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Preparation of *N,N*-Dialkylcarbamato Lanthanide Complexes by Extraction of Lanthanide Ions from Aqueous Solution into Hydrocarbons

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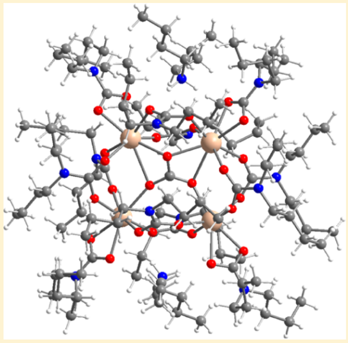
Supporting Information

ABSTRACT: Lanthanides are easily extracted as *N,N*-dibutylcarbamato complexes from aqueous solutions of their chlorides into heptane solutions of dibutylamine saturated with CO_2. The products are recovered in high yields and are soluble in hydrocarbons. The derivatives $[Ln(O_2CNBu_2)_3]_n$ [Ln = Nd (**1**), Eu (**2**), Tb (**3**)], $[NH_2Bu_2]_2[Ln_4(CO_3)(O_2CNBu_2)_{12}]$ [Ln = Tb (**4**), Sm (**5**), Eu (**6**)], and $[Sm_4(CO_3)(O_2CNBu_2)_{10}]$, **7**, have thus been obtained. The crystal and molecular structure of **4** has been solved; the samarium and europium complexes **5** and **6** were found to be isostructural. Mass spectra of the complexes **1**−**3**, **4**, and **7** (in MeCN/toluene) reveal that equilibria are present in solution. Compound **2** has been reacted in toluene with $NHBz_2$ in the presence of CO_2 affording $[NH_2Bz_2][Eu(O_2CNBz_2)_4]$, **8**, through a ligand exchange process. By thermal treatment, **8** afforded $[Eu(O_2CNBz_2)_3]_n$, **9**. With a similar procedure $[Sm(O_2CNBz_2)_3]_n$, **10**, was obtained from **5**. According to the photoluminescence study carried out on solid samples of **2**, **4**, **5**, **7**, and **8**, the metal centered f−f transitions represent the only effective way to induce lanthanide luminescence in these complexes.



INTRODUCTION

Lanthanide compounds are presently used in several fields of fundamental and applied chemistry, such as organic synthesis and catalysis.[1] Moreover, they have played a relevant role in the development of new technologies, being used, for instance, in superconductors and magnetic materials,[2] luminescent sensors,[3] contrast reagents, and shift reagents in NMR spectroscopy.[4] Additionally, lanthanide recycling from industrial residues or from lanthanide-containing end-of-life products has become economically interesting, in view of the increasingly limited export quota by China, presently producing more than 90% of the global lanthanide output.[5] To this regard, the U.S. Department of Energy (DOE) indicated neodymium (Nd), europium (Eu), terbium (Tb), dysprosium (Dy), and yttrium (Y) as the five lanthanides with the highest supply risk in the near future. Moreover, samarium is considered a strategic metal for the development of high performance permanent magnets (samarium cobalt alloys, $SmCo_5$ or Sm_2Co_{17}) and for use in niche fields which require particular temperature and corrosion resistance (e.g., on-board aircraft).[5]

Thus, the development of simple and fast synthetic procedures to lanthanide derivatives generated by lanthanide oxides or carbonates is of considerable interest.

The extraction of some metal ions from aqueous solutions into hydrocarbons by the NHR_2/CO_2 system (for instance with R = butyl, hexyl, cyclohexyl, benzyl) was previously patented.[6] Later on, the complexes $[Cu(O_2CNR_2)_2(NHR_2)_2]$ and $[Zn_4(O)(O_2CNR_2)_6]$ (R = butyl, Bu; benzyl, Bz), as obtained by this method in high yields, have been reported. The benzyl derivative of copper and the butyl derivative of zinc were structurally characterized.[7] It is reasonable to suppose that the success in the use of the NHR_2/CO_2 system as metal ion extraction agent from aqueous solutions into hydrocarbons[6,7] is due to (a) the fast reaction rate of CO_2 with the amine (with formation of $[NH_2R_2][O_2CNR_2]$);[8,9] (b) the choice of secondary amines containing bulky, nonbranched, R groups;[9] and (c) the use of labile metal centers, assuring the fast substitution of the first coordination sphere ligands by the *N,N*-diakylcarbamato groups and the formation of lipophilic metal complexes which migrate from the aqueous solution to the hydrocarbon layer. About point b, it is worthwhile to recall that the requested lipophilic character of the amine must be associated with a lack of steric hindrance adjacent to the nitrogen atom.[9b]

The synthesis of metal carbamato complexes starting from commercial metal oxides or carbonates, without preliminary dehydrating procedures, was in our view particularly attractive and deserved further attention in order to define the conditions

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of extraction of some lanthanides and to determine the nature of the products.

Here we report that neodymium(III), samarium(III), europium(III), and terbium(III) are conveniently extracted into heptane as their *N,N*-dibutyl carbamato complexes from aqueous solutions of their salts, obtained by their metal oxides. X-ray diffraction methods, HRMS spectrometry, and photoluminescence studies have been used for the product characterization.

The lanthanide centers herein studied have been selected among the ones which present interest for particular applications and/or risk of supply.[5] For instance, samarium, europium, and terbium(III) are suitable for the preparation of species showing photoluminescence in the visible region.[3] Moreover, neodymium(III), because of its relatively intense color, was useful to easily monitor the efficiency of the extraction process.

■ EXPERIMENTAL SECTION

Materials and Instrumentation. Commercial neodymium, samarium, europium, and terbium oxides [Nd_2O_3 (Aldrich, 99.9%); Sm_2O_3 (Aldrich, 99.9%); Eu_2O_3 (Strem Chemicals, 99.99%); Tb_4O_7 (Strem Chemicals, 99.9%)] were used without further purification. Aqueous solutions of the lanthanide 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.[10]

All manipulations after extraction were performed in anhydrous conditions under a dinitrogen or CO_2 atmosphere, as specified. FTIR spectra in the solid state were recorded with a Spectrum One Perkin Elmer spectrometer, with ATR technique. The metal 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 [Ln_2O_3 (Ln = Nd, Sm, and Eu) or Tb_4O_7] was determined. The carbon dioxide content of the 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.[11] C, H, N elemental analyses are not reported because the sensitivity of the compounds to moisture prevented the acquisition of reliable results.

High resolution mass spectrometry (HRMS) analysis was performed on a 7 T 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.[12] The solutions were injected with a flow rate of 50 μL/min. The ion source was equipped with a vacuum ultraviolet gas (Kripton) discharge lamp. Nitrogen was used as the nebulizing gas, the vaporizer temperature was 350 °C, the capillary voltage was 15 V, the capillary temperature was 270 °C, and the tube lens voltage was 140 V. Mass spectra were recorded in positive mode with a mass range of 400−4000 m/z, with an average resolving power of 400 000 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 distributions of the main species of the mass spectra have been compared.

The luminescence spectra were recorded on solid samples at room temperature in a front-face acquisition geometry with a spectrofluorimeter (Fluorolog-3, Horiba Jobin Yvon) equipped with double-grating monochromator in both the excitation and emission sides coupled to a R928P Hamamatsu photomultiplier and a 450 W Xe arc lamp as the excitation source. The emission spectra were corrected for detection and optical spectral response of the spectrofluorimeter supplied by the manufacturer. The excitation spectra were corrected for the spectral distribution of the lamp intensity using a photodiode reference detector.

$NHBu_2$ Solubility in Water. By operating under a dinitrogen atmosphere, water (150.0 mL) and $NHBu_2$ (20.0 mL) were introduced in a flask. After stirring for 2 h and standing for 5 h, an aliquot of the aqueous layer (25.0 mL) was transferred to a Schlenk tube and titrated with 0.1 N HCl. The amine concentration (M) in the saturated solutions corresponded to (temperature/°C in parentheses): 44.0×10^{-3} (16.0), 42.8×10^{-3} (16.5), 40.8×10^{-3} (17.0), 40.0×10^{-3} (18.1), 38.5×10^{-3} (18.5), 37.6×10^{-3} (20.0), 36.0×10^{-3} (21.0), 33.2×10^{-3} (23.0), 30.2×10^{-3} (25.0), 28.5×10^{-3} (27.0).

Distribution of $NHBu_2$ in the Heptane/Water Biphasic System under N_2. Four separated experiments were carried out. Under dinitrogen atmosphere, water (50.0 mL), heptane (50.0 mL), and $NHBu_2$ (5.0, 10.0, 15.0, or 20.0 mL) were introduced into a flask. After stirring for 2 h and standing for 5 h at 20 °C, a sample of the aqueous layer (25.0 mL) was transferred to a Schlenk tube and titrated with 0.10 N HCl. The average distribution ratio *D* (corresponding to the $[\text{amine}]_{\text{hept}}/[\text{amine}]_{\text{aq}}$ ratio) was found to be 70.

Uptake of CO_2 by $NHBu_2$. In a reactor, supplied with a magnetic bar, toluene (25 mL) was introduced under CO_2. The reactor was then connected to a gasvolumetric apparatus under CO_2 (T = 25 °C; P_{toluene} = 40 Torr; P_{total} = 760 Torr; P_{CO2} = 760−40 = 720 Torr). A sealed, fragile ampule containing $NHBu_2$ (220 mg; 1.70 mmol) was introduced in the reactor. After the thermal equilibrium was reached the ampule was broken by magnetic stirring, and the CO_2 uptake was measured up to saturation (about 1 h). The gas absorption corresponded to 20.6 mL [($CO_2/NHBu_2$) molar ratio 0.47].

Distribution of $NHBu_2$ in the Heptane/Water Biphasic System under CO_2. Solutions of $NHBu_2$ in heptane (0.30 M) were treated under CO_2 (P_{CO2} about 760 Torr) at 20 °C with formation of $[NH_2Bu_2][O_2CNBu_2]$.[8] An equivalent volume of water was added, and the biphasic system was stirred for about 2 min. After standing for 5 min, a sample of the aqueous layer was transferred to a Schlenk tube and titrated with 0.10 N HCl. The NBu_2 group could be present as $NHBu_2$, $[NH_2Bu_2][O_2CNBu_2]$, and $[NH_2Bu_2][HCO_3]$: for each species 1 equiv of HCl is required per NBu_2 unit. Average distribution ratio *D* = 0.60.

Extraction of Lanthanide Ions from Aqueous Solution into Heptane by the $NHBu_2/CO_2$ System. Synthesis of $[Ln(O_2CNBu_2)_3]_n$ (Ln = Nd, 1; Eu, 2; Tb, 3). (1) The neodymium case is described at length. A solution of dibutylamine (10.5 mL, 62.0 mmol) in heptane (50 mL) was saturated with carbon dioxide and then added to 20.0 mL of an aqueous solution of hydrated neodymium chloride (obtained by 1.04 g of Nd_2O_3, corresponding to 6.20 mmol of Nd) at 0 °C. Upon shaking for a few seconds at 0 °C, discoloration of the aqueous layer was observed while the organic phase became violet. The organic layer was then separated and evaporated at reduced pressure (1.0×10^{-3} Torr). A violet oil was obtained which was dissolved in a few milliliters of heptane. The solution was evaporated again, and the process was repeated twice. A violet solid (3.63 g) was obtained (89% yield). Anal. Calcd for $C_{27}H_{54}N_3NdO_6$: CO_2, 20.0; Nd, 21.8%. Found: CO_2, 19.5; Nd: 21.5%. IR, PCTFE mull (the most significant bands in the range 1700−1250, cm^{-1}): 1528s, 1490s, 1430s, 1378m, 1325m cm^{-1}. The aqueous layer after extraction was evaporated to dryness to control its metal content by calcination of the solid residue. A 42 mg portion of Nd_2O_3 was weighed corresponding to about 4% of the total neodymium. (2) The product was obtained (3.55 g, 88% yield) starting from an aqueous solution of hydrated europium chloride obtained by 1.063 g of Eu_2O_3 (6.04 mmol of Eu), and dibutylamine (10.0 mL, 59.0 mmol) saturated with CO_2 in heptane (50 mL). Anal. Calcd for $C_{27}H_{54}EuN_3O_6$: CO_2, 19.7 ; Eu, 22.7%. Found: CO_2, 19.8; Eu: 22.8%. ATR IR, solid (the most significant bands in the range 1700−1250 cm^{-1}): 1581m, 1485s, 1422s, 1375m, 1313s, 1265m cm^{-1}. (3) The product was obtained (3.84 g, 89% yield) starting from an aqueous solution of hydrated

Table 1. Crystal Data and Structure Refinement details for Sm and Tb Carbonate Carbamates

	5	4	4
empirical formula	$C_{125}H_{256}N_{14}O_{27}Sm_4$	$C_{125}H_{256}N_{14}O_{27}Tb_4$	$C_{125}H_{256}N_{14}O_{27}Tb_4$
fw	2993.59	3023.12	3023.12
wavelength (Å)	0.710 73	0.710 73	0.710 73
T (K)	293	293	100
cryst syst	orthorhombic	orthorhombic	monoclinic
space group	*Cmca*	*Cmca*	$P2_1/c$
a (Å)	32.7594(11)	32.7086(6)	31.399(6)
b (Å)	17.5962(5)	17.5952(3)	27.759(5)
c (Å)	28.2090(9)	28.1698(5)	17.295(3)
β (deg)			92.963(2)
V (Å^3)	16260.8(9)	16212(5)	15053.9(5)
Z	4	4	4
density (calcd) (g/cm^3)	1.236	1.239	1.334
abs coeff (mm^{-1})			1.922
reflns collected			141 804
indep reflns			36 027 [0.1169]
restraints/params			104/1527
GOF			1.089
final R indices [$I > 2\sigma(I)$]			R1 = 0.1186, wR2 = 0.2909
R indices (all data)[a]			R1 = 0.2179, wR2 = 0.3472

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o$, wR2 = $\{\Sigma[w(F_o^2 - F_c^2)]/\Sigma[w(F_o^2)]\}^{1/2}$.

terbium chloride obtained by 1.199 g of Tb_4O_7 (6.41 mmol of Tb) and dibutylamine (11.0 mL, 65.0 mmol) saturated with CO_2 in heptane (50 mL). Anal. Calcd for $C_{27}H_{54}N_3O_6Tb$: CO_2, 19.5; Tb, 23.5%. Found: CO_2, 20.0; Tb: 23.5%. ATR IR, solid (the most significant bands in the range 1700−1250 cm^{-1}): 1584s, 1485s, 1422s, 1374m, 1313s, 1264m cm^{-1}.

Preparation of $[NH_2Bu_2]_2[Tb_4(CO_3)(O_2CNBu_2)_{12}]$, 4. An aqueous solution of hydrated terbium chloride obtained by 1.200 g of Tb_4O_7 (6.42 mmol of Tb) was added to a solution of dibutylamine (11.0 mL, 65.0 mmol) saturated with CO_2 in heptane (50 mL). Upon shaking for a few seconds at 0 °C the organic layer was separated and evaporated to dryness at room temperature. The oily residue was dissolved in anhydrous heptane (50 mL) under N_2, and the solution was cooled at −30 °C. Crystals of **4** were filtered and dried *in vacuo* (1.06 g; 22% yield). Anal. Calcd for $Tb_4C_{125}H_{256}N_{14}O_{27}$: CO_2, 18.9; Tb, 21.0%. Found: CO_2, 18.9; Tb: 21.1%. ATR IR (the most significant bands in the range 1700−1250 cm^{-1}): 1584m, 1487s, 1422s, 1374m, 1313s, 1261m cm^{-1}. Single crystals were selected to carry out X-ray diffraction studies (298 and 100 K).

Crystallization of $[NH_2Bu_2]_2[Ln_4(CO_3)(O_2CNBu_2)_{12}]$, (Ln = Tb, 4; Sm, 5; Eu, 6). Single crystals of **4** were also obtained by storing for about 40 h at room temperature the oily residue obtained by the concentration under vacuum at room temperature of the organic phase derived from the extraction process carried out as described in the previous paragraph. Crystals were selected and studied by X-ray diffraction methods (298 K).

Single crystals of **5** and **6** were obtained similarly. They were studied by X-ray diffraction methods (298 K).

Conversion of 5 into $Sm_4(CO_3)(O_2CNBu_2)_{10}$, 7. A sample of **5** was treated *in vacuo* (10^{-3} Torr) at 40 °C up to constant weight. The resulting product showed CO_2 and metal contents consistent with the composition $Sm_4(CO_3)(O_2CNBu_2)_{10}$. Anal. Calcd for $C_{91}H_{180}N_{10}O_{23}Sm_4$: CO_2, 20.3; Sm, 25.2%. Found: CO_2, 20.6; Sm: 25.1%.

Preparation of $[NH_2Bz_2][Eu(O_2CNBz_2)_4]$, 8. To a solution of **2** (3.603 g; 5.39 mmol) in toluene (50 mL) was addedNHBz$_2$ (4.2 mL, 22 mmol). The solution was saturated with CO_2. After 2 days, the solution was concentrated to a small volume (about 5 mL) *in vacuo*. Toluene (20 mL) and $NHBz_2$ (4.2 mL, 22 mmol) were added to the oily residue, and the solution was saturated with CO_2. After 3 h of stirring the solution was evaporated to an oily residue, with the treatment being repeated three times. Heptane (50 mL) was added to the residue, and after 15 h of stirring, the resulting suspension was filtered. The product was dried *in vacuo* at room temperature (5.01 g, 71% yield). Anal. Calcd for $[NH_2Bz_2][Eu(O_2CNBz_2)_4]$, $C_{74}H_{72}EuN_5O_8$: CO_2, 13.4; Eu, 11.6%. Found: CO_2, 13.3; Eu: 11.3%. ATR IR, solid (the most significant bands in the range 1700−1250 cm^{-1}): 1586w, 1514m, 1482s, 1452s, 1430s, 1323m, 1294m, 1270s cm^{-1}.

Preparation of $[Eu(O_2CNBz_2)_3]_n$, 9. A suspension of **8** (1.310 g, 1.00 mmol) in toluene (30 mL) was evaporated to dryness under reduced pressure at 60 °C. The residue was treated *in vacuo* at 60 °C for about 2 h. Toluene was then added (30 mL), and the treatment was repeated four times. Finally, heptane (30 mL) was added to the residue, and the final suspension was filtered. The product was dried *in vacuo* (0.57 g; 65% yield). Anal. Calcd for $[Eu(O_2CNBz_2)_3]_n$, $C_{45}H_{42}EuN_3O_6$: CO_2, 15.1; Eu, 17.4%. Found: CO_2, 15.4; Eu: 17.4%. ATR IR, solid (the most significant bands in the range 1700−1250 cm^{-1}): 1586w, 1512s, 1476s, 1452s, 1429s, 1323s, 1294m, 1269s cm^{-1}.

Preparation of $[Sm(O_2CNBz_2)_3]_n$, 10. To a solution of **7** (0.919 g; 1.56 mmol of Sm) in toluene (10 mL) was added $NHBz_2$ (5.0 mL, 26.0 mmol). The solution was saturated with CO_2, stirred at room temperature for 1 h, and then evaporated under reduced pressure to an oily residue. The residue was treated *in vacuo* at 60 °C for about 2 h, and toluene was then added (30 mL). The suspension was again treated as described for 4 times. Finally, heptane (30 mL) was added to the residue, and the suspension was filtered. The product was dried *in vacuo* (0.95 g; 70% yield). Anal. Calcd for $[Sm(O_2CNBz_2)_3]_n$, $C_{45}H_{42}N_3O_6Sm$: CO_2, 15.2; Eu, 17.3%. Found: CO_2, 14.8; Eu: 17.2%. ATR IR, solid (the most significant bands in the range 1700−1250 cm^{-1}): 1586w, 1512s, 1483s, 1452s, 1430s, 1323m, 1294m, 1271s cm^{-1}.

Single-Crystal X-ray Diffraction. Crystals of **4**, **5**, and **6** were selected at room temperature (293 K) under a nitrogen atmosphere, glued to glass fibers, and analyzed with a Bruker Smart Breeze CCD diffractometer. All the compounds show an orthorhombic symmetry with similar cell parameters. Table 1 lists the measured values for the terbium (**4**) and samarium (**5**) compounds. Cell parameters of the europium compound are a = 32.7(3), b = 17.64(16), c = 28.2(2) Å. Intensity data were collected up to a max 2θ angle of 55.47° for **4** and of 48.17° for **5**. After correction for Lorentz and polarization effects and for absorption, the structure solution procedure was started on both the data series. The molecular structures, which are clearly isotypical, consist of a tetrameric anion $[Ln_4(CO_3)(O_2CNBu_2)_{12}]^{2-}$ characterized by a symmetry $2/m$ linked by ionic and hydrogen interactions with two cations $[NH_2Bu_2]^+$. Since a large disorder present in the butyl moieties and in the carbonate group did not allow us to complete the model, new intensity data were collected on the crystal of **4** at 100 K with the intent to minimize disorder. At low temperature the sample underwent a transition to a monoclinic phase with a slight shortening of lattice parameters, tilting of β angle, and removal of the lattice centering. Table 1 lists the more relevant parameters of the low temperature polymorph. The transformed sample, however, is twinned by rotation about the axis [100] and, due to the tilting of β angle, the two reciprocal lattices are misaligned by about 5.92°. The tilting causes the superposition or the approximate superposition of only a limited number of the diffraction spots. There is perfect superposition of diffraction spots in the plane (hk0) and an imperfect superposition in the planes (hk11), (hk22), and so on. Moreover, several spots are elongated and broadened. For these reasons, the accuracy of the intensity collection was limited. The lattice parameters, the intensity data statistics, and the systematic extinctions suggest the monoclinic space group $P2_1/c$ as the only reasonable choice. However, the internal R factor calculated on 36 027 intensity data, mediated out from 141 804 collected up to a 2θ angle of 57.5°, was still high (0.117).

The structure solution was obtained by combining the direct methods with the difference Fourier maps. The structural model could be completed, but a residual degree of disorder was still present in some butyl groups, as denounced by certain inconsistent bond lengths and by the excessive anisotropy of some thermal ellipsoids. Two butyl groups were introduced in the model as distributed on two limit positions, fixing to 1 the total occupancy of the site. In order to obtain reasonable bond lengths some restraints had to be introduced in their geometry. Restraints were, moreover, introduced in the anisotropy of the thermal ellipsoids of a few atoms. After the introduction of the hydrogen atoms in calculated positions, the final refinement cycle gave the figures of merit shown in Table 1. Further limits of the refined model are the high residual electron density peaks (up to 5 e/Å^3) present in the final difference Fourier map around the positions of the heavier atoms. Crystallographic calculations have been done using SHELX program,[13] and other control calculations were performed with the programs contained in the suite WINGX.[14]

■ RESULTS AND DISCUSSION

Syntheses. Primary and secondary amines (both sketched in the following reactions, 1−3 and 5, as NHR_2) react exothermically with CO_2 with formation of alkylcarbamic acid and/or alkylammonium alkylcarbamate (see eqs 1, 2 and 3, eq 3 being the sum of eqs 1 and 2).[8] In the presence of water the CO_2 hydration equilibria (eq 4) and the hydrolysis of the carbamato anion (eq 5) must in addition be considered.

$$NHR_2(solv) + CO_2(solv) \rightleftharpoons R_2NCOOH(solv) \tag{1}$$

$$\begin{aligned} &NHR_2(solv) + R_2NCOOH(solv) \\ &\quad \rightleftharpoons [NH_2R_2][O_2CNR_2](solv) \end{aligned} \tag{2}$$

$$2NHR_2(solv) + CO_2(solv) \rightleftharpoons [NH_2R_2][O_2CNR_2](solv) \tag{3}$$

$$\begin{aligned} &H_2O(aq) + CO_2(aq) \\ &\quad \rightleftharpoons H_2CO_3(aq) \\ &\quad \rightleftharpoons HCO_3^-(aq) + H^+(aq) \end{aligned} \tag{4}$$

$$[NR_2CO_2]^-(aq) + H_2O(1) \rightleftharpoons NHR_2(aq) + H_2CO_3(aq) \tag{5}$$

N,N-Dialkylcarbamato metal complexes are normally prepared by reacting the appropriate metal halide (usually the chloride) with NHR_2 and CO_2 in organic solvents (for instance hydrocarbons) under strictly anhydrous conditions (eq 6),[8] in view of the fact that these derivatives easily undergo partial or exhaustive hydrolysis producing oxo- or carbonato derivatives (eq 7).[8,15]

$$\begin{aligned} &MX_n + n[NH_2R_2][O_2CNR_2] \\ &\quad \rightarrow [M(O_2CNR_2)_n] + n[NH_2R_2]X \end{aligned} \tag{6}$$

$$\begin{aligned} &c/a[M(O_2CNR_2)_n]_a + mH_2O \\ &\quad \rightarrow 1/b[M_c(Y)_m(O_2CNR_2)_{nc-2m}]_b + zmCO_2 \\ &\qquad + 2mNHR_2 \end{aligned} \tag{7}$$

$$Y = O \quad z = 2$$

$$Y = CO_3 \quad z = 1$$

Lanthanide *N,N*-dialkylcarbamato complexes have been prepared according to this procedure, and the diisopropyl derivatives $[Ln\ (O_2CN^iPr_2)_3]_n$ (Ln = Ce, Pr, Nd, Eu, Gd, Ho, Er, Yb, Lu) have been structurally characterized. They are tetranuclear and, with the exception of the cerium complex, isostructural.[16]

With the aim of avoiding tedious dehydration procedures we have studied the biphasic water/hydrocarbon system for the extraction of lanthanide ions from aqueous solution in the form of carbamato complexes, taking into consideration the results earlier obtained with copper(II) and zinc(II).[7] In view of the utilization of the system $NHBu_2/H_2O/CO_2$/hydrocarbon, we have studied its behavior in the conditions that would have been used for the metal extraction. It is known that neat $NHBu_2$ absorbs CO_2 (T = 10 °C, P_{CO_2} = 760 Torr) to a final ($CO_2/NHBu_2$) molar ratio 0.5, with formation of $[NH_2Bu_2][O_2CNBu_2]$.[8] We have monitored the CO_2 uptake by a dibutylamine solution in toluene (0.067 M) measuring a CO_2/amine molar ratio equal to 0.47 (T = 25 °C, P_{CO_2} = 720 Torr), corresponding to nearly complete amine carbonation to $[NH_2Bu_2][O_2CNBu_2]$ also in solution.

Moreover, the solubility of $NHBu_2$ in water[17] was measured in the temperature range 16−27 °C: it decreases from 0.044 M at 16 °C to 0.029 M at 27 °C (corresponding to $\Delta H°$ and $\Delta S°$ approximately −28 kJ mol^{-1} and −64 J mol^{-1} K^{-1}, respectively). In aqueous solution the anion $[O_2CNBu_2]^-$ is partially hydrolyzed (eq 8) with an equilibrium constant (T = 18 °C) equal to 1.9×10^{-1}.[18]

$$[NBu_2CO_2]^-(aq) + H_2O(l) \rightleftharpoons NHBu_2(aq) + HCO_3^-(aq) \tag{8}$$

We have measured the distribution ratio of the amine in the biphasic system (H_2O/heptane = 1.1 as the volumetric ratio) under N_2. The ratio of the equilibrium molar concentrations in heptane and in water was found to be about 70 (T = 20 °C) in the ratio range 0.5−1.7 mol L^{-1} of the (total amine moles)/(total solvent volume). Under CO_2, the situation drastically changed, as a consequence of the amine reaction with CO_2. When a solution of $NHBu_2$ saturated with CO_2 ($P_{CO_2} \approx 760$ Torr, T = 20 °C) in heptane was stirred with water for a few minutes, a distribution ratio of 0.6 was measured. The formation of $[NH_2R_2][O_2CNR_2]$ justifies this behavior.

The extractions of lanthanide ions from water into hydrocarbons were carried out either in toluene or in heptane; the best results, here reported, have been obtained in heptane. The experiments were carried out starting from aqueous solutions obtained by dissolving the metal oxide in hydrochloric acid as described in the Experimental Section. We presume that these solutions contain the hydrated lanthanide ions $[LnCl_x(H_2O)_n]^{(3-x)+}$ ($0 \leq x \leq 3$). In fact, according to the literature data, the hydrated lanthanide trichlorides (Ln = Pr, Nd, Sm, Tb, Dy, Ho, Tm, Yb) can be obtained by dissolving the corresponding metal oxide in hydrochloric acid and evaporating the resulting solutions to dryness.[10]

Metal extraction was carried out at about 0 °C by adding the hydrocarbon solution of dibutylamine, previously saturated with CO_2, to the aqueous solution of the lanthanide chloride. An amine excess was used with respect to the (amine/metal) molar ratio 6, as requested by the formation of $[Ln(O_2CNBu_2)_3]$ (eq 9) to favor the formation of ionic complexes, of the type $[NH_2Bu_2]_x[Ln_m(O_2CNBu_2)_{3m+x}]$ (eq 10). Ionic species $[NH_2R_2]_x[M_m(O_2CNR_2)_{ym+x}]$ often show a lower nuclearity and a greater solubility in hydrocarbons than the corresponding neutral species $[M(O_2CNR_2)_y]_n$, as observed for instance for complexes of zinc[19] and boron (eq 11).[20]

$$\begin{aligned} &Ln^{3+} + 6NHBu_2 + 3CO_2 \\ &\quad \rightarrow 1/n[Ln(O_2CNBu_2)_3]_n + 3[NH_2Bu_2]^+ \end{aligned} \qquad (9)$$

$$\begin{aligned} &1/n[Ln(O_2CNBu_2)_3]_n + 2x/mNHBu_2 + x/mCO_2 \\ &\quad \rightleftharpoons 1/m[NH_2Bu_2]_x[Ln_m(O_2CNBu_2)_{3m+x}] \end{aligned} \qquad (10)$$

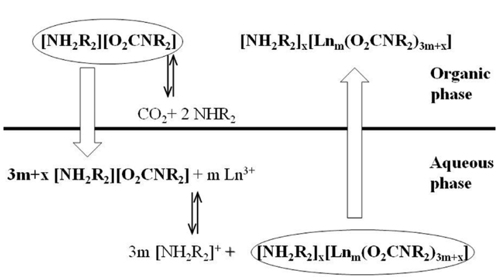
$$\begin{aligned} &1/n[M(O_2CNR_2)_y]_n + 2x/mNHR_2 + x/mCO_2 \\ &\quad \rightleftharpoons 1/m[NH_2R_2]_x[M_m(O_2CNR_2)_{ym+x}] \end{aligned} \qquad (11)$$

y = metal oxidation number $\quad m < n$

The biphasic mixture was stirred for a few seconds: when a colored lanthanide ion was involved, the nearly immediate fading of the aqueous solution was observed with concomitant transfer of the color to the organic phase. The two phases were easily separated, and the *N,N*-dibutylcarbamato metal complex was obtained in yields as high as 90% from the hydrocarbon solution. The efficiency of the lanthanide transfer to the organic layer is confirmed by the lanthanide content of the aqueous layer after the extraction, corresponding to about 4% of the initially used metal. The process is sketched in Scheme 1.

The above-described procedure was applied to aqueous solutions of neodymium, samarium, europium, and terbium salts. Concerning the details of the product recovery, when the heptane solution from the extraction process was evaporated *in vacuo* at room temperature, a viscous oily residue was obtained, probably containing an ionic derivative of the type $[NH_2R_2]_x[Ln_m(O_2CNR_2)_{3m+x}]$ (see eq 10 and Scheme 1) and minor amounts of $NHBu_2$ and water. This residue afforded two different products in dependence of the experimental procedure: (a) When the oily residue was promptly dissolved in heptane and evaporated to dryness and the process was repeated for three or four times in rapid succession, the elemental analysis of the final solid residue corresponded to the formula $[Ln(O_2CNBu_2)_3]_n$ (Ln = Nd, **1**; Eu, **2**; Tb, **3**). (b) When the oily residue was stored for about 40 h at room temperature, crystals of $[NH_2Bu_2]_2[Ln_4(CO_3)(O_2CNBu_2)_{12}]$ (Ln = Tb, **4**; Sm, **5**, and Eu, **6**) separated out. Moreover, **4** was obtained also by dissolving the oily residue in heptane and then cooling the solution at −30 °C.

Scheme 1. Lanthanide Ion Extraction from the Aqueous Phase by the NHR_2/CO_2 System (R = Bu)



Regarding the extraction process, we suggest that $[NH_2Bu_2][O_2CNBu_2]$, initially formed in heptane by reaction of $NHBu_2$ with CO_2, is partially transferred from the organic solvent into the aqueous solution of the lanthanide salt, where the *N,N*-dibutylcarbamato anions rapidly react with the lanthanide ions replacing the metal-coordinated water and/or chloride with formation of lipophilic complexes, which migrate to the organic layer (see Scheme 1). Since the lanthanide ions are labile centers (k in the range 10^7−10^9 s^{-1}, for H_2O exchange in the first coordination sphere of the aquo-ion[21]), the process is sufficiently rapid to avoid the hydrolysis of the metal *N,N*-dibutylcarbamato complex. In Scheme 1, the composition of the metal *N,N*-dibutylcarbamato complex is not specified since it depends on the experimental conditions. As discussed before, equilibria of the type reported in eq 11 have been observed in hydrocarbon solution in the presence of an excess of the amine under CO_2.[21,22]

Concerning the different nature of the products obtained from the two different procedures, a and b, it is reasonable that when the oily residue undergoes repeated dissolution/evaporation cycles (method a), the modest amounts of free amine and water that it contains are removed. Moreover, the initially obtained ionic species $[NH_2Bu_2]_x[Ln_m(O_2CNBu_2)_{3m+x}]$ is expected to release *in vacuo* amine and CO_2 affording $[Ln(O_2CNBu_2)_3]_n$, according to the reverse of eq 10, a type of evolution earlier described for the ionic *N,N*-dialkylcarbamato complexes of titanium(III),[22] zinc,[19] boron,[20] and magnesium.[23] Although there are no direct data confirming the nuclearity of the final species, we suggest that the derivatives are tetranuclear, as found for a large number of lanthanide diisopropylcarbamato complexes of known structure.[16] When the second procedure is followed (method b), probably the tetranuclear ionic species $[NH_2Bu_2]_2[Ln_4(O_2CNBu_2)_{14}]$, in the presence of some residual water, slowly reacts to afford $[NH_2Bu_2]_2[Ln_4(CO_3)(O_2CNBu_2)_{12}]$ according to eq 12.

$$\begin{aligned} &[NH_2Bu_2]_2[Ln_4(O_2CNBu_2)_{14}] + H_2O \\ &\quad \rightleftharpoons [NH_2Bu_2]_2[Ln_4(CO_3)(O_2CNBu_2)_{12}] + 2NHBu_2 \\ &\quad\quad + CO_2 \end{aligned} \qquad (12)$$

It can be assumed that the hydrolytic process is slow, since the metal centers are protected by a thick lipophilic shield, so that if the residue is rapidly worked up as described in procedure a, water is removed and hydrolysis avoided. Nevertheless, the solid products or their solutions, once the amine excess and CO_2 are removed, are promptly hydrolyzed.

On the basis of our previous experience,[19,23] this behavior must be ascribed to the role played in solution by free amine and CO_2. Equation 12, or more generally eq 7, is more or less displaced to the left in dependence of the H_2O, amine, and CO_2 concentrations. As a consequence, as long as an amine excess is present under CO_2 atmosphere, hydrolysis is prevented.

In summary, compounds **1**−**3** show CO_2 and metal contents corresponding to the formula $Ln(O_2CNBu_2)_3$ with a CO_2/Ln molar ratio equal to 3, while the products **4**−**6** appear, through X-ray diffraction studies, to be isostructural species with the composition $[NH_2Bu_2]_2[Ln_4(CO_3)(O_2CNBu_2)_{12}]$. On the basis of the great reproducibility of the results (every preparation was repeated for 4−6 times) we consider acceptable our interpretation of the product identity. Products **1**−**6** do not differ significantly as far as their IR spectra are concerned, probably because the complexes have a similar skeleton and the bands due to the carbonato group lie in the same region[24] of the strong absorptions due to the carbamato ligands. We have tried to confirm the product identity through structural studies. Nevertheless, the presence of bulky alkyl groups, that had guaranteed the success of the lanthanide extraction, frustrated the formation of crystals suitable for structural studies by X-ray diffraction methods. Despite that, we succeeded in growing single crystals of **4**−**6**, and the results of the structural studies are reported in the next paragraph.

Regarding the samarium derivative **5**, its thermal treatment (T = 40 °C) under vacuum was monitored up to the composition $[Sm_4(CO_3)(O_2CNBu_2)_{10}]$, **7** (eq 13), and the final species was characterized. According to literature data, also ionic compounds like $[NH_2R_2]_m[M_n(Y)_x(O_2CNR_2)_z]$ (Y = O or CO_3) undergo progressive loss of amine and CO_2 under vacuum up to the composition $[M_n(Y)_x(O_2CNR_2)_{z\text{-}m}]$.[19,20,22]

$$\underset{\mathbf{5}}{[NH_2Bu_2]_2[Sm_4(CO_3)(O_2CNBu_2)_{12}]} \rightarrow \underset{\mathbf{7}}{[Sm_4(CO_3)(O_2CNBu_2)_{10}]} + 4NHBu_2 + 2CO_2 \quad (13)$$

In addition to the preparation of the described lanthanide *N,N*-dibutylcarbamato complexes, we have exploited the reactivity of these species for the preparation of other derivatives. In effect, metal *N,N*-dialkylcarbamato complexes are excellent precursors of other metal compounds as the carbamato ligand is easily removed, for instance by reaction with Brønsted acids (eq 14).[8]

$$[M(O_2CNR_2)_n] + nHA \rightleftharpoons [MA_n] + nNHR_2 + nCO_2 \quad (14)$$

By treating a dialkylcarbamato complex $[M(O_2CNR_2)_n]$ with the appropriate secondary amine NHR′R″ under CO_2, the substitution reaction 15 is observed.[8,21,25]

$$[M(O_2CNR_2)_n] + nNHR'R'' \rightleftharpoons [M(O_2CNR'R'')_n] + nNHR_2 \quad (15)$$

If NHR_2 is more volatile than NHR′R″, the difficulties arising from possible equilibria leading to mixtures of products are readily overcome. Formally these reactions are amine exchange processes; however, they do not occur in the absence of carbon dioxide. Thus, the presence of ammonium carbamate, $[NH_2R'R''][O_2CNR'R'']$, and/or of carbamic acid, $NR'R''CO_2H$, deriving from the $NHR'R''/CO_2$ equilibria, is essential to trigger the reaction.

N,N-Dibenzylcarbamato complexes of europium and samarium have been prepared starting from their *N,N*-dibutylcarbamato complexes. By repeated treatments with an excess of dibenzylamine ($NHBz_2$) under CO_2 in toluene, **2** underwent substitution of the carbamato group. The ionic derivative **8** was initially obtained (eq 16). By prolonged treatment *in vacuo* at 60 °C, **8** was converted to **9** (eq 17).

$$\underset{\mathbf{2}}{1/n[Eu(O_2CNBu_2)_3]_n} + 5NHBz_2 + CO_2 \rightarrow \underset{\mathbf{8}}{[NH_2Bz_2][Eu(O_2CNBz_2)_4]} + 3NHBu_2 \quad (16)$$

$$\underset{\mathbf{8}}{[NH_2Bz_2][Eu(O_2CNBz_2)_4]} \rightarrow 2NHBz_2 + CO_2 + \underset{\mathbf{9}}{1/n[Eu(O_2CNBz_2)_3]_n} \quad (17)$$

On the other hand, when the samarium carbonato-carbamato complex **7** was treated with an excess of $NHBz_2$ under CO_2 in toluene, **10** was obtained after removal of all volatiles *in vacuo* at 60 °C. Both the *N,N*-dibutylcarbamato ligands and the carbonato groups were displaced by the *N,N*-dibenzylcarbamato anions present in solution in high concentration. Most likely, in analogy with the europium case, the initial product of the reaction was the ionic derivative $[NH_2Bz_2][Sm(O_2CNBz_2)_4]$ (eq 18), which was thermally converted to $[Sm(O_2CNBz_2)_3]_n$ (eq 19) under vacuum.

$$\underset{\mathbf{7}}{[Sm_4(CO_3)(O_2CNBu_2)_{10}]} + 20NHBz_2 + 5CO_2 \rightarrow 4[NH_2Bz_2][Sm(O_2CNBz_2)_4] + H_2O + 10NHBu_2 \quad (18)$$

$$[NH_2Bz_2][Sm(O_2CNBz_2)_4] \rightarrow 2NHBz_2 + CO_2 + \underset{\mathbf{10}}{1/n[Sm(O_2CNBz_2)_3]_n} \quad (19)$$

As discussed above, reactions similar to 17 and 19, affording a neutral metal *N,N*-dialkylcarbamato complex from an ionic species containing the dialkylammoium as cations, have been previously reported.[19,20,22]

X-ray Crystallography. The X-ray diffraction study of both **4** and **5** at room temperature gave an incomplete structural model due to the disorder present in the crystals. Measurements carried out at low temperature (100 K) on **4** showed that a partial ordering occurred to a monoclinic phase, which could be studied more easily. Nevertheless, problems related to the presence of twinning were observed. Actually, the lattice tilting due to the phase transition from a more symmetric phase (orthorhombic) to a less symmetric one (monoclinic, see Experimental Section) is equally probable in opposite directions, so that twinning is produced. Anyway, although the precision of the obtained model is limited, it is sufficient to describe the molecular architecture. A sketch of the molecular structure of **4** is drawn in Figure 1. The anion is made by a cage of four metal atoms gathered around a carbonato ion and each coordinated by a terminal carbamato group and by other four bridging carbamates. The Tb atoms are kept at the apexes of a roughly planar trapezoid, with the major base at the Tb(1) and Tb(2) atoms connected to different carbonato oxygen atoms, and the minor one at the Tb(3) and Tb(4) atoms connected to

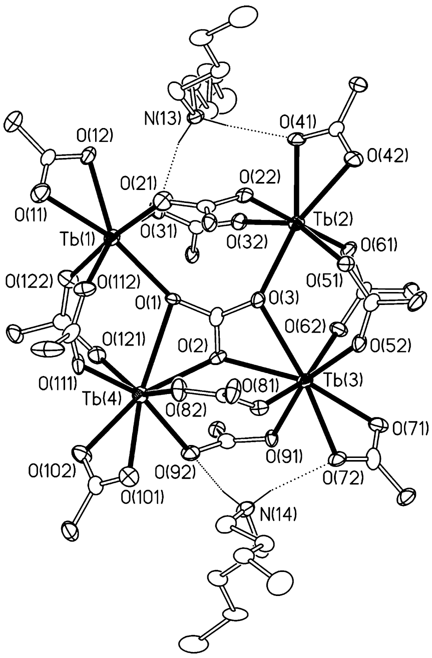


Figure 1. View of the molecular structure of the ionic triplet $[NH_2Bu_2]_2[Tb_4(CO_3)(O_2CNBu_2)_{12}]$ in **4**. Thermal ellipsoids are at 30% probability. The butyl groups present in the anion have been omitted for clarity.

the same carbonato oxygen. The carbonato ligand makes with the four metal atoms four shorter bonds and two longer ones, namely O(1)−Tb(4) and O(3)−Tb(3). A similar coordination of the carbonato group has been described in several polynuclear lanthanide derivatives.[26] The carbonato plane is tilted with respect to the plane of the metal atoms. As can be seen in the figure, Tb(1) and Tb(2) are heptacoordinated with a geometry approaching the pentagonal bipyramid, while Tb(3) and Tb(4) are 8-coordinated with a geometry which can be defined as distorted dodecahedral.

Two dibutylammonium cations face on the opposite grooves of each anion. In addition to the ionic interactions, two couples of hydrogen bonds are observed between the cation nitrogen atoms and four oxygen atoms of the carbamato ligands. N(13) interacts with O(41) and O(31), and N(14) interacts with O(72) and O(92).

HRMS Spectra. To gain more information about their nuclearity, the complexes **1**−**3**, **4**, and **7** were characterized by HRMS(+). Regardless of the specific complex analyzed, two groups of intense signals attributed to the cations $[Ln_2(O_2CNBu_2)_5]^+$ and $[Ln_4O(O_2CNBu_2)_9]^+$ (Ln = Nd, Sm, Eu, Tb) were observed in all the mass spectra. Only in the case of **3**, a weak signal at 2722.1 Da was detected and attributed to the ion $[Tb_4(O_2CNBu_2)_{12}Na]^+$, which was formed by interaction between a tetranuclear neutral species with the cation Na^+, presumably introduced through the solvent employed for the analysis. In all the other mass spectra no molecular ion matching with the presumed tetranuclear molecular formula was identified. We suppose that the cation $[Ln_2(O_2CNBu_2)_5]^+$ might derive from the loss of a $[Bu_2NCO_2]^-$ fragment from the dinuclear species $Ln_2(O_2CNBu_2)_6$ or more likely from the breakup of the tetranuclear derivatives $Ln_4(O_2CNBu_2)_{12}$. The latter hypothesis is supported by the following: (a) the previously established nuclearity 4 for lanthanides(III) *N,N*-diisopropylcarbamato complexes,[16] (b) the identification of the signal corresponding to $[Tb_4(O_2CNBu_2)_{12}Na]^+$, and (c) the presence, in all the mass spectra here reported, of the signal attributable to the tetranuclear fragments $[Ln_4O(O_2CNBu_2)_9]^+$. These last fragments might draw from the partial hydrolysis of the homoleptic tetranuclear carbamato complexes (eq 20), due to adventitious water in the solvents, followed by loss of one carbamato ligand.

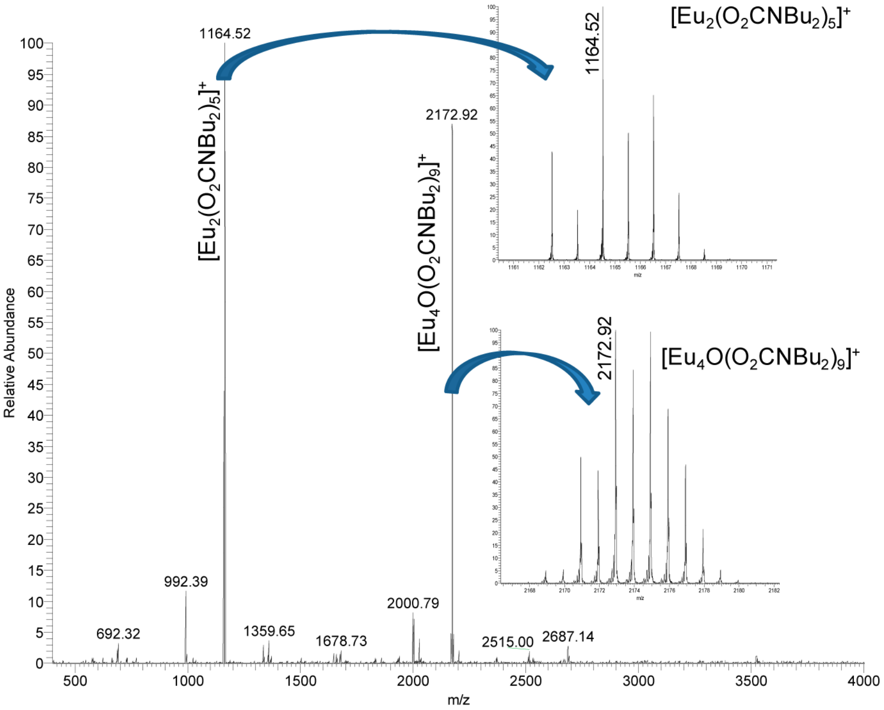


Figure 2. APPI FTICR positive mass spectrum of the complex $[Eu(O_2CNBu_2)_3]_n$, **2**. Blow ups of the isotopic cluster distributions are in the insets.

$$\begin{aligned} &Ln_4(O_2CNBu_2)_{12} + H_2O \\ &\quad \rightleftharpoons Ln_4(O)(O_2CNBu_2)_{10} + [NH_2Bu_2][O_2CNBu_2] \\ &\qquad + CO_2 \end{aligned} \tag{20}$$

It is interesting that the mass spectrum of **4** is quite similar to that of **3** (Supporting Information Figures S2 and S3). This behavior can be explained by assuming that in solution equilibrium reactions of the type hereafter reported (eqs 21 and 22) are rapidly established. Consequently, the two systems do not differ appreciably if we consider that the carbonato tetranuclear complex releases CO_2 in the instrument ion source conditions (350 °C and low CO_2 partial pressure) producing the μ-oxo tetranuclear fragment.

$$\begin{aligned} &\underset{\mathbf{4}}{[NH_2Bu_2]_2[Tb_4(CO_3)(O_2CNBu_2)_{12}]} \\ &\quad \rightleftharpoons Tb_4(CO_3)(O_2CNBu_2)_{10} + 2[NH_2Bu_2][O_2CNBu_2] \end{aligned} \tag{21}$$

$$\begin{aligned} &Tb_4(CO_3)(O_2CNBu_2)_{10} + [NH_2Bu_2][O_2CNBu_2] \\ &\quad \rightleftharpoons \underset{\mathbf{3}}{Tb_4(O_2CNBu_2)_{12}} + H_2O \end{aligned} \tag{22}$$

The attributions of the more abundant ions, in all the samples examined, have been confirmed both with accurate mass calculation (from the HRMS mass spectra) and by comparing the experimental isotope cluster distributions with the theoretical ones. In Figure 2 the APPI FTICR (atmospheric pressure photo ionization Fourier transform ion cyclotron resonance) mass spectrum of **2** is reported, where the two main cations $[Eu_2(O_2CNBu_2)_5]^+$ and $[Eu_4O(O_2CNBu_2)_9]^+$ and the corresponding isotope clusters are evidenced. Generally the variance between the experimental and the theoretical mass was below 0.002% for all the samples analyzed, and we have always obtained an excellent match between the experimental and calculated isotope clusters. The whole series of the mass spectra, together with the comparison between the experimental and calculated isotope clusters and accurate masses, are reported in the Supporting Information.

Photoluminescence Studies. In order to investigate the influence of the carbamato ligands on the emission behavior of the lanthanides ions, a photoluminescence (PL) study has been carried out. Concerning europium, the excitation spectra from both **2** and **8** (Figure 3) have been recorded by monitoring the $^5D_0 \rightarrow {}^7F_2$ transition at ca. 615 nm, with the exact shape and position being dependent on the coordination geometry and the nature of the ligands (polarizability, bond strength, and so forth).[27]

The spectra are composed of several sharp lines characteristic of Eu^{3+} f–f transitions whose shape and relative intensity do not markedly change upon substitution in the europium coordination sphere of the *N,N*-dibutylcarbamato with the *N,N*-dibenzylcarbamato ligands. Despite the presence of a strongly absorbing aromatic moiety in **8**, which in principle could act as sensitizer for lanthanide emission,[27b,28] there is no evidence of an indirect excitation channel, and the luminescent excited states of europium can be effectively populated only by exploiting the Eu^{3+} centered f–f transitions. Conversely, the emission behavior of the lanthanide centers is quite different in **2** compared to **8** (Figure 4).

Whereas the spectroscopic properties of europium are not affected by the value of the excitation wavelength, the emission

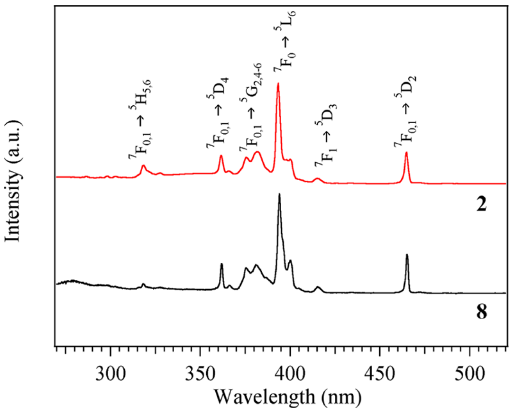


Figure 3. Room temperature excitation spectra of $[Eu(O_2CNBu_2)_3]_n$, **2**, and $[NH_2Bz_2][Eu(O_2CNBz_2)_4]$, **8**, complexes. The spectra have been obtained by monitoring the $^5D_0 \rightarrow {}^7F_2$ transition at 615 nm.

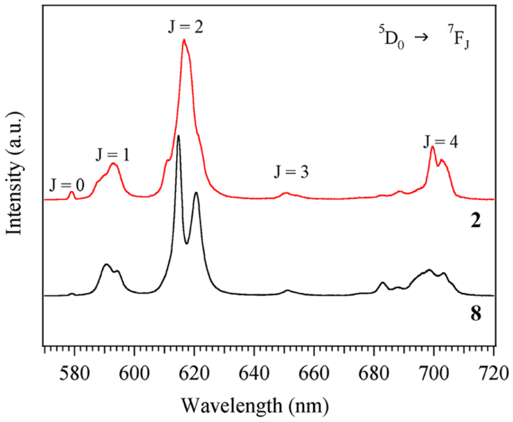


Figure 4. Room temperature emission spectra of $[Eu(O_2CNBu_2)_3]_n$, **2**, and $[NH_2Bz_2][Eu(O_2CNBz_2)_4]$, **8**, complexes excited within the $^7F_0 \rightarrow {}^5L_6$ transition at 394 nm.

spectra of Eu^{3+} in the complexes, dominated by the $^5D_0 \rightarrow {}^7F_2$ transition ($\lambda_{max} \approx 615$ nm), present major modifications depending on the nature of the ligand. In particular, the variation in the number and intensity ratio of the crystal field levels of each ^7F_J ($J = 1$, 2 and 4) multiplet is observed. This behavior is consistent with a change in the Eu^{3+} coordination sphere.[27a−c] Although the molecular structures of these complexes are not known, it is reasonable that **2** is formed by polynuclear molecules, presumably tetranuclear, and that **8** contains mononuclear anions where the four bidentate carbamato ligands provide the coordination number 8 for the lanthanide, like for instance in the *N,N*-dialkyldithiocarbamate derivatives $[Q][Eu(S_2CNR_2)_4]$ ($Q = Na$, $R = Et$; $Q = NH_2Me_2$, $R = Me$).[29]

The samarium complexes **5** and **7** present quite similar spectroscopic properties.

The excitation spectra of the two compounds monitored at 600 nm show the same profile, and the Sm^{3+} f–f transitions labeled in Figure 5 can be exploited for the excitation of samarium luminescence. The variation of the excitation wavelength does not induce any change in the emission spectra which are characterized by the $^4G_{7/2} \rightarrow {}^6H_J$ ($J = 5/2$, 7/2, 9/2, and 11/2)[30] transitions situated in the orange-red spectral region (Figure 6).

In analogy to what is observed for Eu^{3+} and Sm^{3+} carbamato complexes, also for the tetranuclear terbium complex **4** the

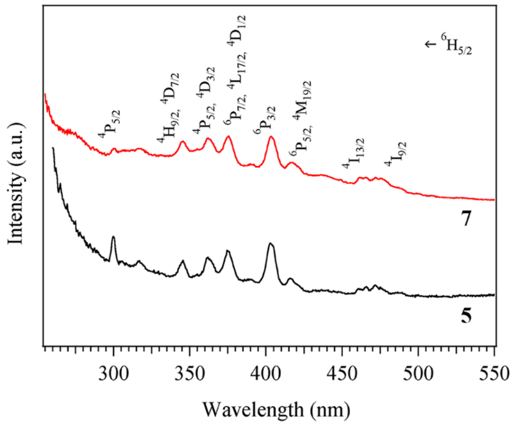


Figure 5. Room temperature excitation spectra of $Sm_4(CO_3)(O_2CNBu_2)_{10}$, **7**, and $[NH_2Bu_2]_2[Sm_4(CO_3)(O_2CNBu_2)_{12}]$, **5**. The spectra have been obtained by monitoring the emission at 600 nm.

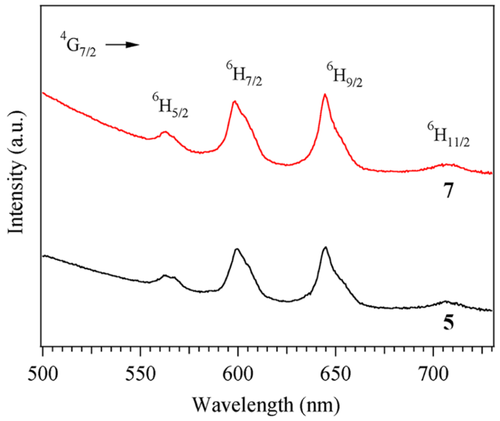


Figure 6. Emission spectra of $Sm_4(CO_3)(O_2CNBu_2)_{10}$, **7**, and $[NH_2Bu_2]_2[Sm_4(CO_3)(O_2CNBu_2)_{12}]$, **5**, complexes obtained under visible excitation at 403 nm.

metal centered f−f transitions represent the only effective way to induce terbium luminescence (Figure 7).

Upon excitation at 360 nm, a bright green luminescence clearly appreciable by the naked eye typical of terbium compounds is observed.

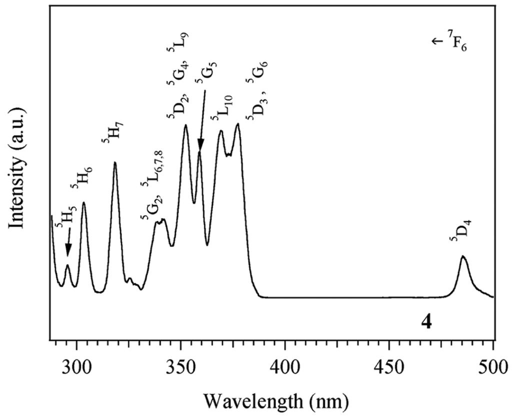


Figure 7. Excitation spectrum of $[NH_2Bu_2]_2[Tb_4(CO_3)(O_2CNBu_2)_{12}]$, **4**, obtained by monitoring the $^5D_4 \rightarrow {}^7F_5$ transition at 545 nm.

The emission spectrum displayed in Figure 8 is characterized by four bands due to the $^5D_4 \rightarrow {}^7F_J$ (J = 6, 5, 4, and 3) transitions[30b,31] whose position, form, and relative intensity are not affected by the excitation wavelength.

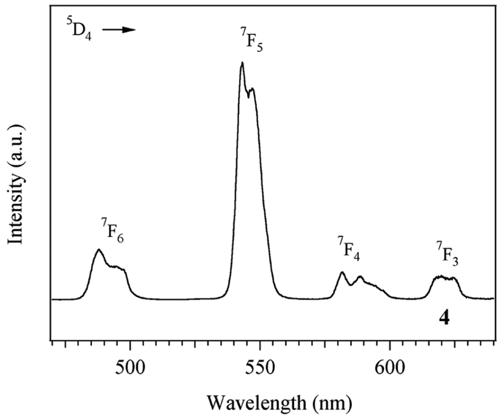


Figure 8. Emission spectrum of $[NH_2Bu_2]_2[Tb_4(CO_3)(O_2CNBu_2)_{12}]$, **4**, obtained under visible excitation at 360 nm.

■ CONCLUSIONS

A simple and efficient system for the extraction of lanthanides(III) from aqueous solution into heptane has been developed for neodymium, samarium, europium, and terbium. The *N,N*-dibutylcarbamato anion, $[Bu_2NCO_2]^-$, generated *in situ* by reaction of $NHBu_2$ with CO_2 appears to be an effective extracting agent of the metal ions from the aqueous layer to the hydrocarbon solution. In the course of the characterization of the extracted complexes, the crystal and molecular structure of $[NH_2Bu_2]_2[Tb_4(CO_3)(O_2CNBu_2)_{12}]$, obtained by single-crystal X-ray diffraction methods, has shown an interesting carbonato centered tetranuclear anion. The analogous samarium and europium complexes are isostructural. Mass spectra of the complexes in MeCN/toluene reveal that rapid equilibria must be present in solution. According to the photoluminescence spectra carried out on solid samples of $[Eu(O_2CNBu_2)_3]_n$, $[NH_2Bu_2]_2[Ln_4(CO_3)(O_2CNBu_2)_{12}]$ (Ln = Sm, Tb), and $[Sm_4(CO_3)(O_2CNBu_2)_{10}]$, the metal centered f−f transitions represent the only effective way to induce lanthanide luminescence in these complexes. The substitution of the dibutyl with the dibenzyl moiety in the europium derivative, affording the species $[NH_2Bz_2][Eu(O_2CNBz_2)_4]$, does not generate any antenna effect, despite the presence of a strongly absorbing aromatic moiety.

The simple syntheses of *N,N*-dialkylcarbamato complexes reported here, besides offering a convenient method of extraction of lanthanide ions from aqueous solutions, produce molecular anhydrous derivatives with potentially excellent features as precursors of a variety of lanthanide compounds. Further studies are underway concerning the extraction of other lanthanide ions and the conversion of the obtained complexes to other derivatives by simple substitution reactions.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Crystallographic data in CIF format. Additional mass spectra and related data. This material is available free of charge via the Internet at http://pubs.acs.org. CCDC 972754 containing the supplementary crystallographic data for the compounds described in this Article can be obtained free of charge from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K. Fax: +44 1223 336 033. E-mail: deposit@ccdc.cam.ac.uk.

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Notes

The authors declare no competing financial interest.

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