New Thermally Stable and Highly Volatile Precursors for Lanthanum MOCVD: Synthesis and Characterization of Lanthanum β-Diketonate Glyme Complexes

Graziella Malandrino,[†] Rosalia Licata, Francesco Castelli, and Ignazio L. Fragalà*

Dipartimento di Scienze Chimiche, Università di Catania, V.le Andrea Doria 6, 95125 Catania, Italy

Cristiano Benelli

Dipartimento di Chimica, Università di Firenze, Via Maragliano 77, 50144 Firenze, Italy

Rare-earth metal β-diketonates[1] and alkoxides[2] have been widely studied for many years, and in particular, during the last 5 years there has been a lot of activity and many novel related complexes have been reported.[3,4] These materials are extensively used in the synthesis of electroceramics, e.g. superconductors such as $LnBa_2Cu_3O_{7-\delta}$[5] and $La_{2-x}Sr_xCuO_4$,[6] piezoelectrics such as $LaCuO_2$,[7] buffer layers of $LaAlO_3$,[8] and NMR shift reagents.[1] In addition, they may find application in the synthesis of LaF_3, both because it represents a suitable solid lubricant, due to its lamellar hexagonal structure, and because it has ionic conductor properties.

The chemical vapor deposition (CVD) technique offers a softer approach with lower processing temperatures and greater throwing power (versatility and adaptability) than alternative techniques[9] for all these applications. To date, conventional lanthanide MOCVD (metal−organic chemical vapor deposition) precursors have had several disadvantages, mainly due to the high residue left in commercial evaporators and to the poor stability in the atmosphere.[10] The general strategy associated with the synthesis of new stable, water-free and volatile rare-earth metal precursors pointed toward the saturation of the metal coordination sphere using glyme ligands.[10−12]

Herein, we report the synthesis and transport characteristics of the new La(hfa)₃·L (Hhfa = hexafluoroacetylacetone, L = bis(2-methoxyethyl) ether, *diglyme*, and 2,5,8,11-tetraoxadodecane, *triglyme*) adducts and discuss their thermal stability and high volatility, compared to conventional lanthanum sources, as well as their application as MOCVD precursors.

The single-step reaction of lanthanum oxide with hexafluoroacetylacetone and polyether in benzene (eq 1) has been found to yield reproducible anhydrous, air-stable adducts in 1 h in air. The adducts are soluble in benzene and can be isolated as

$$\tfrac{1}{2}La_2O_3 + 3Hhfa + L \rightarrow La(hfa)_3 \cdot L \qquad (1)$$
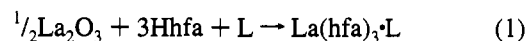
1, La(hfa)₃·diglyme

2, La(hfa)₃·triglyme

white crystalline powders by removal of the solvent. They have been characterized by ¹H, ¹³C NMR, mass spectrometry, and elemental analyses.[13] The adducts are soluble in common organic solvents such as ethanol, chloroform, acetone, pentane, and toluene and slightly soluble in cyclohexane. **1** and **2** are nonhygroscopic, can be handled in air, and melt at 74−76 °C (760 mmHg) and 88−90 °C (760 mmHg),[14] respectively. They sublime quantitatively at 65−70 °C (10^{-3} mmHg) and at 95−105 °C (10^{-3} mmHg) contrasted to 180−190 °C (10^{-3} mmHg) found for the currently used La(tmhd)₃·H₂O precursor.

In regard to mass transport properties and thermal behavior of the as-synthesized, raw[15] adducts, atmospheric pressure thermal gravimetric analyses (TGA, 10 °C/min under N₂) reveal that the sublimation processes of **1** and **2** take place in the 115−295 °C (residue = 2% to 300 °C) and 143−296 °C (residue = 1% to 300 °C) temperature ranges, respectively. No carbonaceous residues have been found in either case. Atmospheric pressure vaporization rate TGA experiments[16] (Figure 1) show that **1** and **2** vaporize ca. 12x and 7x more rapidly than La(tmhd)₃·H₂O. Even more interestingly, they can be also used in atmospheric-pressure MOCVD deposition at temperatures lower than 200 °C.

To our knowledge **1** and **2** represent the first examples of thermally stable lanthanum β-diketonate polyether adducts since the previously reported La(tmhd)₃·tetraglyme (the only other example of a lanthanum β-diketonate polyether adduct) decomposes upon sublimation to yield the unadducted tmhd complex.[10]

† Istituto Nazionale Fisica della Materia (INFM, U.O. Catania, Italy).
(1) Mehrotra, R. C.; Bohra R.; Gaur, D. P. *Metal β-diketonates and Allied Derivatives*; Academic Press: London, 1978.
(2) Bradley, D. C.; Mehrotra R. C.; Gaur, D. P. *Metal Alkoxides*; Academic Press: London, 1978.
(3) Mehrotra, R. C.; Singh, A.; Tripathi, U. M. *Chem Rev.* **1991**, *91*, 1287.
(4) Bradley, D. C.; Chudzynska, H.; Hursthouse, M. B.; Motevalli, M.; Wu, R. *Polyhedron* **1994**, *13*, 1.
(5) (a) Yang, K. N.; Dalichaouch, Y.; Ferreira, J. M.; Lee, B. W.; Neumeier, J. J.; Torikachvili, M. S.; Zhou, H.; Maple, M. B.; Hake, R. R. *Solid State Commun.* **1987**, *63*, 515. (b) Engler, E. M.; Lee, V. Y.; Nazzal, A. I.; Beyers, R. B.; Lim, G.; Grant, P. M.; Parkin, S. S. P.; Ramirez, M. L.; Vasquez, J. E.; Savoy, R. J. *J. Am. Chem. Soc.* **1987**, *109*, 2848.
(6) Cava, R. J.; van Dover, R. B.; Batlagg, B.; Rietman, E. A. *Phys. Rev. Lett.* **1987**, *58*, 408.
(7) Müller-Buschbaum, H. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1472.
(8) Meng, X. F.; Pierce, F. S.; Wong, K. M.; Amos, R. S.; Xu, C. H.; Deaver, B. S., Jr.; Poon, S. J. *IEEE Trans. Magn.* **1991**, *27*, 1638.
(9) Spencer, J. T. In *Progress in Inorganic Chemistry*; Karlin, D. K., Ed.; John Wiley & Sons Inc.: New York, 1994, Vol. 41, p 145.
(10) Drake, S. R.; Lyons, A.; Otway, D. J.; Slawin, A. M. Z.; Williams, D. J. *J. Chem. Soc., Dalton Trans.* **1993**, 2379.
(11) Drake, S. R.; Hursthouse, M. B.; Malik, K. M. A.; Miller, S. A. S.; Otway, D. J. *Inorg. Chem.* **1993**, *32*, 4464.
(12) Bradley, D. C.; Chudzynska, H.; Hursthouse, M. B.; Motevalli, M. *Polyhedron* **1994**, *13*, 7.

(13) *La(hfa)₃·diglyme.* ¹H NMR (200 MHz, CDCl₃): δ 3.53 (s, 6H, OC*H*₃), 3.87 (m, 8H, OC*H*₂), 6.08 (s, 3H, C*H*). ¹³C NMR (50 MHz, CDCl₃): 60.3 (s, O*C*H₃), 71.0 (s, O*C*H₂), 71.4 (s, O*C*H₂), 90.8 (s, *C*H), 117.6 (q, 286 Hz, *C*F₃), 176.8 (q, 34 Hz, *C*O). Anal. Calcd for LaC₂₁-H₁₇F₁₈O₉: C, 28.19; H, 1.91. Found: C, 28.26; H, 1.90. MS (FAB; *m/z* (fragment); M = La(hfa)₃·diglyme): 687, (M − hfa)⁺; 553, (M − hfa − diglyme)⁺; 499, (M − 2hfa + F)⁺; 365, (M − 2hfa − diglyme ● F)⁺; 346 (M − 2hfa − diglyme); 311, (M − 3hfa + 2F)⁺. *La(hfa)₃ triglyme.* ¹H NMR (200 MHz, CDCl₃): δ 3.36 (s, 6H, OC*H*₃), 3.68−3.90 (m, 12H, OC*H*₂), 6.00 (s, 3H, C*H*). ¹³C NMR (50 MHz, CDCl₃): 60.4 (s, O*C*H₃), 70.4 (s, O*C*H₂), 70.6 (s, O*C*H₂), 71.2 (s, O*C*H₂), 89.6 (s, *C*H), 117.8 (q, 286 Hz, *C*F₃), 175.7 (q, 34 Hz, *C*O). Anal. Calcd for LaC₂₃H₂₁F₁₈O₁₀: C, 29.42; H, 2.26. Found: C, 29.45; H, 2.17. MS (FAB; *m/z* (fragment); M = La(hfa)₃·triglyme): 731, (M − hfa)⁺; 553, (M − hfa − triglyme)⁺; 543 (M − 2hfa + F)⁺, 365, (M − 2hfa − triglyme + F)⁺, 355 (M − 3hfa + 2F)⁺.
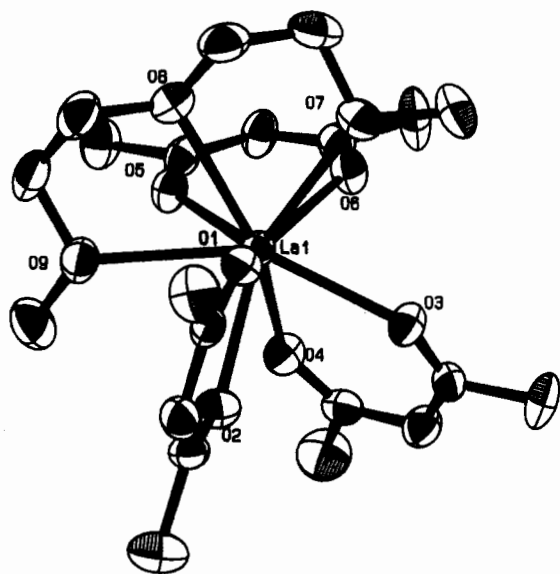(14) Obtained from comparison of DSC data and optical microscopy.
(15) Used without any further purification.
(16) Experiments were performed with a temperature ramp up of 5 °C/min under N₂ and with a 4 mm alumina sample pan.
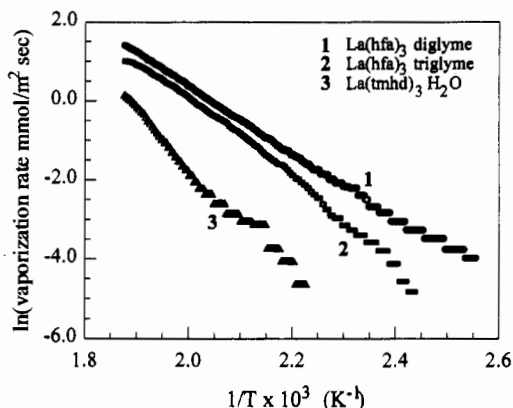
Figure 1. Atmospheric-pressure TGA data of La(hfa)₃·diglyme and La(hfa)₃·triglyme compared to La(tmhd)₃·H₂O as a function of temperature.

Figure 2. 2. ORTEP drawing of the crystal structure of complex **1**. CF₃ groups have been omitted for clarity. Important bond distances (Å) are La1−O1 = 2.515(5), La1−O2 = 2.485(5), La1−O3 = 2.462-(6), La1−O4 = 2.472(6), La1−O5 = 2.635(6), La1−O6 = 2.629(6), La1−O7 = 2.523(5), La1−O8 = 2.475(5), and La1−O9 = 2.642(6).

The crystal structure of **1**[17] (Figure 2) consists of a mononuclear complex in which three hfa and the diglyme ligands are coordinated through all the oxygen atoms thus resulting in

a lanthanum coordination of 9. A square-antiprismatic geometry, analogous to the geometry found for the related La-(tmhd)₃·tetraglyme,[10] is obtained with the ninth coordinating oxygen atom (O8) capping one of the square faces. The La−O(diketone) bond distances range from 2.462 to 2.635 Å. The shorter La−O(diglyme) bond distances (2.475−2.642 Å), compared to the corresponding La−O(ether) bond distances in the nine-coordinated complex La(tmhd)₃·tetraglyme[10] (2.706−2.781 Å), are indicative of strong coordinative bonds between the metal center and the donor atoms of the polyether. These results agree well with sublimation studies.

Atmospheric-pressure MOCVD depositions have been performed, under O₂ (80 sccm) flow, using a horizontal quartz hot-wall reactor from the La(hfa)₃·diglyme precursor. The source temperature was controlled in the 160−170 °C range. Silicon-(111) substrates were used for the deposition of LaF₃. The substrate temperature was varied in the range 400−600 °C. Wavelength dispersive X-ray analyses are indicative of minor (<3%) amounts of carbon contamination. Note that the fluorinating agent is supplied from the source material itself.

Finally, note that the present one-pot synthesis produces, with very high yields (≈90%) and through a viable low-cost route, raw materials that represent pure, final products since no foreign species are introduced in the one-pot synthesis. The present synthetic strategy is of general application[18,19] and opens a new route to an interesting generation of water-free lanthanide precursors.[20]

In summary, the new adducts La(hfa)₃·diglyme and La-(hfa)₃·triglyme have better mass transport properties in terms of volatility and thermal stability than conventional lanthanum CVD precursors. Their vapor-phase transport characteristics at low and atmospheric pressures make them attractive candidates not only for laboratory MOCVD processes but also for industrial applications. Further studies are focusing on the encapsulation of other metals and the effect of the Ln ionic radius on the adduct formation.

Supporting Information Available: Complete listings of crystal structure analysis data, atom positions, thermal parameters, bond distances, and bond angles and an ORTEP plot of **1** (Figure S1), a TGA plot of **1** and **2** (Figure S2), and an XRD pattern of a LaF₃ film (Figure S3) (11 pages). Ordering information is given on any current masthead page.

IC941424V

(17) Crystal data for **1**: LaC₂₁H₁₇O₉F₁₈, monoclinic, $P2_1/c$, a = 10.075(2) Å, b = 15.599(4) Å, c = 21.038(9) Å, β = 103.48(5)°, Z = 4, ϱ_{calc} = 1.85 g/cm³, V = 3215.25(43) Å³, T = 294 K, Mo Kα λ = 0.7107 Å, 3076 unique data collected (θ−2θ technique, 5° < 2θ < 43°) of which 2850 have F_o > 2σ(F^o) and were used for structure solution and refinement, with R = 0.0477, and R_w = 0.0507.

(18) Malandrino, G.; Castelli, F.; Fragalà, I. L. *Inorg. Chim. Acta* **1994,** *224,* 203.

(19) Malandrino, G.; Fragalà, I. L.; Neumayer, D. A.; Stern, C. L.; Hinds, B. J.; Marks, T. J. *J. Mater. Chem.* **1994,** *4,* 1061.

(20) Malandrino, G.; Fragalà, I. L.; et al. Manuscript in preparation.