Reactions of Coordinated Ligands: Topological and Stoichiometric Control for Mixed-metal Alkoxides: Synthesis and Molecular Structure of $[La\{(OC_2H_4)_3N\}_2\{Nb(OPr^i)_4\}_3]$

Vadim G. Kessler,[a] **Liliane G. Hubert-Pfalzgraf,***[a] **Sabine Halut**[b] **and Jean-Claude Daran**[b]

[a] *Laboratoire de Chimie Moléculaire, URA-CNRS, Université de Nice-Sophia Antipolis, Parc Valrose, 06108 Nice Cédex 2, France*

[b] *Laboratoire de Chimie des Métaux de Transition, URA-CNRS, Place Jussieu, 75230 Paris Cedex 05, France*

The reaction of lanthanum isopropoxide with 2 equivalents of triethanolamine leads to a novel 'diatrane' complex $H_3La[(OC_2H_4)_3N]_2$; its reaction with $Nb(OPr^i)_5$ provides a soluble and volatile mixed-metal species $[La\{(OC_2H_4)_3N\}_2\{Nb(OPr^i)_4\}_3]$ whose molecular structure is based on a central 'diatrane' core with eight-coordinate lanthanum while all niobium centres are six-coordinate.

One of the most interesting problems in the application of metal alkoxides for the preparation of ceramics remains the necessity to maintain the stoichiometry of heterometallic species in the course of the hydrolysis process or during their transition into the gaseous phase.[1] Research has recently drawn attention to the synthesis of heteroleptic derivatives where the labile alkoxo bridging ligands are replaced by ligands more stable to hydrolysis or thermal treatment, such as oxo-, β-diketonates or acetate.[2–4] Heterometallic species *e.g.* $[CdNb_2(OAc)_2(OPr^i)_{10}]$ retain the metals ratio during hydrolysis, but were found to be non-volatile and, besides, neither oxo nor acetate ligands are able to fix the stoichiometry between the metals since this is subject to the thermodynamic control of the reaction. In the absence of a control of the stoichiometry, the geometry of the final molecule is also rarely predictable.

We report here the use of triethanolamine [H_3tea, $N(C_2H_4OH)_3$] as a ligand able to achieve control of the stoichiometry as well as the geometry of mixed-metal species. Structural studies reveal a common coordination mode—tetradentate and encapsulating—of the triethanolamine ligand in compounds as different as $B(OC_2H_4)_3N$,[5] $Sn[N(C_2H_4OH)(C_2H_4O)_2]_2$[6] $MCl[N(C_2H_4O)(C_2H_4OH)_2]_2$, (M = Zn,[7] Cu[8]) and $Ba[N(C_2H_4O)(C_2H_4OH)_2]_2{\cdot}2EtOH$.[9] A bridging–chelating behaviour of this polydendate alcohol, although less common, has also been observed for $[Cu\{N(OC_2H_4)(OC_2H_4OH)\}]_4{\cdot}3N(C_2H_4OH)_3$ giving oligomeric derivatives.[10] For the lanthanides only polymeric species of formula $Ln(OC_2H_4)_3N$[11,12] or ionic derivatives $[Ln\{(N(C_2H_4OH)_3\}_2]^{3+}$[13] have been reported. A large variety of electrooptic ceramics are based on lanthanum oxides and show that lanthanum is often associated with niobium.[14]

A novel triethanolamine lanthanum derivative, $H_3La(tea)_2$ **1**,[†] precipitates slowly (within 12–14 h) after addition of 2 equiv. of triethanolamine to the propan-2-ol solution of lanthanum isopropoxide (obtained by electrochemical oxidation of the metal in Pr^iOH[15]). The precipitate of tiny colourless platelet triangular or rhombic crystals, is insoluble in all usual organic solvents and decomposes without melting at about 280 °C. Its IR spectrum differs from that of $La(OC_2H_4)_3N$, prepared in accordance with ref. 12 by the presence of hydroxy groups (3380 cm^{-1}), by higher intensities of the bands at 615 and 590 cm^{-1}, corresponding to the terminal La–O–C bonds, and by the absence of a strong band at 518 cm^{-1}, which can be attributed to the vibration of the alkoxo bridging bonds. It shows also a clear resemblance with that of $Ba\{N(C_2H_4O)(C_2H_4OH)_2\}_2{\cdot}2EtOH$[9] in the ν-MO area, all absorption bands being slightly (10 cm^{-1}) shifted to higher frequencies, thus suggesting a similar structure for the La(tea)$_2$ core. Extremely broad bands for ν-OH vibrations suggest that the hydrogen atoms are involved in intermolecular hydrogen bonds, which hinder dissolution or volatilization but might offer sites of latent reactivity.

Indeed, **1** dissolves readily at room temp. in toluene in the presence of $Nb(OPr^i)_5$ according to eqn. (1).

$$H_3La(tea)_2 + 3Nb(OPr^i)_5 \rightarrow [La\{(OC_2H_4)_3N\}_2\{Nb(OPr^i)_4\}_3] + 3\,Pr^iOH \quad (1)$$

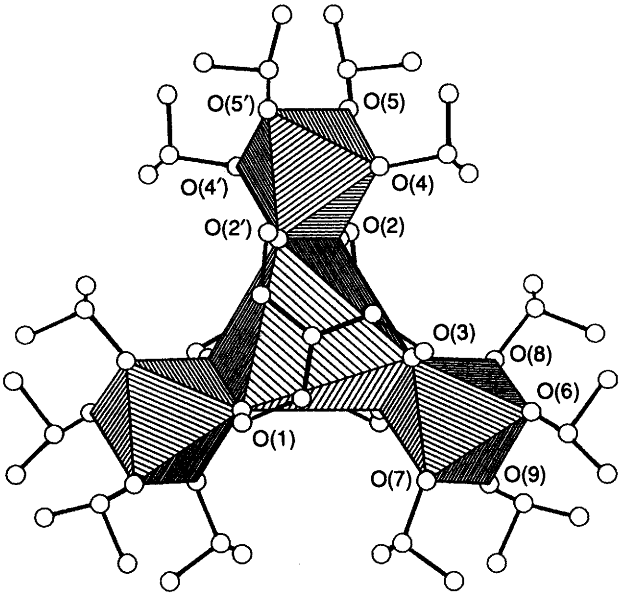

Fig. 1 Polyhedral representation of **2**

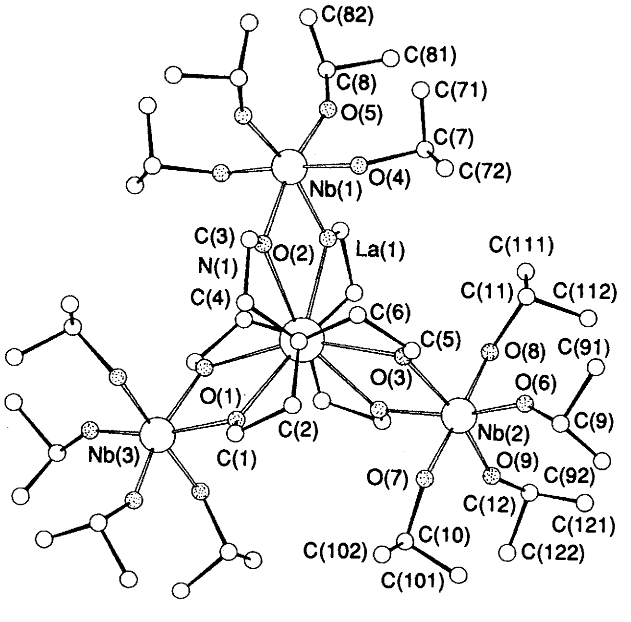

Fig. 2 Molecular structure and atom-labelling scheme for **2** [view along the N(1)–La–N(2) direction]. Selected bond distances (Å) and angles (°) (av.): La–N 2.680(7), La–O 2.499(6), Nb–O_t 1.915(8), Nb–O_b 2.078(6); La–O–Nb 117.3(7), N–La–O 65.4(2) (for the O atoms of the nearest basis), N–La–O 115.6(2) (for the oxygen atoms of the other basis).

The resulting product $[La\{(OC_2H_4)_3N\}_2\{Nb(OPr^i)_4\}_3]$ **2**‡ is obtained in high yield (93%) and crystallizes easily at low temp. as rhombic colourless crystals. It is scarcely soluble in Pr^iOH, but readily in hydrocarbons, especially on heating. Complex **2** sublimes at reduced pressure (10^{-1} mmHg) at about 180–250 °C without decomposition.

The heterometallic character of **2** was established by X-ray diffraction.§ The crystals of **2** are built up by $[La(tea)_2\{Nb(OPr^i)_4\}_3]$ molecules possessing a pseudo-*third*-order symmetry axis orthogonal to the C_2 axis that exists in the structure. Lanthanum and niobium are eight- and six-coordinate, respectively. The molecular structure of **2** can be shown using a polyhedral model (Fig. 1). The central polyhedron around lanthanum—a bicapped trigonal antiprism—is formed by two deprotonated triethanolamine molecules and has a nearly regular character: the N–La–N configuration is almost linear [179.8(4)°], the La–O distances are similar (av. 2.5 Å), as well as the corresponding N–La–O angles (Fig. 2). The capping nitrogen atoms occupy both bases of the prism. The structure of the central core is close to that described for barium in the complex $[Ba\{N(C_2H_4O)(C_2H_4OH)_2\}_2{\cdot}2EtOH$,[9] differing from it only by higher regularity, provided, obviously, by identical structural function of all oxygen atoms. The La–N bond distances (2.68 Å) fall in the range commonly observed.[16] Three NbO_6 octahedra are each sharing one edge of their equatorial plane with one of the side-edges of the antiprism. The Nb–O bond lengths range from 2.081(6) to 1.899(8) Å, the bridging ones [av. 2.078(6) Å] being the longest ones and lie within the usual range. The large size of lanthanum atom permits an increase of the intrabridge O–Nb–O angle [av. 75.7(3) *vs.* 70.4(3)° in $Nb_2(OMe)_{10}$ for example[17]]. The Nb–OPr^i bond lengths are slightly longer for the axial alkoxo groups [av. 1.929(9) Å] than for the equatorial ones [av. 1.901(8) Å] and this difference is also reflected for the corresponding Nb–O–C angles [av. 141.2(12)° for axial in comparison with 149.3(13)° av. for equatorial ones]; the *trans* effect, which was not observed for the homometallic alkoxide has thus reappeared.

The IR spectrum of **2** is in accordance with the solid-state structure: the sharp and intense band at 642 cm^{-1} is to be attributed to La–O vibrations, the broader bands at 569 and 474 cm^{-1} corresponding to terminal and bridging Nb–OR vibrations, respectively. The ^1H NMR spectra give evidence that the structure of **2** is retained in solution. The molecule is fluxional but the exchange between the magnetically non-equivalent equatorial and axial OR groups in the NbO_6 octahedron is slown down at −30 °C.

The high symmetry associated to the polydentate and encapsulating character of the bridging triethanolamine ligands probably results in the stability and volatility of compound **2**.

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Footnotes

† H_3 stands for the hydrogens of the hydroxy functionalities, the compound is actually not a hydride. *Selected spectroscopic data* for **1**, IR (mineral oil, ν/cm^{-1}): 3380 s br(ν-OH), 615m, 590m, 568w, 545m, 480sh, 422w (ν-LaO), 390w (ν-LaN?). Satisfactory elemental analyses (C,H,N) were obtained.

‡ Complex **2** is also obtained by reaction of $LaNb_2(OPr^i)_{13}$ with triethanolamine. *Selected spectroscopic data* for **2**: IR (mineral oil, ν/cm^{-1}): 588s, 553sh, 475vs, 459sh, 433sh; ^1H NMR (25 °C, $CDCl_3$), δ 4.68 (m, 12H, CH), 4.28 (t, *J* 5.6 Hz, 12H, CH_2O), 2.77 (t, *J* 5.6 Hz, 12H, CH_2N), 1.22 (d, *J* 6 Hz, 72H, Me); −30 °C. 4.69m. 4.55m (1 : 1, 12H, CH); 3.55 (br, 12H, CH_2O), 2.74 (br, 12H, CH_2N) 1.18, 1.12 (d, 1 : 1, *J* 6 Hz, 72H).

§ *Crystal data* for $C_{48}H_{108}LaN_2Nb_3O_{18}$ **2**: $M = 1417.6$, monoclinic, space group *C2/m*, $a = 26.30(1)$, $b = 15.183(2)$, $c = 19.209(2)$ Å, $\beta = 117.15(2)°$, $U = 6825(3)$ Å^3, $D_c = 1.37$ g cm^{-3} for $Z = 4$. μ(Mo-Kα) = 11.9 cm^{-1}.

6180 Data were collected at room temp. on a CAD-4 difractometer using graphite-monochromatized Mo-Kα radiation (λ = 0.71073). Computations were performed by using CRYSTALS adapted on a Micro Vax II.[18] The structure was solved by Patterson method and subsequent Fourier maps. Of the 5981 unique refections, 1431 with $I > 3\sigma(I)$ were used to solve and refine the structure. All atoms were refined anisotropically. Least squares refinements with approximation in three blocks to the normal matix were carried out minimizing the function $w(|F_o| - |F_c|)^2$, were F_o and F_c are the observed and calculated structure factors. Unit weights were used. Models reached convergence with $R[= (|F_o| - |F_c|)/|F_o|]$ and R_w of 0.047 and 0.050, respectively; 328 variables. Criteria for a satisfactory complete analysis were the ratios of rms shift to standard deviation being less than 0.1 and no significant features in the final difference map. Anomalous dispersion terms were applied. Empirical absorption corrections were made.[19]

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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