Metrical Comparison and Alkali Metal NMR Spectroscopic Investigation of a Congener Set of Alkali Metalated Titanium(IV) Isopropoxides: X-ray Structures of $[NaTi(OCHMe_2)_5]_\infty$ and $[KTi(OCHMe_2)_5]_\infty$

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The congeners of the alkali metal substituted titanium isopropoxide compound, $[LiTi(OCHMe_2)_5]_2$ (**1**) have been identified as $[NaTi(OCHMe_2)_5]_\infty$ (**2**) and $[KTi(OCHMe_2)_5]_\infty$ (**3**). Both **2** and **3** are polymeric species, wherein the alkali metal acts as a bridge between discrete, mononuclear, trigonal-bipyramidal, titanium pentaisopropoxide moieties. The infinite linear chains formed in **2** consist of alternating five coordinate titanium moieties and tetrahedral sodium atoms. Compound **3** forms a nonlinear continuous chain with the potassium atoms in an *extremely* distorted trigonal-bipyramidal geometry. A comparison of the metrical data of **1**–**3** and literature data reveals that the bond distances and angles of **1**–**3** agree with expected values. Compound **2** crystallized from pentane at −25 °C in the space group $P2_1/a$ with $a = 12.616(1)$ Å, $b = 10.078(4)$ Å, $c = 17.573(4)$ Å, and $\beta = 103.20°$, for $Z = 4$. Least squares refinement of the model based on 3801 reflections ($|F_o| > 3.0\sigma(|F_o|)$) converged to a final $R_F = 8.57\%$. Crystals of **3** formed in the space group $P2_1/n$ with $a = 12.213(2)$ Å, $b = 9.792(2)$ Å, $c = 18.442(3)$ Å, and $\beta = 106.944(12)°$, for $Z = 4$. Least squares refinement of the model based on 3083 reflections ($|F_o| > 3.0\sigma(|F_o|)$) converged to a final $R_F = 4.2\%$. Alkali metal (^7Li, ^{23}Na) NMR spectroscopy data reveal that, in solution, **1** exists as a dimer with rapid alkoxide ligand exchange, whereas, for **2**, a tight ion pair exists between Na^+ and the $Ti(OCHMe_2)_5^-$.

Introduction

Metal alkoxide compounds are often used in the so-called hydrolysis "sol–gel" process as molecular precursors to metal oxides.[1–7] In general, this method involves three basic steps: (1) generation of an appropriate precursor solution (prehydrolysis may be initiated), (2) deposition of the solution onto a substrate followed by hydrolysis (due to ambient humidity) and condensation of the deposited film, and (3) thermal treatment to complete the conversion of these metalloorganic precursors to the desired metal oxide phase.[4] The ceramic materials produced by this method are employed in several areas of technology,[2–6] ranging from monometallic oxide membranes for gas separation to multicomponent perovskite materials for thin film electronic memories. A number of excellent reviews exist on metal alkoxides and their uses as "sol–gel" precursors.[1–2]

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For a complete understanding of the characteristics of these complex ceramic powders generated from mixed-metal precursor species, well-characterized heteronuclear compounds are required.[5] The ability to observe the differences in these structures as the alkali metal is altered allows for interpretation of synthetic results and identification of potential precursors. The majority of crystallographically characterized[8] mixed alkali metal—early transition metal systems have only two alkali congeners. Examples of these systems include $[Y(O_2CCH_3)_4(H_2O)_xA]_\infty$ (A = Na, K),[9] "$AZr(OCHMe_2)_xO_y$" (A = Li, K),[10] and "$AM(O_4C_2)_x$" [M = Zr (A = Na, K);[11] V (A = K, Cs);[12] Mo (A = K, Cs)[13]]. It is rare to find a mixed-metal system, as above, that exists with three or more alkali metal congener compounds;[8,14,15] however, the heteroleptic "$AWH_5(PMe_3)_3$" [A = Li, $Na(O_5C_{10}H_{20})$, $K(O_6C_{12}H_{24})$] system is one example.[14,15] The main group metal, tin, is one of the few examples of a well-characterized mixed-metal homoleptic alkoxide system, "$MSn(OCMe_3)_3$" [M = Li, Na, K, Rb, Cs].[16] In this system it was found that as the size of the alkali metal was increased, the "$ASn(OCMe_3)_3$" species was altered from discrete molecular species (A = Li, Na) to infinite polymeric chains (A = K, Rb, Cs). This change is most likely due to the presence of larger alkali metals that require higher coordination numbers.

Group 4 metal—alkali metal derivatives are of particular interest to us since these compounds may serve as precursors to titanium containing ceramic materials. In an attempt to prepare useful reagents for materials processing, a variety of synthetic approaches are under investigation. Simple metathesis of the alkali metal in "$ATi(OR)_5$" (A = Li, Na, K) compounds with metal halides (MX_4) is one possible synthetic route that can be used for formation of heteronuclear species (eq 1).[1] It

$$MX_4 + 4\text{“}ATi(OR)_5\text{”} \rightarrow M[Ti(OR)_5]_4 + 4AX \qquad (1)$$

M = transition metal
X = halide
A = alkali metal

has been found that the "$Ti(OR)_5^-$" moiety does not always transfer, as shown in eq 1.[1-3] The role of the alkali metal ions in these systems is not known, and little structural information exists for these reagents to provide insight into the reactivity of these systems and to allow for a rational choice of an alkali metal to promote a given reaction.[1-3,7]

The syntheses of $ATi(OR)_5$ (A = Li, **1**; Na, **2**; K, **3**) have been previously reported,[7] wherein, **1** was shown to be the dimer, $[Li(OCHMe_2)_5]_2$ in the solid state and dimeric in benzene solutions. Compounds **2** and **3** were also found to be dimeric in benzene solutions. In this work, we report the structural data for $[AM(OCHMe_2)_5]_\infty$ (A = Na, **2**; K, **3**) and compare the metrical data for **1**−**3**. The opportunity for this type of comparison is rare for early transition metal alkoxide chemistry[14,15] and can provide insight into characteristic trends in these systems. We have further investigated the solution structural characteristics of **1**−**3** using alkali metal (^7Li, ^{23}Na, ^{39}K) NMR spectroscopy. Initial studies of "$A_xTi(OCHMe_2)_{4+x}$" (A = Li, Na, K; x = 0.25, 0.50, 1.0, 2.0) complexes have been undertaken, and preliminary results are reported.

Experimental Section

All reactions were performed under a dry nitrogen or argon atmosphere, using standard Schlenk, vacuum line, and glovebox techniques. Solvents were dried, as previously described.[17] The crystal structure and synthesis of **1** have been previously reported, as well as high yield routes for the preparations of both **2** and **3**.[7] $LiOCHMe_2$ (purified by sublimation) was isolated from a reaction between Li metal and $HOCHMe_2$.

NMR Studies. NMR spectra were obtained on a Bruker AC-250 (^7Li, ^{39}K) and a Bruker WH-400 (^{23}Na) spectrometer. The field strengths of these alkali metals are as follows: at 5.875 T, 250 MHz for ^1H, 97.16 MHz for ^7Li, 66.13 MHz for ^{23}Na, and 11.67 MHz for ^{39}K spectra; at 9.34 T, 400 MHz for ^1H, 155.45 MHz for ^7Li, 105 MHz for ^{23}Na, and 18.66 MHz for ^{39}K spectra.[18] The relative sensitivities for an equal number of nuclei at a constant field (constant frequency)[19a] of these nuclei are as follows for ^1H, 1.00 (1.00); for ^7Li, 0.293 (1.94); for ^{23}Na, 9.25×10^{-2} (1.32), and for ^{39}K, 5.08×10^{-4} (0.233). The standard external reference solutions used were a 1.0 M solution of LiCl in D_2O, a saturated solution of NaCl in D_2O, a 1.0 M solution of KCl in D_2O for ^7Li, ^{23}Na, ^{39}K, respectively.

"$Li_xTi(OCHMe_2)_{4+x}$" (1).[7] In a glovebox, a sample of $LiOCHMe_2$ was dissolved in C_6D_6, transferred to an NMR tube, and sealed with a septum. Aliquots of $Ti(OCHMe_2)_4$ were added under nitrogen immediately prior to obtaining the spectrum. Long term NMR studies

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were conducted on separate samples prepared by dissolving preweighed $LiOCHMe_2$ in a minimum amount of C_6D_6 and adding $Ti(OCHMe_2)_4$ under nitrogen. The NMR tubes were sealed with parafilm and stored in the ambient atmosphere for the 72-h studies.

$[NaTi(OCHMe_2)_5]_\infty$ (2).[7,20] The complex was prepared according to literature methods.[7a,20] The product was readily recrystallized from pentane at −25 °C, yielding colorless crystals. These were shown by X-ray analysis to be **2**. ^1H NMR results were identical to those reported.[7a] Anal. Calcd for $C_{15}H_{35}O_5TiNa$: C, 52.03; H, 10.11. Found: C, 51.45; H, 9.75.

$[KTi(OCHMe_2)_5]_\infty$ (3).[7a] **Crystal Study.** Attempts to grow crystals of **3** from the reaction of $KOCHMe_2/Ti(OCHMe_2)_4$ have not been successful. However, a crystal of **3** was obtained as a byproduct from the reaction mixture of "$KPb(OCHMe_2)_3$",[21] $Ti(OCHMe_2)_4$, and $^1/_2[Zr(OCHMe_2)_4{\cdot}HOCHMe_2]_2$ in toluene. The details of this complex reaction are not fully understood to date; however, concentration of this mixture and allowing it to stand at ambient glovebox temperatures, over a 1-week period, yielded crystalline material. A crystal was selected, and the structure was determined by single crystal X-ray crystallography to be **3**.

X-ray Collection, Structure Determination, and Refinement for $[NaTi(OCHMe_2)_5]_\infty$ (2). A suitable crystal was selected and mounted in a 0.7-mm fluoroborate glass capillary using a glass fiber in an argon atmosphere and then sealed. Crystal quality was determined by oscillation photographs, and full diffraction data were collected on an Enraf-Nonius CAD4 four circle automatic diffractometer, fitted with a liquid nitrogen cooling accessory.

The crystal system was monoclinic, and the systematic absences unequivocally showed the space group to be $P2_1/a$. Corrections were applied to the data for decomposition during collection and for nonuniform absorption of X-rays. Lorentz and polarization effects were corrected for during initial data processing, using a CAD4 program.[22a] Structure determination was performed using the SHELX 80 program.[22b]

After locating the Ti atom via Patterson map, the remaining non-hydrogen atoms were located by difference Fourier methods. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were not included at idealized positions. Refinement of positional and thermal parameters led to converge with $R_F = 8.57\%$; $R_{wF} = 9.3\%$, and GOF = 1.25 for 351 variables refined against those 3081 data with $|F_o| > 3.0\sigma(|F_o|)$. The maximum and minimum values of residual electron density were +0.66 and −0.34 e Å^{-3}.

Table 1. Crystallographic Collection Data for $[Na(TiOCHMe_2)_5]_\infty$ (**2**) and $[K(TiOCHMe_2)_5]_\infty$ (**3**)

	2	**3**
chemical formula	$C_{15}H_{35}O_5NaTi$	$C_{15}H_{35}O_5KTi$
fw	345.9	382.4
temp (K)	273	163
space group	$P2_1/a$ (No. 14)	$P2_1/n$ (No. 14)
a (Å)	12.616(1)	12.213(2)
b (Å)	10.078(4)	9.792(2)
c (Å)	17.573(4)	18.442(3)
β (deg)	103.2	106.94(1)
V (Å^3)	2175.0(2)	2109.7 (6)
Z	4	4
λ (Mo Kα radiation) (Å)	0.710 730	0.710 730
D_{calcd} (mg/m^3)	1.055	1.204
μ (Mo Kα, mm^{-1})	0.378	0.619
$R_F{}^a$ (%)	8.57	4.2
$R_{wF}{}^b$ (%)	9.3^c	4.8^d

[a] $R_F = \sum|(F_o| - F_c|/\sum|F_o|$. [b] $R_{wF} = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|)^2]^{1/2}$, where w^{-1} are given by footnotes *c* and *d*. [c] $w^{-1} = \sigma^2|F_o| + 0.005405|F_o|^2$. [d] $w^{-1} = \sigma^2|F_o| + 0.0010|F_o|^2$.

X-ray Collection, Structure Determination, and Refinement for $[KTi(OCHMe_2)_5]_\infty$ (3). A colorless crystal of approximate dimensions 0.27 × 0.30 × 0.30 mm was oil-mounted[23] on a glass fiber and transferred to a Siemens P3 automated four circle diffractometer that is equipped with a modified LT-2 low temperature system. The determination of Laue symmetry, crystal class, unit cell parameters, and the crystal's orientation matrix was carried out by previously described methods similar to those of Churchill et al.[24] Intensity data were collected at 163 K using a $\theta-2\theta$ scan technique with Mo Kα radiation under the conditions described in Table 1. All 4181 data were corrected for Lorentz and polarization effects and were placed on an approximately absolute scale. The diffraction symmetry was $2/m$ with systematic absences $0k0$ for $k = 2n + 1$ and $h0$ for $h+ = 2n + 1$. The centrosymmetric monoclinic space group $P2_1/n$, a nonstandard setting of $P2_1/c$ [C_{2h}^5, No. 14], is therefore uniquely defined.

All crystallographic calculations were carried out using either the UC-Irvine modified version of the UCLA crystallographic computing package[25] or the SHELXTL PLUS program set.[26] The analytic scattering factors for neutral atoms were used throughout the analysis;[27] both the real ($\Delta f'$) and imaginary ($i\Delta f''$) components of anomalous dispersion were included. The quantity minimized during least-squares analysis was $\sum w(|F_o| - |F_c|)^2$ where $w^{-1} = \sigma^2(|F_o|) + 0.0010(|F_o|)^2$.

The structure was solved by direct methods (SHELXTL PLUS) and refined by full-matrix least-squares techniques. Hydrogen atoms were located from a difference Fourier synthesis and included with isotropic thermal parameters. Refinement of positional and thermal parameters led to convergence with $R_F = 4.2\%$; $R_{wF} = 4.8\%$, and GOF = 1.27 for 340 variables refined against those 3083 data with $|F_o| > 3.0\sigma(|F_o|)$. A final difference Fourier synthesis yielded was featureless, ρ(max) = 0.6901 Å^{-3}.

Results and Discussion

Both **2** and **3** were structurally characterized in the solid state by single crystal X-ray crystallography. Compound **2** was prepared and isolated as previously reported.[7,20] A single crystal of **3** was fortuitously isolated from a complex reaction mixture, which to date is not understood; however, a complete high-yield synthesis has been previously detailed.[7] Table 1 lists the data collection parameters for **2** and **3**. Tables 2 and 3 list selected atomic coordinates for **2** and **3**, respectively. Table 4 is a comparison of some representative bond distances and angles for **1**−**3**. Table 5 is a compilation of atomic alkali metal to metal (A/M) ratios (A = alkali metal and M = Ti, Sn, and W), and Table 6 is a tabulation of the alkali metal NMR spectral results.

As shown in Figure 1, $[LiTi(OCHMe_2)_5]_2$ (**1**) is dimeric, adopting a standard M_4O_{16} ($M_2M'_2O_{16}$) arrangement.[7] The metrical data for this compound have been previously reported.[7] The titanium metal center adopts a distorted trigonal-bipyramidal (TBP) geometry with the lithium atoms in a tetrahedral

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(21) "$KPb(OCHMe_2)_3$" was formed as the major product of the reaction between 2 $KN(SiMe_3)_2$, $PbCl_2$, and (excess) $HOCHMe_2$. Preliminary characterization of this compound using ^1H and ^{39}K NMR indicates the presence of potassium. Another reaction mixture consisting of 2"$Pb(OCHMe_2)_2$", $Ti(OCHMe_2)_4$, and $^1/_2$ $[Zr(OCHMe_2)_4{\cdot}HOCHMe_2]_2$ in toluene yielded crystals of the previously characterized complex $K_4Zr_2(OCHMe_2)_{10}O$.[10]

(22) (a) The CAD 4 program used to automatically correct for Lorentz and polarization effects and applying a *fade* correction where necessary due to crystal decomposition was written by J. E. Davis, Queen Mary College, University of London (date unknown). (b) Sheldrick, G. M. SHELX 80 - Program for Crystal Structure Solution; University of Gottingen, FRG, 1980.

(23) The crystal was immersed in a lube-oil additive which allows for manipulation on the bench-top and prevents decomposition due to air or moisture. The crystal was secured to a glass fiber (the oil acts as the adhesive) which is attached to an elongated brass mounting pin. Further details appear in: Hope, H. *Experimental Organometallic Chemistry: A Practicum in Synthesis and Characterization*; Wayda, A. L., Darensbourg, M. Y., Eds.; ACS Symposium Series No. 357; American Chemical Society: Washington, D.C., 1987.

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Table 2. Selected Atomic Coordinates ($\times 10^4$) for $[Na(TiOCHMe_2)_5]_\infty$ (**2**)[a]

	x	*y*	*z*
Ti(1)	2235(1)	3321(2)	2496(1)
Na(1)	4852(3)	2580(4)	2785(2)
O(1)	1542(5)	3363(8)	3326(4)
O(2)	970(5)	2430(7)	1901(4)
O(3)	2040(7)	4731(8)	1841(5)
O(4)	3098(5)	1820(7)	2445(4)
O(5)	3598(5)	4081(7)	3061(4)

[a] U_{eq} not determined.

Table 3. Selected Atomic Coordinates ($\times 10^5$) for $[K(TiOCHMe_2)_5]_\infty$ (**3**)

	x	*y*	*z*	U_{eq}[a]
Ti(1)	87912(4)	5593(5)	68236(3)	160 (2)
K(1)	73167(6)	−12859(6)	77604(4)	289(2)
O(1)	92811(15)	5557(21)	78787(10)	268(7)
O(2)	80167(16)	−10476(18)	64131(10)	219(6)
O(3)	72741(15)	10840(18)	69184(10)	182(6)
O(4)	88415(16)	22789(19)	63726(11)	226(6)
O(5)	101413(15)	91(20)	66966(10)	228(6)

[a] U_{eq} defined as one-third of the trace of the orthogonalized U_{ij} tensor.

arrangement. The four coordinate lithium atoms use terminal OR, μ-OR, and μ_3-OR ligands to achieve this arrangement.

$[NaTi(OCHMe_2)_5]_\infty$ (**2**) crystallized as an infinite, approximately linear chain of alternating distorted TBP titanium isopropoxide moieties and bridging *very* distorted tetrahedral sodium atoms [O(5)−Na−O(4) = 66.9°], Figure 2. The dihedral angles of the chain range from 146.0(5)° (Na···Ti···Na′) to 162.5(5)° (Ti···Na···Ti′). The titanium center shows little distortion from ideal TBP geometry with angles ranging from 87.5(4)° to 174.2(3)° (four μ-$OCHMe_2$ ligands and one terminal $OCHMe_2$ ligand).

$[KTi(OCHMe_2)_5]_\infty$ (**3**) (Figure 3) is structurally similar to **2**, however, the infinite alternating chain is nonlinear. The potassium atoms are five coordinated and appear to be in an intermediate geometry between square base prismatic and TBP [angles of 53.8(1)°−154.7(1)°]. The potassium atoms interact with four of the five alkoxides of the titanium using μ-$OCHMe_2$ and μ_3-$OCHMe_2$ ligands. The distortion around the titanium metal center [angles range from 83.0(1)° to 176.8(1)°] is similar to that reported for **2**. Unlike **2**, however, the dihedral angles of **3** are wide ranging [93.5° (K···Ti···K′) to 151.0° (Ti···K···Ti′)]. This type of decreased linearity with increased alkali metal radii has also been observed for other inorganic systems such as $\{[\mu$-η^5:η^5-$C_5H_4(SiMe_3)]A\}_\infty$ (A = Li, K).[28] The differences between the general spatial arrangement of **2** and **3** can be discerned from the unit cell packing diagrams, which are shown in Figures 4 and 5, respectively.

The Ti−OR distances of **1**−**3** appear unaffected by the alkali metal coordination and fall within the range of 1.782(9) to 1.988(9) Å, which is representative of Ti−OR (OR = $OCHMe_2$) distances.[1,7,29−35] The Li−μ-OR distances for **1** are on average 1.929(1) Å, the Na−μ-OR distances of **2** span from 2.288(9) to 2.320(9) Å, and the K−μ-OR distances of **3** range from 2.657(1) to 2.958(1) Å. The reduced terminal Ti−OR distances and Ti−O−C terminal angles are consistent with significant O p to Ti dπ bonding, suggesting reduced pπ−dπ bonding. This is in accordance with literature reports for other transition metal complexes, as are the longer Ti−O distances observed due to a higher degree of bonding (i.e., distance of terminal OR < μ-OR < μ_3-OR).[7,36] The Na−O bond distances (average 2.30 Å) are similar to those found for $NaW_2(H)(OCHMe_2)_8\cdot$(diglyme)[37] and $(THF)_2NaTi(OAr$-i-$CHMe_2)_4$ (THF = tetrahydrofuran).[38] The K−μ-O (average 2.82 Å) and K−μ_3-O [2.784(1) Å] distances are cognate to those reported for $KZr_2(OCHMe_2)_9\cdot$(DME) (DME = dimethoxyethane),[10] $K_4ZrO(OCHMe_2)_{10}$,[10] and $[KAl(OCHMe_2)_5(HOCHMe_2)_2]_\infty$.[39]

As mentioned above, the titanium atoms of **1**−**3** posses a 5-fold coordination. Few five-coordinate titanium[29] alkoxide compounds are reported in the literature and would include the following: $Ti_2(O_2C_{22}H_{16})_2(OCHMe_2)_4$,[30] $Ti_3(OPh)_9(TMEDA)_2$,[31] $[LiTiO(OCHMe_2)_3]_4$,[32] $\{[(R)(CO)_5Cr{=})CO]Ti(OCHMe_2)_3\}_2$ [R = n-$(CH_2)_3Me$, $C(Me)CH_2$],[33] $Ti_8O_6(OCH_2C_6H_5)_{20}\cdot OEt_2$[34] and $TiSm_4(O)(OCHMe_2)_{14}$.[35] The majority of these complexes have titanium atoms in a distorted TBP arrangement; however, a five-coordinate square-base pyramidal (SBP) titanium atom is present in the $Ti_3(OPh)_9(TMEDA)_2$ (TMEDA = tetramethylenediamine) molecule.[31] The deviations of the titanium atoms of **1** and **2** from the ideal TBP geometry are very similar to the angles observed for the above compounds. On the other hand, the angles around the titanium atom in **3** are very distorted, resulting in a geometry between the ideal SBP and TBP arrangements. None of these compounds possess distinct five-coordinated titanium anions as is found in **2** and **3**.

A couple of trends are noteworthy in both of the A···Sn[27] and A···Ti systems. For the tin mixed-metal system, the lithium and sodium derivatives exist as dimers, whereas for the potassium and later congeners, one dimensional infinite poly-

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Table 4. Comparison of the Interatomic Distances (Å) and Angles (deg) for $[Li(TiOCHMe_2)_5]_2$ (**1**), $[Na(TiOCHMe_2)_5]_\infty$ (**2**), and $[K(TiOCHMe_2)_5]_\infty$ (**3**)

Distances (Å)

	1	2	3
Ti···Ti′	5.125	6.52(8)	6.688
A···Ti[a]	2.895(22), 2.896(21)	3.289	3.362(1), 3.545(1)
A···A′	2.697(41)	6.31(8)	5.034(1)
Ti−OR[b]	1.782(9), 1.829(9)	1.811(10)	1.814(1)
Ti−μ-OR	1.886(8), 1.900(9)	1.865(8), 1.919(8), 1.936(8), 1.878(8)	1.862(1), 1.878(1), 1.887(1)
Ti−μ_3-OR	1.988(8)		1.979(1)
A−μ-OR	1.930(23), 1.928(23)	2.288(9), 2.320(9)	2.657(1), 2.802(1), 2.863(1), 2.958(1)
A−μ_3-OR	1.984(23), 1.982(23)		2.784(1)

Angles (deg)

	1	2	3
OR−Ti−μ-OR	94.1(4), 94.5(4), 115.6(4), 116.5(4)	89.4(4), 92.6(4), 117.4(5), 126.7(4)	93.5(1), 94.0(1), 96.1(1)
μ-OR−Ti−μ-OR	125.3(4)	83.5(4), 87.5(4), 90.9(4), 96.4(4), 115.9(4), 174.2(3)	113.0(1), 114.9(1), 130.3(1)
OR−Ti−μ_3-OR	95.1(4), 167.4(4)		176.8(1)
μ-OR−Ti−μ_3-OR	80.0(3), 80.2(3)		83.0(1), 86.1(1), 87.6(1)
μ-OR−A−μ-OR	160.1(12)	66.9(3)	58.7(1), 64.8(1), 100.8(1), 118.6(1), 142.9(1), 149.8(1)
OR−A−μ_3-OR	114.6(11), 79.3(9), 79.4(9)		53.8(1), 54.3(1), 143.7(1), 154.7(1)
A−μ_3-OR−A′	85.7(9)		135.4(1)
A−μ_3-OR−Ti	93.6(7), 93.7(7)		88.1(1), 98.7(1)
A−μ-OR−Ti	98.7(7)	104.7(4), 101.7(4)	85.3(1), 87.8(1), 96.3(1)
A···Ti···A′	55.5(7)	146.0(5)	93.5
Ti···A···Ti′	124.5(7)	162.5(5)	151.0

[a] A = Li, Na, K. [b] OR = $OCHMe_2$.

Table 5. *A*/*M* Ratios (A = Alkali Metal, M = Metal Radii) and the Morphology for the $ATi(OR)_5$, $ASn(OR)_3$, and $WH_5(PMe_3)_3A$ Systems

		M = Ti^{4+} (r = 0.68 Å)		M = Sn^{2+} (r = 0.93 Å)		M = W^{4+} (r = 0.70 Å)	
A	radius (r) of A (Å)	*A*/*M*	morphology	*A*/*M*	morphology	*A*/*M*	morphology
Li^+	0.68	1.00	molecule	0.73	molecule	0.971	molecule
Na^+	0.97	1.42	polymer	1.04	molecule	1.39	cmplxd[a]
K^+	1.33	1.95	polymer	1.43	polymer	1.90	cmplxd[a]
Cs^+	1.67	2.45	unsolved	1.79	polymer	2.38	unsolved
Rb^+	1.47	2.16	unsolved	1.58	polymer	2.10	unsolved

[a] Cmplxd = the final structure had an alkali metal complexed by a crown ether.

Table 6. Alkali NMR Spectral Results. ^7Li NMR Resonances for $Li_xTi(OCHMe_2)_{5+x}$ (C_6D_6), ^{23}Na NMR Resonances for $Na_xTi(OCHMe_2)_{5+x}$ (C_6D_6/THF), and ^{39}K NMR (C_6D_6) Resonance for $KOCHMe_2$

	temp (K)	ppm at 0 h	$\Delta\omega_{1/2}$ (Hz)	LiOR (mg/mL)	ppm at 24 h	$\Delta\omega_{1/2}$ (Hz)	ppm at 72 h	$\Delta\omega_{1/2}$ (Hz)
$^7Li^{a,b}$								
$Li_{0.25}Ti(OR)_{4.25}$	298	−1.81	7.3	10/1.2	−2.01	7.2	−1.99	7.8
		−1.91			−2.14	*e*	−2.14	5.8
	343						−2.02	3.3
$Li_{0.5}Ti(OR)_{4.5}$	298	−1.78	4.8	11/0.4	−1.82	5.3	−1.81	7.6
					−1.97	*e*	−1.98	*e*
	343						−1.86	2.9
$LiTi(OR)_5$	298	−1.76	5.2	12/0.3	−1.80	4.9	−1.79	6.0
	343						−1.82	3.8
$Li_2Ti(OR)_6$	298	−1.29	*e*	12/0.3	−1.30	*e*	−1.32	*e*
		−1.76	6.3		−1.77	13.2	−1.77	12.4
		−2.10	*e*		−2.11	*e*	−2.08	*e*
	343						−2.09	*e*
							−1.55	*e*
							−1.80	*e*
LiOR	298	−1.80	14.2	12/0.3	−1.79	18.5	−1.77	17.5
	343						−1.81	10.4
$^{23}Na^c$								
$Na_{0.5}Ti(OR)_{4.5}$	298	−14.14	846					
$NaTi(OR)_5$	298	−15.04	952					
	353	−16.03	423					
$Na_2Ti(OR)_6$	298	−15.59	740					
	353	−21.31	846					
NaOR	298	−23.48	634					
$^{39}K^d$								
KOR	343	+16.00	300					

[a] OR = $OCHMe_2$. [b] External reference $LiCl/D_2O$. [c] External reference $NaCl/D_2O$. [d] External reference KCl/D_2O. [e] Half-height width could not be determined.

mers with "$ASnO_3$" cages were isolated. For the titanium series, the A···M distances (2.90 Å, **1**; 3.29 Å, **2**; 3.36−3.55, **3**), and the M···M′ distances (5.125 Å, **1**; 6.52(8) Å, **2**; 6.688 Å, **3**) aggrandize upon descending group I. These trends are also reported for the A···Sn series.[27] The A···A distances (2.697(41) Å, **1**; 6.31(8) Å, **2**; 5.034(1) Å, **3**) do not increase, but the differences in linearity of the polymeric chains between **2** and **3** would account for this deviation. Besides the size of the alkali metal present, the increase in the size of the alkoxide from $OCHMe_2$ to $OCMe_3$ for the tin system affects the onset of oligomerization versus the titanium system; however, there is also a correlation between alkali metal to metal radius (*A*/*M*) ratio.[19b,40]

Table 5 is a list of alkali metal and metal radii, *A*/*M* ratios, and the morphology of the compound isolated (molecule, complexed alkali metal, polymer, or unsolved) for the $ATi(OR)_5$, $ASn(OR)_3$, and $WH_5(PMe_3)_3A$ systems. In the $ATi(OR)_5$ and $ASn(OR)_3$ systems, discrete molecules have been reported for an *A*/*M* ratio of less than 1.4, whereas, for *A*/*M* ratios greater than 1.4, polymers have been isolated. These reported radii do not take into account the degree of coordination due to limited information provided about the calculated radii[19b,40] and can only be used as a very rough guide. For the heteroleptic $WH_5(PMe_3)_3A$ series, $WH_5(PMe_3)_3Li$ exists as two isomers (*A*/*M* = 0.97). One is a discrete molecule of $LiWH_5(PMe_3)_3$, while the other is a tetramer with lithium or hydrogen bridges.[14] The sodium (*A*/*M* = 1.39) and potassium analogues (*A*/*M* = 1.90) are crystallized using 15-crown-5 and 18-crown-6, respectively.[14b] On the basis of the *A*/*M* radius ratios of this system (see Table 5), it is probable that both the sodium and potassium−tungsten

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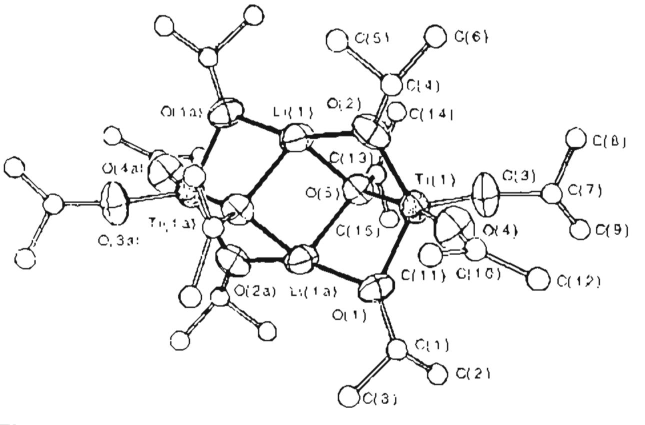

Figure 1. Thermal ellipsoid drawing of $[LiTi(OCHMe_2)_5]_2$ (**1**). Thermal ellipsoids drawn at 30% probability.

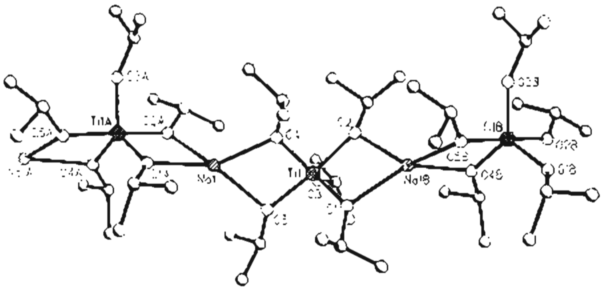

Figure 2. Ball and stick drawing of $[NaTi(OCHMe_2)_5]_\infty$ (**2**).

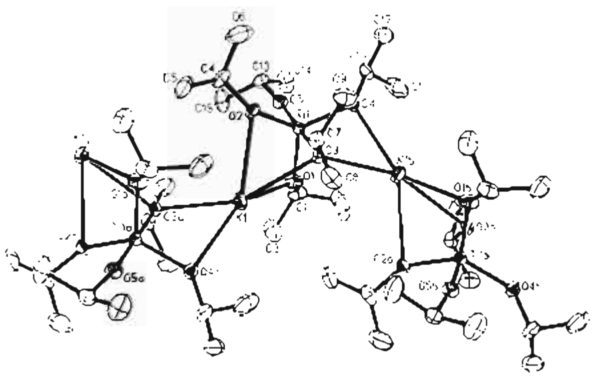

Figure 3. Thermal ellipsoid drawing of $[KTi(OCHMe_2)_5]_\infty$ (**3**). Thermal ellipsoids drawn at 50% probability.

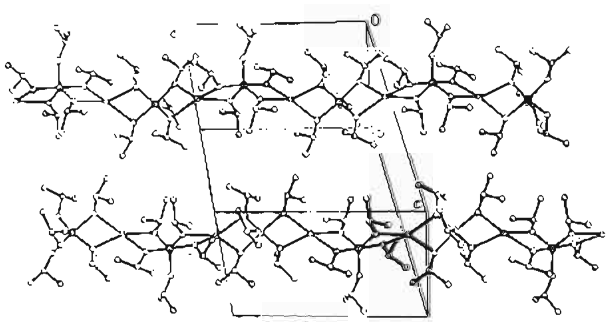

Figure 4. Packing diagram of the unit cell of $[NaTi(OCHMe_2)_5]_\infty$ (**2**).

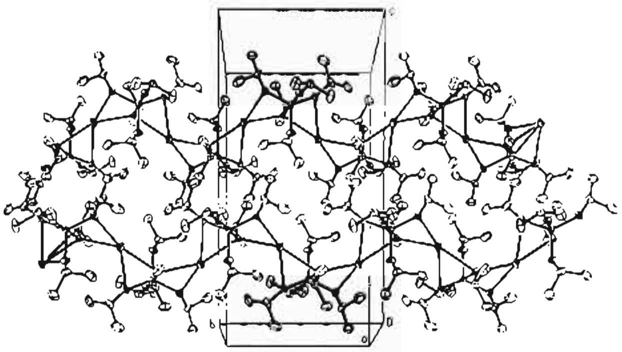

Figure 5. Packing diagram of the unit cell of $[KTi(OCHMe_2)_5]_\infty$ (**3**).

compounds exist as polymers in the solid state without the complexing agents present.

Alkali Metal NMR Studies

Solution characteristics of **1**−**3** were investigated using alkali metal NMR spectroscopy. This technique is a convenient and direct means for studying the general solution structural types and the coordination number of the alkali metal. ^{7}Li, ^{23}Na, and ^{39}K all have a spin of $^3/_2$'s and possess natural abundances of 92.58, 100, and 93.10%, respectively.[18,19] Both ^{7}Li and ^{23}Na are more sensitive than ^{13}C nuclei and are easily detected (small number of scans <10) at relatively low concentrations. C_6D_6 was used to investigate the solution species presented, and these spectral results are transcribed in Table 6.

^{7}Li NMR Spectroscopy. Crystals grown from a mixture of $Ti(OCHMe_2)_4$ and $LiOCHMe_2$ were found to be consistent with the previously reported structure (a slightly smaller unit cell was found due to data collection temperature differences).[7d] Therefore, the reaction mixtures of stoichiometrically prepared samples, $Li_xTi(OCHMe_2)_{4+x}$ (x = 0.25, 0.50, 1.0, 2.0) in C_6D_6 were investigated, and the ^{7}Li NMR resonances of these compounds are listed in Table 6. The chemical shift of $LiOCHMe_2$ was found to be concentration dependent (δ −1.79 was recorded for 12 mg/0.3 mL of C_6D_6). Due to this, a titration of $LiOCHMe_2$ (10 mg/0.3 mL of C_6D_6) with neat $Ti(OCHMe_2)_4$ was performed to minimize volume changes. For the stoichiometries investigated, the line widths were on average 7.2 Hz ($LiOCHMe_2$ average 16.8 Hz) which is typical for ^{7}Li NMR spectra.[41] On the basis of the ^{1}H and ^{7}Li NMR spectra, rapid exchange of the alkoxide ligands is obviously occurring in these samples. Unexpectedly, at the stoichiometries where x = 0.25 or 2.0, more than one resonance was observed. These spectra were monitored over time (72 h) for further changes and revealed the ingrowth of peaks which were minimally present in the initial spectra (see Figure 6). Elevated temperature (343 K) spectra showed a coalescence of peaks coupled with a decrease in line widths (average 3.3 Hz). Due to the number of resonances present, line width, temperature dependence, and previous molecular weight studies,[7] a number of discrete Li···Ti alkoxide molecules exist which can be readily interconverted or scrambled by variations in temperature or stoichiometry. The intermediate stoichiometric ratios agree with the previously reported solution molecular species.[7] At the stoichiometries where x = 0.5 or 2.0, it is apparent a number of lithium/titanium species are being generated in solution. Characterization of these species is the basis of continuing investigations.

^{23}Na NMR Spectroscopy. ^{23}Na NMR spectra of $Na_xTi(OCHMe_2)_{4+x}$ (x = 0.50, 1.0, 2.0) in C_6D_6/THF show single resonances at 353 K (see Table 6). The line widths obtained are comparable to signals previously reported for Na^+ ions complexed to crown ethers or compounds in which the anion effectively competes with the solvent in the Na^+ coordination sphere.[42] These line widths (average 850 Hz) may also be

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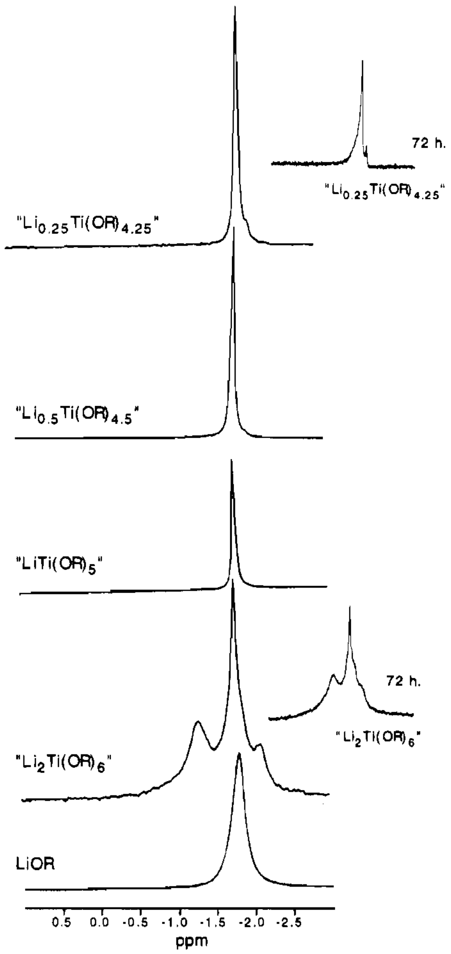

Figure 6. ^{7}Li NMR spectra of $Li_xTi(OR)_{4+x}$ (x = 0.25, 0.50, 1.0, 2.0; OR = $OCHMe_2$) with C_6D_6, at 97.211 MHz for 24 h.

contrasted with the line widths of ~10 Hz for NaCl−H_2O and 40 Hz for $NaBPh_4$ in THF. The averaged signal for the excess $NaOCHMe_2$ sample suggests rapid exchange of the $NaOCHMe_2$ on the NMR time scale and an asymmetric electric field gradient around the sodium.[42] These results are consistent with those previously reported,[20] wherein conductometric and volatility measurements on **2** indicated that the molecule had low stability. Another preliminary investigation of different sodium double metal alkoxide complexes[43] show similar line broadening. This is consistent with the view that these compounds are presumably existing as tight ion pairs, which creates a symmetric environment about the Na atom. In contrast to these rapidly exchanging compounds, $[NaL]BPh_4$ (L = 1,4,7-tris(pyrozole-1-ylmethyl)-1,4,7-triazacyclononane or 1,4,7,10-tetrakis(pyrozole-1-ylmethyl)-1,4,7,10-tetraazacyclononane) shows a dramatic decrease in line widths δ 12.51 ($\Delta\omega_{1/2}$ = 48 Hz) and 9.69 ($\Delta\omega_{1/2}$ = 98 Hz) which was ascribed to either slow or no exchange of the Na^+ cations on the NMR time scale.[44] This apparent lack of alkoxide ligand exchange is further evidenced by the presence of an asymmetric Na^+ ion environment. On the basis of previous molecular weight studies,[7] it is likely that deoligomerization occurs for **2**, which would be consistent with the covalent nature of these compounds.

^{39}K NMR Spectroscopy. Potassium has the least relative sensitivity at a constant field (constant frequency)[19a] of these alkali metal nuclei; however, resonances for both KCl (D_2O, external reference) and $KOCHMe_2$ [C_6D_6 (343 K) δ 16; $\Delta\omega_{1/2}$ = 300 Hz] were readily obtained (<10 scans). Informative spectra were not obtained on the $K_xTi(OCHMe_2)_{4+x}$ (x = 0.25, 0.50, 1.0, 2.0) samples. Overnight, elevated temperature experiments did not lead to resolution of spectral peaks, which were extremely broad (>400 Hz) and difficult to distinguish from the rolling base line.

Conclusion

Both **2** and **3** have been isolated and characterized in the solid state as polymeric species. The alkali metal acts as a bridge between discrete mononuclear, trigonal-bipyramidal titanium pentaisopropoxide moieties. The five-coordinate titanium metal centers observed in both **2** and **3** are unusual in that they exist as discrete anions in the solid state; however, this has little effect on the bond distances and angles observed for **2** or **3**. For the systems investigated, an alkali metal to metal ratio greater than 1.4 was consistent with the formation of a polymeric species in the solid state. Alkali metal NMR was found to be a convenient and easy method for identifying the solution characteristics of alkali metalated transition metal complexes. For **1**, rapid alkoxide exchange is observed. With the addition of excess amounts of lithium or titanium isopropoxide, the ^{7}Li NMR spectra reveal a number of different species are present. A tight ion pair was found to exist for **2** in solution, based on a comparison of ^{23}Na NMR spectral line widths. The behavior of **3** in solution could not be further elucidated using ^{39}K NMR.

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Supporting Information Available: For **2** and **3** a complete set of crystal data including tables of positional parameters, bond distances and angles, and thermal parameters (14 pages). Ordering information is given on any current masthead page.

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[42] (a) Laszlo, P. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 254. (b) Lin, J. D.; Popov, A. I. *J. Am. Chem. Soc.* **1981**, *103*, 3773.

[43] ^{23}Na NMR of (1) $Na_2Zr_3(OCHMe_2)_{14}$, δ −12.50 (C_7D_8, 298 K, $\Delta\omega_{1/2}$ = 592 Hz), −12.10 (353 K, $\Delta\omega_{1/2}$ = 296 Hz); (2) $NaNb(OCHMe_2)_6$, δ −14.92 (C_7D_8/THF, 298 K, $\Delta\omega_{1/2}$ = 465 Hz), −15.31 (353 K, $\Delta\omega_{1/2}$ = 571 Hz); and (3) $NaTa(OCHMe_2)_6$, δ −17.29 (C_7D_8/THF, 353 K, $\Delta\omega_{1/2}$ = 508 Hz). Compounds prepared according to ref 37.

[44] Di Vaira, M.; Cosimelli, B.; Mani, B.; Stoppioni, P. *J. Chem. Soc., Dalton Trans.* **1991**, 331.