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Synthesis and Characterization of a Series of Rubidium Alkoxides and Rubidium–Titanium Double Alkoxides

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This report investigates the structural aspects of the products isolated from the reactions of a series of titanium alkoxides $\{[\mathrm{Ti(OR)_4}]_n$ $n = 2$, OR = $\mathrm{OCH_2C(CH_3)_3}$ (ONep) (**1**); $n = 1$, $\mathrm{OC_6H_3(CH_3)_2}$-2,6 (DMP) (**2**)$\}$ with rubidium alkoxides $\{[\mathrm{Rb(OR)}]_\infty$ where OR = (ONep) (**3**), (DMP) (**4**), and $\mathrm{OC_6H_3(CH(CH_3)_2)_2}$-2,6 (DIP) (**5**)$\}$. The resultant double alkoxides were determined by single crystal X-ray diffraction to be $[\mathrm{Rb}(\mu\text{-ONep})_4(\mathrm{py})\mathrm{Ti(ONep)}]_2$ (**6**), $[\mathrm{Rb}(\mu\text{-DMP})\mathrm{Ti(DMP)_4}]_\infty$ (**7**), and $[\mathrm{Rb}(\mu\text{-DMP})_2(\mu\text{-ONep})_2\mathrm{Ti(ONep)}]_\infty$ (**8**). Compound **1** is the previously reported dinculear species with trigonal bipyramidal Ti metal centers whereas compound **2** is a monomer with a tetrahedral Ti center. Suitable X-ray quality crystals of **3** were not isolated. Compounds **4** and **5** demonstrate extended polymeric networks with Rb coordination ranging from two to five utilizing terminal μ- and μ_3-OR ligands and π-interactions of neighboring OAr ligands. The double alkoxide **6** revealed a simple tetranuclear structure with μ-ONep acting as the bridge, terminal ONep ligands on the Ti, and one terminal py on the Rb. For **7** and **8**, the π-interaction facilitated the formation of extended polymeric systems. All complexes were further characterized by FT-IR and multinuclear NMR spectroscopy.

Introduction

Mixed metal alkoxides are ideal precursors to technologically important ceramic oxides via chemical vapor deposition (CVD), sol–gel processes, and, more recently, nanocrystal fabrication.[1–8] These so-called "single-source" precursors are of interest since they can greatly simplify processing, control stoichiometry of final materials, and increase throughput. To synthesize such precursors, metathesis routes involving alkali metal (lithium, sodium, and potassium) cations are widely employed.[9–13] We previously presented full reports on the syntheses and structures of a wide variety of alkali alkoxide reagents [A(OR)][14–16] and alkali–titanium double alkoxide derivatives, $[\mathrm{ATi(OR)_5}]_n$, OR = $\mathrm{OCHMe_2}$ ($\mathrm{OPr^i}$)[15] and $\mathrm{OCH_2CMe_3}$ (ONep).[1] However, attempts to use these compounds in metathesis reactions often resulted in undesired retention of alkali metalated species.[17] This lack of reactivity was attributed to the steric hindrance around the alkali metals which was readily apparent from the final solved structures; however, a general trend was noted for the $\mathrm{OPr^i}$ system, wherein as the alkali metal increased in size, the alkali metal became more accessible. It was of interest to determine if the larger congener, rubidium, used in the same synthetic strategy, could generate alkali-metal-free transition metal

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complexes of interest. Given the general enhanced reactivity of heavier alkali metal alkoxides versus their lithium counterparts, this seemed reasonable. We chose to investigate double alkoxides based on Ti due to the ubiquity of Ti in complex ceramic materials and our previous experience with alkali metal titanium alkoxides $[ATi(OR)_5]_n$ (A = Li, Na, K; and OR = OPr^{i}[15] and ONep[1]).

In order to initiate the synthesis of the double alkoxides, it was necessary to have both well-characterized titanium alkoxide ($Ti(OR)_4$) and rubidium alkoxide (Rb(OR)) precursors readily available. For the $Ti(OR)_4$, we used the previously reported $[Ti(\mu\text{-ONep})(ONep)_3]_2$ (**1**),[18] and in order to introduce substantially varied steric bulk we isolated the aryloxide $Ti(DMP)_4$ (**2**, DMP = $OC_6H_3Me_2$-2,6), previously predicted to be a monomer,[19] from the alcohol exchange reaction, shown in eq 1.

A large number of structurally characterized lithium-, sodium-, and potassium-containing alkoxide complexes have been reported;[16,20−31] however, there is a considerable dearth of information concerning structurally characterized rubidium alkoxides. Previously reported examples include $[Rb(OBu^t)]_4$ where $OBu^t = OC(CH_3)_3$,[32] $[Rb(OBu^t)(HOBu^t)]_n$,[32] $[Rb^+][^-OSiMe_3]$,[33] $[Rb(OAr)]_n$ where OAr = 2,6-diphenylphenoxide,[34] bis(μ_4-4-hydroxyphenolato-O,O′),[35] 2-(2-carboxyphenol),[36] 4-nitrophenol,[37] and 2,4,6-trinitrophenol (picrate).[38] Typically, the limited number of structurally characterized Rb species is attributed to the oligomerization that results from the large cation size. Because of the lack of reported "Rb(OR)" compounds, it was necessary to synthesize (eq 2) and characterize some of these, including $[Rb(ONep)]_x$ ((**3**) not structurally identified), $[Rb_4(\mu\text{-DMP})_4(THF)_2]_\infty$ (**4**), and $[Rb_2(\mu\text{-DIP})_2(\mu\text{-THF})]_\infty$ (**5**) (DIP = $OC_6H_3(CHMe_2\text{-}2,6)_2$).

$$Ti(OR')_4 + 4HOR \rightarrow \text{“}Ti(OR)_4\text{”} + 4HOR' \qquad (1)$$

$$Rb^0 + HOR \rightarrow \text{“}Rb(OR)\text{”} \qquad (2)$$

$$\text{“}Rb(OR)\text{”} + Ti(OR)_4 \rightarrow \text{“}RbTi(OR)_5\text{”} \qquad (3)$$

where OR = ONep, DMP, DIP; OR′ = OPr^i.

These two sets of complexes were envisioned to provide a good baseline for the synthesis and characterization of a series of "$RbTi(OR)_5$" complexes which were isolated as $[Rb(\mu\text{-ONep})_4(py)Ti(ONep)]_2$ (**6**), $[Rb(\mu\text{-DMP})Ti(DMP)_4]_\infty$ (**7**), and $[Rb(\mu\text{-DMP})_2(\mu\text{-ONep})_2Ti(ONep)]_\infty$ (**8**), from eq 3. The combination of such a fundamental structural and spectroscopic study is notably scarce in the field of rubidium chemistry and should serve as a starting point for the synthesis of additional heterometallic alkoxides and the resulting mixed metal oxide ceramic materials.[39] The full set of synthetic conditions, analytical information, and comparison to literature compounds is discussed below.

Experimental Section

All compounds described here were handled with rigorous exclusion of air and water using standard Schlenk line and glovebox techniques under an argon atmosphere. All solvents were stored under argon and used as received (Aldrich) in sure seal bottles, including hexanes (hex), toluene (tol), tetrahydrofuran (THF), and pyridine (py). The following chemicals were used as received (Aldrich): $Ti(OPr^i)_4$, Rb^0 metal, H-ONep, H-DMP, and H-DIP. Compound **1** was synthesized by a literature procedure.[18]

FT-IR data were obtained on a Bruker Vector 22 Instrument using KBr pellets under an atmosphere of flowing nitrogen. Elemental analysis was performed on a Perkin-Elmer 2400 CHN-S/O elemental analyzer. All NMR samples were prepared from dried crystalline materials that were handled and stored under an argon atmosphere and redissolved in the appropriate deuterated solvent (THF-d_8, pyridine-d_5) as saturated solution concentrations. All solution spectra were obtained on a Bruker DRX400 spectrometer at 399.8 and 100.5 MHz for ^1H and ^{13}C experiments, respectively. A 5 mm broadband probe was used for all experiments. ^1H NMR spectra were obtained using a direct single pulse excitation, with a 10 s recycle delay and 8 scan average. The $^{13}C\{^1H\}$ NMR spectra were obtained using a WALTZ-16 composite pulse ^1H decoupling, a 5 s recycle delay, and a $\pi/4$ pulse excitation.

$Ti(DMP)_4$ (2). To a solution of $Ti(OPr^i)_4$ (4.69 g, 16.5 mmol) in toluene 4.5 equiv of DMP-H (2.02 g, 66.0 mmol) were added while stirring. After 12 h, the yellow solution was concentrated and cooled to −35 °C to yield X-ray quality crystals. Yield: 5.44 g (61.9%). FTIR: (KBr, ν/cm^{-1}) 2917(m), 1591(m), 1477(s), 1268(s), 1268(s), 1211(s), 1085(m), 922(s), 764(s), 724(m), 584(m), 480(w), 410(w); ^1H NMR (399.8 MHz, THF-d_8) δ 6.84 (2.0H, d, $OC_6H_3(CH_3)_2$)), 6.58 (1.0H, m, $OC_6H_3(CH_3)_2$)), 2.17 (6.0H, s, $OC_6H_3(CH_3)_2$)). Anal. Calcd for $C_{32}H_{36}O_4Ti$: C, 72.19; H, 6.77. Found: C, 71.84; H, 6.77.

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Because of the similarity of syntheses of **3**−**5** and **6**−**8**, a general description is supplied for the general synthesis of (a) Rb(OR) and (b) $RbTi(OR)_5$.

(a) General Synthesis of Rb(OR). The appropriate alcohol was added dropwise to a vial containing a mixture of Rb^0 in ∼10 mL of THF. Bubbling was observed. After stirring for 12 h, the colorless solution was concentrated and cooled to −35 °C to form X-ray quality crystals. *Note: This reaction is very exothermic and great care must be taken in handling* Rb^0 *and the subsequent generated waste.*

$[Rb(ONep)]_x$ (3). This reaction used Rb^0 (1.00 g, 11.8 mmol) and H-ONep (1.00 g, 11.8 mmol) in ∼10 mL of THF. Yield 1.72 g (84.3%). FTIR: (KBr, ν/cm^{-1}) 2949(s), 2862(m), 1582(w), 1451(s), 1426(m), 1391(m), 1347(m), 1113(m), 1013(m), 876(m), 765(w), 540(m). ^1H NMR (399.8 MHz, THF-d_8) δ 5.23 (2.0H, s, $OCH_2C(CH_3)_3$), 2.65 (9.0H, s, $OCH_2C(CH_3)_3$). $^{13}C\{^1H\}$ NMR (100.5 MHz, THF-d_8) δ 78.7 ($OCH_2C(CH_3)_3$), 35.1 ($OCH_2C(CH_3)_3$), 27.7 ($OCH_2C(CH_3)_3$). Anal. Calcd for $C_5H_{11}ORb$: C, 34.78; H,6.38. Found: C, 33.59; H, 6.39.

$[Rb_4(\mu\text{-DMP})_4(THF)_2]_\infty$ (4). This reaction used Rb^0 (1.21 g, 14.1 mmol) and H-DMP (1.74 g, 14.1 mmol) in ∼20 mL of THF. Yield 3.11 g (90.0%). IR: (KBr, ν/cm^{-1}): 2953(s), 2864(m), 1582(m), 1425(s), 1350(s), 1281(m), 1261(m), 1133(m), 1103(m), 1037(m), 947(w) 883(m), 839(s), 765(s), 677(w), 523(m), 428(w). ^1H NMR (399.8 MHz, THF-d_8) δ 6.62 (2.0H, d, $OC_6H_3(CH_3)_2)$), 5.85 (1.0H, m, $OC_6H_3(CH_3)_2)$), 2.02 (6.0H, s, $OC_6H_3(CH_3)_2)$). $^{13}C\{^1H\}$ NMR (100.5 MHz, THF-d_8) δ 168.3, 128.4, 124.7, 109.1 ($OC_6H_3(CH_3)_2$), 18.9 ($OC_6H_3(CH_3)_2$). Anal. Calcd for $C_{40}H_{52}O_6Rb_4$: C, 49.48; H, 5.36. Found: C, 49.89; H, 6.11.

$[Rb_2(\mu\text{-DIP})_2(\mu\text{-THF})]_\infty$ (5). This reaction used Rb^0 (0.570 g, 6.62 mmol) and H-DIP (1.18 g, 6.62 mmol) in ∼10 mL of THF. Yield 1.52 g (76.8%). FTIR: (KBr, ν/cm^{-1}) 2963(s), 1584(s), 1427(s), 1365(s), 1312(m), 1234(w), 1088(s), 972(s), 934(w), 909(w), 844(s), 753(s), 678(w), 496(s). ^1H NMR (399.8 MHz, THF-d_8) δ 6.70 (2.0H, d, $OC_6H_3(CH(CH_3)_2)_2$), 6.03 (1.0H, t, $OC_6H_3Me_2$), 3.52 (2.0H, m, $OC_6H_3(CH(CH_3)_2)_2$), 1.14 (12.0H, d, $OC_6H_3(CH(CH_3)_2)_2$). $^{13}C\{^1H\}$ NMR (100.5 MHz, THF-d_8) δ 168.3, 135.5, 122.6, 108.9 ($OC_6H_3(CH(CH_3)_2)_2$), 27.2 ($OC_6H_3(CH(CH_3)_2)_2$), 24.3 ($OC_6H_3(CH(CH_3)_2)_2$). Anal. Calcd for $C_{28}H_{42}O_3Rb_2$: C, 56.25; H, 7.03. Found: C, 55.64; H, 7.62.

(b) General Synthesis of Rb−Ti Double Alkoxides. A solution of the appropriate $[Ti(OR)_4]_x$ was added slowly to a vial of the stirring solution of $[Rb(OR)]_x$ dissolved in the appropriate solvent. The resultant clear reaction mixture was stirred overnight, concentrated by rotary evaporation, and then either cooled at −35 °C or left at room temperature until crystals formed.

$[Rb(\mu\text{-ONep})_4(py)Ti(ONep)]_2$ (6). This reaction used **1** (0.500 g, 1.26 mmol), **3** (0.220 g, 1.26 mmol), and 10 mL of pyridine. Yield 0.532 g (74.3%). ^1H NMR (399.8 MHz, py-d_5) δ 3.52 (2.0H, s, $OCH_2C(CH_3)_3$), 1.05 (9.0H, s, $OCH_2C(CH_3)_3$). $^{13}C\{^1H\}$ NMR (100.5 MHz, py-d_5) δ 72.68 ($OCH_2C(CH_3)_3$), 33.14 ($OCH_2C(CH_3)_3$), 26.6 ($OCH_2C(CH_3)_3$). Anal. Calcd for $C_{25}H_{55}O_5RbTi$: C, 52.78; H, 9.68. Found: C, 51.67; H, 9.12.

$[Rb(\mu\text{-DMP})Ti(DMP)_4]_\infty$ (7). This reaction used **2** (0.500 g, 0.94 mmol), **4** (0.910 g, 0.94 mmol), and ∼10 mL of THF. Yield 0.38 g (54.7%). ^1H NMR (399.8 MHz, THF-d_8) δ 6.82 (2.0H, d, $OC_6H_3(CH_3)_2$), 6.53 (1.0H, m, $OC_6H_3(CH_3)_2)$), 2.30 (6.0H, s, $OC_6H_3(CH_3)_2)$). $^{13}C\{^1H\}$ NMR (100.5 MHz, THF-d_8): δ 215.9, 128.6, 119.5, 109.1 ($OC_6H_3(CH_3)_2$), 18.9 ($OC_6H_3(CH_3)_2$). Anal. Calcd for $C_{40}H_{45}O_5RbTi$: C, 65.00; H, 6.09. Found: C, 64.35; H, 6.14.

$[Rb(\mu\text{-DMP})_2(\mu\text{-ONep})_2Ti(ONep)]_\infty$ (8). This reaction used **1** (0.500 g, 1.26 mmol), **4** (1.22 g, 1.26 mmol), and ∼10 mL of THF. Yield 0.52 g (64.8%). FTIR: (KBr, ν/cm^{-1}) 2654(s), 2907(m), 2867(m), 1591(w), 1479(m), 1466(m), 1439(w), 1392(m), 1376(m), 1362(m), 1294(m), 1229(m), 1069(s), 1022(s), 865(m), 751(m), 699(s), 650(w), 539(m). ^1H NMR (399.8 MHz, THF-d_8) δ 6.84 (4.0H, d, $OC_6H_3(CH_3)_2$), 6.58 (2.0H, m, $OC_6H_3(CH_3)_2)$), 2.17 (12.0H, s, $OC_6H_3(CH_3)_2)$), 3.13 (6.0H, s, $OCH_2C(CH_3)_3$), 0.85 (27.0H, s, $OCH_2C(CH_3)_3$). $^{13}C\{^1H\}$ NMR (100.5 MHz, THF-d_8) δ 168.3, 128.4, 124.7, 109.1 ($OC_6H_3(CH_3)_2$), 78.7 ($OCH_2C(CH_3)_3$), 35.1 ($OCH_2C(CH_3)_3$), 27.7 ($OCH_2C(CH_3)_3$), 18.9 ($OC_6H_3(CH_3)_2$). Anal. Calcd for $C_{31}H_{51}O_5RbTi$: C, 58.45; H, 8.01. Found: C, 55.19; H, 8.44.

General X-ray Crystal Structure Information.[40] Each crystal was mounted onto a thin glass fiber from a pool of Fluorolube and immediately placed under a liquid N_2 stream, on a Bruker AXS diffractometer. The radiation used was graphite monochromatized Mo Kα radiation (λ = 0.7107 Å). The lattice parameters were optimized from a least-squares calculation on carefully centered reflections. Lattice determination and data collection were carried out using SMART Version 5.054 software. Data reduction was performed using SAINT Version 6.01 software. The structure refinement was performed using XSHELL 3.0 software. The data were corrected for absorption using the SADABS program within the SAINT software package.

Each structure was solved using direct methods. This procedure yielded the heavy atoms, along with a number of the C, N, and O atoms. Subsequent Fourier synthesis yielded the remaining atom positions. The hydrogen atoms were fixed in positions of ideal geometry and refined within the XSHELL software. These idealized hydrogen atoms had their isotropic temperature factors fixed at 1.2 or 1.5 times the equivalent isotropic U of the C atoms to which they were bonded. The final refinement of each compound included anisotropic thermal parameters on all non-hydrogen atoms. Table 1 lists the data collection parameters for **2** and **4**−**8**. Tables 2 and 3 list interatomic distances and angles for **2** and **4**−**8**. We attempted numerous times to grow X-ray quality crystals of **3** but were unsuccessful. All CIF files were checked for errors using the free on-line Checkcif service provided by the International Union of Crystallography (available on the Web at http://www.iucr.org/acs/checkcif.html). Any problematic aspects of the structural solutions are discussed in the following paragraphs. Additional information concerning the data collection and final structural solutions of these compounds can be found in the Supporting Information or by accessing CIF files through the Cambridge Crystallographic Data Base.

$[Rb_4(\mu\text{-DMP})_4(THF)_2]_\infty$ (4). The structure was solved in the space group $P2_12_12_1$ using Patterson synthesis. This solution yielded the Rb, O, and some of the C atoms. Subsequent refinements yielded the remaining C atoms. THF was observed in the structural model as a disordered solvent. Attempts to structurally model the disordered THF failed, and so, the disordered THF was modeled using the PLATON/SQUEEZE program (Ver. 01-11-99). The SQUEEZE program located the solvent centers at (0.153 0.526 0.514), (0.347 0.474 1.014), (0.653 0.974 0.486), and (0.847 0.026 −0.014). These four sites had a total potential volume of 714.3 Å^3 and electron count of 157 electrons/cell, consistent with four THF molecules. The disordered THF molecules were added to the contents of the unit cell during the final refinement series so that the proper crystal data could be calculated. Because of complications with Rb interactions, it was difficult to model the hydrogen atoms. Therefore, hydrogen atoms were left off of the structural model but were added to the formula during the final refinement.

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(40) The listed versions of SAINT, SMART, XSHELL, and SADABS Software from Bruker Analytical X-ray Systems Inc., 6300 Enterprise Lane, Madison, WI 53719, were used in analysis.

Table 1. Data Collection Parameters for **2** and **4**−**8**

	2	**4**	**5**	**6**	**7**	**8**
chemical formula	$C_{32}H_{36}O_4Ti$	$C_{56}H_{84}O_6Rb_4$	$C_{44}H_{60}O_7Rb_4$	$C_{60}H_{120}N_2O_{10}$ Rb_2Ti_2	$C_{80}H_{90}O_{10}Rb_2Ti_2$	$C_{78}H_{134}O_{14}Rb_2Ti_2$
fw	532.51	1195.11	1042.80	1296.32	1478.26	1562.59
temp (K)	168(2)	168(2)	168(2)	178(2)	178(2)	178(2)
space group	triclinic $P\bar{1}$	monoclinic $P2_1/c$	orthorhombic $P2_12_12_1$	monoclinic $P2_1/c$	orthorhombic $Pna2_1$	monoclinic $P2_1/c$
a (Å)	9.1661(17)	12.970(7)	15.709(3)	11.3747(19)	17.101(2)	13.986(4)
b (Å)	9.6351(18)	11.549(6)	16.580(4)	20.282(4)	10.5715(14)	13.874(4)
c (Å)	16.736(3)	19.582(11)	17.556(4)	16.399(3)	19.698(3)	20.684(6)
α (deg)	78.234(3)					
β (deg)	86.085(3)	97.196(9)		101.573(3)		101.688(7)
γ (deg)	88.549(3)					
V (Å^3)	1443.5(5)	2910(3)	4572.4(17)	3706.4(11)	3561.2(8)	3215.3(15)
Z	2	2	4	2	2	2
D_{calcd} (Mg/m^3)	1.225	1.515	1.515	1.162	1.379	1.320
μ (Mo Kα) (mm^{-1})	0.330	3.388	4.302	1.568	1.641	1.494
R1^a (%) (all data)	5.89 (7.73)	4.34 (7.02)	7.66 (14.00)	3.53 (6.72)	5.32 (7.03)	11.02 (26.60)
wR2^b (%) (all data)	13.02 (14.01)	8.91 (9.81)	15.83 (173.84)	5.59 (5.91)	8.55 (9.01)	14.46 (28.80)

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o| \times 100$. [b] $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum(w|F_o|^2)^2]^{1/2} \times 100$.

Table 2. Selected Interatomic Distances (Å) and Angles (deg) for **2**, **4**, and **5**

		Complex **2**			
Ti(1)−O(1)	1.7853(17)	Ti(1)−O(3)	1.7979(18)	Ti(1)−O(4)	1.7990(18)
Ti(1)−O(2)	1.7841(18)				
O(2)−Ti(1)−O(1)	109.70(8)	O(1)−Ti(1)−O(3)	108.38(9)	O(2)−Ti(1)−O(4)	109.05(8)
O(2)−Ti(1)−O(3)	108.38(9)	O(3)−Ti(1)−O(4)	110.22(9)	O(1)−Ti(1)−O(4)	111.07(9)
		Complex **4**			
Rb(1)−O(1)	2.851(7)	Rb(3)−O(4)	2.825(7)	Rb(1)−C(7)	3.445(12)
Rb(1)−O(2)	2.715(8)	Rb(3)−O(6)	2.925(10)	Rb(2)−C(13)	3.271(11)
Rb(1)−O(4)	2.851(7)	Rb(4)−O(1)	2.851(6)	Rb(2)−C(14)	3.297(10)
Rb(2)−O(1)	2.868(7)	Rb(4)−O(3)	2.864(7)	Rb(3)−C(3)	3.385(10)
Rb(2)−O(3)	2.909(7)	Rb(4)−O(4)	2.755(7)	Rb(3)−C(16)	3.439(11)
Rb(3)−O(2)	2.990(7)	Rb(4)−O(5)	3.003(7)	Rb(4)−C(9)	3.517(11)
Rb(3)−O(3)	2.786(7)	Rb(1)−C(1)	3.473(10)	Rb(4)−C(15)	3.647(11)
O(2)−Rb(1)−O(1)	117.7(2)	O(3)−Rb(3)−O(6)	89.9(3)	O(1)−Rb(4)−O(5)	81.6(2)
O(3)−Rb(3)−O(2)	75.5(2)	O(4)−Rb(4)−O(5)	110.3(2)	O(4)−Rb(4)−O(1)	153.2(2)
		Complex **5**			
Rb(1)−O(1)	2.713(3)	Rb(2)−O(2)	2.701(3)	Rb(2)−C(2)	3.313(4)
Rb(1)−O(2)	2.714(3)	Rb(2)−O(3)	3.190(3)	Rb(2)−C(3)	3.262(4)
Rb(1)−O(3)	2.972(3)	Rb(2)−C(1)	3.358(4)	Rb(2)−C(4)	3.263(4)
Rb(2)−O(1)	2.724(3)				
O(1)−Rb(1)−O(2)	89.13(8)	O(2)−Rb(1)−O(3)	84.55(8)	O(2)−Rb(2)−O(3)	80.62(8)
O(1)−Rb(1)−O(3)	80.91(9)	O(2)−Rb(2)−O(1)	89.15(8)	O(1)−Rb(2)−O(3)	76.86(8)

[Rb(μ-DMP)$_2$(μ-ONep)$_2$Ti(ONep)]$_\infty$ (8). The structure was solved in the space group $P2_1/c$ using a Patterson refinement. This solution yielded the Rb, O, and some of the C atoms. Subsequent refinements yielded the remaining C atoms. THF was observed in the structural model as a disordered solvent. Attempts to structurally model the disordered THF failed, and so, the disordered THF was modeled using the PLATON/SQUEEZE program (Ver. 01-11-99). The SQUEEZE program located the solvent centers at (0.513 0.292 0.945), (0.487 0.792 0.555), (0.513 0.208 0.445), and (0.487 0.708 0.055). These four sites had a total potential volume of 830.8 Å^3 and electron count of 174 electrons/cell, consistent with four (THF) molecules. The disordered (THF) molecules were added to the contents of the unit cell during the final refinement series so that the proper crystal data could be calculated.

Results and Discussion

Previously, we explored the use of alkali metals as a means to generate complex precursors through a metathesis route with titanium alkoxides.[1,15] It is envisioned that these conveniently synthesized compounds could be used as templates for mixed metal complexes. However, the majority of these structures revealed cations that were too sterically encumbered to be exchanged.[1,15] Therefore, we decided to investigate Tl cations as potential metathesis agents and reported the synthesis of a series of $TlTi(OR)_5$ compounds.[41] While Tl is a good complexing agent for halide atoms, it is highly toxic (even in small amounts) and under further studies did not facilitate the formation of heteronuclear compounds.[17] We therefore reinvestigated the alkali metals of the $ATi(OR)_5$ series using the larger congener, Rb. In the following discussion, we detail the synthesis and characterization of sterically varied titanium aryloxide, rubidium alkoxides, and rubidium titanium double alkoxides. This study demonstrates the ability to generate Rb cations with various degrees of accessibility via the steric bulk of the coordinated alkoxy ligand.

Synthesis. Compounds **1**[18] and **2** were isolated from the reaction of $Ti(OPr^i)_4$ with 4 equiv of the respective alcohol in toluene (eq 1). In order to confirm the previously reported monomeric nature of **2**,[19,41] a crystallographic investigation was undertaken. A thermal ellipsoid plot of **2** is shown in Figure 1 which confirms the literature prediction.

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(41) Boyle, T. J.; Zechmann, C. A.; Alam, T. M.; Rodriguez, M. A.; Hijar, C. A.; Scott, B. L. *Inorg. Chem.* **2002**, *41*, 946.

Table 3. Selected Interatomic Distances (Å) and Angles (deg) for **6−8**

		Complex **6**			
Ti(1)−O(1)	1.8901(16)	Ti(1)−O(4)	1.8709(16)	Rb(1)−O(1)	3.1566(17)
Ti(1)−O(2)	1.9101(17)	Ti(1)−O(5)	1.9119(17)	Rb(1)−O(5)	3.0890(18)
Ti(1)−O(3)	1.8369(17)	Rb(1)−O(2)	2.9226(17)	Rb(1)−N(1)	3.087(3)
O(1)−Ti(1)−O(2)	89.11(7)	O(3)−Ti(1)−O(4)	122.30(8)	O(3)−Ti(1)−O(1)	122.35(8)
O(3)−Ti(1)−O(2)	91.03(7)	O(4)−Ti(1)−O(2)	89.72(7)	O(1)−Ti(1)−O(5)	87.52(7)
O(2)−Ti(1)−O(5)	173.99(7)	O(1)−Rb(1)−N(1)	119.58(6)	O(2)−Rb(1)−N(1)	103.44(6)
O(4)−Rb(1)−N(1)	106.72(6)	O(4)−Rb(1)−O(5)	50.93(4)	O(2)−Rb(1)−O(5)	143.10(5)
O(1)−Rb(1)−O(5)	128.24(5)	O(5)−Rb(1)−O(1)	49.79(4)	O(1)−Rb(1)−O(4)	87.24(5)
		Complex **7**			
Ti(1)−O(1)	1.945(5)	Rb(1)−O(1)	3.094(4)	Rb(1)−C(28)	3.306(7)
Ti(1)−O(2)	1.862(5)	Rb(1)−C(18)	3.623(8)	Rb(1)−C(29)	3.270(7)
Ti(1)−O(3)	1.896(4)	Rb(1)−C(19)#1	3.342(8)	Rb(1)−C(30)	3.301(7)
Ti(1)−O(4)	1.872(5)	Rb(1)−C(24)	3.746(11)	Rb(1)−C(37)	3.176(7)
Ti(1)−O(5)	1.857(4)	Rb(1)−C(27)	3.337(7)		
O(2)−Ti(1)−O(1)	87.5(2)	O(5)−Ti(1)−O(4)	92.8(2)	O(1)−Rb(1)−C(28)	102.49(18)
O(3)−Ti(1)−O(1)	92.5(2)	O(2)−Ti(1)−O(4)	92.2(2)	O(1)−Rb(1)−C(36)	100.33(15)
O(4)−Ti(1)−O(1)	178.2(2)	O(5)−Ti(1)−O(2)	119.6(2)	Ti(1)−O(1)−Rb(1)	144.4(2)
O(5)−Ti(1)−O(1)	85.8(2)				
		Complex **8**			
Ti(1)−O(1)	1.980(6)	Rb(1)−O(1)	2.901(6)	Rb(1)−C(2)	3.432(9)
Ti(1)−O(2)	1.847(6)	Rb(1)−O(3)	2.985(6)	Rb(1)−C(3)	3.388(9)
O(2)−Ti(1)−O(1)	87.5(3)	O(2)−Ti(1)−O(4)	124.5(3)	O(5)−Ti(1)−O(4)	91.8(3)
O(3)−Ti(1)−O(4)	124.6(3)	O(3)−Rb(1)−O(2)	60.21(17)	O(5)−Ti(1)−O(2)	95.9(3)
O(5)−Ti(1)−O(3)	95.9(3)	O(1)−Rb(1)−O(2)	53.45(17)	O(4)−Rb(1)−O(2)	148.07(18)
O(3)−Ti(1)−O(1)	87.1(3)	O(4)−Rb(1)−O(3)	147.99(18)	O(4)−Rb(1)−O(1)	122.49(17)

The novel rubidium complexes **3−5** were obtained via reaction of the pure metal with a THF solution of the appropriate alcohol (eq 2). In the syntheses of **3−5**, upon addition of a slight excess of the alcohol, evolution of a gas, presumed to be hydrogen, was observed. After stirring for 12 h, the Rb^0 had been consumed, and the reaction mixture was clear. X-ray quality crystals were isolated through slow evaporation of the volatile materials for **4** and **5**, and thermal ellipsoid plots are shown in Figures 2 and 3, respectively.

Heterometallic alkoxides were prepared in an analogous manner as we presented previously,[1,15,41] wherein a Rb(OR) and a $Ti(OR)_4$ were mixed together in a 1:1 stoichiometry and stirred overnight, and then, the volatile material was removed by slow evaporation. If X-ray quality crystals were not isolated by this method, the solution mixture was placed in a freezer at −35 °C until crystals formed. The products isolated from various combinations of the parent alkoxides were identified as the homoleptic **6−8**.

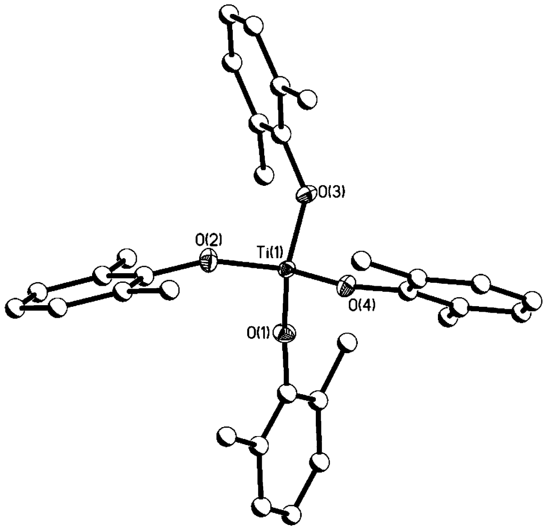

Figure 1. Thermal ellipsoid plot of **2** (C atoms are shown as a ball-and-stick plot for clarity). Ellipsoids are drawn at the 30% level.

Crystals of **2−8** were dried in vacuo to yield the bulk powder that was used in the following analyses. The FTIR spectra of **2−8** show no stretches associated with −OH ligands indicative of complete substitution for eqs 1−3. The standard alkyl and aryl stretches for the aryloxide as well as alkoxide stretches are present in each sample with small variations based upon the ligand substitution. Because of the complexity of the M−O region, it was not possible to definitively assign a Rb−O stretch. Elemental analyses for the bulk powders of the aryloxides are consistent with their respective crystal structures. However, for the ONep derivatives, the elemental analyses varied slightly. This is often attributed to the high volatility of the ONep derivatives for which it is notoriously difficult to get acceptable analyses.[18] For complex **8**, another explanation was uncovered. On the basis of stoichiometry, the assumed presence of $RbTi(ONep)_5$ as a byproduct in this reaction was observed by spectroscopic investigations and explains the variations noted.

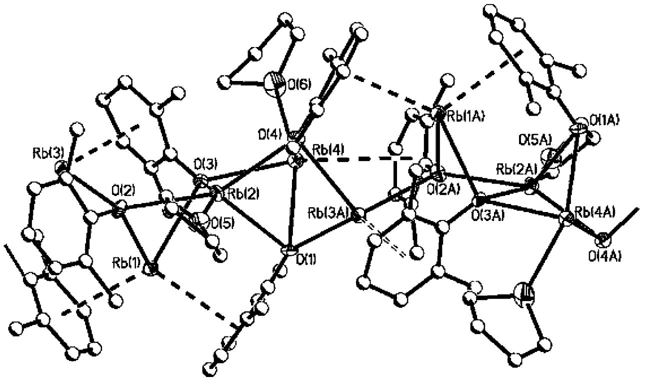

Figure 2. Thermal ellipsoid plot of **4** (C atoms are shown as a ball-and-stick plot for clarity). Ellipsoids are drawn at the 30% level.

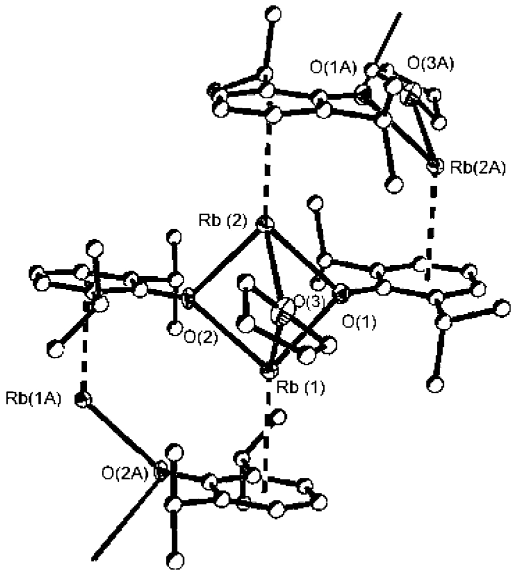

Figure 3. Thermal ellipsoid plot of **5** (C atoms are shown as a ball-and-stick plot for clarity). Ellipsoids are drawn at the 30% level.

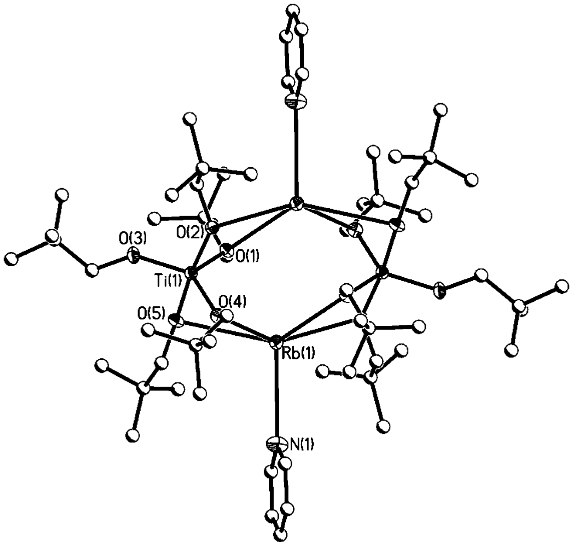

Figure 4. Thermal ellipsoid plot of **6** (C atoms are shown as a ball-and-stick plot for clarity). Ellipsoids are drawn at the 30% level.

X-ray Crystallographic Structures. Table 1 lists the data collection parameters for **2** and **4**−**8**, respectively. Tables 2 and 3 list interatomic distances and angles for **2** and **4**−**8**. Thermal ellipsoid plots of **2** and **4**−**8** are presented in Figures 1−6, respectively. Because of the lack of Rb(OR) and hence $RbTi(OR)_5$ complexes available in the literature, there are no representative model compounds to use for comparison. However, the structures observed for the double alkoxides are reminiscent of other mixed metal species (i.e., $TlTi(OR)_5$)[41] that we have previously investigated, and discussions of these compounds are included when appropriate.

Compound **2** is a simple discrete monomeric species (Figure 1) wherein the central Ti atom is tetrahedrally (Td) coordinated to four aryloxide ligands. The metrical parameters for **2** are similar to the structural reports of other homoleptic four coordinate Ti aryloxides, such as $Ti(DIP)_4$,[42,43] $Ti(OC_6H_4(C(CH_3)_3)\text{-}2)_4$,[44] and $Ti(OC_6H(CH_3)_4\text{-}2,3,5,6)_4$.[44]

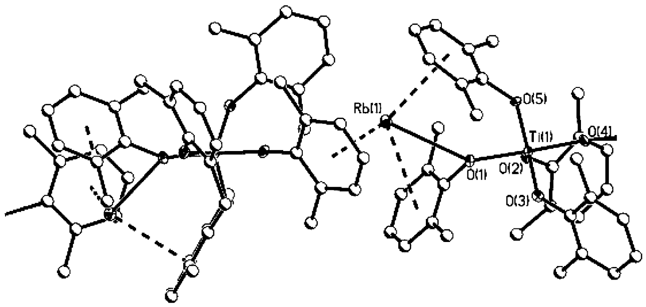

Figure 5. Thermal ellipsoid plot of **7** (C atoms are shown as a ball-and-stick plot for clarity). Ellipsoids are drawn at the 30% level.

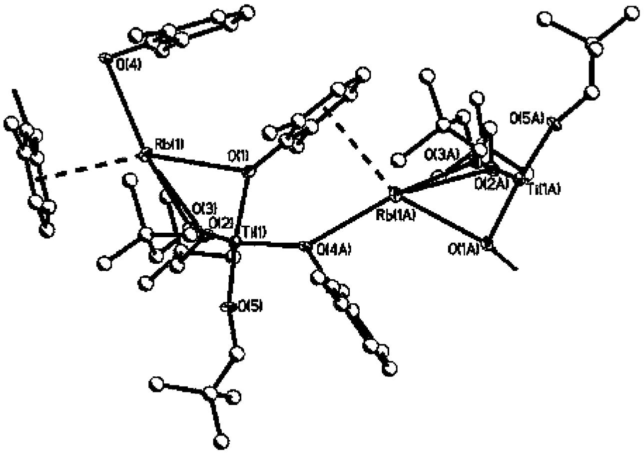

Figure 6. Thermal ellipsoid plot of **8** (C atoms are shown as a ball-and-stick plot for clarity). Ellipsoids are drawn at the 30% level.

Compounds **4** and **5** crystallize in an extended infinite array of Rb and μ-OAr groups. The unique construct of compound **4** consists of an asymmetric arrangement of four Rb atoms linked by a variety of μ-DMP ligands (Figure 2). The Rb(1) metal center is Td coordinated to one μ_3-DMP ligand and one μ-DMP ligand, and it interacts with the π-electrons of the aromatic rings of two neighboring DMP ligands. Square based pyramidal (SBP) Rb(2) is coordinated to four μ_3-DMP ligands, and one terminal THF molecule. The Td Rb(3) is coordinated to three μ_3-DMP ligands, and bound to the π-ring of a neighboring DMP ligand. And the SBP Rb(4) is coordinated to three μ_3-DMP ligands and one terminal THF molecule, and it interacts with the π system of a neighboring DMP ligand.

The structure of **5** consists of two Rb atoms bridged equally by two μ-DIP ligands and one μ-THF molecule (Figure 3). Each 3-coordinate Rb atom fills its coordination sphere through an interaction with the π-ring of the neighboring DIP ligand adopting a Td geometry. This differs from the structure of the K-DIP adduct, $[K(\eta^6,\mu\text{-DIP})]_\infty$,[14] wherein it was reported that this unsolvated structure was generated regardless of the coordinating solvent, including the use of THF. This can be attributed to the larger coordination sphere Rb possesses versus its smaller congeners. The metrical data

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[42] Minhas, R.; Duchateau, R.; Gambarotta, S.; Bensimon, C. *Inorg. Chem.* **1992**, *31*, 4933.

[43] Durfee, L. D.; Latesky, S. L.; Rothwell, I. P.; Huffman, J. C.; Folting, K. *Inorg. Chem.* **1985**, *24*, 4569.

[44] Toth, R. T.; Stephan, D. W. *Can. J. Chem.* **1991**, *69*, 172.

are consistent with the literature reports on simple Rb(OR) sytems reported by both Chishom[32,35] and Couhorn.[32,35]

Crystallized from pyridine, compound **6** is tetranuclear, forming a ring of alternating Rb and Ti atoms linked by μ-ONep ligands. A thermal ellipsoid plot is shown in Figure 4. In addition to the four μ-ONep ligands, each trigonal bipyramidal (TBP) Ti atom also possesses a single terminal ONep ligand. The Rb atoms fill their SBP coordination sphere through coordination of a py molecule. In comparison to the $[ATi(OR)_5]_2$,[1,15,41] the structure is much more open with the μ_3-OR now reduced to μ-OR; however, the open coordination site on the Rb is now occupied by a py solvent molecule. This indicates that the Rb is more accessible to interactions than the previous $[ATi(OR)_5]_2$[1,15,41] systems.

Increasing the steric bulk to DMP for both metal centers yielded the polymeric species **7**. The $Ti(DMP)_5^-$ moieties of **7** were found to possess a trigonal bypyramidal Ti metal center with one μ-DMP binding to the Rb metal center. The Rb metal center was found to additionally interact with the π-ring of two DMP ligands from the parent moiety and one neighboring DMP π-ring to form an SBP coordinated Rb atom. None of the congener species adopted this polymeric structure; however, the π-rings were not present in all of these other systems. For the "$TlTi(OR)_5$" species investigated, the $TlTi(DMP)_5$ adopts a very similar arrangement. This complex reported a "naked" Tl atom solely supported by π-arene ring interactions. This differs from the coordination behavior found in **6** due to the covalent bond to the parent Ti. Apparently, the decreased electronegativity of rubidium versus thallium facilitates the additional coordination of one μ-DMP ligand to the Rb atom; however, the atom does appear accessible if the π-interaction can be reduced.

Using a heteroleptic ligand set consisting of the ONep and DMP ligands, compound **8** was isolated as an infinite chain of alternating Rb and Ti atoms linked by μ-DMP and μ-ONep ligands. The TBP Ti atoms utilize two DMP and three ONep ligands to fill its coordination sphere. The parent Ti moiety possesses one terminal ONep ligand and bridges to the distorted SBP coordinated Rb atom with two μ-ONep and one μ-DMP ligands. The other DMP acts as a bridge to a neighboring Rb atom. The Rb atom completes its coordination sphere by interacting with the π-ring of the parent μ-DMP.

Solution NMR. Understanding the solution behavior of these compounds is of interest in order to unravel the accessibility of the Rb atoms in a number of these compounds. Crystalline material of **3**−**8** was redissolved in the appropriate parent deuterated solvent for this study. For each derivative, only the resonances associated with the pendant alkoxide chains were observed. The simplistic spectra imply for the mixed alkoxide species that the various π-interactions must be destroyed in solution; otherwise, much more complex spectra would be observed. While additional work is being undertaken to further understand the behavior of these species, it appears that the Rb species are much more accessible than previously observed in the other congener $[ATi(OR)_5]_2$ systems.[1,15,41]

Summary and Conclusion

We have successfully synthesized and characterized a family of structurally varied "Rb(OR)" (**3**−**4**) and "$RbTi(OR)_5$" alkoxide compounds (**6**−**8**). For the aryloxide derivatives, the Rb atoms were found to form polymeric structures due to π-interactions with the aryl groups of the phenoxide ligands. These structural characteristics contrast with those of the lighter group 1 aryloxide complexes, which had a tendency to form di-, tri-, and tetranuclear structures but do appear similar to what was noted for the heavier group 1 aryloxide derivatives.[14,16,20] Numerous structural arrangements are expected for the "Rb(OR)" systems on the basis of concentration of the reaction mixture, solvents used, temperature of crystallization, and many other factors, but the structures reported here represent examples of the structure types available for Rb(OAr).

The addition of the heavier congener to the family of $[ATi(OR)_5]_n$ results in the formation of simple molecular and polymeric homoleptic $RbTi(OR)_5$ species. It appears that the degree of interaction can be fine-tuned through the use of mixed ligand sets. For all of these systems, the Rb atom appears much more accessible than noted for the lighter group 1 $[ATi(OR)_5]_n$ members. Currently, the chemical accessibility of the Rb atoms in these and other $RbTi(OR)_5$ system are being explored through metathesis reactions with metal halides.

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Supporting Information Available: X-ray crystallographic files in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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