition with 20 % sulfuric acid. The gas volumetric apparatus was substantially similar to that previously described by Cotton and Calderazzo [17]. Both determinations were carried out in controlled atmosphere to avoid the sample hydrolysis by exposure to air. Volumetric analyses via EDTA titration were also carried out on the aqueous layer discarded after extraction [18].

SEM-EDX analyses were carried out on a Philips XL 30 instrument. Samples were prepared placing a portion of the powder on a pin stub covered with a conductive tape and then metalized with graphite.

High resolution mass spectrometry (HRMS) analysis was performed on a 7 Tesla LTQ FT-Ultra instrument (Thermo Scientific) equipped with an APPI (Atmospheric Pressure Photo Ionization) ionization source. The samples were dissolved [0.02 mg/ml] in a 1:1 v/v mixture of MeCN/toluene. Toluene acted both as solvent and as dopant in the ionization process [19]. The solutions were injected with a flow rate of 50 $\mu\text{l}/\text{min}$. The ion source was equipped with a vacuum ultraviolet gas (Krypton) discharge lamp. Nitrogen was used as the nebulizing gas, the vaporizer temperature was 350 $^{\circ}\text{C}$, the capillary voltage 15 V, the capillary temperature 270 $^{\circ}\text{C}$, and the Tube Lens Voltage 140 V. Mass spectra were recorded in positive mode with a mass range of 400-4000 m/z , with an average resolving power of 400000 at m/z 400, in profile mode, microscan 1, max injection time 1000, and with an automatic gain control (AGC) on the ICR (Ion Cyclotron Resonance) cell of 10^6 . A minimum of 100 scans were collected and averaged for each analysis to improve the signal to noise ratio. Data were processed by the software Xcalibur (Thermo Scientific). For the molecular formula assignments, the experimental (accurate) m/z values have been compared with the calculated ones, and as additional confirmation the experimental and theoretical isotope cluster distribution of the main species of the mass spectra have been compared.

The thermogravimetric analysis (TGA) of $[\text{La}_4(\text{CO}_3)(\text{O}_2\text{CNBu}_2)_{10}]$, **3**, was carried out through a Netzsch Jupiter F1 Thermogravimetric balance (TGA). About 20 mg of **3** were moved first into an alumina basket (sample holder) in a N_2 atmosphere dry box (in order to avoid hydrolysis). Then the sample was rapidly transferred into the instrument for the analysis. The sample was heated from 40 $^{\circ}\text{C}$ to 550 $^{\circ}\text{C}$ at a heating rates, 20 $^{\circ}\text{C min}^{-1}$, in a nitrogen flow of 50 ml min^{-1} .

The amount of the volatile components in the mixed lanthanide carbonates was determined through a simultaneous thermal analyzer Netzsch 449, which combines a sensitive balance for use in thermogravimetric analysis (TG), with a heat-flux differential scanning calorimetry (DSC) for simultaneous TG-DSC analysis.

TG and DSC analyses were obtained in the following instrumental conditions: open alumina crucibles, heating rate of 10 °C/min under 30 ml/min nitrogen gas flow, 25 mg of sample dried at room temperature.

2.1.1. Synthesis of $[La(O_2CN^iPr_2)_3]$, **1**, from $[LaCl_3(DME)]$

A solution of NH^iPr_2 (13.5 mL, 96.5 mmol) in 200 mL of toluene was stirred under CO_2 up to complete amine carbonation equilibrium was reached. $[LaCl_3(DME)]$ (4.57 g, 13.6 mmol) was then introduced and the suspension was stirred under CO_2 for 2 days. The suspension was filtered and the solid, principally formed of $NH_2^iPr_2Cl$, was discarded. The filtrate was concentrated to dryness and the colourless residue was dried *in vacuo* at room temperature for 3 h. The solid was then treated with heptane (25 mL). The suspension was filtered and the solid was dried *in vacuo* (3.78 g; 48.6 % yield). Anal. Calcd for $C_{21}H_{42}LaN_3O_6$: CO_2 , 23.1; La, 24.3. Found: CO_2 , 23.2; La: 24.3 %. IR (1700-1300, cm^{-1}): 1578s, 1524m, 1468s, 1450s, 1382s, 1354s.

2.1.2. Partial hydrolysis of $[La(O_2CN^iPr_2)_3]$, (La/ H_2O) molar ratio = 4. Formation of $[La_4O(O_2CN^iPr_2)_{10}]$, **2**

$[La(O_2CN^iPr_2)_3]$ (478 mg, 0.836 mmol) was dissolved in heptane (50 mL). A solution of water (50 μ L, 2.78 mmol) in THF (50 mL) was prepared and a portion of this solution (3.70 mL, 0.205 mmol) was added dropwise to the lanthanum complex solution. After 12 h crystals were formed (100 mg, 24 % yield). After having selected some single crystals of suitable dimensions to carry out X-Ray diffraction studies, the product was dried *in vacuo*. Anal. Calcd for $[La_4O(O_2CN^iPr_2)_{10}]$, $C_{70}H_{140}La_4N_{10}O_{21}$: CO_2 , 21.9; La, 27.6. Found: CO_2 , 21.4; La: 27.5 %.

2.1.3. Extraction of lanthanum ions from aqueous solution into heptane by the $NHBu_2/CO_2$ system with formation of $[La_4(CO_3)(O_2CNBu_2)_{10}]$, **3**

A solution of dibutylamine (10.0 mL, 66 mmol) in heptane (50 mL) was saturated with carbon dioxide and cooled at 0 °C. An aqueous solution of lanthanum chloride (20 mL, 0.33 M, 6.6 mmol) was cooled at 0°C. The two solutions were mixed and shaken for a few seconds at 0 °C. The aqueous layer was removed and the organic layer was separated and evaporated at reduced pressure (1.0×10^{-3} Torr). The colorless oil was dissolved in a few mL of heptane. The solution was evaporated again and the process was repeated three times. The colorless solid was dried *in vacuo* at 35 °C (1.95 g, 50.5 % yield). Anal. Calcd for

$\text{La}_4(\text{CO}_3)(\text{O}_2\text{CNBu}_2)_{10}$, $\text{C}_{91}\text{H}_{180}\text{LaN}_{10}\text{O}_{23}$: CO_2 , 20.7; La, 23.8. Found: CO_2 , 21.0; La: 23.4 %. IR ATR (1700-1300, cm^{-1}): 1519m, 1481ms, 1423ms, 1375m, 1313s. Mass spectrometry, APPI (m/z ratio; relative abundance; fragment): 1138.51 $[\text{La}_2(\text{O}_2\text{CNBu}_2)_5]^+$ (60%); 2120.92 $[\text{La}_4(\text{O})(\text{O}_2\text{CNBu}_2)_9]^+$ (100 %); 2315.96 $[\text{La}_4(\text{O})(\text{O}_2\text{CNBu}_2)_{10}]\text{Na}^+$ (3%).

2.1.4. Partial hydrolysis of $[\text{Ln}(\text{O}_2\text{CN}^i\text{Pr}_2)_3]$, $\text{Ln} = \text{Nd, Eu, Gd}$, ($\text{Ln}/\text{H}_2\text{O}$) molar ratio = 2. Formation of $[\text{Ln}_2(\text{CO}_3)(\text{O}_2\text{CN}^i\text{Pr}_2)_4]$ (**4**, $\text{Ln} = \text{Nd}$; **5**, $\text{Ln} = \text{Eu}$; **6**, $\text{Ln} = \text{Gd}$).

The reactions were carried out following the same procedure. The case of neodymium is reported at length.

Neodymium. A solution of water (33 μL , 1.83 mmol) in THF (50 mL) was added to a solution of $[\text{Nd}(\text{O}_2\text{CN}^i\text{Pr}_2)_3]$ (2.14 g; 3.71 mmol) in heptane (150 mL). The solution was stirred at room temperature for 48 h. The solution was concentrated to dryness and the violet residue was dried *in vacuo* for 3 h (1.22 g, 71.1 % yield). Anal. Calcd for $[\text{Nd}_2(\text{CO}_3)(\text{O}_2\text{CN}^i\text{Pr}_2)_4]$, $\text{C}_{29}\text{H}_{56}\text{N}_4\text{Nd}_2\text{O}_{11}$: CO_2 , 23.8; Nd, 31.2. Found: CO_2 , 23.5; Nd: 31.3 %. IR (1700-1300, cm^{-1}): 1544s, 1521s, 1490s, 1466s, 1440s, 1385s, 1354s.

Europium. $[\text{Eu}(\text{O}_2\text{CN}^i\text{Pr}_2)_3]$ (1.38 g; 2.36 mmol); water (8.4 mL of a 0.14 M solution of water in THF, corresponding to 1.18 mmol of H_2O). 0.86 g, yield 77.5 %. Anal. Calcd for $[\text{Eu}_2(\text{CO}_3)(\text{O}_2\text{CN}^i\text{Pr}_2)_4]$, $\text{C}_{29}\text{H}_{56}\text{N}_4\text{Eu}_2\text{O}_{11}$: CO_2 , 23.4; Eu, 32.3. Found: CO_2 , 23.2; Eu: 32.0 %. IR (1700-1300, cm^{-1}): 1569s, 1532s, 1512s, 1484s, 1467s, 1451, 1384s, 1353s.

Gadolinium. $[\text{Gd}(\text{O}_2\text{CN}^i\text{Pr}_2)_3]$ (1.05 g; 1.78 mmol); water (6.2 mL of a 0.14 M solution of water in THF, corresponding to 0.87 mmol of H_2O). 0.73 g, 86 % yield. Anal. Calcd for $[\text{Gd}_2(\text{CO}_3)(\text{O}_2\text{CN}^i\text{Pr}_2)_4]$, $\text{C}_{29}\text{H}_{56}\text{N}_4\text{Gd}_2\text{O}_{11}$: CO_2 , 23.1; Gd, 33.1. Found: CO_2 , 22.1; Gd: 32.7 %. IR (1700-1300, cm^{-1}): 1526s, 1483s, 1468s, 1450s, 1385s, 1354s.

2.1.5. Exhaustive hydrolysis of $[\text{Ln}(\text{O}_2\text{CNR}_2)_3]$, $\text{Ln} = \text{Nd, Eu, Gd, Tb}$; $\text{R} = ^i\text{Pr}$ and/or Bu , with formation of $[\text{Ln}_2(\text{CO}_3)_3].n\text{H}_2\text{O}$

The reactions were carried out following the same procedure. The case of neodymium N,N -dibutylcarbamato complex is reported at length.

$\text{Ln} = \text{Nd}$; $\text{R} = \text{Bu}$. To a solution of $[\text{Nd}(\text{O}_2\text{CNBu}_2)_3]$ (0.93 g; 1.41 mmol) in heptane (100 mL) a solution of water (250 μL , 13.89 mmol) in THF (50 mL) was added dropwise. The solution was stirred at room temperature for 48 h. The suspension was filtered and the pink solid was dried *in vacuo* (0.35 g, 89 % yield). Anal. Calcd for $[\text{Nd}_2(\text{CO}_3)_3].5\text{H}_2\text{O}$, $\text{C}_3\text{H}_{10}\text{Nd}_2\text{O}_{14}$: CO_2 , 23.6; Nd, 51.6. Found: CO_2 , 23.0; Nd: 51.8 %. IR (the most significant bands, cm^{-1}): 3367s, broad, 1630sh, 1494s, 1427s.

$Ln = Eu; R = Bu$. $[Eu(O_2CNBu_2)_3]$ (1.09 g; 1.63 mmol); water (300 μ L, 16.7 mmol) in THF (15 mL). 0.37 g, 79 % yield. Anal. Calcd for $[Eu_2(CO_3)_3] \cdot 5H_2O, C_3H_{10}Eu_2O_{14}$: CO₂, 23.0; Eu, 52.9. Found: CO₂, 24.0; Eu: 53.6 %. IR (the most significant bands, cm^{-1}): 3367s, broad, 1632sh, 1510s, 1400s.

$Ln = Gd; R = Bu$ $[Gd(O_2CNBu_2)_3]$ (0.95 g; 1.41 mmol); water (280 μ L, 15.6 mmol). 0.157 g, 73 % yield. Anal. Calcd for $[Gd_2(CO_3)_3] \cdot 5H_2O, C_3H_{10}Gd_2O_{14}$: CO₂, 22.6; Gd, 53.8. Found: CO₂, 23.1; Gd: 54.1 %. IR (the most significant bands, cm^{-1}): 3370s, broad, 1640sh, 1500s, 1413s.

$Ln = Tb; R = Bu$ $[Tb(O_2CNBu_2)_3]$ (7.61 g; 11.3 mmol); water (11 mL, 611 mmol, H₂O/metal molar ratio 51.7). 3.20 g, 91 % yield. Anal. Calcd for $[Tb_2(CO_3)_3] \cdot 7H_2O, C_3H_{14}Gd_2O_{16}$: Tb, 50.9. Found: Tb: 50.6 %. IR (the most significant bands, cm^{-1}): 3370s, broad, 1579sh, 1494s, 1410s.

$Ln = Eu; R = {}^iPr$. $[Eu(O_2CN{}^iPr_2)_3]$ (1.00 g; 1.71 mmol); water (320 μ L, 17.8 mmol) in THF (16 mL). 0.34 g, 68 % yield. Anal. Calcd for $[Eu_2(CO_3)_3] \cdot 6H_2O, C_3H_{12}Eu_2O_{15}$: CO₂, 22.3; Eu, 51.3. Found: CO₂, 21.9; Eu: 51.6 %. IR (the most significant bands, cm^{-1}): 3370 broad, 1640sh, 1500s, 1410s.

$Ln = Gd; R = {}^iPr$. $[Gd(O_2CN{}^iPr_2)_3]$ (0.73 g; 1.24 mmol); water (260 μ L, 14.4 mmol) in THF (13 mL). 0.30 g, 83 % yield. Anal. Calcd for $[Gd_2(CO_3)_3] \cdot 5H_2O, C_3H_{10}Gd_2O_{14}$: CO₂, 22.6; Gd, 53.8. Found: CO₂, 22.4; Gd: 53.2 %. IR (the most significant bands, cm^{-1}): 3370s, broad, 1640sh, 1500s, 1413s.

2.1.6. Exhaustive hydrolysis of copper(II) carbamate complexes

$[Cu(O_2CNEt_2)_2(NHEt_2)]_2$. A solution of $[Cu(O_2CNEt_2)_2(NHEt_2)]_2$ (2.46 g; 6.7 mmol of copper) in absolute EtOH (50 mL) was treated under N₂ with 3.40 mL of H₂O (189 mmol). A pale blue suspension was obtained. After 3 h stirring at room temperature the suspension was filtered. The solid was dried *in vacuo* (0.59 g; 71% yield with respect to the copper content). Anal. Calcd for $[Cu_2(CO_3)(OH)_2] \cdot 1.5 H_2O, C_1H_5Cu_2O_{6.5}$: CO₂, 17.7; Cu, 51.2. Found: CO₂, 16.0; Cu: 51.0 %, CO₂/Cu molar ratio: 0.45. IR (the most significant bands, cm^{-1}): 3400s, broad, 1510s, 1430sh, 1400s.

$[Cu(O_2CN{}^iPr_2)_2]$. A solution of $[Cu(O_2CN{}^iPr_2)_2]$ (3.78 g; 10.7 mmol) in absolute EtOH (80 mL) was treated under N₂ with 4.50 mL of H₂O (250 mmol). A pale blue suspension was obtained. After 3 h stirring at room temperature the suspension was filtered. The solid was dried *in vacuo* (1.15 g; 89 % yield with respect to the copper content). Anal. Calcd for $[Cu_2(CO_3)(OH)_2] \cdot 1.5 H_2O, C_1H_5Cu_2O_{6.5}$: CO₂, 17.7; Cu, 51.2. Found: CO₂, 17.0; Cu: 52.0 %,

CO₂/Cu molar ratio: 0.47. IR (the most significant bands, cm⁻¹): 3400s, broad, 1510s, 1430sh, 1400s.

2.1.7. Preparation of a mixed La/Ce oxide by exhaustive hydrolysis of [Ce(O₂CNBu₂)₃] and La₄(CO₃)(O₂CNBu₂)₁₀ (La/Ce molar ratio 0.11)

A solution of [Ce(O₂CNBu₂)₃] (7.88 g; 12 mmol) and La₄(CO₃)(O₂CNBu₂)₁₀ (0.75 g; 0.32 mmol) in anhydrous toluene (70 mL) was treated under vigorous stirring with a solution of water (11 mL, 611 mmol, (H₂O/metal) molar ratio 46) in THF (50 mL). The progressive formation of a waxy light yellow solid was observed. After decantation the solid was washed with THF/toluene (1:2 in volume; 75 mL) for three times and then dried *in vacuo* at room temperature *in vacuo* for 4 h (3.89 g; 97 % yield as Ln₂(CO₃)₃·8H₂O). Anal. Calcd for [Ce_{1.80}La_{0.20}(CO₃)₃]·8 H₂O, C₃H₁₆Ce_{1.80}La_{0.20}O₁₇: Ce+La, 46.4. Found: Ce+La, 46.8 %. After treatment at 250°C (24 h) the weight loss was 42.9 % (versus 43.0 % theoretical value from Ce_{1.80}La_{0.20}(CO₃)₃·8 H₂O to Ce_{1.80}La_{0.20}O_{3.90}).

SEM EDS analyses revealed that the material was homogeneous and showed a La/Ce molar ratio of 0.12 (used 0.11).

The compound was treated at 250 °C in air for 12 h and a pale yellow solid was obtained. The product was subsequently treated at 850 °C for 12 h. Powder XRD measurements were carried out on both samples.

2.1.8. Preparation of a mixed Ce/Tb oxide by exhaustive hydrolysis of [Ce(O₂CNBu₂)₃] and [Tb(O₂CNBu₂)₃] (Tb/Ce molar ratio 0.21)

A solution of [Ce(O₂CNBu₂)₃] (10.11 g; 15.4 mmol) and [Tb(O₂CNBu₂)₃] (2.22 g; 3.29 mmol) in anhydrous toluene (160 mL) was treated under vigorous stirring with a solution of water (17 mL, 944 mmol, H₂O/metal molar ratio 50.5) in THF (85 mL). A light yellow gelatinous suspension formed. After 12 h stirring the suspension was decanted, the mother liquor was removed and the solid was washed with THF/toluene (1:2 in volume; 75 mL) for three times. The solvent was every time removed after decantation and added to the mother liquor. The solid was dried *in vacuo* at 35 °C for 1 h and at room temperature for 6 h (4.74 g; 94.1 % yield as Ln₂(CO₃)₃·4H₂O).

Anal. Calcd for [Ce_{1.65}Tb_{0.35}(CO₃)₃]·4H₂O, C₃H₈Ce_{1.65}Tb_{0.35}O₁₃: Ce+Tb, 53.2. Found: Ce+Tb, 52.3 %. IR (the most significant bands, cm⁻¹): 1470s, 1355s, br. The mother liquor and the washing solvent, once evaporated to dryness, left a negligible amount of solid residue. SEM EDS analyses revealed that the material was homogeneous and showed a Tb/Ce molar ratio of 0.21 (used 0.21).

The compound was treated at 250 °C in air for 12 h and a pale brown solid was obtained. The product was treated at 850 °C for 12 h and a brown powder was obtained. Powder XRD measurements were carried out on both samples.

2.2. Crystallographic Determinations.

The X-ray diffraction experiments were carried out at room temperature ($T = 293$ K) by means of a Bruker Smart Breeze CCD diffractometer operating with graphite-monochromated Mo- K_{α} radiation. The samples were sealed in glass capillaries under CO₂ atmosphere. Due to the limited quality of the crystals the diffraction intensities drop out rapidly to zero at growing of diffraction angle, so the intensity data collection was limited to a 2θ maximum of 23.2°. The intensities were corrected for Lorentz and polarization effects and for absorption by means of a multi-scan method [20]. Some relevant crystal parameters are listed in Table 3.

The structure solution has been obtained by the automatic direct methods contained in SHELX97 [21]. In the next refinement with anisotropic thermal parameters, the thermal ellipsoids of many carbon atoms appeared abnormally elongated revealing a conformational disorder of several isopropyl groups. In a first time we tried to describe the disorder as a statistical distribution of interested isopropyl groups on two different conformations. But with the introduction of the fifth disordered group the refinement program began to diverge. So we decided to continue the structure refinement giving up to develop a model of the disorder. After the introduction of hydrogen atoms in calculated positions the structural model included extensive cavities in correspondence of inversion centers containing some broad maxima of electron density. The disposition of maxima has been interpreted as the presence of a disordered molecule of lattice solvent that could not comply with the inversion centre. The coordinates of a molecule of heptane, taken from the literature [22], were introduced in the structural model through a fitting procedure on the residual maxima and were refined as a rigid block with isotropic thermal parameters. The final reliability factors are listed in Table 3. Notwithstanding the limited quality of the structural refinement, mainly due to the severe disorder present in the crystal, the molecular core geometry is well defined. In addition to the aforementioned software, other control calculations and preparation of publication material were performed with the programs contained in the suite WINGX [23].

Table 3. Crystal data and selected structure refinements details for 2·0.5 *n*-heptane

empirical formula	C _{73.5} H ₁₄₈ La ₄ N ₁₀ O ₂₁
<i>M</i>	2063.65
crystal system	monoclinic
space group	<i>P</i> 2 ₁ / <i>n</i> (no. 14)
<i>a</i> / Å	13.3446(3)
<i>b</i> / Å	24.8018(6)
<i>c</i> / Å	30.7205(7)
β / °	90.2420(10)
<i>U</i> / Å ³	10167.5(4)
<i>Z</i>	4
<i>D</i> _c / Mg·m ⁻³	1.348
μ / mm ⁻¹	1.708
no. measured	63086
no. unique [<i>R</i> _{int}]	14412 [0.0813]
no. parameters	956
<i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> > 2σ(<i>I</i>)] ^a	0.0504, 0.0911
<i>R</i> ₁ , <i>wR</i> ₂ [all data] ^a	0.0911, 0.1057
GOF ^a on <i>F</i> ²	1.065

^a $R(F_o) = \sum ||F_o| - |F_c|| / \sum |F_o|$; $Rw(F_o^2) = [\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]]^{1/2}$; $w = 1 / [\sigma^2(F_o^2) + (AQ)^2 + BQ]$ where $Q = [\text{MAX}(F_o^2, 0) + 2F_c^2] / 3$; $\text{GOF} = [\sum [w(F_o^2 - F_c^2)^2] / (N - P)]^{1/2}$, where *N*, *P* are the numbers of observations and parameters, respectively

Results and discussion

The *N,N*-di-iso-propylcarbamato complex of lanthanum, [La(O₂CN^{*i*}Pr₂)₃], **1**, was prepared by reacting the solvated metal chloride, LaCl₃·DME, with NH^{*i*}Pr₂ and CO₂ in toluene, according to the procedure previously used for the synthesis of a series of lanthanide complexes, [Ln(O₂CN^{*i*}Pr₂)₃]₄ (Ln = Ce, Pr, Nd, Eu, Gd, Ho, Er, Yb, Lu) [16]. Nuclearity four was established for all the derivatives, so it is probable that compound **1** shows the same molecular complexity. The partial hydrolysis of **1**, carried out with a La/H₂O molar ratio of 4 in heptane/THF, yielded the oxo-derivative [La₄(μ₄-O)(O₂CN^{*i*}Pr₂)₁₀], **2**. Single crystals of the product were obtained that allowed a structural study by X-Ray diffraction methods. This is the first lanthanide μ-oxocarbamate complex obtained by hydrolysis of a homoleptic carbamate.

A simplified view of the core of the lanthanum-oxo-carbamate is shown in Fig. 1. The four metal atoms are disposed around the μ₄-oxo ligand in an approximately tetrahedral geometry. The disposition does not possess any symmetry element, although an approximately twofold axis crossing the middle points between La(1)···La(2) and La(3)···La(4) may be found. La(1) and La(2) are octa-coordinated, the La–O distances being in the range 2.40–2.74 Å (Table 4), while La(3) and La(4) may be considered ennea-coordinated, although the longest La–O distance, La(3)–O(61) 2.913 Å, is near to the upper limit of bond distances for lanthanum carboxylates reported in the CCDC database [24] (mean value 2.601 Å).

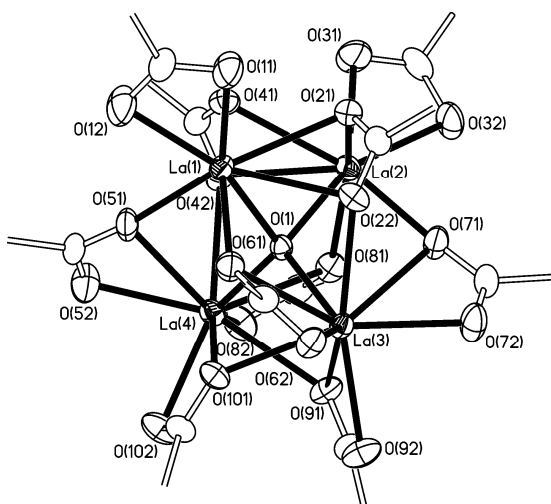
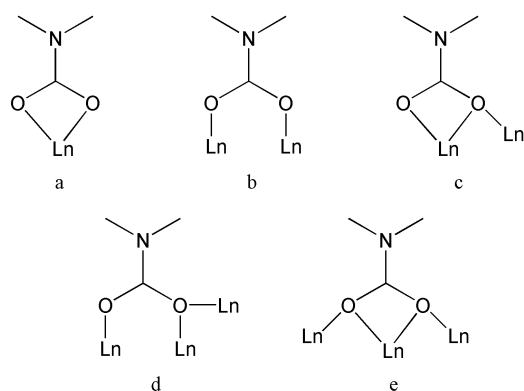


Figure 1. View of the molecular structure of $[\text{La}_4(\mu_4\text{-O})(\text{O}_2\text{CN}^t\text{Pr}_2)_{10}]$, **2**. Thermal ellipsoids are at 30% probability. The di-*iso*-propylamino groups have been omitted for clarity.

Table 4. Selected bond lengths (Å) and angles (°) for **2**·0.5 heptane

La(1)–O(1)	2.423(4)	La(2)–O(1)	2.398(4)
La(3)–O(1)	2.309(4)	La(4)–O(1)	2.304(4)
La(1)–O(11)	2.515(6)	La(2)–O(31)	2.481(5)
La(1)–O(12)	2.506(6)	La(2)–O(32)	2.493(5)
La(1)–O(21)	2.673(5)	La(2)–O(41)	2.737(5)
La(1)–O(22)	2.709(5)	La(2)–O(42)	2.610(5)
La(1)–O(41)	2.507(5)	La(2)–O(21)	2.516(5)
La(1)–O(51)	2.455(5)	La(2)–O(71)	2.457(5)
La(1)–O(61)	2.416(5)	La(2)–O(81)	2.453(6)
La(3)–O(22)	2.646(5)	La(4)–O(42)	2.746(5)
La(3)–O(61)	2.913(5)	La(4)–O(81)	2.796(5)
La(3)–O(62)	2.465(5)	La(4)–O(82)	2.490(5)
La(3)–O(71)	2.857(5)	La(4)–O(51)	2.852(5)
La(3)–O(72)	2.488(5)	La(4)–O(52)	2.454(6)
La(3)–O(91)	2.665(5)	La(4)–O(101)	2.642(5)
La(3)–O(92)	2.492(5)	La(4)–O(102)	2.482(5)
La(3)–O(101)	2.608(5)	La(4)–O(91)	2.644(5)

Two carbamate ligands, no. 1 and 3, are terminal bidentate (coordination mode a in Scheme 1), two carbamate ligands, no. 2 and 4, connect three different metals (coordination mode e in Scheme 1) and the remaining ones, no. 5-10, bridge two different metals (coordination mode c in Scheme 1). The different types of coordination of the ligands make the geometry around the lanthanum atoms rather irregular and prevent to define it in terms of a semi-regular polyhedron.



Scheme 1. Different coordination modes of carbamate ligands.

It can be of some interest a comparison between the geometry of the tetrameric $\text{La}_4(\mu_4\text{-O})(\text{O}_2\text{CN}^i\text{Pr}_2)_{10}$, **2**, and that of the tetramers $[\text{Ln}_4(\text{O}_2\text{CN}^i\text{Pr}_2)_{12}]$, known for several lanthanides [15]. Since the structure of the lanthanum homoleptic compound $[\text{La}_4(\text{O}_2\text{CN}^i\text{Pr}_2)_{12}]$ is not known, the geometry of **2** is compared with the one of $[\text{Nd}_4(\text{O}_2\text{CN}^i\text{Pr}_2)_{12}]$. In both compounds the metal atoms are approximately arranged at the vertices of a tetrahedron, but the presence of the central μ_4 -oxo in **2** significantly reduces the size of tetrahedron itself. The mean distances $\text{Ln}\cdots\text{Ln}$ are 3.85 and 4.66 Å in $\text{La}_4(\mu_4\text{-O})(\text{O}_2\text{CN}^i\text{Pr}_2)_{10}$ and $[\text{Nd}_4(\text{O}_2\text{CN}^i\text{Pr}_2)_{12}]$, respectively. The lanthanum ions, although larger [25] than neodymium ions, are brought closer by the oxo-ligand. The high coordination numbers shown by the lanthanum centers in **2** are saturated by the rather flexible carbamate ligands (Scheme 1) which adopt a high denticity. The compounds of the series $[\text{Ln}_4(\text{O}_2\text{CN}^i\text{Pr}_2)_{12}]$ contain four carbamates of type a, four of type b and four of type d (Scheme 1).

The preparation of the *N,N*-dibutylcarbamato complex of lanthanum was carried out by extraction of the lanthanum ion from the aqueous solution of its chloride into heptane by NHBu_2 saturated with CO_2 , according to a method previously used with success with other lanthanides [5]. By this approach, the homoleptic derivatives $[\text{Ln}(\text{O}_2\text{CNBu}_2)_3]$ or the carbonato-carbamato species $[\text{NH}_2\text{Bu}_2]_2[\text{Ln}_4(\text{CO}_3)(\text{O}_2\text{CNBu}_2)_{12}]$ or $[\text{Ln}_4(\text{CO}_3)(\text{O}_2\text{CNBu}_2)_{10}]$ are obtained, in dependence of the reaction conditions and/or the lanthanide identity. With lanthanum, according to the CO_2 and La content, a product with composition $[\text{La}_4(\text{CO}_3)(\text{O}_2\text{CNBu}_2)_{10}]$, **3**, was obtained several times with good reproducibility. The IR spectrum of the compound (Figure 2) shows strong bands in the 1700-1300 cm^{-1} region.

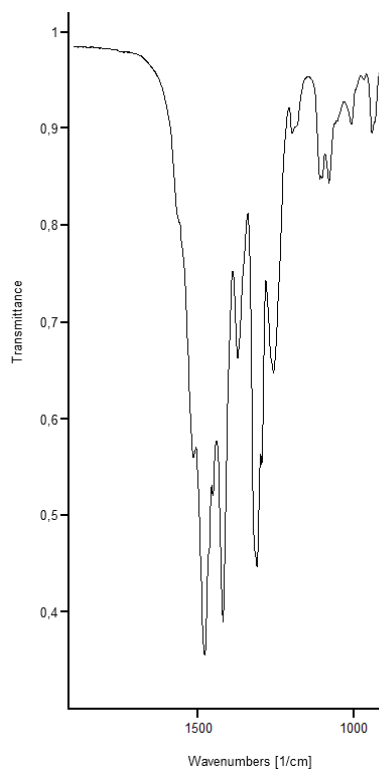


Figure 2. IR spectrum of $[\text{La}_4(\text{CO}_3)(\text{O}_2\text{CNBu}_2)_{10}]$, **3** in the range $1700\text{-}1000\text{ cm}^{-1}$.

Several lanthanide μ_n -carbonato complexes have been reported in the literature and in a few cases bands at about 1550 and 1350 cm^{-1} have been assigned to carbonate vibrations [26]. Unfortunately, the presence of the carbamato ligands in **3** prevents a reliable attribution of the bands, because intense and broad absorptions due to the O_2CN moiety stretching vibrations are in the same range.

The compound mass spectrum (Figure 3) showed the main peak at m/z 2120.92, attributable to the fragment $[\text{La}_4\text{O}(\text{O}_2\text{CNBu}_2)_9]^+$, together with minor peaks at 1138.51 attributable to the cation $[\text{La}_2(\text{O}_2\text{CNBu}_2)_5]^+$, and at 2315.96 assigned to the $[\text{La}_4\text{O}(\text{O}_2\text{CNBu}_2)_{10}]\text{Na}^+$ ion. As a comparison, in the mass spectrum of $[\text{Sm}_4(\text{CO}_3)(\text{O}_2\text{CNBu}_2)_{10}]$ [5], recorded in similar conditions, the peak related to the ion $[\text{Sm}_4\text{O}(\text{O}_2\text{CNBu}_2)_9]^+$ was found to be the most abundant. We suppose that these μ -oxo tetranuclear fragments derive from the loss of one $[\text{Bu}_2\text{NCO}_2]^-$ group by the tetranuclear carbonato complexes followed, or preceded, by the release of CO_2 in the instrument ion source conditions (350°C and low CO_2 partial pressure). This hypothesis is supported by a TGA experiment performed on **3**, in which a well-defined transition was detected, in the range $95\text{-}180^\circ\text{C}$ (Fig. S1), corresponding to 9.4 % of the sample weight, very close to the calculated value expected for the loss of CO_2 and one *N,N*-dibutylcarbamato ligand. Moreover, the $[\text{La}_4\text{O}(\text{O}_2\text{CNBu}_2)_{10}]\text{Na}^+$ ion formation can be justified by the decarboxylation of the product accompanied by the addition of the

cation Na^+ , presumably present as impurity in the solvent employed for the analysis. The attributions of the more abundant ions of the mass spectrum have been confirmed with accurate mass calculation (from the HRMS mass spectra).

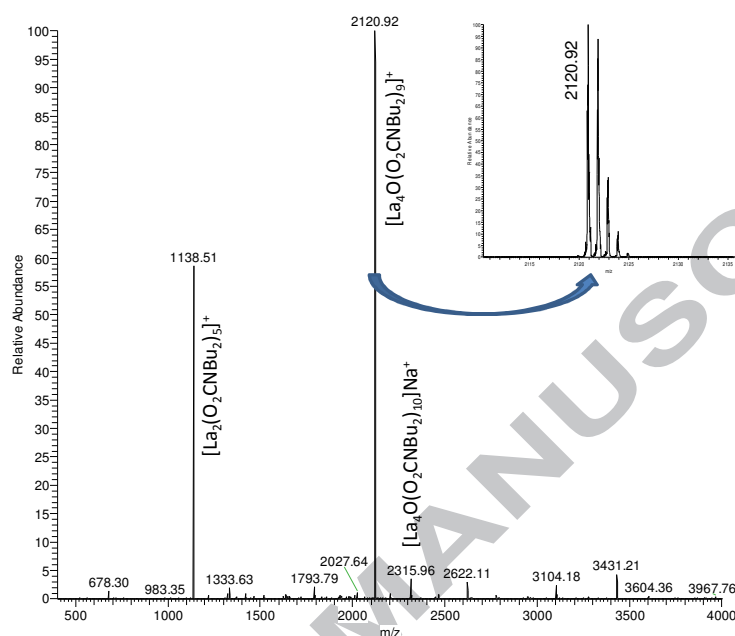
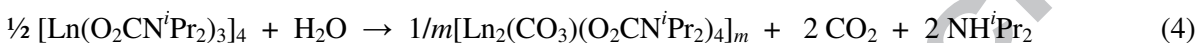


Figure 3. APPI FTICR positive mass spectrum of the complex $[\text{La}_4(\text{CO}_3)(\text{O}_2\text{CNBu}_2)_{10}]$. The blow up of the isotopic cluster distribution is in the inset. The cluster is mainly due to the ^{13}C contribution, since La is a monoisotopic species.

The evolution of a system like $[\text{Ln}(\text{O}_2\text{CNR}_2)_3]_n + x \text{H}_2\text{O}$ towards the oxo- or the carbonato derivative can be influenced by a variety of parameters as for instance: a) the nature of the R residue, b) the nuclearity of the precursor, c) the CO_2 partial pressure d) the concentrations of the reacting species, e) the temperature, f) the $(\text{M}/\text{H}_2\text{O})$ molar ratio. From a chemical point of view (acid-base interactions), we can expect that lanthanide complexes evolve towards the formation of carbonates. Nevertheless, the formation of the μ -oxo derivative **2** appears to be in contrast with this hypothesis, although reminiscent of several cases involving metals of the blocks *s* and *d* discussed in the Introduction. Presumably, in the arrangement of polynuclear molecular derivatives not only acid-base interactions have to be considered, because the μ -oxo cores, with respect to the μ -carbonato ones, assure a greater compactness, that guarantees a more efficient bridging coordination of the residual carbamate groups. Concerning this aspect a comparison of the core structures of **2** and $[\text{NH}_2\text{Bu}_2]_2[\text{Tb}_4(\text{CO}_3)(\text{O}_2\text{CNBu}_2)_{12}]$ [5] can be useful. In the terbium anionic complex the four Tb atoms form a roughly planar trapezoid around the carbonato ligand with rather long $\text{Tb}\cdots\text{Tb}$ distances, the shortest one being 4.280 Å. The metal centers are connected by eight bridging carbamates (Scheme 1, b) and each terbium atom is coordinated by a terminal carbamate (Scheme

1, a). In **2** the closeness of the metal atoms allows the coordination modes c and e (Scheme 1) to be adopted permitting to lanthanum to saturate its high coordination numbers (8 and 9).

Although the compactness of the μ_n -O cores in molecular polynuclear complexes has to be taken into consideration, it is reasonable that the formation of carbonato- or oxo- derivatives is the result of a fine balance of several effects. As a matter of fact, when the partial hydrolyses of the lanthanide complexes $[\text{Ln}(\text{O}_2\text{CN}^i\text{Pr}_2)_3]$ (Ln = Nd, Eu, Gd) were carried out with a (Ln/H₂O) molar ratio = 2, the carbonato-carbamato complexes $[\text{Ln}_2(\text{CO}_3)(\text{O}_2\text{CN}^i\text{Pr}_2)_4]$ were obtained.



In the case of exhaustive hydrolysis, the formation of oxo- or carbonato derivatives is expected to depend on the metal oxide basicity. In the course of this work, the exhaustive hydrolyses of $[\text{Ln}(\text{O}_2\text{CNBu}_2)_3]$ (Ln = Nd, Eu, Gd, Tb) and of $[\text{Ln}(\text{O}_2\text{CN}^i\text{Pr}_2)_3]$, Ln = Eu, Gd) were carried out at room temperature in a toluene/THF mixture. The formation of $[\text{Ln}_2(\text{CO}_3)_3] \cdot n\text{H}_2\text{O}$ was always observed, n being in the range 5-7, probably depending on the duration of the drying process usually carried out *in vacuo* at room temperature. The products were characterized by their metal and CO₂ contents, corresponding to a CO₂/Ln molar ratio 1.5. Therefore, lanthanide carbonates formed, independently of the lanthanide nature and of the NR₂ complexity, consistently with the basic nature of the lanthanide(III) oxides, Ln₂O₃ [27].

To compare the lanthanide behavior with that of a *d* metal centre in this type of reaction, we selected copper(II) for its lability, similar to that of lanthanide(III). It has been previously reported that the partial hydrolysis of $[\text{Cu}(\text{O}_2\text{CN}^i\text{Pr}_2)_2]$ (Cu/H₂O molar ratio = 4) gives the structurally characterized μ -oxo derivative $[\text{Cu}_8(\mu_4\text{-O})_2(\text{O}_2\text{CNR}_2)_{12}]$ [2b]. The complete hydrolyses of both $[\text{Cu}(\text{O}_2\text{CNEt}_2)_2(\text{NH}_2\text{Et}_2)]_2$ and $[\text{Cu}(\text{O}_2\text{CN}^i\text{Pr}_2)_2]$ complexes were carried out at room temperature in ethanol. In both cases a copper basic carbonate analyzing as Cu₂(CO₃)(OH)₂·nH₂O was obtained.

Among the lanthanide carbonates obtained by the hydrolysis of their *N,N*-dibutylcarbamates, the terbium carbonate was thermally decarboxylated at about 250 °C in air with formation of terbium oxide. The product appeared amorphous at the X-Ray diffraction powder analysis. After the thermal treatment at 850 °C, the powder acquired a more crystalline aspect and its X-Ray diffraction pattern corresponded to the one of the Tb₇O₁₂ phase (JCP2:01-085-180 [28]), with a fluorite-like (CaF₂) structure [29]. The broad reflections observed suggest small crystallite size, of the order of 5-10 nm according to the Sherrer's formula.

The availability of suitable lanthanide precursors urged us to try the preparation of mixed oxides starting from solutions containing two different lanthanide complexes in a specific molar ratio, to

check the composition of the final oxide and verify if the selected molar ratio was maintained in the product.

The mixed cerium/terbium carbonate, obtained by the hydrolysis of the *N,N*-dibutylcarbamato precursors (Tb/Ce molar ratio 0.21) in nearly quantitative yield, showed an IR spectrum similar to those of hydrated carbonates discussed before.

After treatment at 250 °C for 12 h a light brown solid formed with a weight loss in good agreement with the leaving of H₂O and CO₂ from Ce_{1.65}Tb_{0.35}(CO₃)₃·4H₂O to yield Ce_{1.65}Tb_{0.35}O_{3.82}. In effect, as previously discussed, the medium oxidation number of terbium in the oxide obtained by calcination in air is higher than III, so it would be more correct to write the formula as Ce_{1.65}Tb_{0.35}O_{3.82+x}. Nevertheless, this implies a negligible effect on the weight loss calculation. Only one crystalline phase was detected by the powder XRD spectra of the product, showing the fluorite type structure corresponding to the face centered cubic space group, like pure cerium dioxide CeO₂ and pure TbO₂ [30]. After treatment at 850 °C the powder diffraction pattern allowed the determination of the cell parameter of the cubic cell, a₀=5.3922 Å, which was intermediate with respect to the ones of CeO₂, 5.409 Å, and TbO₂, 5.213 Å [30].

The TG-DSC analysis carried out under N₂ on the mixed Ce/Tb carbonate (Fig. 4) shows a mass loss in the range 20-250 °C slightly higher than expected for the water loss by Ce_{1.65}Tb_{0.35}(CO₃)₃·4H₂O, probably due to absorbed water (the sample was weighted on air). The mass loss in the range 250-700 °C is close to the theoretical value (Δ = -0.64 %). The curve of the differential scanning calorimetry shows a clear exothermic peak at approximately 480 °C caused by the oxidation of the sample.

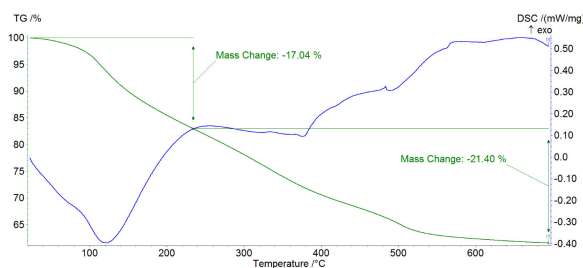


Figure 4. TG-DSC curves of Ce_{1.65}Tb_{0.35}(CO₃)₃·4H₂O

SEM-EDS analyses (Fig. 5) revealed that the material, apparently homogeneous, showed a Tb/Ce molar ratio of 0.21 (in agreement with the used one, 0.21).

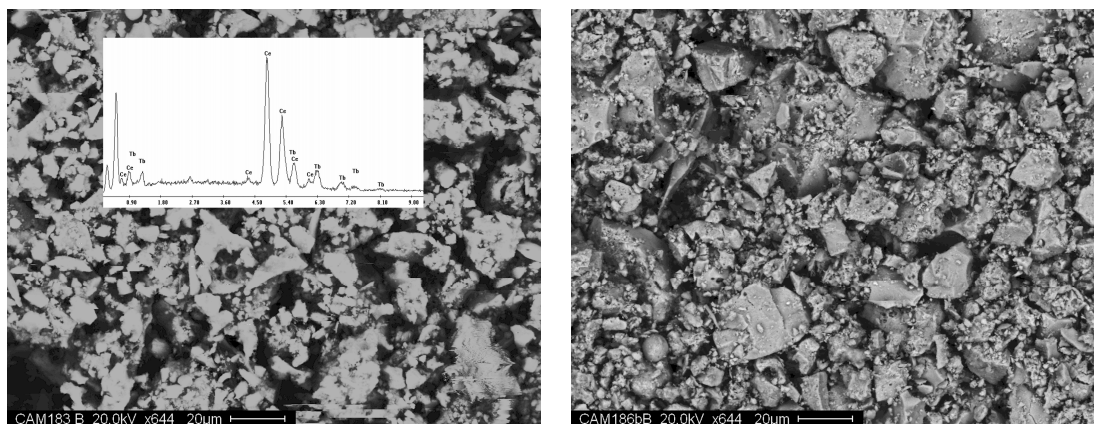


Figure 5. Electron micrographs (SEM) for mixed Tb/Ce carbonate (left, EDS in the inset) and the corresponding oxide obtained at 250 °C (right).

The mixed cerium/lanthanum carbonate obtained by complete hydrolysis of a solution of cerium and lanthanum *N,N*-dibutylcarbamato complexes (La/Ce molar ratio 0.11) was treated at 250°C for 12 h undergoing a weight loss in good agreement with the leaving of H₂O and CO₂ from Ce_{1.80}La_{0.20}(CO₃)₃·8H₂O to yield Ce_{1.80}La_{0.20}O_{3.90}.

The TG-DSC analysis carried out under N₂ on the mixed Ce/La carbonate (Fig. 6) shows a mass loss between 20 °C and 200 °C, slightly higher than the expected one for the loss of water by Ce_{1.80}La_{0.20}(CO₃)₃·8H₂O probably attributable to absorbed water. During the subsequent heating, the mass loss of the sample is close to that expected ($\Delta = -0.17\%$).

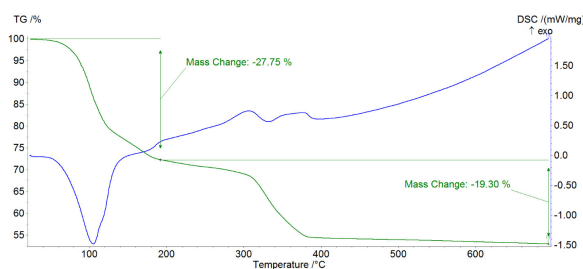


Figure 6. TG-DSC curves of Ce_{1.80}La_{0.20}(CO₃)₃·8H₂O

A SEM-EDS analysis of the powders (Fig. 7) showed that the Ce/La molar ratio respected the one used in the parent solution and the metals were homogeneously distributed.

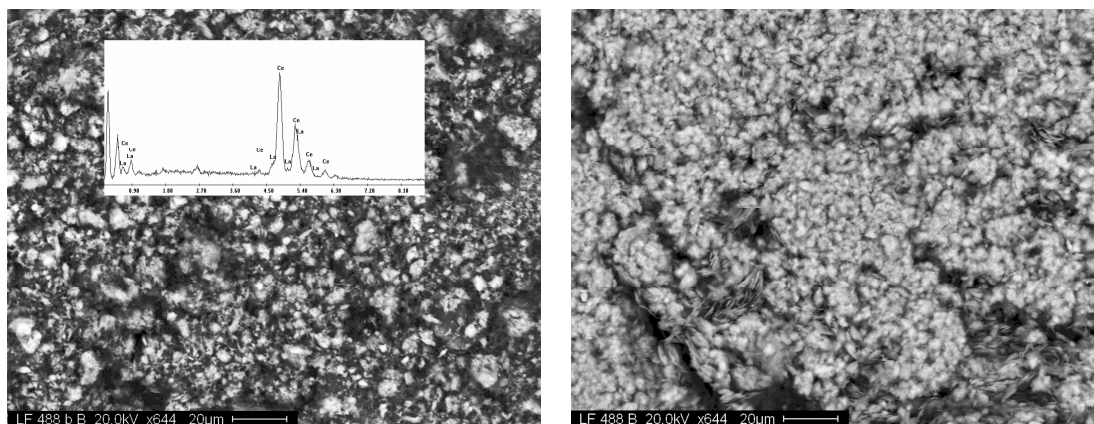


Figure 7. Electron micrographs (SEM) for mixed La/Ce carbonate (left, EDS in the inset) and the corresponding oxide obtained at 250 °C (right).

The powder XRD spectrum carried out on the product showed the presence of a single crystalline phase with the CaF₂ (fluorite) type structure [30]. Crystallite size corresponding to 5-8 nm was calculated by the Sherrer's formula. Calcination at 850 °C afforded a solid whose powder diffraction pattern allowed the determination of the cell parameter of the cubic cell, $a_0=5.4316 \text{ \AA}$, which was slightly larger than the one of CeO₂, 5.409 Å [30], as expected for the presence of the lanthanum(III).

4. Conclusions

By partial hydrolysis of lanthanide *N,N*-dialkylcarbamato complexes, oxo-carbamato or carbonato-carbamato complexes were produced. Although carbonato derivatives were expected for the lanthanide centers, associated to rather basic oxides, probably the compactness demand of the molecular oligo-nuclear products can afford the formation of oxo-derivatives. The complete hydrolysis of [Ln(O₂CNR₂)₃] (Ln = Nd, Tb, R = Bu; Ln = Eu, Gd, R = ⁱPr, Bu) produced hydrated lanthanide carbonates, Ln₂(CO₃)₃ · *n* H₂O.

Mixed lanthanide oxides were obtained by thermal decarboxylation of the carbonates precipitated out by complete hydrolysis of lanthanide *N,N*-dibutylcarbamato complexes. Cerium/lanthanum and cerium/terbium nano-crystalline mixed oxides were prepared, containing a single crystalline phase and the two metals in the desired molar ratio. The similar lability of the metal centers can account for this outcome. This method of preparation of mixed lanthanide oxides appears to be promising. Moreover, the results of the present work pave the way to the synthesis of d/f heterometallic oxides involving the labile copper(II) center. Further studies on this field are in course in our laboratories.

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Appendix A. Supplementary data

CCDC 1402498 contains the supplementary crystallographic data for complex **2**. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1002/j.poly.1234567>.

References

- [1] D. Belli Dell'Amico, F. Calderazzo, L. Labella, F. Marchetti, G. Pampaloni, *Chem. Rev.* 103 (2003) 3857.
- [2] (a) F. Calderazzo, G. Dell'Amico, M. Pasquali, G. Perego, *Inorg. Chem.* 17 (1978) 474. (b) E. Agostinelli, D. Belli Dell'Amico, F. Calderazzo, D. Fiorani, G. Pelizzi, *Gazz. Chim. Ital.* 118 (1988) 729. (c) A. Bacchi, D. Belli Dell'Amico, F. Calderazzo, U. Giurlani, G. Pelizzi, L. Rocchi, *Gazz. Chim. Ital.* 122 (1992) 429. (d) D. Belli Dell'Amico, F. Calderazzo, F. Gingl, L. Labella, J. Strähle, *Gazz. Chim. Ital.* 124 (1994) 375. (e) D. Belli Dell'Amico, F. Calderazzo, L. Labella, C. Maichle-Mössmer, J. Strähle, *Chem. Commun.* (1994) 1555. (f) U. Abram, D. Belli Dell'Amico, F. Calderazzo, S. Kaskel, L. Labella, F. Marchetti, R. Rovai, J. Strähle, *Chem. Commun.* (1997) 1941. (g) D. Belli Dell'Amico, D. Boschi, F. Calderazzo, S. Ianelli, L. Labella, F. Marchetti, G. Pelizzi, E. G. F. Quadrelli, *Inorg. Chim. Acta* 300-2 (2000) 882. (h) D. Belli Dell'Amico, F. Calderazzo, F. Marchetti, G. Pampaloni, *Metal Clusters in Chemistry* Wiley-VCH, vol. 1 (1999) 209-220. P. Braunstein, L. Oro, P. Raithby, Eds. (i) D. Belli Dell'Amico, F. Calderazzo, L. Labella, F. Marchetti, G. Pampaloni, *Inorg. Chem. Commun.* 5 (2002) 733. (j) D. Belli Dell'Amico, C. Bradicich, F. Calderazzo, A. Guarini, L. Labella, F. Marchetti, A. Tomei, *Inorg. Chem.*, 41 (2002) 2814. (k) D. Belli Dell'Amico, F. Calderazzo, L. Labella, F. Marchetti, I. Mazzoncini, *Inorg. Chim. Acta* 359 (2006) 3371. (l) D. Belli Dell'Amico, F. Calderazzo, L. Costa, E. Franchi, L. Gini, L. Labella, F. Marchetti, *J. Molec. Struct.* 890 (2008) 295.
- [3] (a) U. Abram, D. Belli Dell'Amico, F. Calderazzo, L. Marchetti, J. Strähle, *J. Chem. Soc., Dalton Trans.* (1999) 4093. (b) D. Belli Dell'Amico, F. Calderazzo, L. Labella, F. Marchetti, *J. Organomet. Chem.* 596 (2000) 144.
- [4] (a) D. Belli Dell'Amico, F. Calderazzo, L. Labella, F. Marchetti, M. Martini, I. Mazzoncini, *C. R. Chimie* 7 (2004) 877. (b) K.-C. Yang, C.-C. Chang, C.-S. Yeh, G.-H. Lee, S.-M. Peng, *Organometallics* 20 (2001) 126.
- [5] L. Armelao, D. Belli Dell'Amico, P. Biagini, G. Bottaro, S. Chiaberge, P. Falvo, L. Labella, F. Marchetti, S. Samaritani, *Inorg. Chem.* 53 (2014) 4861.
- [6] R. Alessio, D. Belli Dell'Amico, F. Calderazzo, U. Englert, A. Guarini, L. Labella, P. Strasser, *Helv. Chim. Acta* 81 (1998) 219.
- [7] (a) E. Hemmer, C. Cavelius, V. Huch, S. Mathur, *Inorg. Chem.* 2015 DOI: 10.1021/acs.inorgchem.5b00529. (b) Ł. John, P. Sobota, *Acc. Chem. Res.* 47 (2014) 470. (c) M. J. Veith, *Chem. Soc., Dalton Trans.*, 12 (2002) 2405. (d) G. A. Seisenbaeva, Kessler, V. G., *Nanoscale* 6 (2014) 6229. (e) P. Dolcet, S. Diodati, M. Casarin, S. Gross, *J. Sol-Gel Sci. Technol.* 73 (2015) 591.
- [8] (a) D. Belli Dell'Amico, F. Calderazzo, M. Dell'Innocenti, *Eur. Pat. Appl. EP* 394669, Oct. 31 1990. (b) D. Belli Dell'Amico, F. Calderazzo, M. Dell'Innocenti, P. Robino, *US Pat.* 5 198 565, Mar. 30 1993.
- [9] D. Belli Dell'Amico, D. Boschi, L. Labella, unpublished results.
- [10] (a) Lorenzo Falchi, *Tesi di Laurea Magistrale in Chimica, Università di Pisa* (2014). (b) D. Belli Dell'Amico, M. De Sanctis, R. Ishak, S. Dolci, L. Labella, M. Lezzerini, F. Marchetti, *Polyhedron* 99 (2015) 170.
- [11] (a) G. Jacobs, L. Williams, U. Graham, D. Sparks, B. H. Davis, *J. Phys. Chem. B* 107 (2003) 10398. (b) K. Sohlberg, S. T. Pantelides, S. J. Pennycook, *J. Am. Chem. Soc.* 123 (2001) 6609. (c) F. Goubin, X. Rocquefelte, M. H. Whangbo, Y. Montardi, R. Brec, S. Jovic, *Chem. Mat.* 16 (2004) 662. (d) D. G. Shchukin, R. A. Caruso, *Chem. Mat.* 16 (2004) 2287.
- [12] (a) A. Trovarelli, *Catalysis Reviews - Science and Engineering* 38 (1996), 439. (b) A. Trovarelli, C. de Leitenburg, M. Boaro, G. Dolcetti, *Catalysis Today* 50 (1999) 353. (c) W.D. Michalak, G.A. Somorjai, *Top. Catal.* 56 (2013) 1611.
- [13] [(a) J. Patakangas, Y. Ma, Y. Jing, P. Lund *J. Power Sources* 263 (2014) 315. (b) J. Patakangas, Y. Ma, Y. Jing, P. Lund *J. Power Sources* 263 (2013) 315. (c) J. W. Fergus *J. Power Sources* 162 (2006) 30.
- [14] (a) H. Gu, M. D. Soucek, *Chem. Mater.* 19 (2007) 1103. (b) Q. Yuan, H.-H. Duan, L.-L. Li, L.-D. Sun, Y.-W. Zhang, C. H. Yan, *J. Colloid Interf. Sci.* 335 (2009) 151. (c) W. Feng, L.-D. Sun, Y.-W. Zhang, C.-H. Yan *Coord. Chem. Rev.* 254 (2010) 1038. (d) V.K. Ivanov, O.S. Polezhaeva, Y.D. Tret'yakov, *Russ. J. Gen. Chem.*, 80 (2010) 604. (e) V.K. Ivanov, A. E. Baranchikov, O. S. Polezhaeva, G. P. Kopitsa, Yu. D. Tret'yakov, *Russ. J. Inorg. Chem.*, 55 (2010) 325. (f) C. Sun, H. Li, L. Chen, *Environ. Sci.* 5 (2012) 8475. (g) D. Zang, X. Du, L. Shi, R. Gao, *Dalton Trans.* 41 (2012) 14455. (h) S. Gangopadhyay, D. D. Frolov, A. E. Masunov, S. Seal, *J. Alloys Comp.* 584 (2014) 199. (i) M. Melchionna, P. Fornasiero, *Materials Today* 17 (2014) 349. (j) F. Hrizi, H. Dhaouadi, F. Touati, *Ceram. Int.* 40 (2014) 25.
- [15] U. Baisch, D. Belli Dell'Amico, F. Calderazzo, R. Conti, L. Labella, F. Marchetti, E. A. Quadrelli, *Inorg. Chim. Acta* 357 (2004) 1538.
- [16] U. Baisch, D. Belli Dell'Amico, F. Calderazzo, L. Labella, F. Marchetti, A. Merigo, *Eur. J. Inorg. Chem.* (2004) 1219.
- [17] F. Calderazzo, F. A. Cotton, *Inorg. Chem.* 1 (1962) 30.
- [18] L. Yu, D. Chen, J. Li, P. G. Wang, *J. Org. Chem.*, 62 (1997) 3580.
- [19] D.B. Robb, T.R. Covey, A.P. Bruins, *Anal. Chem.* 72 (2000) 3653.
- [20] G. M. Sheldrick, SADABS, Program for empirical absorption correction, University of Göttingen, Germany (1996).
- [21] SHELX97 - Programs for Crystal Structure Analysis (Release 97-2). G.M. Sheldrick, Institut für Anorganische Chemie der Universität, Tammanstrasse 4, D-3400 Göttingen, Germany (1998).

-
- [22] D. J. Brauer, C. Liek, O. Stelzer, J. Organomet. Chem. 626 (2001) 106.
- [23] L. J. Farrugia, J. Appl. Crystallogr. 32 (1999) 837.
- [24] F. H. Allen, Acta Cryst. B58 (2002) 380.
- [25] R. D. Shannon, Acta Cryst. A32 (1976) 751.
- [26] L. Zhang, H.-R. Zhang, K.-B. Yu, L.-M. Zheng, Angew. Chem. Int. Ed. 48 (2009) 3499. M. Sarkar, G. Arom, J. Cano, V. Bertolasi, D. Ray, Chem. Eur. J. 16 (2010) 13825. H. Tian, L. Zhao, Y.-N. Guo, Y. Guo, J. Tang, Z. Liub, Chem. Commun. 48 (2012) 708. L. Zhao, S. Xue, J. Tang, Inorg. Chem. 51 (2012) 5994.
- [27] N. N. Greenwood, A. Earnshaw, Chemistry of the Elements, 2nd Edition, Elsevier, Amsterdam, 1997.
- [28] Database JCPZ.ZCA International Centre for Diffraction Data (ICDD), 12, Campus Boulevard, New Town Square, PA 19673-3273, USA.
- [29] Zhang, J.; von Dreele, R. B.; Eyring, L., J. Solid State Chem. 104 (1993) 21.
- [30] A. B. Hungría, A. Martínez-Arias, M. Fernández-García, A. Iglesias-Juez, A. Guerrero-Ruiz, J. J. Calvino, J. C. Conesa, J. Soria, Chem. Mat. 15 (2003) 4309.