



# Heterometallic lithium niobium complexes: synthesis and molecular structures of $\text{LiNbO}(\text{O}-2,6\text{-PhMe}_2)_4 \cdot 3\text{THF}$ and $[\text{LiNbCl}_3(\text{O}-2,6\text{-PhMe}_2)_2 \cdot 2\text{THF}]_2$

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Received 13 October 1999; accepted 24 February 2000

## Abstract

The methathesis reactions between  $\text{NbCl}_5$  and lithium-2,6-dimethylphenoxide,  $\text{LiO}-2,6\text{-PhMe}_2$ , afford  $\text{LiNbO}(\text{O}-2,6\text{-PhMe}_2)_4 \cdot 3\text{THF}$  (**1**) and  $[\text{LiNbCl}_3(\text{O}-2,6\text{-PhMe}_2)_2 \cdot 2\text{THF}]_2$  (**2**). The complexes **1** and **2** were characterized by X-ray single crystal diffraction analyses, elemental analyses, and FT-IR,  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy. Complex **1** exists as a monomeric binuclear lithium niobium complex which has a terminal oxo ligand, and complex **2** exists as a dimeric tetranuclear lithium niobium complex where metal atoms are linearly connected by  $\mu_2$ -chloride linkages, respectively. Lithium metal is coordinated by THF molecules as a counter ion. ©2000 Elsevier Science Ltd All rights reserved.

**Keywords:** Heterometallic aryloxides; Lithium niobate; Monomeric compounds; Niobium; Precursors

## 1. Introduction

Transition metal alkoxides are not only important starting materials for studying organometallic chemistry but are also extremely attractive precursors for the preparation of metal oxides. In particular, heterometallic alkoxides are potential single-source precursors for the fabrication of bimetallic (or multimetallic) oxides owing to the significant advantages they offer to the composition control of final ceramic materials and simplification of processes [1–10]. With the development of processes such as sol-gel and metal-organic chemical vapor deposition (MOCVD), demand for molecularly defined precursors has been increased [1–10]. Therefore, there has been many studies on the preparation of heterometallic alkoxides in recent years.

In particular, lithium niobium alkoxides are in an area of intense current interest owing to their utility as precursors for electro-optic materials [11–23]. However, the chemistry of lithium niobium alkoxides remains relatively unexplored. Since the first report of the syntheses of lithium niobium(V) alkoxides,  $[\text{LiNb}(\text{OR})_6]_x$  ( $\text{R} = \text{Me}, \text{Et}, \text{}^i\text{Pr}, \text{}^t\text{Bu}$ ) [15], a few complexes have been synthesized and characterized:

$[\text{LiNb}(\text{OEt})_6]_x$  of helical structure [16] and  $[\text{LiNbO}(\text{OEt})_4 \cdot \text{EtOH}]_2$  [1,11,17] as intermediate in a hydrolysis reaction to  $[\text{LiNb}(\text{OEt})_6]_x$ . More recently,  $[\text{LiNb}(\text{OR})_6]_2$  ( $\text{R} = \text{CH}_2\text{CMe}_3, \text{CH}_2\text{SiMe}_3$ ), dimeric molecular precursors, have been prepared and characterized [18].

Our motivation for exploring lithium niobium alkoxides concerns the development of improved molecular single-source precursors for lithium niobate,  $\text{LiNbO}_3$ . To obtain molecular lithium niobium complexes without any intermolecular bonds or bridging units, we have introduced bulky aryl groups containing methyl side chains [24]. Syntheses and structural characterizations of niobium(V) aryl compounds such as homoleptic niobium aryloxides,  $\text{Nb}(\text{O}-2,6\text{-PhMe}_2)_5$ ,  $[\text{Nb}(\text{O}-4\text{-PhMe})_5]_2$ , and  $[\text{Nb}(\text{O}-3,5\text{-PhMe})_5]_2$ , niobium oxo aryloxides,  $\text{NbO}(\text{O}-2,6\text{-PhMe}_2)_3$  and  $\text{NbO}(\text{O}-2,6\text{-Ph}^t\text{Bu}_2)_3$ , and niobium chloro aryloxides,  $\text{NbCl}(\text{MTP})_2$  ( $\text{MTP} = 2,2'\text{-CH}_2(\text{O}-2,4\text{-C}_6\text{H}_2\text{Bu}_2)_2$ ),  $[\text{Nb}(\text{O}-2,6\text{-Ph}^i\text{Pr}_2)_2 \cdot \text{Cl}_3]_2$ , and  $\text{Nb}(\text{O}-2,6\text{-PhMe}_2)_2\text{Cl}_3 \cdot \text{THF}$  ( $\text{THF} = \text{tetrahydrofuran}$ ) have been reported [25–29]. However, lithium niobium aryloxides, oxo aryloxides, or chloro aryloxides have not been synthesized yet. This study reports the syntheses and structural characterizations of the first examples of a monomeric lithium niobium(V) oxo aryloxide,  $\text{LiNbO}(\text{O}-2,6\text{-PhMe}_2)_4 \cdot 3\text{THF}$  (**1**), and a dimeric lithium niobium(IV) chloro aryloxide,  $[\text{LiNbCl}_3(\text{O}-2,6\text{-PhMe}_2)_2 \cdot 2\text{THF}]_2$  (**2**).

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## 2. Experimental

All reactions and manipulations were carried out under dry inert gas using standard Schlenk line techniques. Solvents were dried and purified by distillation from sodium benzophenone ketyl under nitrogen. Niobium chloride, lithium, and 2,6-dimethylphenol were used as received from Strem Chemicals and Aldrich Chemical Co. Lithium-2,6-dimethylphenoxide was prepared from 2,6-dimethylphenol and metallic lithium in diethyl ether. IR spectra were obtained as KBr pellet technique on a Nicolet Magna-IR 760 spectrometer. NMR spectra were registered on a Varian Gemini 300 spectrometer. Analytical data were obtained with a Thermoquest EA-1110 CHNS analyzer.

### 2.1. Synthesis of $\text{LiNbO}(\text{O}-2,6\text{-PhMe}_2)_4 \cdot 3\text{THF}$ (**1**)

A solution of  $\text{NbCl}_5$  (2 g, 7.4 mmol) in THF (50 ml) was added dropwise to a solution of 4 equiv.  $\text{LiO}-2,6\text{-PhMe}_2$  (3.8 g, 29.7 mmol) in THF (50 ml). The resultant mixture was stirred at ambient temperature for 24 h. After removal of THF solvent, diethyl ether (150 ml) was added, and the mixture was filtered to eliminate  $\text{LiCl}$ . After concentration to half volume, THF (50 ml) was added and the solution was layered with *n*-hexane. Complex **1** was obtained as yellow crystals with 72% (4.35 g) yield. *Anal.* Found: C, 64.74; H, 7.67. Calc. for  $\text{C}_{44}\text{H}_{60}\text{O}_8\text{LiNb}$ : C, 64.70; H, 7.40%. FT-IR ( $\text{cm}^{-1}$ ): 3010w, 2976m, 2880m, 1594w, 1467s, 1426s, 1372w, 1273vs, 1225vs, 1088m, 1048m, 918m, 880s, 754s, 737m, 713s, 566m, 546m.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $25^\circ\text{C}$ , ppm): 6.94–6.51 (m, 12H,  $\text{OC}_6\text{H}_3\text{Me}_2$ ); 3.66 (t, 12H,  $\text{OCH}_2\text{CH}_2$ ); 2.15 (s, 24H,  $\text{OC}_6\text{H}_3\text{Me}_2$ ); 1.76 (quintet, 12H,  $\text{OCH}_2\text{CH}_2$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ,  $25^\circ\text{C}$ , ppm): 160.5, 128.5, 127.8,

127.2, 123.5, 121.1, 119.6, 118.9 ( $\text{OC}_6\text{H}_5\text{Me}_2$ ); 68.2 ( $\text{OCH}_2\text{CH}_2$ ); 25.4 ( $\text{OCH}_2\text{CH}_2$ ); 17.0, 16.2 ( $\text{OC}_6\text{H}_5\text{Me}_2$ ).

### 2.2. Synthesis of $[\text{LiNbCl}_3(\text{O}-2,6\text{-PhMe}_2)_2 \cdot 2\text{THF}]_2$ (**2**)

A solution of 4 equiv.  $\text{LiO}-2,6\text{-PhMe}_2$  (3.8 g, 29.7 mmol) in THF (50 ml) was added dropwise to  $\text{NbCl}_5$  (2 g, 7.4 mmol). After a similar procedure to the preparation of complex **1**, complex **2** was obtained as dark brown crystals in a small amount. Satisfactory C and H analyses were obtained for complex **2**. FT-IR ( $\text{cm}^{-1}$ ): 3010w, 2976m, 2881m, 1587w, 1467s, 1420m, 1379w, 1266s, 1208vs, 1092m, 1044m, 891s, 767m, 730s, 571m.  $^1\text{H}$  NMR ( $\text{CD}_3\text{OD}$ ,  $25^\circ\text{C}$ , ppm): 6.89–6.61 (m, 12H,  $\text{OC}_6\text{H}_3\text{Me}_2$ ); 3.73 (t, 16H,  $\text{OCH}_2\text{CH}_2$ ); 2.19 (s, 24H,  $\text{OC}_6\text{H}_3\text{Me}_2$ ); 1.87 (quintet, 16H,  $\text{OCH}_2\text{CH}_2$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CD}_3\text{OD}$ ,  $25^\circ\text{C}$ , ppm): 129.3, 125.5, 120.7 ( $\text{OC}_6\text{H}_5\text{Me}_2$ ); 68.8 ( $\text{OCH}_2\text{CH}_2$ ); 26.5 ( $\text{OCH}_2\text{CH}_2$ ); 16.6 ( $\text{OC}_6\text{H}_5\text{Me}_2$ ).

### 2.3. Crystallography of $\text{LiNbO}(\text{O}-2,6\text{-PhMe}_2)_4 \cdot 3\text{THF}$ and $[\text{LiNbCl}_3(\text{O}-2,6\text{-PhMe}_2)_2 \cdot 2\text{THF}]_2$

Single crystals suitable for X-ray diffraction studies were grown from THF and *n*-hexane for complexes **1** and **2**. A suitable crystal of each compound was mounted inside a glass capillary under nitrogen atmosphere and sealed with a flame. Diffraction data were collected on a Bruker P4 four circle instrument, with graphite-monochromated  $\text{Mo K}\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). The unit cell parameters and basic information about data collection and structure refinement are given in Table 1. The structures were solved by direct methods with SHELXS-86 and refined against  $F^2$  on all data by full-matrix least-squares with SHELXL-93. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms

Table 1  
Crystal data for  $\text{LiNbO}(\text{O}-2,6\text{-PhMe}_2)_4 \cdot 3\text{THF}$  and  $[\text{LiNbCl}_3(\text{O}-2,6\text{-PhMe}_2)_2 \cdot 2\text{THF}]_2$

Formula	$\text{C}_{44}\text{H}_{60}\text{O}_8\text{LiNb}$	$\text{C}_{48}\text{H}_{68}\text{O}_8\text{Cl}_6\text{Li}_2\text{Nb}_2$
FW	816.77	1184.4
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$
<i>a</i> (Å)	13.226(1)	11.953(1)
<i>b</i> (Å)	20.709(2)	17.383(2)
<i>c</i> (Å)	16.559(2)	13.724(1)
$\beta$ (°)	90.54(1)	95.94(1)
<i>V</i> (Å <sup>3</sup> )	4535.3(8)	2836.2(5)
<i>Z</i>	4	2
Density $\rho_{\text{calc}}$ (g cm <sup>-3</sup> )	1.196	1.388
Linear absorption coefficient $\mu$ (mm <sup>-1</sup> )	0.312	0.732
Temperature of measurement (K)	293(2)	293(2)
Scan type	$\theta-2\theta$	$\theta-2\theta$
Data collection range (°)	$1.83 \leq \theta \leq 22.52$	$1.90 \leq \theta \leq 22.51$
Octants collected	–14.0; –22.0; –17.17	0.12; –18.0; –14.14
<i>F</i> (000)	1728	1220
No. of data collected	6149	3895
No. of unique data collected	5877	3690
$R_{\text{int}}$	0.1737	0.0334
$R_1 = \sum   F_o  -  F_c   / \sum  F_o $	0.0673(0.0889)	0.0369(0.0501)
$wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum wF_o^4]^{1/2}$ for data with $I > 2\sigma(I)$	0.2030(0.2418)	0.0916(0.1036)
GOF = $[\sum w(F_o^2 - F_c^2)^2 / \sum (n-p)]^{1/2}$	1.028	1.011
Min./max. residual electron density (e Å <sup>-3</sup> )	–0.707/0.575	–0.377/0.364
No. of variables	547	332

were included at geometrically calculated positions and refined using a riding model.

### 3. Results and discussion

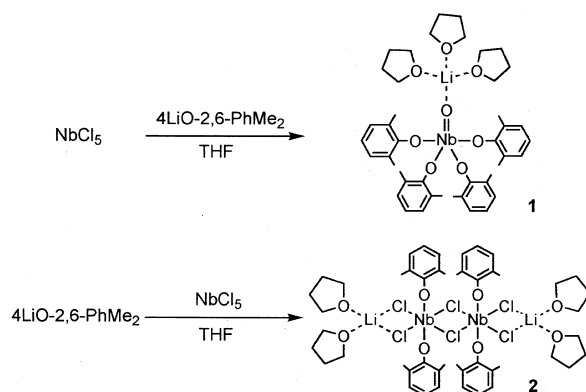
#### 3.1. Synthesis and characterization

The metathesis reactions of niobium chloride,  $\text{NbCl}_5$ , with lithium-2,6-dimethylphenoxide,  $\text{LiO}-2,6\text{-PhMe}_2$ , were investigated in THF at room temperature. Complexes of formula  $\text{LiNbO}(\text{O}-2,6\text{-PhMe}_2)_4 \cdot 3\text{THF}$  (**1**) and  $[\text{LiNbCl}_3(\text{O}-2,6\text{-PhMe}_2)_2 \cdot 2\text{THF}]_2$  (**2**) were obtained (Scheme 1). Complex **1** was prepared by adding a THF solution of  $\text{NbCl}_5$  to a THF solution of 4 equiv.  $\text{LiO}-2,6\text{-PhMe}_2$  with 72% yield. Complex **1** was formed irrespective of the ligand-to-metal molar ratio,  $R$ , used (from 4 to 6) and was obtained in the same yield for each ratio. The formation of a terminal oxo ligand in situ may result from the abstraction of the oxygen atom from THF by  $\text{NbCl}_5$  at the initial stage of the reaction [14,23,29,30]. However, the direct reaction between  $\text{NbOCl}_3 \cdot 2\text{CH}_3\text{CN}$  and 4 equiv.  $\text{LiO}-2,6\text{-PhMe}_2$  did not seem to be a useful route to complex **1**. On the other hand, the addition of a THF solution of 4 equiv.  $\text{LiO}-2,6\text{-PhMe}_2$  to  $\text{NbCl}_5$  led to the formation of complex **2**. The reaction of  $\text{NbCl}_5$  with  $\text{Li}-2,6\text{-OPhMe}_2$  in 1:2–1:6 molar ratio was carried out. An amount of complex **2** was obtained with the formation of a niobium chloro-aryloxide,  $\text{NbCl}_x(\text{OR})_{5-x}$ , as the major product. The maximum yield of complex **2** was  $> 10\%$  at  $R=4$ . Complexes **1** and **2** were characterized by spectroscopic and analytical techniques.

The FT-IR spectra exhibit stretching modes from  $\nu(\text{C}-\text{O}-\text{C})$  of the coordinated THF molecules at 1048 (m) and 880 (s)  $\text{cm}^{-1}$  for complex **1** and at 1044 (m) and 891 (s)  $\text{cm}^{-1}$  for complex **2** and a sharp band at 918 (m)  $\text{cm}^{-1}$  for complex **1** from  $\nu(\text{Nb}=\text{O})$  which is shifted to lower frequencies compared to  $\nu(\text{Nb}=\text{O})$ , 962  $\text{cm}^{-1}$  of the  $[\text{NbOCl}_4(\text{THF})]^-$  anion [31]. The bands at 566 (m) and 546 (m)  $\text{cm}^{-1}$  in complex **1** and at 571 (m)  $\text{cm}^{-1}$  in complex **2** are assigned to  $\nu(\text{Nb}-\text{O})$  vibrations from aryloxo ligands [32]. In the  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra of complex **2** in  $\text{CD}_3\text{OD}$ , the resonance signals corresponding to only one type of 2,6-dimethylphenoxy ligand and coordinated THF molecules are observed at room temperature, while those of complex **1** in  $\text{CDCl}_3$  show two types of peaks for 2,6-dimethylphenoxy ligands. The presence of two types of signals suggests magnetically non-equivalent surroundings for 2,6-dimethylphenoxy ligands.

#### 3.2. Molecular structures of $\text{LiNbO}(\text{O}-2,6\text{-PhMe}_2)_4 \cdot 3\text{THF}$ and of $[\text{LiNbCl}_3(\text{O}-2,6\text{-PhMe}_2)_2 \cdot 2\text{THF}]_2$

To establish the solid state structures, X-ray single crystal diffraction analyses of complexes **1** and **2** were used. The ORTEP diagrams of complexes **1** and **2** are presented in Figs. 1 and 2, respectively.



Scheme 1. Syntheses of lithium niobium oxo-aryloxides and chloro-aryloxides.

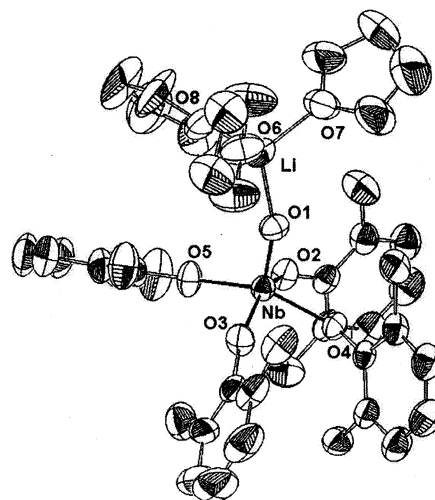


Fig. 1. ORTEP diagram of complex **1** in the solid state. The hydrogen atoms are omitted for clarity.

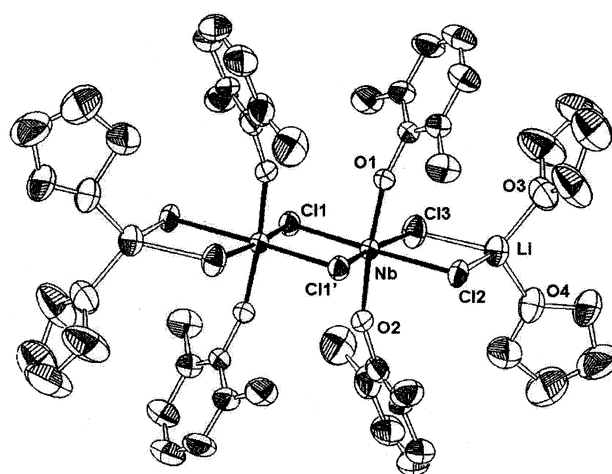


Fig. 2. ORTEP diagram of complex **2** in the solid state. The hydrogen atoms are omitted for clarity.

Complex **1** exists as a monomeric binuclear complex (Fig. 1). Selected bond lengths and angles are given in Table 2. The structure of complex **1** can be described as  $[\text{NbO}(\text{O}-2,6\text{-PhMe}_2)_4]^-$  capped by an  $\text{Li}^+$  cation which is solvated with three THF molecules. The molecular structure of com-

Table 2  
Selected bond lengths (Å) and angles (°) for  $\text{LiNbO}(\text{O}-2,6\text{-PhMe}_2)_4 \cdot 3\text{THF}$

Nb–O1	1.730(5)	Li–O1	1.88(2)
Nb–O2	1.948(4)	Li–O6	1.95(2)
Nb–O3	1.940(5)	Li–O7	1.96(2)
Nb–O4	1.985(4)	Li–O8	1.90(2)
Nb–O5	1.922(5)		
O1–Nb–O2	106.8(2)	O1–Li–O6	109.3(8)
O1–Nb–O3	103.2(2)	O1–Li–O7	112.5(8)
O1–Nb–O4	103.1(2)	O1–Li–O8	112.1(9)
O1–Nb–O5	101.5(2)	O6–Li–O7	106.3(9)
O2–Nb–O4	82.8(2)	O6–Li–O8	110.8(8)
O2–Nb–O5	87.3(2)	O7–Li–O8	105.6(8)
O3–Nb–O4	86.6(2)	C1–O2–Nb	144.6(4)
O3–Nb–O5	90.7(2)	C9–O3–Nb	158.0(6)
O2–Nb–O3	149.7(2)	C17–O4–Nb	138.7(4)
O4–Nb–O5	155.2(2)	C25–O5–Nb	169.9(5)
Nb–O1–Li	154.0(6)		

plex **1** includes niobium square pyramid and lithium tetrahedron units sharing a corner corresponding to the oxo ligand ( $\text{Li}-\text{O}1=\text{Nb}$   $154.0(6)^\circ$ ). The niobium is five-coordinated by a terminal oxo ligand in an axial position and four 2,6-dimethylphenoxy ligands in the basal plane of the square pyramid. The lithium is four-coordinated by three oxygen atoms of THF molecules and the terminal oxo ligand in the  $[\text{NbO}(\text{O}-2,6\text{-PhMe}_2)_4]^-$  unit. The steric hindrance of the 2,6-dimethylphenoxy ligands stabilizes a low coordination number, with a terminal  $\text{Nb}=\text{O}$  bond [12,13,23].

The square pyramidal geometry around the niobium metal is severely distorted ( $\text{O}-\text{Nb}=\text{O}$  angles ranging from  $101.5(2)$  to  $106.8(2)^\circ$ , *cis*  $\text{O}-\text{Nb}-\text{O}$  angles ranging from  $82.8(2)$  to  $90.7(2)^\circ$ , and *trans*  $\text{O}-\text{Nb}-\text{O}$  angles ranging from  $149.7(2)$  to  $155.2(2)^\circ$ ), while the lithium tetrahedron is quite regular ( $\text{O}-\text{Li}-\text{O}$  angles ranging from  $105.6(8)$  to  $112.5(8)^\circ$ ). The average  $\text{Nb}-\text{O}$  bond length of  $1.949$  Å is significantly longer than those in analogous compounds such as  $[\text{LiNb}(\text{OEt})_6]_x$  ( $1.88$  Å) [16],  $[\text{LiNb}(\text{OCH}_2\text{SiMe}_3)_6]_2$  ( $1.893$  Å) [18], and  $\text{Nb}(\text{O}-2,6\text{-PhMe}_2)_5$  ( $1.899$  Å) [25]. This is probably due to the formation of a double bond between niobium and the terminal oxygen in axial position, which results in the elongation of  $\text{Nb}-\text{O}$  bonds in *trans* positions. Interestingly, the four 2,6-dimethylphenoxy ligands in complex **1** are not identical. The bond distance  $\text{Nb}-\text{O}5$  ( $1.922(5)$  Å) is shorter than those of the other  $\text{Nb}-\text{O}$  bonds in complex **1**. It can be assumed that the partial  $\pi$  interaction between the d orbital of niobium and p orbital of oxygen in  $\text{Nb}-\text{O}5$  might cause the strong bond. The nearly linear  $\text{Nb}-\text{O}5-\text{C}25$  angle ( $169.9(5)^\circ$ ) supports this assumption. In addition, the  $\text{Nb}=\text{O}1$  bond length ( $1.730(5)$  Å) is longer than those in the following complexes:  $1.710$  Å in  $[\text{NbO}(\text{SPh})_4]^-$  [33],  $1.699$  Å in  $\text{NbO}(\text{N}(\text{SiMe}_3)_2)_3$  [30], and  $1.67$ – $1.71$  Å in six-coordinated oxo niobium complexes [34]. This probably results from the interaction between the terminal oxo ligand and lithium ion that makes the  $\text{Nb}=\text{O}$  bond relatively weaker.

Complex **2** exists as a dimeric tetranuclear complex (Fig. 2). Selected bond lengths and angles are given in Table 3. The center of the dimeric molecule is located on the crystallographic inversion center. The molecular structure of complex **2** can be described as niobium octahedra and lithium tetrahedra which are linearly connected by  $\mu_2$ -chloride linkages along the  $\text{Li}-\text{Nb}-\text{Nb}-\text{Li}$  axis. The niobium is six-coordinated by four  $\mu_2$ -chloride ligands and two 2,6-dimethylphenoxy ligands in *trans* positions. The lithium is four-coordinated by two  $\mu_2$ -chloride ligands and two oxygen atoms of THF molecules.

The coordination environments of niobium and lithium are quite distorted (*cis*  $\text{X}-\text{Nb}-\text{X}$  ( $\text{X}=\text{O}$  or  $\text{Cl}$ ) angles ranging from  $83.62(4)$  to  $104.01(3)^\circ$  and  $\text{X}-\text{Li}-\text{X}$  angles ranging from  $90.3(3)$  to  $117.8(5)^\circ$ ). The average  $\text{Nb}-\text{O}$  bond length,  $1.888$  Å, is similar to those in previously known compounds but shorter than those in complex **1** by  $0.06$  Å [16,18,25]. The decrease in  $\text{Nb}-\text{O}$  bond length of complex **2** can be explained by the absence of an  $\text{Nb}=\text{O}$  bond. The average  $\text{Nb}-\mu_2\text{-Cl}$  bond length,  $2.484$  Å, is significantly longer than those in chloride derivatives of niobium, probably as a consequence of interaction between the bridging chloride ligand and the lithium counter ion [14,27–29,31,34–36].

Complex **1** is the first monomeric lithium niobium(V) oxo aryloxide and complex **2** is also the first dimeric lithium niobium(IV) chloro aryloxide. Complex **1** is expected to act as a potential precursor for the fabrication of  $\text{LiNbO}_3$  owing to its solubility in a variety of organic solvents and reduced sensitivity to hydrolytic processes [2]. In addition, complex **2** is an invaluable intermediate to interpret the formation of heterometallic alkoxides in organometallic chemistry. Further study will verify more detailed reaction mechanisms and reactivities of complexes **1** and **2**. In a preliminary study,

Table 3  
Selected bond lengths (Å) and angles (°) for  $[\text{LiNbCl}_3(\text{O}-2,6\text{-PhMe}_2)_2 \cdot 2\text{THF}]_2$

Nb–O1	1.887(3)	Nb–Nb'	3.0360(8)
Nb–O2	1.888(3)	Nb'–Cl1	2.4690(12)
Nb–Cl1	2.4626(11)	Li–Cl2	2.364(10)
Nb–Cl1'	2.4690(12)	Li–Cl3	2.358(10)
Nb–Cl2	2.5095(12)	Li–O3	1.905(11)
Nb–Cl3	2.5117(13)	Li–O4	1.896(11)
O1–Nb–Cl1	93.19(9)		
O1–Nb–Cl1'	89.65(9)		
O1–Nb–Cl2	87.91(9)	Nb–Cl1–Nb'	75.99(3)
O1–Nb–Cl3	88.74(9)	Nb–Cl2–Li	92.9(2)
O2–Nb–Cl1	92.55(10)	Nb–Cl3–Li	93.0(3)
O2–Nb–Cl1'	90.96(10)	Cl2–Li–Cl3	90.3(3)
O2–Nb–Cl2	86.05(10)	O3–Li–Cl2	108.5(5)
O2–Nb–Cl3	89.73(10)	O3–Li–Cl3	117.8(5)
Cl1–Nb–Cl1'	104.01(3)	O4–Li–Cl2	117.5(5)
Cl1–Nb–Cl3	84.77(4)	O4–Li–Cl3	113.1(5)
Cl2–Nb–Cl1'	87.63(4)	O3–Li–O4	108.9(5)
Cl2–Nb–Cl3	83.62(4)	C1–O1–Nb	163.4(3)
O1–Nb–O2	173.90(12)	C9–O2–Nb	157.1(3)
Cl1–Nb–Cl2	168.31(4)		
Cl3–Nb–Cl1'	171.15(4)		

complex **1** yields pure LiNbO<sub>3</sub> powder after heat treatment at 600°C in air. We are continuing the investigation into the application of complex **1** as a molecular precursor for fabrication of LiNbO<sub>3</sub>.

### Supplementary data

Supplementary data are available from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-223-336033; e-mail: deposit@ccdc.cam.ac.uk) on request, quoting the deposition numbers CCDC 130855 for structure **1** and 136586 for structure **2**.

### Acknowledgements

This work has been generously supported by grants from the Korea Science and Engineering Foundation (KOSEF-97K3-0603-02-05-3) through the Ceramic Processing Research Center at Hanyang University.

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