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Communication

A Decanuclear Lithium Niobium(V) Heterometallic Oxo Phenoxide Complex : The Synthesis and Structural Characterization of $[Li_6Nb_4O_6(OPh)_{14}(THF)_6]LL'$(THF = tetrahydrofuran, L = 1/2hexane, L = 1/2H_2O)

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Recently, the use of transition metal alkoxides as molecular precursors for high-tech ceramic materials has resulted in an intense activity in the field of coordination chemistry.[1] The sol-gel process for hydrolytic condensation has been used for many years as a low-temperature method for conversion of transition metal alkoxides to metal oxides.[2] Although there are many examples of the use of this process for the synthesis of metal oxides,[3] the chemistry involved in this process is very little known.

Increasing interest has been devoted to the study of transition metal oxo alkoxo clusters.[4] The coordination compounds play an important role in understanding and characterizing transition metal oxo based materials prepared by sol-gel process.[2a,5a] Numerous metal oxo alkoxide clusters (metal = Si, Ti, Zr, etc.) synthesized through hydrolysis and condensation reactions have received much attention and have been structurally characterized.[5] In contrast, much less work have been devoted to niobium oxo alkoxide complexes. Particularly, structural information of heterometallic niobium oxo alkoxides remains scarce. Since octanuclear compound, $Nb_8O_{10}(OEt)_{20}$,[6] was first obtained through controlled hydrolysis of niobium ethoxide, and its structure was resolved by single crystal X-ray diffraction analysis, the tetranuclear complex, $[Li_2Nb_2O_2(OEt)_8] \cdot 2EtOH$,[7] as an intermediate in a hydrolysis reaction to $[LiNb(OEt)_6]_x$,[8] and the decanulcear complex, $Pb_6Nb_4O_4(OEt)_{24}$,[9] have been reported. Recently, tetranuclear compounds capped by chelating ligands, $Nb_4O_4(OAc)_4(O^iPr)_8$[10] and $Nb_4O_4(Mc)_4(O^iPr)_8$ (Mc = $O_2CCMeCH_2$),[11] have been prepared and characterized.

In this communication, we report the synthesis and structural characterization of the novel decanuclear lithium niobium(V) oxo-aryloxide complex, $[Li_6Nb_4O_6(OPh)_{14}(THF)_6]LL'$ (THF = tetrahydrofuran, L = 1/2hexane, L′ = 1/2H_2O), which may be an intermediate in hydrolysis and/or condensation reactions of lithium niobium phenoxide.

The synthesis of $[Li_6Nb_4O_6(OPh)_{14}(THF)_6]LL'$ was accomplished by the methathesis reaction of niobium chloride, $NbCl_5$, with lithium phenoxide, LiOPh, in THF (eq. 1). At room temperature under N_2 atmosphere, THF solution (50 mL) of $NbCl_5$ (2 g, 7.4 mmol) was added dropwise to THF solution (50 mL) of 6 equivalent LiOPh (4.45 g, 44.4 mmol), and the reaction mixture was stirred for 24 h. After the yellow solution was concentrated to half volume and ether (150 mL) was added, the resultant mixture was filtered to eliminate LiCl. The filtrate was then concentrated to half volume, layered with n-hexane, and the yellow crystals of $[Li_6Nb_4O_6(OPh)_{14}(THF)_6]LL'$ was obtained in > 60% yield.

$$\text{(4-6 eq.)LiOPh} + NbCl_5 \rightarrow [Li_6Nb_4O_6(OPh)_{14}(THF)_6]LL' \quad \text{(RT, in THF)} \qquad (1)$$

The molecular structure of $[Li_6Nb_4O_6(OPh)_{14}(THF)_6]LL'$ was determined by X-ray single crystal diffraction analysis.[12] The spectroscopic analyses of these compounds supported the crystal structure.[13] The ORTEP diagram and schematic view of the structure of $[Li_6Nb_4O_6(OPh)_{14}(THF)_6]LL'$ are shown in Figures 1 and 2, respectively, which reveals that this compound exists as a decanuclear cluster with oxo bridging units.

The selected bond distances and angles of $[Li_6Nb_4O_6(OPh)_{14}(THF)_6]LL'$ are given in Table 1.

The $[Li_6Nb_4O_6(OPh)_{14}(THF)_6]LL'$ exists as a tetrameric decanuclear complex occupying a special position on the two-fold symmetry axis. The molecular structure of the decanuclear species $[Li_6Nb_4O_6(OPh)_{14}(THF)_6]LL'$ includes

the tetrahedron of the central core consisting of $Nb_4(\mu_2\text{-}O)_4(\mu_4\text{-}O)_2$ unit and the cubes of the side consisting of $NbLi_3(\mu_3\text{-}O)_3(\mu_4\text{-}O)$ units. The tetrahedron and cubes are linked by a μ_4-oxo ligand, two μ_2-OPh ligands, and two μ_3-OPh ligands, with sharing the edges mutually. The tetrahedron contains four niobium octahedra and the cubes contain a niobium octahedron and three lithium atoms in its alternating vertices. The niobium atoms are coordinated by three oxo ligands (μ_2-O and μ_4-O bridging) and three OPh ligands (terminal, μ_2-O, and/or μ_3-O bridging). The lithium atoms are of two structually independent types: one is four-coordinated by three μ_3-OPh ligands and a THF ligand, the other five-coordinated by a μ_4-oxo ligand, a μ_2-OPh ligand, two μ_3-OPh ligands, and a THF ligand.

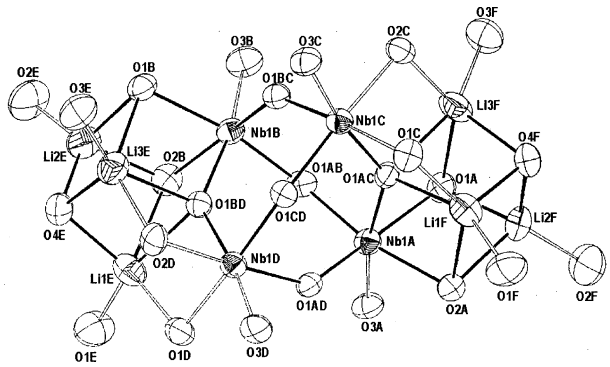

Figure 1. ORTEP diagram of $[Li_6Nb_4O_6(OPh)_{14}(THF)_6]LL'$ in the solid state. The hydrogen atoms and the carbon atoms in ligands are omitted for clarity.

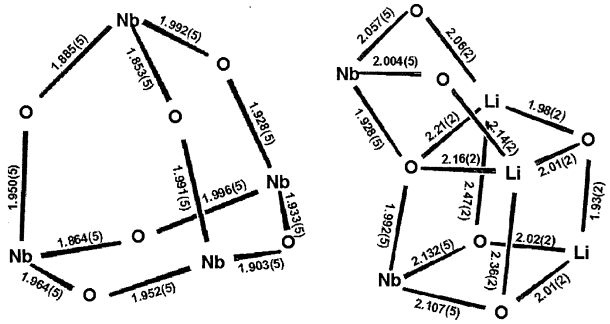

Figure 2. Schematic view of the structure of $Li_6Nb_4(\mu_2\text{-}O)_8(\mu_3\text{-}O)_6(\mu_4\text{-}O)_2$ (a) Tetrahedral central core of $Nb_4(\mu_2\text{-}O)_4(\mu_4\text{-}O)_2$ unit, (b) Cubic side of $NbLi_3(\mu_3\text{-}O)_3(\mu_4\text{-}O)$ unit.

The oxygen environments of the various metal atoms are significantly distorted: octahedron for the niobium atom, trigonal-bipyramid and tetrahedron for the lithium atom. Each octahedron exhibits Nb-O bond distances from 1.853(5) to 2.136(5) Å, cis O-Nb-O bond angles from 79.8(2) to 98.6(2)°, and trans O-Nb-O bond angles from 168.4(2) to 173.9(2)°. The Nb-OPh bond distances are close to those of previously known complexes[8,14] (1.88-1.90 Å in terminal bonds and 1.98-2.05 Å in bridging bonds) with the following pattern, terminal-OPh < μ_2-OPh < μ_3-OPh, but the Nb-μ_2-O and Nb-μ_4-O bond distances are significantly increased compared with those of the other structurally characterized complexes (1.81-1.85 Å).[6,10,11] It should be emphasized that the Nb-O bond distances in this complex are practically independent of the bond character of oxo group (μ_4-O or μ_2-O bridging).[15] The large deviations of cis O-Nb-O bond angles are similar to those in $Nb_4O_4(OAc)_4(O^iPr)_8$[10] (from 79.7 to 100.6°), while the trans O-Nb-O bond angles exhibit very small difference in their values. The differences between the cis O-Nb-O bond angles and the reduction in the trans O-Nb-O bond angles presumably result from the geometric constraints of $Nb_4(\mu_2\text{-}O)_4(\mu_4\text{-}O)_2$ core.[10] The structure of $NbLi_3(\mu_3\text{-}O)_3(\mu_4\text{-}O)$ corresponding to three lithium atoms is analogous to opened cube observed previously for $[LiTi(O^iPr)_5]_2$.[16] The coordination environments of lithium atoms could be described as severely distorted trigonal-bipyramid with Li-O bond distances from 1.92(2) to 2.47(2) Å and O-Li-O bond angles from 69.0(5) to 159.6(10)° and tetrahedron with Li-O bond distances from 1.90(2) to 2.04(2) Å and O-Li-O bond angles from 84.5(6) to 127.6(9)°.

The oxo units were generated during the substitution of LiOPh into niobium center, which compose central tetrahedral $Nb_4(\mu_2\text{-}O)_4(\mu_4\text{-}O)_2$ core. The formation of bridging oxo ligands in situ might results from side reaction of $NbCl_5$ with THF at initial stage of reaction or induction by trace amounts of water.[17] It is also surprising that the extra LiOPh bearing cubic structure exists in $NbLi_3(\mu_3\text{-}O)_3(\mu_4\text{-}O)$ unit. The existence of extra LiOPh introduces the five coordination geometry of lithium in spite of the small atomic size.[18]

Table 1. Selected Bond Distances (Å) and Angles (deg) for $[Li_6Nb_4O_6(OPh)_{14}(THF)_6]LL'$

Distances					
Bond Types	Averages	Ranges	Bond Types	Averages	Ranges
Nb-OPh	1.902	1.891(5)-1.919(5)			
Nb-(μ_2-O)Ph	2.032	2.004(5)-2.057(5)	Li-OPh	2.10	1.90(2)-2.47(2)
Nb-(μ_3-O)Ph	2.121	2.107(5)-2.136(5)	Li-O	2.16	2.12(2)-2.21(2)
Nb-(μ_2-O)	1.922	1.853(5)-1.996(5)	Li-O (THF)	1.94	1.91(2)-1.95(2)
Nb-(μ_4-O)	1.959	1.928(5)-1.992(5)			
Angles					
O-Nb-O (cis)	89.9	79.8(2)-98.6(2)	O-Li-O	105.5	69.0(5)-159.6(10)
O-Nb-O (trans)	170.7	168.4(2)-173.9(2)	Nb-O-Li	101.0	95.8(5)-112.4(5)
Nb-O-Nb	140.4	137.9(3)-144.1(3)	Li-O-Li	86.4	77.8(7)-93.2(8)

The five-coordinated lithium has never been reported in lithium niobium complexes.

The structure adopted by $[Li_6Nb_4O_6(OPh)_{14}(THF)_6]LL'$ in the solution state was investigated using NMR spectroscopy. The ^{13}C NMR spectra show resonances for two coordination types of OPh groups attributed to the bridging and the terminal OPh ligands of the niobium octahedra as well as THF molecules coordinated to lithium at room temperature. The ^1H NMR spectra also reveal multiplet resonances for two types of OPh groups in agreement with the ^{13}C NMR spectra. In FT-IR spectra of this complex, the presence of a broad band at 590cm^{-1} is assigned to vibration of a oxo ligands (μ_2-O and μ_4-O bridging) and the doublet bands at 638 and 621 cm^{-1} are also attributed to OPh ligands (terminal, μ_2-O, and μ_3-O bridging), which is significantly shifted compared to those of neutral niobium compounds.[19]

Lithium niobium oxo phenoxide, $[Li_6Nb_4O_6(OPh)_{14}(THF)_6]$ LL′, represents the first example of an oxo aryloxide adduct. Due to its compact structure connected by bridging oxo ligands, this compound could be strongly favoured precursor for the preparation of lithium niobate, $LiNbO_3$, in the respect of ceramic yield and hydrolysis control. Further studies will verify a more detailed reaction mechanism, reactivity in solution, and behaviour towards hydrolysis of this complex.

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12. Crystal and refinement data: Yellow crystal of $[Li_6Nb_4O_6(OPh)_{14}(THF)_6] \cdot 1/2$hexane $\cdot 1/2H_2O$ is monoclinic, space group $P2_1/c$ with a = 26.796(6) Å, b = 15.404(4) Å, c = 28.217(6) Å, β = 94.640(10)°, and Z = 4. Single X-ray diffraction data for the crystal was collected on Bruker P4 four circle diffractometer using Mo-Kα radiation (λ = 0.71073 Å). The solution of the structure was carried out by a combination of heavy atom Patterson techniques, direct methods, and Fourier techniques. The refinement of the structure by full matrix least squares methods was based on 14945 unique reflections (2θ = 45, I > 2σ). Anisotropic temperature factors were used for all non-hydrogen. At the current stage of refinement on 1334 parameters with all atoms present in the asymmetric units, R = 0.0638, Rw = 0.1644.
13. Spectroscopic data for $[Li_6Nb_4O_6(OPh)_{14}(THF)_6] \cdot 1/2$ hexane $\cdot 1/2H_2O$: FT-IR (cm^{-1}; KBr) ν = 3060 (w), 3029 (w), 3010 (w), 2955 (w, br), 2873 (w), 1592 (m), 1483 (s), 1448 (w), 1371 (w), 1270 (m), 1243 (m), 1161 (w), 1068 (w), 1040 (w), 1020 (w), 996 (w), 893 (w), 851 (w), 827 (w), 757 (s, br), 691 (m), 638 (w), 621 (w), 590 (m, br), 498 (w): ^1H NMR (300 MHz, C_6D_6, 25 °C) δ = 7.53-6.59 (m, 70H, OC_6H_5), δ = 4.60 (s, 1H, H_2O), δ = 3.52 (t, 24H, OCH_2CH_2), δ = 1.33 (q, 24H, OCH_2CH_2), δ = 1.25 (s, 4H, hexane), δ = 0.89 (t, 3H, hexane): ^{13}C NMR (300 MHz, C_6D_6, 25 °C) δ = 163.6, 161.9 (ipso-C_6H_5), δ = 129.8, 129.2, 128.6, 128.2 (o-C_6H_5), δ = 121.4, 120.9, 120.5, 119.9 (m-C_6H_5), δ = 117.6 (p-C_6H_5), δ = 70.8, 68.1 (OCH_2CH_2), δ = 27.0, 25.0 (OCH_2CH_2), δ = 31.8, 22.9, 14.2 (hexane): Anal. calcd. for $C_{111}H_{126}O_{26.5}Li_6Nb_4$: C 58.03, H 5.53; found: C 58.19, H 5.17.
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