N,*N*-Dialkylcarbamato Lanthanide Complexes, a Series of Isotypical Coordination Compounds

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The preparations of the *N*,*N*-dialkylcarbamato complexes with analytical formulae $[Ln(O_2CNR_2)_3]$ (Ln = Pr, Nd, Eu, Gd, Ho, Er, Yb, Lu, R = *i*Pr; Ln = Nd, Eu, Gd, R = Bu; Ln = Nd, R = Et), using $[LnCl_3(ether)_x]$ (ether = THF or dimethoxyethane, DME), NHR_2, and CO_2 are reported. X-ray diffraction of the diisopropylcarbamato derivatives, including a reinvestigation of $[Yb_4(O_2CNiPr_2)_{12}]$, showed these complexes to be tetranuclear and isotypical over a range of 12 atomic numbers. The lanthanide contraction has been evaluated based on the lengths of four different types of Ln–O bond.

Introduction

The synthesis, characterization, and reactivity of *N*,*N*-dialkylcarbamato transition metal complexes have been extensively studied in these laboratories and elsewhere.[1–6] As far as lanthanide (Ln) derivatives are concerned, the structurally characterized examples have resulted from work carried out within this research group,[7,8] with the sole exception of the heteroleptic binuclear complex $[Sm_2(C_5Me_5)_4(THF)\{\mu\text{-}\eta^2\text{-}:\eta^1\text{-}NN(CO_2)Ph_2\}]$, prepared[9] by carbonation of the precursor $[Sm_2(C_5Me_5)_4\{\mu\text{-}\eta^2\text{-}:\eta^1\text{-}NNPh_2\}]$. Moreover, structurally defined homoleptic derivatives of lanthanides with oxygen donors are rather rare. A literature survey has in fact shown that, with these restrictions, even the well-established classes of the β-diketonato[10–12] and carboxylato[13,14,15] complexes are not extensively represented. However, it appears that when bulky coordinated ligands are present, isostructural behavior may be more easily observed. This is evidenced by the synthesis of the isopropoxy μ_5-oxo derivatives of general formula $[Ln_5(\mu_5\text{-}O)(OiPr)_{13}]$ which have been shown to crystallize in the $P2_1/n$ (no. 14) space group for Ln = Nd, Gd, Er, i.e. over a range of nine atomic numbers.[16]

Recently, a preliminary communication from these laboratories showed that the metrical data of the isotypical tetranuclear complexes $[Ln_4(O_2CNiPr_2)_{12}]$ allowed the lanthanide contraction in these complexes to be evaluated in the sequence from neodymium to ytterbium.[17] In this paper, the preparation of the derivatives $[Ln(O_2CNR_2)_3]$ (R = *i*Pr, Ln = Pr, Nd, Eu, Gd, Ho, Er, Lu; R = Et, Ln = Nd; R = Bu, Ln = Nd, Eu, Gd) and the full details of the crystal and molecular structures of the isotypical compounds $[Ln_4(O_2CNiPr_2)_{12}]$ (Ln = Nd, Eu, Gd, Ho, Er, Yb, Lu) are reported.

Results and Discussion

The carbamato complexes $[Ln(O_2CNR_2)_3]$ have been mainly prepared[7,8,17] starting from the derivatives $[LnCl_3(ether)_x]$ (ether = THF or dimethoxyethane, DME),[18] which have a low nuclearity and react promptly with NHR_2 and CO_2 according to Equation (1).

$$[LnCl_3(ether)_x] + 6\,NHR_2 + 3\,CO_2 \rightarrow [Ln(O_2CNR_2)_3] + 3\,[NH_2R_2]Cl + x\text{ ether} \quad (1)$$

As previously reported, in the cases of erbium and ytterbium,[7,8,17] the unsolvated chlorides $LnCl_3$ have been found to be useful starting materials for the synthesis of the carbamato complexes. Consistent with the fact that erbium and ytterbium are late lanthanide elements, and in the hypothesis that the chemical properties of these compounds are mainly governed by the ionic radius of the central metal cation, the preparation of the carbamato derivative was also attempted with lutetium trichloride. This has now been found to react with the $NHiPr_2/CO_2$ system giving the corresponding carbamato derivative in good yield. Conversely, this synthetic route met with failure for the lighter lantha-

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nides. The extended structures of the anhydrous lanthanide chlorides could be responsible for their poor or even lack of reactivity. In this context, it is useful to point out that the anhydrous trichlorides have the structure of UCl_3 ($CN = 9$) from lanthanum to gadolinium, while from dysprosium to lutetium the structures are like that of YCl_3 ($CN = 6$).[19] The lower coordination number towards the end of the series, associated with the usual trend towards smaller ionic radii in the same direction, may be responsible for the higher reactivity of the heavier metal halides. In fact, it is reasonable that the primary stage of the reaction sequence towards the formation of the carbamato derivatives is amine association. This is presumably more likely to occur with ytterbium and lutetium with a reduced coordination number, thus initiating the chain of reactions towards the final product.

The yields of the *N,N*-dialkylcarbamato complexes (R = *i*Pr, Bu) varied from moderate to good. The workup was rather simple, requiring a preliminary filtration of the reaction mixture to eliminate the dialkylammonium chloride, followed by concentration of the filtrate containing the product.

The solubility of the products in non-polar solvents depends on the nature of the R group. For instance, the *N,N*-diethylcarbamato complex of neodymium $[Nd(O_2CNEt_2)_3]$, presumably possessing a polynuclear structure, is only sparingly soluble in hydrocarbons. For this reason it is more conveniently prepared by treatment of the soluble $[Nd(O_2CNBu_2)_3]$ in a hydrocarbon solution with $NHEt_2$ and CO_2 according to an $O_2CNR_2/O_2CNR'_2$ substitution reaction, originally reported for the titanium(III) complexes,[20] and more latterly extended to other metal cations.[5,21]

Table 1. IR spectra of the tetranuclear complexes $[Ln_4(O_2CN\textit{i}Pr_2)_{12}]$ in the 1650−1350 cm^{-1} region

Ln	Medium	Wavenumber[a] (cm^{-1})			
Pr	PCTFE	1591	1527	1518	1353
Nd	Nujol	1593	1515	1479	1354
Eu	PCTFE	1597	1533	1488	1354
Gd	PCTFE	1598	1537	1485	1355
Ho	Nujol	1601	1538	1489	1354
Er	Nujol	1602	1540	1490	1355
Yb	Nujol	1604	1541	1491	1355
Lu	Nujol	1610	1530	1490	1354

[a] Bands at about 1460 and 1380 cm^{-1}, attributable to the CH_3 and CH_2 groups. Bending vibrations are not reported.

The IR spectra of these derivatives show intense and broad bands in the 1650−1350 cm^{-1} region due to the stretching vibrations of the O_2CN moieties (see Table 1, and the Exp. Sect.). As expected for complexes having analogous molecular structures, the spectra of $[Ln_4(O_2CN\textit{i}Pr_2)_{12}]$ are almost identical, except for a shift of the highest frequency band towards higher wavenumbers along the series. Chisholm and Extine[3] studied the effect of isotopic substitution ($^{18}O_2CN$ and $O_2{}^{13}CN$) on the position of the highest frequency band for some dialkyl-carbamato complexes of zirconium, niobium and tantalum. They concluded that for a bidentate group the vibration is mostly NC in character, while for a monodentate arrangement there is a predominant OC contribution. According to this interpretation, the data in Table 1 would tend to suggest an increase of the NC bond order from Pr to Lu. The following data within this paper on the observed trend of Ln−O bond lengths (vide infra) are relevant to this specific point.

Magnetic susceptibility measurements have been carried out on $[Nd_4(O_2CN\textit{i}Pr_2)_{12}]$, $[Eu_4(O_2CN\textit{i}Pr_2)_{12}]$, and $[Gd(O_2CNBu_2)_3]$, see Table 2. The magnetic moments at room temperature agree with the experimental values usually encountered with these paramagnetic centers and, for neodymium and gadolinium, they correspond to the calculated values.[22,23] The europium (III) derivatives frequently show more complicated magnetic behavior as the first excited level is close to the ground state (about 250 cm^{-1} higher) so that it may become thermally populated. Variable temperature studies have been performed for the europium and gadolinium compounds. In the range 70−270 K, the magnetic susceptibility of the gadolinium derivative follows the Curie−Weiss law. On the contrary, the europium compound in the 70−170 K range shows, as expected, a temperature dependent μ value, the magnetic moment becoming independent of temperature above 170 K.

The diisopropyl derivatives can be easily recrystallized from heptane with formation of single crystals suitable for X-ray diffraction studies. They are isotypical and the complete structural determination was performed for the neodymium, europium, gadolinium, holmium, erbium and lu-

Table 2. Magnetic susceptibilities of the $[Ln(O_2CNR_2)_3]$ derivatives

Ln	R[a]	T /K	χ_{corr} /cgsu	Diam. Corr,[b]/cgsu	μ_{eff} /BM ($\mu_{calcd.}$)[c]	Ref.
Nd	*i*Pr	297	$5250 \cdot 10^{-6}$	$-302 \cdot 10^{-6}$	3.53 (3.62)	this work
Eu[d]	*i*Pr	295	$3210 \cdot 10^{-6}$	$-302 \cdot 10^{-6}$	2.76 (0)	this work
Gd[d]	Bu	270	$24400 \cdot 10^{-6}$	$-373 \cdot 10^{-6}$	7.28 (7.94)	this work
Er	*i*Pr	295	$35400 \cdot 10^{-6}$	$-302 \cdot 10^{-6}$	9.11 (9.58)	[8]
Yb	Et	295	$7645 \cdot 10^{-6}$	$-231 \cdot 10^{-6}$	4.23 (4.54)	[8]
Yb	*i*Pr	295	$7576 \cdot 10^{-6}$	$-302 \cdot 10^{-6}$	4.21 (4.54)	[8]

[a] The compounds are tetranuclear for R = *i*Pr; the nuclearity of the ethyl and butyl derivatives is unknown. [b] Pascal constants have been used for H, C, N, and O, the diamagnetic correction for Ln^{3+} being $-16 \cdot 10^{-6}$ cgsu. [c] $\mu_{calcd.} = g[J(J+1)]^{1/2}$; $g = 3/2 + [S(S+1) - L(L+1)]/2J(J+1)$]. [d] See text for the variable−temperature measurements.

tetium complexes.[24] Although the ytterbium compound had been previously studied, a new crystallographic determination was carried out in order to have more accurate bond parameters.

The molecules of $[Ln_4(O_2CN\textit{i}Pr_2)_{12}]$ are slightly prolate spheroids with a maximum diameter of about 16.4 Å. The external shell of the molecules is composed of isopropyl groups, and this accounts for the solubility of these species in hydrocarbons. The crystal packing of these large molecules leaves relatively large cavities which can accommodate solvent molecules such as toluene, heptane, or isooctane. The different nature of the lattice solvent, however, does not affect either the space group or the molecular structure of the compounds, as shown by the smooth trend of the Ln−O distances vs. the number of *f* electrons (Figure 2).

The lanthanide carbamato molecules have C_2 symmetry, the carbamato ligands being situated around four metal atoms as shown in Figure 1. Two metal atoms are related to the other two by a two-fold axis, the quadruplet building a sort of elongated tetrahedron (ditrigon). Three different coordination modes are exhibited by the ligands, which chelate three, two, or one metal atom, labelled **[a]**, **[b]**, and **[c]**, respectively.

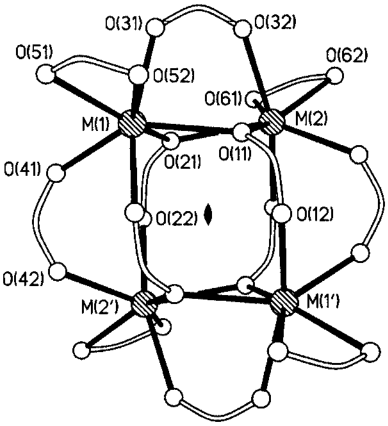
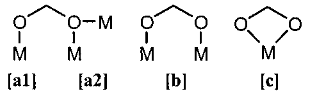


Figure 1. Schematic representation of the $[Ln_4(O_2CN\textit{i}Pr_2)_{12}]$ core projected down the two-fold axis, showing the metal and oxygen labelling



The ligands chelating three metal atoms have a tri-coordinated oxygen atom which shows the longest Ln−O distances and has been indicated as the **[a2]** type and a di-coordinated one, the **[a1]** type. Table 3 shows the Ln−O distances found in the known structures of $[Ln_4(O_2CN\textit{i}Pr_2)_{12}]$ listed by metal and by ligation type. For each type the weighted means are also reported. The mean values and the standard deviations have been calculated using the expressions below.[25]

$$\bar{x} = \frac{\sum_i \left(\frac{x_i}{\sigma_i^2} \right)}{\sum_i \left(\frac{1}{\sigma_i^2} \right)}$$

$$\sigma(\bar{x}) = \sqrt{\frac{1}{\sum_i \left(\frac{1}{\sigma_i^2} \right)}}$$

The lanthanide is hepta-coordinated and the coordination polyhedra of M(1) and M(2) are almost superimposable. They may be considered as a heavy distortion of a pentagonal bipyramid (idealized symmetry D_{5h}), according to the catalogue of seven-vertex polyhedra proposed by Britton and Dunitz.[26]

Taking into account the mean values of the Ln−O distances of Table 3, the **a2** distance is the longest, being about 6% greater than the **a1** type (see Table 3 for the individual M−O distances). This lengthening is certainly due to the tri-coordination of the oxygen in the **a2** type. In contrast, the Ln−O distances of type **c** are stretched by about 4%, with a small O−Ln−O angle of about 56°. Finally, for each compound the Ln−O distances of types **a1** and **b** are rather similar, the differences being within 1%.

In order to show the trend of the Ln−O distances as a function of the nature of the lanthanide, the mean values of the distances for each bond type (**a1**, **a2**, **b**, and **c**) have been plotted against the number of *f* electrons of the metal cation. Figure 2 shows the result when the distances of each type were fitted with the quadratic function $d(\mathrm{Ln{-}O}) = A_0 - A_1{\cdot}n + A_2{\cdot}n^2$, where d is the distance, n is the number of *f* electrons and A_0, A_1, and A_2 are the fitting parameters. The curves show rather similar slopes, suggesting that the metal radius contraction should mainly account for the trend. In the case of the Ln−O **a1** distances some adjacent couples, such as Yb/Lu or Ho/Er, do not show a significant contraction. However, the trend along the series is analogous to that found for the other bond types.

As has been underlined in a previous preliminary communication[17] from these laboratories, the trend of the Ln−O bond shortening is parabolic,[27] i.e. the early lanthanides contract their radii slightly more rapidly than the later ones (Figure 2). Since we now add the data for the Eu, Er and Lu derivatives and the more accurate data for the Yb derivative, we further confirm the general trend of the distances. The A_2 parameter of the fitting is $1.71{\cdot}10^{-4}$ for the Ln−O distances of the **b** type compared with a mean value of $4.87{\cdot}10^{-4}$ for the other types. The well−known lanthanide contraction was originally recognized[27b] on the basis of X-ray crystallographic determinations on the oxides and fluorides of the Ln^{3+} ions, which are not isostructural along the whole series. The contraction was evaluated to be 15% from cerium to lutetium, a correction being required for the decreased coordination number along the series. [27c,27d]

The **a1** bonds represent the maximum approach of the oxygen to the metal. The **a1** fitting corresponds to the equa-

Table 3. M−O distances in isotypical diisopropylcarbamato derivatives of lanthanides. See text for the classification of bond types **[a1]**, **[a2]**, **[b]**, and **[c]**

		Nd	Eu	Gd	Ho	Er	Yb	Lu
O(12)−M(1′)[a]	**[a1]**	2.320(10)	2.273(4)	2.259(4)	2.223(5)	2.225(3)	2.198(4)	2.192(6)
O(22)−M(2′)	**[a1]**	2.336(10)	2.295(5)	2.288(4)	2.247(5)	2.229(4)	2.213(5)	2.218(6)
O**[a1]**−M (mean)		**2.328(7)**	**2.282(3)**	**2.274(3)**	**2.235(4)**	**2.226(2)**	**2.204(3)**	**2.205(4)**
O(11)−M(2)	**[a2]**	2.499(10)	2.453(4)	2.427(5)	2.398(5)	2.348(3)	2.361(4)	2.342(5)
O(21)−M(1)	**[a2]**	2.466(10)	2.429(4)	2.379(5)	2.371(5)	2.392(3)	2.345(4)	2.328(5)
O(11)−M(1)	**[a2]**	2.474(9)	2.420(4)	2.401(4)	2.364(5)	2.348(3)	2.329(4)	2.313(5)
O(21)−M(2)	**[a2]**	2.484(9)	2.416(4)	2.404(4)	2.367(5)	2.346(3)	2.326(4)	2.315(5)
O**[a2]**−M (mean)		**2.481(5)**	**2.430(2)**	**2.403(2)**	**2.375(3)**	**2.359(2)**	**2.340(2)**	**2.325(3)**
O(31)−M(1)	**[b]**	2.373(10)	2.306(5)	2.298(4)	2.264(5)	2.246(4)	2.221(5)	2.219(6)
O(32)−M(2)	**[b]**	2.362(10)	2.305(5)	2.295(4)	2.272(5)	2.273(4)	2.233(5)	2.227(6)
O(41)−M(1)	**[b]**	2.338(10)	2.296(5)	2.275(4)	2.239(6)	2.251(4)	2.217(5)	2.212(6)
O(42)−M(2′)	**[b]**	2.307(10)	2.304(6)	2.304(5)	2.262(5)	2.245(4)	2.231(5)	2.221(6)
O**[b]**−M (mean)		**2.345(5)**	**2.303(3)**	**2.292(2)**	**2.261(3)**	**2.254(2)**	**2.226(3)**	**2.220(3)**
O(51)−M(1)	**[c]**	2.407(10)	2.340(6)	2.324(5)	2.298(6)	2.298(4)	2.278(5)	2.269(7)
O(52)−M(1)	**[c]**	2.420(10)	2.382(6)	2.375(6)	2.342(6)	2.342(4)	2.320(5)	2.312(6)
O(61)−M(2)	**[c]**	2.434(10)	2.380(5)	2.373(5)	2.338(6)	2.329(4)	2.321(5)	2.309(6)
O(62)−M(2)	**[c]**	2.421(10)	2.375(5)	2.364(5)	2.321(6)	2.302(4)	2.290(5)	2.280(6)
O**[c]**−M (mean)		**2.421(5)**	**2.371(3)**	**2.358(3)**	**2.325(3)**	**2.318(2)**	**2.302(3)**	**2.294(3)**

[a] ′: $-x, y, 3/2 - z$.

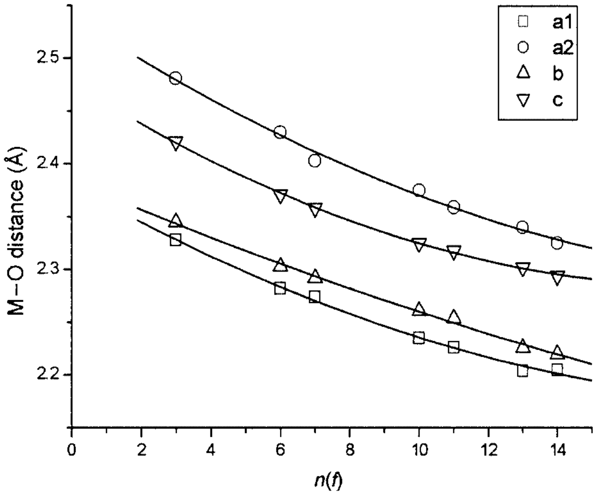


Figure 2. Polynomial fittings of different types of Ln−O distances in the isotypical $[Ln_4(O_2CN\textit{i}Pr_2)_{12}]$ vs. the 4*f* electronic configuration.

tion $d(\text{Ln-O}) = 2.381 - 0.0188 \cdot n + (4.24 \cdot 10^{-4}) \cdot n^2$. By extrapolation it can be anticipated that 2.381 Å should be shortest La−O distance of this type if the lanthanum carbamato derivative had the same structure as the compounds reported in this paper.

It is remarkable that the cerium(III) derivative $[Ce_4(O_2CN\textit{i}Pr_2)_{12}]$ also turned out to be a tetranuclear species.[28] It shows a less symmetrical molecular structure than the compounds described herein. In the molecule the coordination number is seven for three of the cerium atoms and eight for the fourth one. Because of the different structural arrangement, a comparison of the Ce−O distances with those found in the isotypical species herein described is in general difficult. On the other hand, the unique Ce−O distance of type **a1** involving hepta-coordinated cerium [Ce(3)−O(82)] in this complex is 2.368 Å corresponding to a length increase of 0.04 Å with respect to the neodymium complex.

Conclusions

A class of molecular compounds of the trivalent lanthanides, i.e. the *N*,*N*-dialkylcarbamato complexes, has been exhaustively defined as far as their preparation and characterization are concerned. The *N*,*N*-diisopropyl derivatives from Nd to Lu are isotypical species, consisting of tetranuclear molecules, $[Ln_4(O_2CN\textit{i}Pr_2)_{12}]$, where the metal center is hepta-coordinated. The structural determinations have allowed the lanthanide contraction over a range of 12 atomic numbers to be monitored.

The solubility of these complexes in hydrocarbons can be tuned by varying the nature of the alkyl group, thus allowing these compounds to be used as precursors to other derivatives in slightly polar, non-coordinating solvents.

Experimental Section

All preparations were carried out under a dry atmosphere (N_2 or CO_2). Solvents were freshly distilled from the usual drying agents under nitrogen. In the case of the lutetium derivative, commercially available anhydrous $LuCl_3$ was used as received (Aldrich). Elemental analyses (C,H,N) were carried out at the Laboratorio di Microanalisi della Facoltà di Farmacia, Università di Pisa, with a Carlo Erba mod. 1106 analyzer. IR spectra were measured with a FT-IR Perkin−Elmer mod. 1725X spectrophotometer. Magnetic measurements were performed with a magnetic balance (Faraday method) using $CuSO_4 \cdot 5H_2O$ for calibration. The lanthanide complexes $LnCl_3(\text{ether})_x$ (ether = DME or THF) were prepared as previously reported.[17]

Synthesis of [$Ln_4(O_2CNiPr_2)_{12}$] (Ln = Pr, Nd, Eu, Gd, Ho, Er, Yb, Lu): The syntheses were carried out by treating the solvated chlorides [$LnCl_3$(ether)$_x$] (ether = DME, x = 0.5, Ln = Nd; x = 1, Ln = Pr; x = 2, Ln = Eu, Gd, Ho, Yb; ether = THF, x = 1.5, Ln = Nd; x = 0, Ln = Lu) with $NHiPr_2$ and CO_2 in toluene. Analysis for $C_{21}H_{42}LnN_3O_6$, Ln = Pr, M = 573.49: calcd. Pr 24.6, CO_2 23.0%; found Pr 25.2; CO_2 23.3%. Ln = Nd, M = 576.83: calcd. Nd 25.0, CO_2 22.9%; found Nd 25.2, CO_2 21.5%. Ln = Eu, M = 584.55: calcd. Eu 26.0, CO_2 22.6%; found Eu 25.2, CO_2 22.5%. Ln = Gd, M = 589.84: calcd. Gd 26.7, CO_2 22.4%; found Gd 25.2, CO_2 21.2%. Ln = Ho, M = 597.52: calcd. Ho 27.6, CO_2 22.1%; found Ho 27.5, CO_2 21.7%. Ln = Er, M = 599.85: calcd. Er 27.9, CO_2 22.0%; found Er 27.5, CO_2 21.7%. Ln = Yb, M = 605.63: calcd. Yb 28.6, CO_2 21.8%; found Yb 28.8, CO_2 20.9%. Ln = Lu, M = 607.56: calcd. Lu 28.8, CO_2, 21.7%; found Lu 29.6; CO_2 21.3%.

Colors of the products are: green (Pr), violet (Nd), pale pink (Eu), colorless (Gd, Yb, Lu), yellow-pink (Ho), and pink (Er). The approximate solubility of the tetranuclear ytterbium compound is $6\cdot 10^{-3}$ M in toluene. Analyses of the products, once dried in vacuo, were consistent with the formula [$Ln(O_2CNiPr_2)_3$]$_n$. When obtained as single crystals by recrystallization from hydrocarbons (C_nH_m = heptane, isooctane, or toluene), their compositions corresponded to $Ln_4(O_2CNiPr_2)_{12}\cdot 2C_nH_m$ (Ln = Nd, n = 8, m = 18; Ln = Eu, Er, n = 7, m = 8; Ln = Gd, Ho, Yb, Lu, n = 7, m = 16).

Two typical experiments are described below.

a) Europium: A solution of $NHiPr_2$ (16.0 mL, 114.2 mmol) was stirred in a flask under CO_2 until gas absorption was complete. At this point, [$EuCl_3(DME)_2$] (5.02 g; 11.45 mmol) was added, the suspension was stirred for 23 h and then filtered. The filtrate was evaporated to dryness and the pale-pink residue was treated with heptane (50 mL). The product was recovered by filtration and dried in vacuo (2.75 g, 41% yield).

b) Lutetium: A solution of $NHiPr_2$ (8.0 mL, 57.08 mmol) in toluene (200 mL) was stirred in a flask under CO_2 up to completion of the gas absorption. Anhydrous $LuCl_3$ (1.58 g, 5.62 mmol) was introduced and the suspension was stirred under CO_2 for 2 days. The mixture was filtered and the filtrate was evaporated to dryness in vacuo. The colorless residue was recrystallized from heptane (1.22 g, 36% yield).

Synthesis of [$Ln(O_2CNBu_2)_3$] (Ln = Nd, Eu, Gd): The syntheses were carried out starting from [$LnCl_3$(DME)$_x$] (x = 0.5, Ln = Nd; x = 2, Ln = Eu, Gd). The dimethoxyethane adduct [$LnCl_3$(DME)$_x$] was treated with $NHBu_2$ and CO_2 in toluene. Analysis for $C_{27}H_{54}N_3LnO_6$. Ln = Nd, M = 660.99: calcd. C 49.1, H 8.2, N 6.4, Nd, 21.8, CO_2, 20.0%; found C 48.7, H 8.7, N 6.1, Nd, 22.1, CO_2, 20.0%. Ln = Eu, M = 668.71: calcd. Eu, 22.7, CO_2, 19.7%; found Eu, 20.8, CO_2, 17.4%. Ln = Gd, M = 674.00: calcd. Gd, 23.3, CO_2, 19.6%; found Gd, 21.7, CO_2, 18.0%.

A typical experiment is described: A solution of dibutylamine (5.0 mL, 29.67 mmol) in heptane (50 mL) was saturated with CO_2 and [$NdCl_3(DME)_{0.5}$] (0.74 g, 2.50 mmol) was then added. After 12 h stirring the suspension was filtered and the violet product was obtained by evaporating the filtrate to dryness (1.23 g, 74% yield). IR (1700−1300 cm^{-1}, Nujol mull, cm^{-1}): 1528 s, 1490 s, 1430 s, 1325 s.

Synthesis of [$Nd(O_2CNEt_2)_3$]: [$Nd(O_2CNBu_2)_3$] (6.77 g, 10.24 mmol) in heptane (100 mL) was treated with $NHEt_2$ (7.0 mL, 67.66 mmol) under CO_2. The violet product precipitated and after 1 h stirring the liquid phase had become colorless. The suspension was filtered and the solid was dried in vacuo (4.36 g, 86% yield). Analysis for $C_{15}H_{30}N_3NdO_6$. M = 492.66: calcd. Nd, 29.3, CO_2, 26.8%; found: Nd, 28.6, CO_2, 26.9%. IR (range 1700−1300 cm^{-1}, PCTFE mull, cm^{-1}): 1610 w, 1545 s, 1493 s, 1457 s, 1436 s, 1313 s.

X-ray Crystallography: Only the structure determination of $Yb_4(O_2CNiPr_2)_{12}\cdot 2C_7H_{16}$ is presented in detail, the other determinations being performed in a similar manner. A summary of data collection is in Table 4. The X-ray measurements were carried out with a Bruker P4 diffractometer equipped with graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). The crystals, prepared as described before, are colorless prisms. One of them was sealed in a glass capillary under a nitrogen atmosphere saturated with heptane vapor and the unit cell parameters listed in Table 4 were derived from the setting angles of 34 intense reflections. Data were collected in the ω/2θ scan mode, and three standard reflections were monitored every 97 measurements for checking crystal decay and equip-

Table 4. Crystal data and structure refinement of isotypical lanthanide carbamates [$Ln_4(O_2CNiPr_2)_{12}$], monoclinic, $C2/c$ space group

Lanthanide	Eu[a]	Er[a]	Yb[b]	Lu[b]
Empirical formula	$C_{98}H_{184}Eu_4N_{12}O_{24}$	$C_{98}H_{184}Er_4N_{12}O_{24}$	$C_{98}H_{200}Yb_4N_{12}O_{24}$	$C_{98}H_{200}Lu_4N_{12}O_{24}$
Molecular mass	2522.5	2583.7	2622.9	2630.6
Temperature [K]	293(2)	293(2)	293(2)	293(2)
Wavelength [Å]	0.71073	0.71073	0.71073	0.71073
a [Å]	29.000(2)	28.369(5)	29.046(2)	29.023(5)
b [Å]	20.357(1)	20.091(3)	19.802(2)	19.749(2)
c [Å]	23.004(1)	22.874(3)	23.088(2)	23.065(2)
β [deg]	107.02(1)	106.368(9)	107.135(8)	107.13(1)
Volume [Å^3]	12985(5)	12509(3)	12690(2)	12634(3)
Z	4	4	4	4
$\rho_{calcd.}$ [Mg·m^{-3}]	1.290	1.372	1.373	1.383
μ [mm^{-1}]	1.967	2.720	2.984	3.162
Data/restr./param.	15257/0/567	19840/0/622	7969/0/592	8738/6/467
$R(F_o)$ [$I > 2\sigma(I)$][c]	0.0418	0.0447	0.0325	0.0406
Rw (F_o^2) [$I > 2\sigma(I)$][c]	0.1082	0.1267	0.0666	0.0888
Goodness-of-fit on F^2 [c]	0.997	1.020	1.045	1.019

[a] Clathrate solvent: toluene. [b] Clathrate solvent: heptane. [c] $R(F_o) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $Rw(F_o^2) = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (AQ)^2 + BQ]$ where $Q = [\max(F_o^2,0) + 2F_c^2]/3$; GOF = $[\Sigma[w(F_o^2 - F_c^2)^2]/(N - P)]^{1/2}$, where N, P are the numbers of observations and parameters, respectively.

ment stability. Data reduction was carried out using the XSCANS program.[29] A set of 7669 reflections was collected between $\theta = 2.3$ and 25.0° and corrected for Lorentz and polarization effects and for absorption by the ψ−scan method. After merging the equivalent reflections $\{R_{\rm int} = [\Sigma|F_o^2 - F_o^2({\rm mean})|/\Sigma(F_o^2)] = 0.0251\}$, 5848 unique reflections satisfying the condition $I > 2\sigma(I)$ were retained for the following calculations. The systematic absences strongly suggested the space groups *Cc* or *C*2/*c*. The solution was found by direct methods in the centrosymmetric space group and completed through the subsequent difference Fourier maps. Calculations were carried out with the SHELX-97 and SHELXTL programs.[30,31] In the final refinement cycles, based on F^2, anisotropic thermal parameters were used for all non hydrogen atoms. The final reliability factors are listed in Table 4.

CCDC-211411 [for $Eu_4(O_2CN\textit{i}Pr_2)_{12}$], -211412 [for $Er_4(O_2CN\textit{i}Pr_2)_{12}$], -211413 [for $Yb_4(O_2CN\textit{i}Pr_2)_{12}$], and -211414 [for $Lu_4(O_2CN\textit{i}Pr_2)_{12}$] contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Center, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

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