Supplementary Material Available: Tables S1-S5 and S78, listing fractional atomic coordinates for non-hydrogen atoms, bond lengths, bond angles, anisotropic temperature factors for all non-hydrogen atoms, calculated atomic positions for hydrogen atoms, and crystallographic experimental conditions (9 pages); Table S6, listing observed and calculated structure factors (18 pages). Ordering information is given on any current masthead page.

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Crystal Structure of $LiNb(OCH_2CH_3)_6$: A Precursor for Lithium Niobate Ceramics

Metal alkoxide complexes have received renewed attention as precursors for metal oxides.[1] A recent application toward ceramic materials, "sol-gel" processing, uses the tendency of metal alkoxides to form polymeric structures upon hydrolysis.[2] Heat treatment of the resultant polymeric structures typically yields amorphous oxides that can be crystallized at higher temperatures.[3] An important example of sol-gel processing is the fabrication of lithium niobate, $LiNbO_3$, ceramics for applications such as optical modulation.[4] However, homogeneous material is a prerequisite in these applications, to eliminate variations in refractive index and electrical properties. Therefore, sol-gel processing has been investigated as a means of producing high-purity homogeneous material of the desired stoichiometric composition. The crystal structure of heterometallic alkoxides may be of particular interest to materials chemists investigating the evolution of molecular structure during sol-gel processing of metal oxides.

In this paper we report the crystal structure of lithium niobium ethoxide, $LiNb(OCH_2CH_3)_6$, which as been used in the preparation of lithium niobate.[5] Mehrotra has previously reported that the reaction of niobium and lithium alkoxides resulted in isolation of white powders corresponding to $LiNb(OR)_6$.[6] We have recently presented further *spectroscopic* evidence for the formation, in solution, of the heterometallic alkoxide lithium niobium ethoxide.[7] However, prior to this report, the *solid-state* structure of lithium niobium ethoxide had not been elucidated.

Equimolar quantities of lithium ethoxide[8] and niobium ethoxide[9] were reacted under reflux in a dry dinitrogen atmosphere for 24 h to give a solution of approximately 0.25 M concentration. Crystals were obtained at room temperature when the ethanolic solution was concentrated to approximately 1 M. The crystals thus obtained were transparent and 2-5 mm in length and were the subject of our crystallographic study.[10]

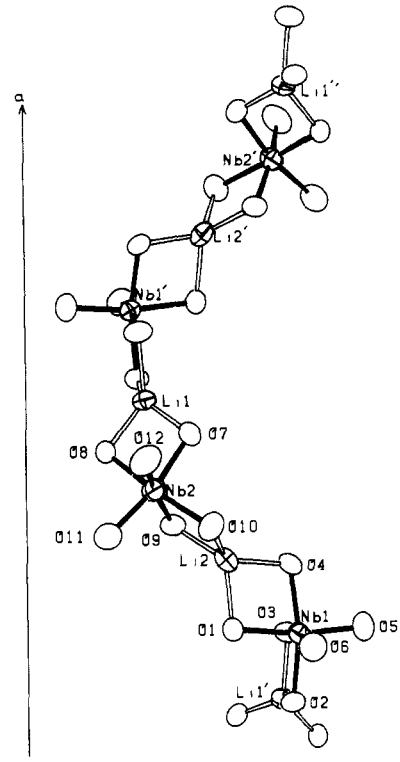

Figure 1. Thermal ellipsoid (35% probability) perspective view normal to the *a* axis, showing one translational unit (ORTEP-II). Carbon atoms were omitted for clarity.

The crystallographic asymmetric unit contains two independent Li atoms and two independent Nb complexes forming infinite helical $LiNb(OCH_2CH_3)_6$ polymers composed of alternating $Nb(OCH_2CH_3)_6$ octahedra cis-linked by (severely distorted) tetrahedral Li atoms. One cis pair of ethoxide ligands is terminal, while the remaining ligands form bis(μ-O) bridges with two Li atoms to generate the polymer (Figure 1). The centrosymmetric unit cell consists of alternating right- and left-handed helical polymers parallel to the *a* axis. There are no intermolecular

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(3) See, for example: Schwartz, R. W. Ph.D. Thesis, University of Illinois at Urbana-Champaign, 1989. Klein, L. C. *Sol-Gel Technology for Thin Films, Fibers, Preforms, Electronic and Specialty Shapes*; Noyes Publications: Park Ridge, NJ, 1988.
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(7) Eichorst, D. J.; Howard, K. E.; Payne, D. A. In *Proceedings of Fourth International Conference on Ultrastructure Processing of Ceramics, Glasses and Composites*; Uhlmann, D. R., Weinberg, M. C., Risbud, S. H., Ulrich, D. R., Eds.; J. Wiley: New York, in press.
(8) Lithium metal (0.347 g, 0.050 mol) was added under N_2 to dry ethanol (100 mL, dried and distilled from magnesium) and stirred until all of the metal had been consumed.
(9) $Nb(OCH_2CH_3)_5$ was prepared according to: Bradley, D. C.; Chakravarti, B. N.; Wardlaw, W. *J. Chem. Soc.* **1956**, 2381. It was purified by successive crystallizations and vacuum distillation. A total of 15.91 g of $Nb(OCH_2CH_3)_5$ was added to 100 mL of dried absolute ethanol.
(10) Crystal data for $LiNb(OCH_2CH_3)_6$: transparent, colorless, equidimensional crystal, 0.3 × 0.3 × 0.4 mm, orthorhombic, space group *Pbca*, a = 17.704 (4) Å, b = 19.736 (5) Å, c = 21.267 (8) Å, V = 7431 (6) Å^3, ρ_{calc} = 1.324 g/cm^3, Z = 16, 198 K. Diffraction data: Enraf-Nonius CAD4 automated κ-axis diffractometer, monochromated Mo radiation ($\lambda(K\bar{\alpha})$ = 0.710 73 Å), range $2 < 2\theta < 46°$ ($+h,+k,+l$) and $2 < 2\theta < 8$ ($\pm h,\pm k,\pm l$), 6054 reflections (5154 unique, R_i = 0.020, 2200 observed, $I > 2.58\sigma(I)$); corrected for anomalous dispersion, Lorentz, and polarization effects but not for absorption (μ = 6.35 cm^{-1}). Solution: Patterson methods (SHELXS-86) located Nb atoms, difference Fourier syntheses gave positions for remaining non-hydrogen atoms (severely disordered alkyl groups). Refinement: (SHELX-76) H atom contributions ignored, normalized site occupancy factors for each ethyl group, common variables for C-O (1.47 Å) and C-C (1.50 Å) bond lengths, a common isotropic thermal parameter for carbon atoms, anisotropic thermal coefficients for non-carbon atoms. Final results: difference Fourier map (range $0.50 > e/Å^+ > -0.54$) located maximum residual electron density in vicinity of ethyl carbon atoms; variance between observed and calculated structure factors depended (slightly) on $\sin\theta$; agreement factors, R = 0.062 and R_w = 0.074.

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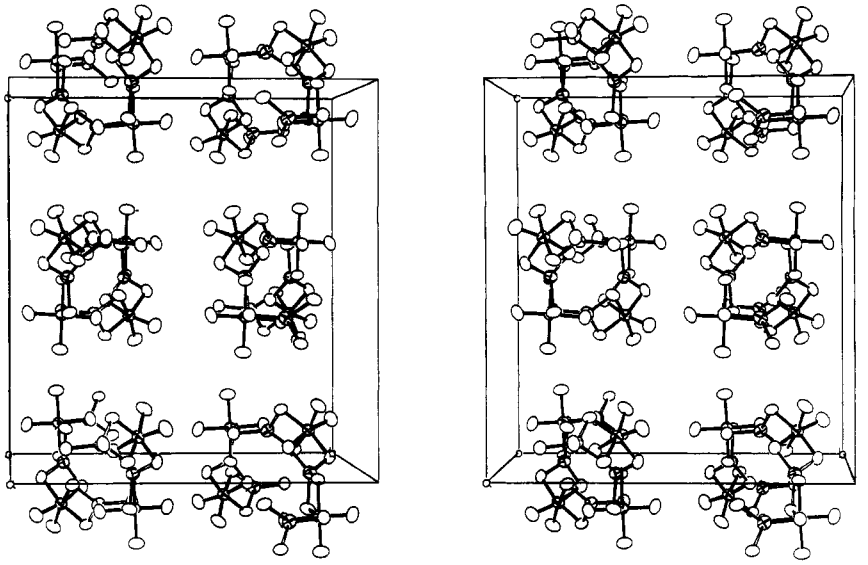

Figure 2. Perspective view (35% probability ellipsoids) parallel to the *a* axis, showing the unit cell packing (ORTEP-II). Carbon atoms were omitted for clarity.

interactions between adjacent polymer chains (Figure 2). The average Nb–O(bridging) bond length, 1.98 (1) Å, is significantly longer than the Nb–O(terminal) bond length, 1.88 (2) Å; the average Li–O bond length is 1.94 (3) Å. For the bis(μ-O) bridge, average angles are 77.8 (8), 80 (1), and 101.0 (8)° for O–Nb–O, O–Li–O, and Nb–O–Li, respectively. The most striking difference between crystallographically independent environments is the orientation of the two Nb octahedra with respect to the polymer axis. The plane containing Nb(1), O(5), and O(6) makes a dihedral angle of 4° with the *b,c* crystal plane, whereas the corresponding plane containing Nb(2), O(11), and O(12) exhibits a dihedral angle of 59°.

The crystal structure demonstrates the required Li/Nb atomic ratio for synthesis of stoichiometric lithium niobate. Successive crystallization of the precursor allows removal of impurities that contribute to optical loss. Furthermore, the polymeric nature may be beneficial for fiber production. In summary, alkoxide processing of lithium niobate allows preparation of high-quality material and may allow new processing possibilities.

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Supplementary Material Available: A complete ORTEP figure and tables of atomic coordinates, thermal parameters, and internuclear distances and angles (10 pages). Ordering information is given on any current masthead page.

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