Tetrameric Lanthanide Neopentoxide Complexes with Agostic Ln···H—C Interactions: X-ray Crystal Structures of $Ln_4(OCH_2\text{-}t\text{-}Bu)_{12}$ (Ln = La, Nd)

David M. Barnhart,[1a] David L. Clark,*,[1b] John C. Gordon,[1b]
John C. Huffman,[1c] John G. Watkin,*,[1b] and Bill D. Zwick[1d]

Los Alamos National Laboratory
Los Alamos, New Mexico, 87545
Indiana University Molecular Structure Center
Bloomington, Indiana 47405

Received June 10, 1993

While the alkoxides of yttrium and the lanthanides have been known for many years,[2] their application as precursors to electronic and ceramic materials has generated a renewed interest in well-characterized homoleptic complexes.[3] Recent developments include characterization of a wide variety of novel structural types and thermal decomposition studies.[4] Such studies have demonstrated that the nature of oligomerization in lanthanide alkoxide complexes and many of their solution properties are highly dependent on the steric requirements of the alkoxide ligands. Herein we report the preliminary results of our study of lanthanide neopentoxide complexes. This work provides a unique example of a lanthanide alkoxide complex with spectroscopic evidence for an agostic Ln···H—C bond both in the solid state *and in solution* and may provide additional insight into the initial steps of alkoxy group breakdown during thermal decomposition reactions.

Reaction of a lanthanide tris(silylamide) ($Ln[N(SiMe_3)_2]_3$, Ln = La or Nd)[5] with 3 equiv of dry neopentanol in hexane solution at 25 °C, followed by cooling to –40 °C, yields colorless [Ln = La (**1**)][6] or pale blue [Ln = Nd (**2**)][7] crystals of the homoleptic lanthanide neopentoxide complexes $[Ln(OCH_2\text{-}t\text{-}Bu)_3]_4$.[8] Compounds **1** and **2** are oxygen- and moisture-sensitive and are soluble in noncoordinating hydrocarbon solvents. Variable-temperature ^1H and ^{13}C NMR spectra of **1** and **2** in toluene-d_8 reveal complex dynamic solution behavior, and interpretation has been hindered by overlapping resonances in **1**, paramagnetism in **2**, and a possible dimer ↔ tetramer equilibrium in solution. The infrared spectra[9] (Nujol mull, KBr plates) of both **1** and **2** show strong absorption bands characteristic of alkoxide ligation[10] and a low ν(C–H) stretching frequency at 2688 (**1**) and 2692 (**2**) cm^{-1}, consistent with the presence of agostic Ln···H—C interactions in the solid state.[11] IR spectra recorded in benzene solution revealed similar absorption features at 2680 (**1**) and 2686 (**2**) cm^{-1}, indicating that an agostic interaction is maintained in solution. While agostic interactions have been proposed for a variety of f-element complexes on the basis of X-ray crystallographic studies,[12] to the best of our knowledge, **1** and **2** represent the first examples of spectroscopic evidence for *solution* agostic M···H—C interactions in an f-element complex.

Single crystals of **1** and **2** were grown at –40 °C from concentrated hexane and toluene-d_8 solutions, respectively, and the solid-state structures were determined from X-ray diffraction data collected at –70 (**1**)[13] and –164 °C (**2**).[14] The X-ray structures revealed a tetrameric $Ln_4(OCH_2\text{-}t\text{-}Bu)_{12}$ unit for both **1** and **2**, as shown in Figures 1 and 2, respectively, with four molecules of toluene per tetramer within the lattice of **2**. Both molecules contain a square of lanthanide metal atoms with averaged (nonbonding) Ln···Ln distances of 3.85 and 3.74 Å for **1** and **2**, respectively. There are eight μ_2-OR ligands, four above and four below the Ln_4 plane, and terminal Ln–O bonds radiate from the corners of the Ln_4 square. The overall structure is

---

[1] (a) Los Alamos National Laboratory. Present address: Department of Chemistry, University of Washington, BG-10, Seattle, WA 98185. (b) Inorganic and Structural Chemistry Group, INC-1, Mail Stop C346, Los Alamos. (c) IUMSC. (d) Nuclear Materials Technology Division, NMT-6, Mail Stop E510, Los Alamos.

[2] Mehrotra, R. C.; Singh, A.; Tripathi, U. M. *Chem. Rev.* **1991**, *91*, 1287.

[3] (a) Hubert-Pfalzgraf, L. G. *New J. Chem.* **1987**, 662. (b) Bradley, D. C. *Chem. Rev.* **1989**, *89*, 1317. (c) Brinker, C. J.; Clark, D. E.; Ulrich, D. R. Better Ceramics Through Chemistry II. *Mater. Res. Soc. Symp. Proc.* **1986**, 73.

[4] (a) Evans, W. J.; Deming, T. J.; Olofson, J. M.; Ziller, J. W. *Inorg. Chem.* **1989**, *28*, 4027. (b) Schumann, H.; Kociok-Köhn, G.; Loebel, J. *Z. Anorg. Allg. Chem.* **1990**, *581*, 69. (c) Bradley, D. C.; Chudzynska, H.; Hursthouse, M. B.; Motevalli, M. *Polyhedron* **1991**, *10*, 1049. (d) Evans, W. J.; Sollberger, M. S. *Inorg. Chem.* **1988**, *27*, 4417. (e) Evans, W. J.; Sollberger, M. S.; Hanusa, T. P. *J. Am. Chem. Soc.* **1988**, *110*, 1841. (f) Evans, W. J.; Olofson, J. M.; Ziller, J. W. *J. Am. Chem. Soc.* **1990**, *112*, 2308. (g) Poncelet, O.; Sartain, W. J.; Hubert-Pfalzgraf, L. G.; Folting, K.; Caulton, K. G. *Inorg. Chem.* **1989**, *28*, 263. (h) Vaartstra, B. A.; Huffman, J. C.; Gradeff, P. S.; Hubert-Pfalzgraf, L. G.; Daran, J. C.; Parraud, S.; Yunlu, K.; Caulton, K. G. *Inorg. Chem.* **1990**, *29*, 3126. (i) Bradley, D. C.; Chudzynska, H.; Frigo, D. M.; Hammond, M. E.; Hursthouse, M. B.; Mazid, M. A. *Polyhedron* **1990**, *9*, 719. (j) McGeary, M. J.; Coan, P. S.; Folting, K.; Streib, W. E.; Caulton, K. G. *Inorg. Chem.* **1989**, *28*, 3283. (k) McGeary, M. J.; Coan, P. S.; Folting, K.; Streib, W. E.; Caulton, K. G. *Inorg. Chem.* **1991**, *30*, 1723. (l) Coan, P. S.; McGeary, M. J.; Lobkovsky, E. B., Caulton, K. G. *Inorg. Chem.* **1991**, *30*, 3570. (m) Evans, W. J.; Golden, R. E.; Ziller, J. W. *Inorg. Chem.* **1991**, *30*, 4963. (n) Poncelet, O.; Hubert-Pfalzgraf, L. G.; Daran, J.-C.; Astier, R. *J. Chem. Soc., Chem. Commun.* **1989**, 1846. (o) Poncelet, O.; Hubert-Pfalzgraf, L. G. *Polyhedron* **1989**, *8*, 2183. (p) Helgesson, G.; Jagner, S.; Poncelet, O.; Hubert-Pfalzgraf, L. G. *Polyhedron* **1991**, *10*, 1559. (q) Stecher, H. A.; Sen, A.; Rheingold, A. L. *Inorg. Chem.* **1989**, *28*, 3282. (r) Hitchcock, P. B.; Lappert, M. F.; Singh, A. *J. Chem. Soc., Chem. Commun.* **1983**, 1499.

[5] Bradley, D. C.; Ghotra, J. S.; Hart, F. A. *J. Chem. Soc., Dalton Trans* **1973**, 1021.

[6] Procedure: in a drybox, 0.40 g (0.64 mmol) of $La[N(SiMe_3)_2]_3$ was dissolved in 60 mL of hexane to give a colorless solution. Cold neopentanol (0.17 g, 1.95 mmol) was added, and the mixture was stirred at room temperature for 2 h. The volume of solution was reduced to 2 mL *in vacuo*, and then the solution was placed at –40 °C. After 1 day, little in the way of a solid product was seen, so the solution was allowed to evaporate slowly under the helium box atmosphere, resulting in the formation of colorless crystals. Yield 0.230 g (87%).

[7] Procedure: in a drybox, 1.50 g (2.40 mmol) of $Nd[N(SiMe_3)_2]_3$ was dissolved in 100 mL of hexane to give a pale blue solution. Neopentanol (0.64 g, 7.26 mmol), dissolved in 10 mL of hexane, was added, and the mixture was stirred at room temperature for 2 h. The volume of solution was reduced to 10 mL *in vacuo*, and then the solution placed at –40 °C. Pale blue crystals were deposited after 2 days. These were decanted free from solvent and allowed to dry under a helium atmosphere. Yield 0.338 g (35%).

[8] Anal. Calcd. for $C_{60}H_{132}La_4O_{12}$ (**1**): C, 45.00; H, 8.31; N, 0.00. Found: C, 44.17; H, 8.14; N, 0.05. Anal. Calcd. for $C_{60}H_{132}Nd_4O_{12}$ (**2**) (sample crystallized from hexane, no toluene present): C, 44.41; H, 8.20; N, 0.00. Found: C, 43.80; H, 7.72; N, 0.00.

[9] IR data. (**1**, Nujol, cm^{-1}): 2688 (w), 1362 (m), 1354 (m), 1254 (w), 1215 (w), 1104 (s), 1063 (s), 1016 (m), 930 (w), 897 (w), 749 (w), 725 (w), 592 (m), 553 (m). (**2**, Nujol, cm^{-1}): 2735 (w), 2692 (m), 2642 (w), 1476 (s), 1394 (m), 1359 (s), 1306 (w), 1293 (w), 1255 (w), 1218 (w), 1105 (s), 1064 (s), 1055 (s), 1019 (s), 933 (m), 897 (m), 749 (w), 727 (w), 599 (s), 554 (m), 419 (s).

[10] For a general review of IR spectra of metal alkoxides, see: Bradley, D. C.; Mehrotra, R. C.; Gaur, D. P. *Metal Alkoxides*; Academic Press: New York, 1978. Malhotra, K. C.; Martin, R. C. *J. Organomet. Chem.* **1982**, *239*, 1159. Chisholm, M. H.; Clark, D. L.; Huffman, J. C. *Polyhedron* **1985**, *4*, 1203.

[11] Brookhart, M.; Green, M. L. H.; Wong, L.-L. *Prog. Inorg. Chem.* **1988**, *36*, 1.

[12] (a) den Haan, K. H.; de Boer, J. L.; Teuben, J. H.; Spek, A. L.; Kojic-Prodic, B.; Hays, G. R.; Huis, R. *Organometallics* **1986**, *5*, 1726. (b) Schaverien, C. J.; Nesbitt, G. J. *J. Chem. Soc., Dalton Trans.* **1992**, 157. (c) Turner, H. W.; Andersen, R. A.; Zalkin, A.; Templeton, D. H. *Inorg. Chem.* **1979**, *18*, 1221. (d) Heeres, H. J.; Meetsma, A.; Teuben, J. H. *J. Chem. Soc., Chem. Commun.* **1988**, 962. (e) Tilley, T. D.; Andersen, R. A.; Zalkin, A. *J. Am. Chem. Soc.* **1982**, *104*, 3725.

[13] Crystal data for $[La_4(OCH_2\text{-}t\text{-}Bu)_{12}]$ (**1**) at –70 °C: orthorhombic space group $P2_12_12$, $a = 17.259(4)$, $b = 19.151(4)$, and $c = 11.771(3)$ Å, $V = 3890.6(16)$ Å^3, $Z = 4$, $d_{calc} = 1.367$ g cm^{-3}. An empirical absorption correction was applied to the diffraction data, and the structure was solved by direct methods and Fourier techniques and refined by full-matrix least-squares using the SHELXTL PLUS program suite. Final discrepancy indices were $R_f = 0.040$ and $R_{wf} = 0.044$ for those 3161 reflections (Enraf-Nonius CAD-4) with $F_o \geq 4\sigma(F_o)$. The limits of data collection were $2° \leq 2\theta \leq 50°$ (Mo Kα). Disorder in the methyl carbons of the *tert*-butyl groups was accommodated by the use of a model with 64% and 36% occupancies of two distinct rotations of the *tert*-butyl groups.

[14] Crystal data for $[Nd_4(OCH_2\text{-}t\text{-}Bu)_{12}]\cdot 4C_7D_8$ (**2**) at –171 °C: tetragonal space group $P\bar{4}2_1c$, $a = 20.383(5)$ and $c = 11.822(3)$ Å, $V = 4911.78$ Å^3, $Z = 2$, $d_{calc} = 1.346$ g cm^{-3}. The structure was solved by direct methods and Fourier techniques and refined by full-matrix least-squares using SHELXS-86. Final discrepancy indices were $R_f = 0.0475$ and $R_{wf} = 0.0503$ for those 1540 reflections (Picker four-circle) with $F_o \geq 2.33\sigma(F_o)$. The limits of data collection were $6° \leq 2\theta \leq 45°$ (Mo Kα).

0002-7863/93/1515-8461$04.00/0

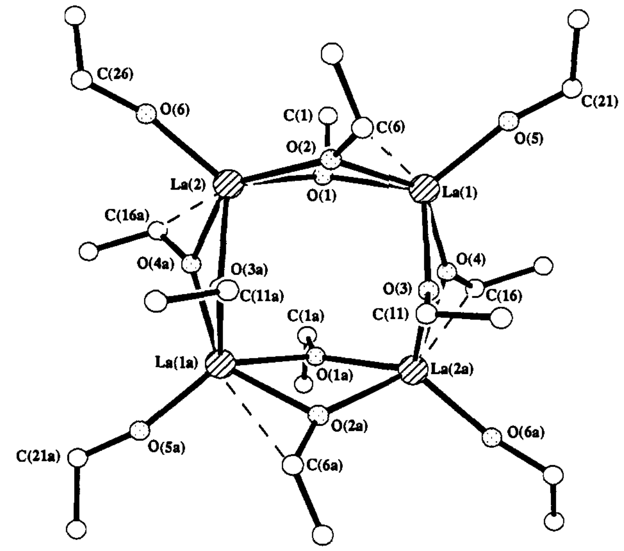

Figure 1. Ball and stick representation of the molecular structure of $La_4(OCH_2\text{-}t\text{-}Bu)_{12}$ (**1**). Methyl carbon atoms omitted for clarity. Selected bond distances (Å) and angles (deg): La(1)–La(2) 3.865(1), La(1)–O(1) 2.407(9), La(1)–O(2) 2.445(9), La(1)–O(3) 2.390(9), La(1)–O(4) 2.376(9), La(1)–O(5) 2.169(7), La(1)–La(2A) 3.850(1), La(2)–O(1) 2.418(9), La(2)–O(2) 2.379(9), La(2)–O(6) 2.157(6), La(2)–O(3A) 2.407(9), La(2)–O(4A) 2.420(10), La(2)–C(16A) 3.099(15), La(1)–C(6) 3.148, La(1)–O(1)–La(2) 106.4(3), La(1)–O(2)–La(2) 106.5(3), La(2A)–O(4)–C(16) 105.2(8), La(1)–O(3)–La(2A) 106.8 (3), La(1)–O(4)–La(2A) 106.8(4), La(1)–O(4)–C(16) 147.6(9), La(1)–O(2)–C(6) 106.5(7), La(2)–O(2)–C(6) 146.7(7).

remarkably similar to that of $Mo_4Cl_4(O\text{-}i\text{-}Pr)_8$,[15] except for the shorter M–M distances in the Mo complex due to the presence of M–M bonding. The longer M–M distances in the Ln tetramers are accompanied by a concomitant opening up of the M–μ-O–M angles [*viz.* 70.4(1)° in the Mo system compared to 106.6(5)° and 106.3(5)° (av) in **1** and **2**]. The local LnO_5 coordination geometry in **1** and **2** may be described as a distorted square-based pyramid, with a terminal alkoxide ligand occupying the apical position. The average La-μ_2-O distance of 2.40 Å (**1**) is similar to the 2.442(14)-Å (av) distance seen in the solid-state structure of $La_3(O\text{-}t\text{-}Bu)_9(HO\text{-}t\text{-}Bu)_2$.[4c] Similarly, the terminal La–O distance of 2.163(7) Å (av) is comparable to the uniquely identified terminal La–O bond of 2.195(13) Å in $La_3(O\text{-}t\text{-}Bu)_9(HO\text{-}t\text{-}Bu)_2$.[4c] The terminal Nd–O distance of 2.138(8) Å (**2**) is comparable to average terminal Nd–O distances of 2.05(2), 2.174(2), and 2.148(16) Å seen in $Nd_6(O\text{-}i\text{-}Pr)_{17}Cl$,[16] $Nd(OC\text{-}t\text{-}Bu_2CH_2PMe_2)_3$,[17] and $Nd_5O(O\text{-}i\text{-}Pr)_{13}(HO\text{-}i\text{-}Pr)_2$,[4p] respectively. Bridging Nd–O distances are, as expected, somewhat longer than those of the terminal alkoxide ligands and average 2.342(12) Å. The Ln–O–C angles of the terminal alkoxide ligands are very obtuse, averaging 162.45° in **1** and 163.9(14)° in **2**.

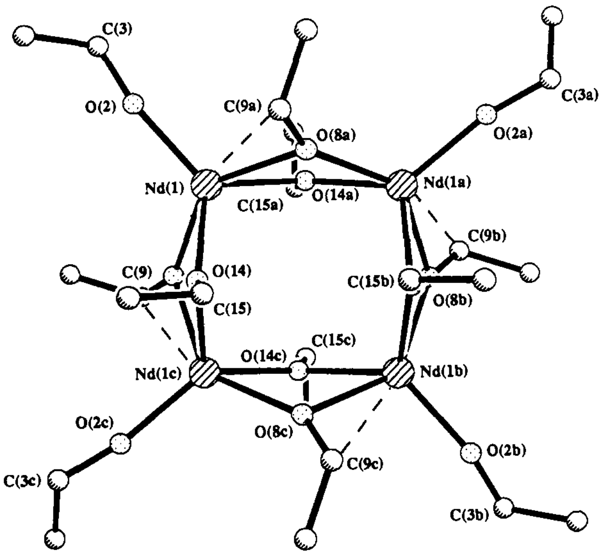

Figure 2. Ball and stick representation of the molecular structure of $Nd_4(OCH_2\text{-}t\text{-}Bu)_{12}$ (**2**). Methyl carbon atoms and lattice toluene molecules omitted for clarity. Selected bond distances (Å) and angles (deg): Nd(1)–Nd(1a) 3.741(3), Nd(1)–O(2) 2.138(8), Nd(1)–O(8) 2.320(12), Nd(1)–O(8a) 2.381(12), Nd(1)–O(14) 2.332(12), Nd(1)–O(14a) 2.333(11), Nd(1)–O(2)–C(3) 163.9(14), Nd(1)–O(8)–C(9) 147.5(10), Nd(1a)–O(8)–C(9) 106.9(10), Nd(1)–O(8)–Nd(1a) 105.4(4), Nd(1)–O(14)–Nd(1a) 106.6(5), Nd(1)–O(14)–C(15) 134.5(10), Nd(1a)–O(14)–C(15) 117.6(10).

Notable features of both structures are the relatively close approach of several bridging methylene carbon atoms to the Ln metal centers [La(2A)–C(16) = 3.099(15) and La(1)–C(6) = 3.148(15) Å in **1**, Figure 1, and Nd(1)–C(9A) = 3.100 Å in **2**, Figure 2], consistent with the IR spectral data for the bulk samples, and the presence of agostic Ln···H—C interactions in the solid state. The close approach of the methylene carbons is accompanied by a distortion and asymmetry in the bridging La–O distances in **1**. Bridging La–O bonds without La···C contacts average 2.406(9) Å, while bridging La–O bonds with close La···C contacts reveal two significantly different La–O distances averaging 2.337(9) and 2.433(9) Å (Figure 1).

Further studies of this fascinating class of agostic lanthanide alkoxide complex are in progress.

Acknowledgment. This work was performed under the auspices of the Office of Energy Research, Division of Chemical Sciences, and the Office of Nuclear Material Production, U.S. Department of Energy. Los Alamos National Laboratory is operated by the University of California for the U.S. Department of Energy under Contract W-7405-ENG-36.

Supplementary Material Available: For **1** and **2**, tables listing crystal data, atomic positional and equivalent isotropic thermal parameters, anisotropic thermal parameters, and selected bond distances and bond angles (11 pages); observed and calculated structure factors (21 pages). Ordering information is given on any current masthead page.

---

[15] Chisholm, M. H.; Clark, D. L.; Errington, R. J.; Folting, K.; Huffman, J. C. *Inorg. Chem.* **1988**, *27*, 2071.

[16] Andersen, R. A.; Templeton, D. H.; Zalkin, A. *Inorg. Chem.* **1978**, *17*, 1962.

[17] Hitchcock, P. B.; Lappert, M. F.; MacKinnon, I. A. *J. Chem. Soc., Chem. Commun.* **1988**, 1557.