Isotypical *N*,*N*-dialkylcarbamato lanthanide complexes covering a range of 11 atomic numbers: direct experimental assessment of the lanthanide contraction in trivalent molecular compounds

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The *N*,*N*-diisopropylcarbamato complexes of lanthanides(III) from neodymium (Z = 60) to ytterbium (Z = 70) were found to be isotypical, with Ln–O distances decreasing steadily with increasing Z, the lanthanide contraction in this series of molecular complexes being provisionally assigned to an increasing bond strength with increasing atomic number of the central metal atom.

The well known lanthanide contraction was originally recognized[1a] on the basis of X-ray diffractometric data on the ionic oxides and fluorides of the trivalent cations and estimated to correspond to about a 15% decrease of the radii on going from cerium to lutetium,[1] a correction[1b,c] being required for the decreasing coordination numbers (CN) along the series. In fact, no isotypical coordination compounds of lanthanides are known, for halide or oxide ligands, to cover the whole series; normally, changes of both space group and CN are encountered, on going from the first part to the second one[1d,e] of the series.

Coordination chemistry of lanthanides (Ln) is a subject of increasing interest,[2] the focus of the current studies being on uncharged complexes of Ln(III),[3] in view of their role in biochemistry[3a] and in carbon–carbon and carbon–nitrogen bond forming reactions,[3b–r] mainly catalyzed by organometallic derivatives [4] of these elements. A better understanding of these systems should originate from the synthesis of isotypical (*i.e.* with constant CN and geometry) and *neutral* compounds and by the determination of their interatomic parameters through diffraction methods.

We now report the preparation of some isotypical *N*,*N*-dialkylcarbamato complexes of the lanthanides. Although *N*,*N*-dialkylcarbamato complexes of transition d elements are well established,[5] such lanthanide derivatives are still in their infancy, mainly due to synthetic difficulties.[6]

The synthesis of the new *N*,*N*-diisopropylcarbamato derivatives of La, Nd, Eu, Gd and Ho, of the same general formula, has now been achieved by using the ether complexes $LnCl_3(ether)_x$ (ether = THF or Et_2O),[7] as starting materials [eqn. (1)]. Yields

$$4\,LnCl_3(ether)_x + 12\,CO_2 + 24\,NHPr^i_2 \longrightarrow$$
$$Ln_4(O_2CNPr^i_2)_{12} + 12\,[NH_2Pr^i_2]Cl + 4x\,ether \qquad (1)$$
$$(Ln = La, f^0; Nd, f^3; Eu, f^6; Gd, f^7; Ho, f^{10}; Er, f^{11})$$

of recrystallized product are generally moderate (20%) to satisfactory (50%).

The new isopropyl derivatives of Nd(III), Eu(III), Gd(III) and Ho(III) were found to be moderately soluble in hydrocarbons; these compounds are isotypical with one another and with the already known Yb(III) analogue.[6]

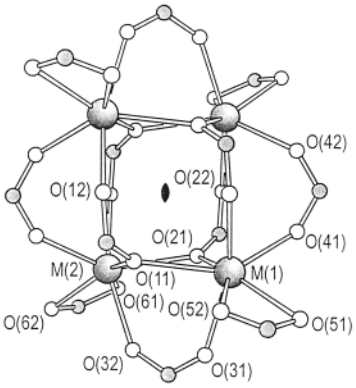
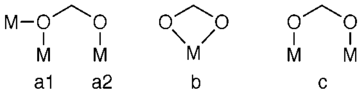


Fig. 1 Molecular structure of the lanthanide derivatives $M_4(O_2CNPr^i_2)_{12}$; M = Nd (Z = 60), Gd (Z = 64), Ho (Z = 67), Yb (Z = 70). The heptacoordinated metal atoms are shown with their oxygen donor atoms.

Complete crystal data were collected for the Nd (Z = 60), Gd (Z = 64), and Ho (Z = 67) derivatives,† to be compared with the already available information for the isostructural Yb species (Z = 70).[6] In these tetranuclear compounds, the heptacoordinate lanthanide is surrounded by terminal bidentate, bridging bidentate and bridging tridentate diisopropylcarbamato groups. The molecular core of the tetranuclear derivatives is schematically shown in Fig. 1.

The Ln–O average bond distances of the new *N*,*N*-diisopropylcarbamato complexes can be factorized as a function of the type of bonding (Table 1, Fig. 2). The Ln–O bond distance contracts along our series with increasing Z; more precisely, by assuming that the lanthanide-coordinated oxygen has the same radius of 1.21 Å as that of bicoordinated oxygen,[1c] the lanthanide contraction, averaged over the four different types of ligands (Table 1) is *ca.* 8% over the eight Z values from Nd to

Table 1 Average Ln–O bond distances (Å) in tetranuclear *N*,*N*-diisopropylcarbamato complexes of lanthanides, for different coordination modes. The quadratic dispersion from the average values is given in parentheses.



	Nd	Gd	Ho	Yb
a1	2.48(1)	2.40(2)	2.37(2)	2.34(5)
a2	2.33(1)	2.27(1)	2.24(1)	2.25(4)
b	2.42(1)	2.36(2)	2.33(2)	2.28(3)
c	2.35(2)	2.29(1)	2.26(1)	2.21(3)

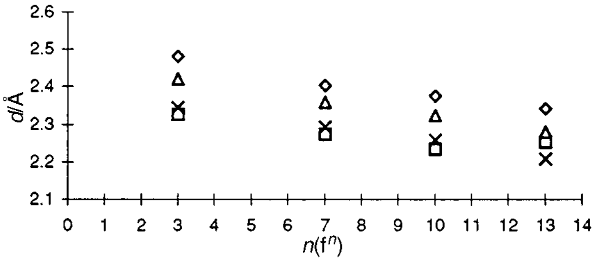


Fig. 2 Lanthanide(III)–oxygen bond distances (Å) *vs.* f^n electronic configuration in the tetranuclear *N,N*-diisopropylcarbamato complexes $M_4(O_2CNPr^i_2)_{12}$; M = Nd (Z = 60), Gd (Z = 64), Ho (Z = 67), and Yb (Z = 70). The ordinate axis shows the average Ln–O bond distances (Å): (◇) type a1, (□) type a2, (△) type b, (×) type c (from top to bottom, see Table 1). The anomalous behavior of the a2 distance for Yb is presumably due to the lower accuracy of the crystal data.[6]

Ho, Yb being excluded because of the lower accuracy of the older structural determination. This result can be linearly extrapolated to the 15 Z series from La to Lu giving a 14% average contraction over the whole series. This is substantially in agreement with the earlier findings for the predominantly ionic oxides.[1c]

An examination of the crystallographic literature[9] has disclosed a few other series of isotypical molecular compounds of lanthanides, namely, (η^6-arene)aryloxides, $Ln(OC_6H_3Pr^i\text{-}2,6)_3(THF)_2$ and THF adducts of tris(cyclopentadienyl), $Ln(\eta^5\text{-}C_5H_5)_3(THF)$, the expected decreasing trend of Ln–O interatomic distances being similarly observed.

A plausible interpretation of the present data is that the bond lanthanides form with oxygen-containing ligands becomes steadily stronger along the series. This suggests that relatively weaker bonds in the oxidation state +III should be found, for lanthanides, at the beginning of the series. This finding may be significant in connection with the catalytic phenomena observed[3e,h,k,n,o–r] with lanthanides.

Work is in progress collecting further accurate crystallographic data on other compounds of this lanthanide series.

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Notes and references

† Complete crystal data were collected for the Nd (Z = 60), Gd (Z = 64), and Ho (Z = 67) derivatives, $Ln_4(O_2CNPr^i_2)_{12}$. The measurements were carried out with a CAD4 and a Siemens P4 diffractometers equipped with Mo-$K\alpha$ radiation (λ = 0.71073 Å). All compounds were monoclinic, space group $C2/c$ (no.15). The intensity data were corrected for Lorentz and polarisation effects by means of the suitable programs.[8] For the Nd and Ho samples, the solvent molecule (octane and heptane, respectively) was found to be slightly disordered; for Gd, the solvent was not localised. Some degree of disorder was occasionally present in the diisopropyl groups. At the end of refinement, residual peaks and holes of *ca.* ± 1 e Å^{-3} were present in the zones of disordered groups or the metal in the difference Fourier maps.

$Nd_4(O_2CNPr^i_2)_{12}\cdot 2C_8H_{18}$: violet crystals, $C_{100}H_{204}Nd_4N_{12}O_{24}$, M = 2535.7, T = 253(2) K, a = 28.97(1), b = 20.064(8), c = 23.549(9) Å, β = 107.44(4)°, U = 13060(9) Å^3, Z = 4; μ = 1.63 mm^{-1}; crystal size = 0.2 × 0.2 × 0.3 mm. Independent reflections 7909. Final reliability factors for 611 parameters: R_1 = 0.067 for 3686 reflections with $I > 2\sigma(I)$, wR_2 = 0.179 for all 7418 reflections in the refinement; GOF = 0.941.

$Gd_4(O_2CNPr^i_2)_{12}\cdot 2C_7H_{16}$: colourless crystals, $C_{98}H_{200}Gd_4N_{12}O_{24}$, M = 2559.7, T = 203(2) K, a = 29.041(8), b = 19.676(2), c = 23.170(8) Å, β = 107.52(1)°, U = 12625(6) Å^3, Z = 4, μ = 2.14 mm^{-1}, crystal size = 0.35 × 0.3 × 0.1 mm. Independent reflections 11367, R_{int} = 0.0257. Final reliability factors for 559 parameters without restraints: R_1 = 0.0489, wR_2 = 0.1209 for 6713 reflections with $I > 2\sigma(I)$; GOF = 1.056.

$Ho_4(O_2CNPr^i_2)_{12}\cdot 2C_7H_{16}$: light yellow crystals, $C_{98}H_{200}Ho_4N_{12}O_{24}$, M = 2590.4, T = 293(2) K, a = 29.130(2), b = 19.844(2), c = 23.131(1) Å, β = 107.24(1)°, U = 12770(2) Å^3, Z = 4; μ = 2.51 mm^{-1}; crystal size = 0.82 × 0.48 × 0.35 mm. 8868 independent reflections. Final reliability factors for 467 parameters: R_1 = 0.039 calculated for 6711 reflections with $I > 2\sigma(I)$, wR_2 = 0.110 for all 8868 reflections in the refinement; GOF = 1.041.

$Eu_4(O_2CNPr^i_2)_{12}\cdot 2C_7H_{16}$: pink crystals, $C_{98}H_{200}Eu_4N_{12}O_{24}$, M = 2538.5, T = 203(2) K, a = 29.074(5), b = 19.699(5), c = 23.211(4) Å, β = 107.65(2)°, U = 12668(4) Å^3, Z = 4. The intensity data of the Eu derivative were not collected.[8] CCDC 182/1404. See http://www.rsc.org/suppdata/cc/1999/2053/ for crystallographic files in .cif format

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