Inorg. Chem. **1997,** *36,* 2391−2399 **2391**

Synthesis and Characterization of New Alkoxotitanates of Yttrium, Barium, and Copper: Single Crystal X-ray Diffraction Structures of $Cl_2Y\{Ti_2(OPr^i)_9\}$, $\{Ti(OPr^i)_5\}Ba\{Ti_2(OPr^i)_9\}$, and $ClCu\{Ti_2(OPr^i)_9\}$[†]

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Received October 31, 1996[⊗]

The synthesis and characterization of new mixed-metal alkoxides of titanium with yttrium, barium, and copper, achieved via salt elimination and acid−base reactions, is described. The metathesis reactions of $KTi_2(OPr^i)_9$ with anhydrous YCl_3 (1:1 and 2:1) and $CuCl_2$ (1:1) afford chloro-functionalized heterobimetallic alkoxides $Cl_2Y\{Ti_2(OPr^i)_9\}$ (**1**), $ClY\{Ti_2(OPr^i)_9\}_2$ (**2**), and $ClCu\{Ti_2(OPr^i)_9\}$ (**3**), respectively, in high yields. The barium−titanium derivatives $[Ba\{Ti_2(OPr^i)_{10}\}]_2$ (**4**), $\{Ti_2(OPr^i)_9\}Ba\{Ti(OPr^i)_5\}$ (**5**), and $Ba\{Ti_2(OPr^i)_9\}_2$ (**6**) result from the reaction between $[Ba(OPr^i)_2]_n$ and $Ti(OPr^i)_4$ in 1:2, 1:3, and 1:4 molar ratios, respectively. All the new derivatives (**1**−**6**) have been characterized by elemental analyses, variable-temperature ^1H and ^{13}C NMR, infrared spectroscopy, cryoscopy, and single crystal X-ray diffraction studies for **1**, **3**, and **5**. The crystallographic study of **1** reveals a mononuclear species where the yttrium atom, coordinated by four alkoxide oxygen atoms of the $\{Ti_2(OPr^i)_9\}^-$ unit and two chloride ligands, is in a pseudo-octahedral arrangement. The NMR (^1H and ^{13}C) and cryoscopic data for **1** indicate that the bioctahedral $\{Ti_2(OPr^i)_9\}$ framework, as observed in the solid state structure, is retained in solution also. The X-ray structure of copper derivative **3** exhibits a triangular heterometallic core $CuTi_2(\mu_2\text{-}OPr^i)_3(\mu_3\text{-}OPr^i)_2$ with chloride as a terminal ligand on copper. Each titanium bears two terminal OPr^i groups and displays a distorted octahedral geometry whereas copper has a pseudotrigonal bipyramidal environment. The high-temperature NMR studies for the paramagnetic **3** are in agreement with Curie law behavior; the isotropic shifts indicate that the OPr^i groups bound directly to the Cu^{II} center experience a greater paramagnetic influence in comparison to OPr^i groups attached to titanium only. Barium titanates reveal an interesting observation of structural and stoichiometry (Ba/Ti) change. The dimeric compound **4** (Ba/Ti, 1:2) reacts with 1 mol of $Ti(OPr^i)_4$ to offer mononuclear **5** with a Ba/Ti stoichiometry of 1:3; on further addition of 1 mol of $Ti(OPr^i)_4$, **5** is converted to **6** (Ba/Ti, 1:4). X-ray crystallography performed on **5** shows the molecular structure to be formed by the coordination of monoanionic $\{Ti(OPr^i)_5\}^-$ and $\{Ti_2(OPr^i)_9\}^-$ units to Ba^{2+} in bi- and tetradentate fashion, respectively. The coordination figure of the central atom, barium, corresponds to a trigonal prism distorted toward an octahedron. Crystal data for **1**: monoclinic space group *Cc*, $a = 21.618(14)$ Å, $b = 9.878(5)$ Å, $c = 19.949(13)$ Å, $\beta = 109.51(4)°$, $V = 4015(4)$ Å^3, $Z = 4$. Crystal data for **3**: triclinic space group $P\bar{1}$, $a = 10.085(2)$ Å, $b = 10.210(2)$ Å, $c = 21.551(4)$ Å, $\alpha = 84.40(3)°$, $\beta = 84.03(3)°$, $\gamma = 60.86(3)°$, $V = 1924.9(6)$ Å^3, $Z = 2$. Crystal data for **5**: triclinic space group $P\bar{1}$, $a = 11.850(2)$Å, $b = 13.888(3)$ Å, $c = 18.716(4)$ Å, $\alpha = 86.08(3)°$, $\beta = 89.15(3)°$, $\gamma = 83.36(3)°$, $V = 3052.3(11)$ Å^3, $Z = 4$.

Introduction

The advent of superconducting properties in the ternary metal oxide system $YBa_2Cu_3O_{7-\delta}$[1] has prompted great interest in the synthesis and characterization of Y-, Ba-, and Cu-containing alkoxides.[2] The synthesis of simple and soluble tris(alkoxides) of yttrium "$Y(OR)_3$" based on isopropoxide and *tert*-butoxide ligands suffer from the preferential formation of pentanuclear alkoxide cluster $Y_5O(OPr^i)_{13}$[3] and retention of halide ligands (e.g., $Y_3(OBu^t)_{10}Cl(THF)_2$ and $Y_2(OBu^t)_4Cl(THF)_4{}^+$),[4] respectively. The conventional barium and copper alkoxides are in general insoluble and nonvolatile species.[5] The solubility of homometallic species has been improved by the use of chelating or sterically crowded alkoxide ligands, which owing to their multidentate behavior or steric bulk reduce the extensive association of metal alkoxides to produce soluble derivatives.[2e] However, the use of chelating or encumbering ligands does not always offer less-associated species and formation of high-nuclearity aggregates with complex structures is frequently observed.[6] An alternative route to incorporate these metals in molecular precursors with precise stoichiometries is the synthesis of heterometallic alkoxides $MM'(OR)_{x+y}$, which are more soluble than the constituting, $M(OR)_x$ and $M'(OR)_y$, components. As a part of our continuing research on heterometallic alkoxides,[7] we are interested in developing synthetic principles for an easy access to molecular alkoxide assemblies containing two, three, or more different metals. To this end, we have reported on the first structural characterization of a heterotermetallic

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[†] Dedicated to Prof. Gottfried Huttner on the occasion of his 60th birthday.

[⊗] Abstract published in *Advance ACS Abstracts,* May 1, 1997.

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S0020-1669(96)01321-3 CCC: $14.00

isopropoxide, $[\{Cd(OPr^i)_3\}Ba\{Zr_2(OPr^i)_9\}]_2$, which demonstrates the versatility of the metalloligand $\{Zr_2(OPr^i)_9\}^-$ in the rational construction of heterometallic clusters.[7a] The chemistry of the face-sharing nonaisopropoxodimetalate unit $\{M_2(OPr^i)_9\}^-$ among early transition metals is dominated by the use of zirconium,[2b−d] and the formation of a similar bioctahedral substructure by the smaller titanium has not been studied; the iodide heterobimetallic, $ICdTi_2(OPr^i)_9$, and the dimeric heterotermetallic isopropoxide, $[\{Cd(OPr^i)_3\}Ba\{Ti_2(OPr^i)_9\}]_2$, derived from it are the only well-characterized examples for the existence of $\{Ti_2(OPr^i)_9\}^-$ (Ti, C.N. (coordination number) = 6) unit in solution and the solid state.[7c] The less-exemplified status of heterometal derivatives containing the $\{Ti_2(OPr^i)_9\}^-$ unit is presumably due to (i) the dissociative tendency of $MTi_2(OPr^i)_9$ (M = Na, K) derivatives (cf. Zr derivatives, $MZr_2(OPr^i)_9$, are isolable solids and can be sublimed in high yields),[5] (ii) the lack of structurally characterized six-coordinate titanium isopropoxide derivatives, which led to the common belief that the smaller titanium (r(Å): Ti, 0.64; Zr, 0.80) might not achieve hexacoordination due to the steric requirements of isopropoxide ligands,[8] and (iii) the monomeric and nonadduct-forming behavior of $Ti(OPr^i)_4$, which supports the preceding argument (cf. zirconium isopropoxide forms a dimeric alcoholate, $[Zr(OPr^i)_4{\cdot}Pr^iOH]_2$).[5] In view of the above and the importance of titanium-containing ceramics, we report herein the synthesis and characterization of a series of alkoxotitanates of yttrium, barium, and copper based on monoanionic $\{Ti(OPr^i)_5\}^-$ and $\{Ti_2(OPr^i)_9\}^-$ units.

Experimental Section

All reactions were carried out under an atmosphere of dry and deoxygenated dinitrogen. All solvents were carefully dried using appropriate drying agents, distilled prior to use, and stored over molecular sieves under dry nitrogen. Anhydrous YCl_3 and $CuCl_2$ were purchased from Aldrich. $Ti(OPr^i)_4$ (Fluka) was purified by distillation. $[Ba(OPr^i)_2]_n$ was prepared by the alcoholysis of $\{Ba[N(SiMe_3)_2]_2\}$.[9] ^1H and ^{13}C NMR spectra were recorded on a Bruker AC-200 NMR spectrometer, and chemical shifts were referenced to the proton impurities of the deuterated solvents and ^{13}C resonance of the solvents, respectively. ^{13}C CP MAS spectra were performed on a Bruker MSL 200S spectrometer. Elemental analyses (C, H) were performed using a LECO elemental analyser CHN 900. Fourier transform infrared spectra were recorded on a Bio-Rad FTS-165 as $CDCl_3$ solutions (s, strong; m, medium; w, weak; br, broad) or as KBr pellets. The IR spectra of new heterobimetallic alkoxides (**1**−**6**) exhibit, in both solution and the solid state, strong absorptions characteristic of the metal-attached isopropoxy groups.[5] The $(CH_3)_2CH$ skeletal vibrations are observed in the range 1176−1117 and 880−721 cm^{-1} while the ν (C−O) stretching vibrations are displayed in the range 1081−950 cm^{-1}. The Cu−Cl stretching frequency is observed as a single band at 668 cm^{-1} whereas ν(Y−Cl) are observed in the range 340−254 cm^{-1}. Standard analytical procedures were employed to estimate metal and chlorine contents in the new derivatives.[10] Molecular weights were determined cryoscopically by the freezing point depression of benzene.

Syntheses. (a) $\mathbf{Cl_2Y\{Ti_2(OPr^i)_9\}}$ (1). Anhydrous YCl_3 (1.52 g, 7.78 mmol) was slurried by stirring in a mixture of isopropyl alcohol−toluene, and a toluene (30 mL) solution of freshly prepared $KTi_2(OPr^i)_9$ [$KOPr^i$ 0.77 g (7.80 mmol); $Ti(OPr^i)_4$ 4.44 g (15.61 mmol)] was added; the resulting mixture was stirred for 16 h at 70 °C. The precipitated KCl was filtered off, and the solvent was removed in vacuo to obtain a viscous mass (5.88 g, 96%) which analyzed to $Cl_2Y\{Ti_2(OPr^i)_9\}$ (**1**). The product has a high solubility in a mixture of toluene−isopropyl alcohol (10:1, v/v); this solution when cooled to −10 °C produced rectangular colorless bars of **1** (1.94 g, 33%). A second crop (20%) of microcrystalline **1** could be obtained on further concentrating the mother liquor. Anal. Calcd for $C_{27}H_{63}Cl_2O_9Ti_2Y$: C, 41.15; H, 8.00; Cl, 9.00; Ti, 12.16; Y, 11.29. Found: C, 40.83; H, 7.64; Cl, 8.90; Ti, 12.01; Y, 11.36. IR (1500−200 cm^{-1}): 1497 s, 1463 m, 1388 m, 1331 s, 1283 m, 1255 m, 1134 s, 1082 s, 1000 m, 880 m, 850 m, 821 s, 730 s, 694 s, 671 m, 644 m, 577 s, 491 m, 352 s, 279 s. ^1H NMR (20 °C, C_6D_6, 200.13 MHz): δ 1.16 (d, J = 6 Hz, 12H), 1.23 (d, J = 6 Hz, 12H), 1.26 (d, J = 6 Hz, 6H), 1.61 (d, J = 6 Hz, 12H), 1.88 (d, J = 6 Hz, 12H) (CH_3); 4.47 (sept, J = 6 Hz, 5H), 4.75 (sept, J = 6 Hz, 4H) (CH). ^{13}C NMR (20 °C, C_6D_6, 50.3 MHz): δ 25.20, 25.54, 25.93, 26.23 (CH_3); 73.65, 73.82, 74.60, 75.81, 81.14 (CH). Molecular weight found 818, against the calculated value of 787.

The colorless compound $ClY\{Ti_2(OPr^i)_9\}_2$ (**2**) was prepared analogously by the reaction of YCl_3 and $KTi_2(OPr^i)_9$ in 1:2 molar ratio.

(b) $\mathbf{ClY\{Ti_2(OPr^i)_9\}_2}$ (2). YCl_3 (0.89 g, 4.57 mmol) and $KTi_2(OPr^i)_9$ [$KOPr^i$ (0.89 g, 9.15 mmol) + $Ti(OPr^i)_4$ (5.21 g, 18.31 mmol)]. Yield of crystallized product: 2.7 g, 45%. Anal. Calcd for $C_{54}H_{126}ClO_{18}Ti_4Y$: C, 46.97; H, 9.13; Cl, 2.57; Ti, 13.88; Y, 6.44. Found: C, 46.38; H, 8.99, Cl, 2.40; Ti, 13.71; Y, 6.35. IR (1500−200 cm^{-1}): 1469 s, 1385 m, 1369 m, 1337 s, 1171 s, 1151 m, 1031 s, 954 s, 863 m, 835 w, 668 s, 580 br, 566 w, 457 m, 419 s, 397 s, 353 s, 290 m, 254 w. ^1H NMR (−30 °C, C_7D_8, 200.13 MHz): δ 1.21 (d, J = 6 Hz, 24H), 1.24 (d, J = 6 Hz, 6H), 1.26 (d, J = 6 Hz, 24H), 1.29 (d, J = 6 Hz, 6H), 1.57 (d, J = 6 Hz, 18H), 1.61 (d, J = 6 Hz, 18H), 1.83 (d, J = 6 Hz, 6H), 1.95 (d, J = 6 Hz, 6H) (CH_3); 4.42 (m, 8H), 4.58 (m, 10H) (CH). ^{13}C NMR (-40 °C, C_7D_8, 50.3 MHz): δ 25.84, 26.07, 26.19, 26.30, 29.00, 30.68 (CH_3); 68.13, 73.66, 74.11, 74.30, 80.45, 80.73 (CH). Molecular weight found 1241, against the calculated value of 1380.

(c) $\mathbf{ClCu\{Ti_2(OPr^i)_9\}}$ (3). A toluene (25 mL) solution of $KTi_2(OPr^i)_9$ [freshly synthesized; obtained by reacting $KOPr^i$ (2.19 g, 22.32 mmol) and $Ti(OPr^i)_4$ (12.70 g, 44.67 mmol) in toluene at 70 °C] was added slowly to a suspension [toluene (10 mL)−isopropyl alcohol (1 mL)] of anhydrous $CuCl_2$ (3.0 g, 22.31 mmol) and the reaction mixture stirred at 40 °C for 24 h. The traces of isopropyl alcohol facilitate the reaction; however, an excess results in the extensive formation of $Cu(OPr^i)_2$ (insoluble), thus drastically reducing the yield. The greenish-white precipitate was filtered over a Celite pad to obtain a dark green solution. The solution was concentrated in vacuum and after adding a few drops of isopropyl alcohol was left at −30 °C for two days when transparent green rectangle-shaped crystals were formed in 35% yield. The crystals were dried in vacuo for analytical and spectral purposes. The analytical data conform to the formulation $ClCu\{Ti_2(OPr^i)_9\}$. Anal. Calcd for $C_{27}H_{63}ClCuO_9Ti_2$: C, 44.59; H, 8.67; Cl, 4.88; Cu, 8.74; Ti, 13.17. Found: C, 44.25; H, 8.39; Cl, 4.65; Cu, 8.59; Ti, 13.01. IR (1500−200 cm^{-1}): 1461 m, 1423 s, 1394 s, 1165 m, 1128 s, 1011 w, 950 m, 670 s, 505 br, 459 m, 422 s, 396 s, 353 s, 329 w, 278 s. ^1H NMR (20 °C, C_6D_6, 200.13 MHz): δ 2.13 (br, 54H) (CH_3). The methine protons are not observed at room temperature. ^1H NMR (+95 °C, C_7D_8, 200.13 MHz): δ 1.21 (d, 30H), 1.23 (d, 24H) (CH_3); 4.49 (br, 9H), (CH). ^{13}C NMR (+95 °C, C_7D_8, 50.3 MHz): δ 26.53 (CH_3), 76.15 (CH). Molecular weight determinations at two different concentrations (167 and 304 mg/20.0 mL) gave an average value of 815 against the calculated value of 727.

(d) $\mathbf{\{Ti_2(OPr^i)_9\}Ba\{Ti(OPr^i)_5\}}$ (5). To a toluene (10 mL) suspension of $Ba(OPr^i)_2$ (1.20 g, 4.69 mmol) was added a solution of $Ti(OPr^i)_4$ (4.01 g, 14.10 mmol) in toluene (20 mL) and isopropyl alcohol (10 mL). The resulting mixture was heated to reflux; the insoluble barium isopropoxide dissolved immediately, indicating the formation of a soluble heterometallic species. The reaction mixture was heated for ∼16 h. The removal of solvent in vacuum gave a colorless oil (5.15 g, 99%) which was dissolved in a minimum amount of toluene and isopropyl alcohol and left at −30 °C. Colorless prismatic crystals of **5** were formed (2.48 g, 48%) over a period of a few weeks. The compound is highly soluble in benzene, toluene, hexane, isopropyl alcohol, and THF. Attempted volatilization under reduced pressure resulted in decomposition, giving $Ti(OPr^i)_4$ as a volatile fragment. Molecular weight determination on $[\{Ti_2(OPr^i)_9\}Ba\{Ti(OPr^i)_5\}]_n$ at a concentration of 210 mg/20.0 mL indicated a monomeric behavior (n

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= 0.9). Anal. Calcd for $C_{42}H_{98}BaO_{14}Ti_3$: C, 45.47; H, 8.84; Ba, 12.39; Ti, 12.39. Found: C, 45.11; H, 8.56; Ba, 12.44; Ti, 12.83. IR (1500−200 cm^{-1}): 1461 s, 1385 m, 1369 m, 1336 br, 1176 s, 1130 m, 1035 s, 961 s, 864 m, 828 w, 730 m, 615 w. ^1H NMR (20 °C, C_6D_6, 200.13 MHz): overlapping set of doublets centered at δ 1.32, 1.37, 1.45, 1.68, 1.76 (CH_3); 4.58 (m, 5H), 4.89 (sept, 9H) (C*H*). ^{13}C NMR (20 °C, C_6D_6, 50.3 MHz): δ 26.27, 26.43, 26.53, 26.84, 27.34 (*C*H_3); 70.08, 70.57, 72.54, 72.23, 75.86, 77.34, 77.81 (*C*H). ^1H NMR (−53 °C, C_7D_8, 200.13 MHz): δ 1.30 (d, $J = 6$ Hz, 6H), 1.32 (d, $J = 6$ Hz, 6H), 1.37 (d, $J = 6$ Hz, 12H), 1.43 (d, $J = 6$ Hz, 6H), 1.46 (d, $J = 6$ Hz, 12H), 1.53 (d, $J = 6$ Hz, 30H), 1.70 (d, $J = 6$ Hz, 12H) (CH_3); 4.58 (m, $J = 6$ Hz, 3H), 4.89 (sept, $J = 6$ Hz, 6H), 5.06 (sept, $J = 6$ Hz, 5H) (C*H*). ^{13}C NMR (−53 °C, C_7D_8, 50.3 MHz): δ 26.47, 26.52, 26.59, 26.89, 27.06, 27.51, 27.95 (*C*H_3); 70.73, 72.82, 73.21, 73.25, 76.51, 77.91, 78.41 (*C*H). ^{13}C CP MAS NMR: 25.23, 25.48, 26.05, 26.45, 27.21, 27.89, 28.50 (*C*H_3); 70.59, 71.60, 71.88, 73.17, 73.92, 77.80, 78.27 (*C*H).

$[\mathrm{Ba\{Ti_2(OPr^i)_{10}\}}]_2$ (**4**) and $[\mathrm{Ba\{Ti_2(OPr^i)_9\}_2}]$ (**6**) could be obtained in a similar manner by treating $\mathrm{Ba(OPr^i)_2}$ with 2 and 4 mol of $\mathrm{Ti(OPr^i)_4}$, respectively.

(e) $[\mathrm{Ba\{Ti_2(OPr^i)_{10}\}}]_2$ (4). $\mathrm{Ba(OPr^i)_2}$ (1.95 g, 7.63 mmol) and $\mathrm{Ti(OPr^i)_4}$ (4.01 g, 14.10 mmol). Yield of crystallized product: 3.17 g, 53%. Anal. Calcd for $C_{30}H_{60}BaO_{10}Ti_2$: C, 43.68; H, 7.28; Ba, 16.66; Ti, 11.62. Found: C, 43.55; H, 7.09; Ba, 16.57; Ti, 11.70. IR (1500−200 cm^{-1}): 1470 s, 1388 m, 1375 s, 1361 m, 1160 vs, 1148 w, 1140 s, 1134 vs, 1117 w, 1081 br, 999 vs, 972 s, 965 s, 850 w, 822 m, 728 m, 694 m, 672 w, 618 m, 603 br. ^1H NMR (20 °C, C_6D_6, 200.13 MHz): δ 1.35 (d, $J = 6$ Hz, 120H) (CH_3); methine protons observed as broad multiplets centered at δ 4.89 and 4.69. ^{13}C NMR (20 °C, C_6D_6, 50.3MHz): δ 26.79 (*C*H_3); 77.60 (*C*H). ^1H NMR (−20 °C, C_7D_8, 200.13 MHz): δ 1.29 (d, $J = 6$ Hz, 24H), 1.34 (d, $J = 6$ Hz, 24H), 1.39 (d, $J = 6$ Hz, 12H), 1.44 (d, $J = 6$ Hz, 30H), 1.65 (d, $J = 6$ Hz, 24H) (CH_3); 4.54 (m, 8H), 4.86 (m, 10H), 5.00 (m, 2H) (C*H*). ^{13}C NMR (−20 °C, C_7D_8, 50.3 MHz): δ 26.22, 26.59, 26.76, 26.87, 27.27, 27.41, 27.70 (*C*H_3); 70.36, 72.64, 72.87, 77.59, 77.76, 77.98 (*C*H). Molecular weight found 1433, against a calculated value of 824.

(f) $\mathrm{Ba\{Ti_2(OPr^i)_9\}_2}$ (6). $\mathrm{Ba(OPr^i)_2}$ (1.06 g, 4.14 mmol) and $\mathrm{Ti(OPr^i)_4}$ (4.72 g, 16.60 mmol). Yield of crystallized product: 2.71 g, 47%. Anal. Calcd for $C_{54}H_{126}BaO_{18}Ti_4$: C, 46.52; H, 9.05; Ba, 9.86; Ti, 13.75. Found: C, 45.89; H, 8.75; Ba, 9.53; Ti, 13.60. IR (1500−200 cm^{-1}): 1492 m, 1463 s, 1388 m, 1371 s, 1337 m, 1165 m, 1125 s, 1003 s, 980 br, 853 s, 819 m, 721 w, 660 m, 612 s, 590 s, 510 w. ^1H NMR (20 °C, C_6D_6, 200.13 MHz): δ 1.38 (d, $J = 6$ Hz, 108H) (CH_3); 4.74 (d, $J = 6$ Hz, 18H) (C*H*). ^{13}C NMR (20 °C, C_6D_6, 50.3 MHz): δ 26.26 (*C*H_3); 76.37 (*C*H). ^1H NMR (−78 °C, C_7D_8, 200.13 MHz): methyl resonances observed as three broad signals centered at δ 1.41, 1.55 and 1.58; methine protons as a broad multiplet at δ 4.92. Molecular weight found 1250, against a calculated value of 1393.

Crystallographic Studies. (a) $\mathrm{Cl_2Y\{Ti_2(OPr^i)_9\}}$ (1). A suitable crystal (0.4 × 0.2 × 0.1 mm) was affixed to the end of a glass fiber using silicone grease and transferred in an atmosphere of dry and deoxygenated nitrogen to a Lindemann capillary of appropriate dimensions. The capillary was sealed and placed on the goniometer head of a Siemens Stoe AED 2 four-circle diffractometer equipped with graphite-monochromated Mo Kα radiation. Unit cell parameters were determined from the least-squares refinement of $(\sin \theta/\lambda)^2$ values for 25 accurately centered reflections. The crystallographic data collection parameters are listed in Table 1. A systematic search of a limited hemisphere of reciprocal space located a set of diffraction maxima corresponding to the two possible monoclinic space groups, noncentrosymmetric *Cc* (No.9) or the centrosymmetric *C*2/*c* (No. 15). Statistics favored the noncentrosymmetric choice *Cc*, which was shown to be the right choice by subsequent solution and refinement of the model. Data were collected at ambient temperature using a standard $\omega-\theta$ scan technique. Reference reflections were periodically monitored for intensity and orientation control; no crystal decay was observed. Intensities were corrected for Lorentz and polarization effects; absorption correction was made. All refinements and calculations were carried out with the SHELXS 86[11] and SHELXL 93[12] software package on a Digital Alpha 4/233 computer. The positions of heavy atoms for the structure were determined by direct methods and the remaining nonhydrogen atoms were located from successive difference Fourier map calculations. The refinements were carried out using full-matrix least-squares techniques. All nonhydrogen atoms were refined as individual anisotropic atoms. The hydrogen atoms were fixed in the idealized positions and were included for refinements in the final cycles. Weights were introduced in the last refinement cycles. A final difference Fourier map was devoid of significant features, ρ (max) = 0.722 e $Å^{-3}$.

Table 1. Summary of the Pertinent Crystallographic Features of Complexes **1**, **3**, and **5**

	1	**3**	**5**
chemical formula	$C_{27}H_{63}Cl_2O_9Ti_2Y$	$C_{27}H_{63}ClCuO_9Ti_2$	$C_{42}H_{98}BaO_{14}Ti_3$
formula weight	787.38	726.56	1108.23
space group	*Cc* (No. 9)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
a	21.618(14) Å	10.085(2) Å	11.850(2) Å
b	9.878(5) Å	10.210(2) Å	13.888(3) Å
c	19.949(13) Å	21.551(4) Å	18.716(4) Å
α	90°	84.40(3)°	86.08(3)°
β	109.51(4)°	84.03(3)°	89.15(3)°
γ	90°	60.86(3)°	83.36(3)°
V	4015(4) $Å^3$	1924.9(6) $Å^3$	3052.3(11) $Å^3$
Z	4	2	4
λ	0.710 73 Å	0.710 73 Å	0.710 73 Å
ρ_{calcd}	1.302 g cm^{-3}	1.254 g cm^{-3}	1.793 g cm^{-3}
μ	19.94 cm^{-1}	10.62 cm^{-1}	18.46 cm^{-1}
T	20 °C	20 °C	20 °C
GOF[a] on F^{2a}	1.124	1.048	1.028
$R(F_o^2)^b$	0.0595	0.0476	0.0731
$R_w(F_o^2)^c$	0.0811	0.0521	0.0786

[a] GOF, $[\sum[w(F_o^2 - F_c^2)^2]/(n - p)]^{1/2}$, where *n* is the number of reflections and *p* is the total number of parameters refined. [b] Conventional $R = \sum||F_o| - |F_c||/|F_o|$ for observed reflections having $F_o^2 > 2\sigma(F_o^2)$. [c] $R_w = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$ for all data.

(b) $\mathrm{ClCu\{Ti_2(OPr^i)_9\}}$ (3) and $\mathrm{\{Ti_2(OPr^i)_9\}Ba\{Ti(OPr^i)_5\}}$ (5). Crystal data, collection, and processing parameters are given in Table 1. A transparent green bar of **3** and a colorless crystal of **5** with approximate dimensions 0.5 × 0.4 × 0.3 and 0.6 × 0.38 × 0.2 mm, respectively, were sealed in thin-walled Lindemann capillaries for diffraction analysis in a manner described for **1**. In both the cases, a careful examination of the preliminary data set revealed no systematic extinctions or any diffraction symmetry suggesting the space group *P*1 or $P\bar{1}$. The centrosymmetric triclinic space group $P\bar{1}$ chosen, in each of the cases, was later proved to be correct by successful solution and refinement of the model. The structures were solved by a combination of direct methods and difference Fourier techniques. The positions of copper and titanium atoms in **3** and barium and titanium atoms in **5** were easily determined from an initial "*E*-map". Subsequent difference Fourier syntheses revealed the positions of the remaining nonhydrogen atoms. All nonhydrogen atoms in **3** and **5** were refined anisotropically, and hydrogen atoms were included as idealized contribution. Weights were introduced in the last refinement cycles. The final difference Fourier maps were featureless with minimum residual electron density of 0.505 (**3**) and 0.722 e $Å^{-3}$ (**5**).

Results and Discussion

Syntheses and Properties. Both metathesis (salt elimination) and Lewis acid−base (adduct formation) reactions are successfully employed in preparing a variety of new alkoxotitanates of yttrium, barium, and copper as illustrated in eqs 1−5. In only one case (eq 6), no heterometallic alkoxide can be isolated.

In general, the new heterobimetallic alkoxides (**1**−**6**) are highly moisture sensitive derivatives, soluble in common nonpolar solvents; the solubility increases remarkably in the

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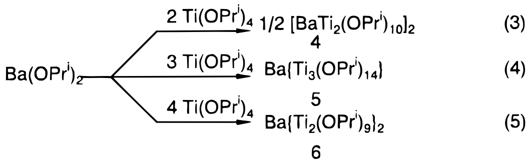
$$YCl_3 + n\,K\{Ti_2(OPr^i)_9\} \longrightarrow Cl_{3-n}Y\{Ti_2(OPr^i)_9\}_n + n\,KCl \qquad (1)$$

1: n = 1
2: n = 2

$$CuCl_2 + K\{Ti_2(OPr^i)_9\} \longrightarrow \underset{\mathbf{3}}{ClCu\{Ti_2(OPr^i)_9\}} + KCl \qquad (2)$$



$$Ba(OPr^i)_2 \xrightarrow{2\,Ti(OPr^i)_4} \underset{\mathbf{4}}{1/2\,[BaTi_2(OPr^i)_{10}]_2} \qquad (3)$$

$$Ba(OPr^i)_2 \xrightarrow{3\,Ti(OPr^i)_4} \underset{\mathbf{5}}{Ba\{Ti_3(OPr^i)_{14}\}} \qquad (4)$$

$$Ba(OPr^i)_2 \xrightarrow{4\,Ti(OPr^i)_4} \underset{\mathbf{6}}{Ba\{Ti_2(OPr^i)_9\}_2} \qquad (5)$$

$$CuCl_2 + 2\,M\{Ti(OPr^i)_5\} \longrightarrow Cu(OPr^i)_2 + 2\,Ti(OPr^i)_4 + 2\,MCl \qquad (6)$$

M = Li, Na, K

presence of very little quantities of isopropyl alcohol (for Y and Cu derivatives). All these derivatives could be purified for spectral and analytical purposes by recrystallization from toluene−isopropyl alcohol at low (−10 to −30 °C) temperatures. The compounds **1**−**3**, **5**, and **6** are monomeric in freezing benzene (molecular complexity, $\eta = 0.9-1.1$) while the derivative **4** tends to exhibit a dimeric behavior ($\eta > 1.7$). These alkoxotitanates are thermally labile, and attempted volatilization resulted in their decomposition to give a colorless oil as one of the volatile products which was shown by spectral and analytical data to be $Ti(OPr^i)_4$.

In a typical reaction, anhydrous YCl_3 reacted (eq 1) with (1:1, toluene−isopropyl alcohol, 70 °C) freshly synthesized potassium nonaisopropoxodititanate, $KTi_2(OPr^i)_9$ to afford $Cl_2Y\{Ti_2(OPr^i)_9\}$, (**1**). The workup (see Experimental Section) of reaction medium gave a viscous product which crystallized from a toluene and isopropyl alcohol mixture. The analytical data of the crystallized product are consistent with the formulation of **1**, which was corroborated by spectral and single crystal X-ray diffraction studies (vide infra). The bis derivative $ClY\{Ti_2(OPr^i)_9\}_2$ (**2**) was synthesized analogously by the reaction of YCl_3 and $KTi_2(OPr^i)_9$ in 1:2 molar ratios.

The chloro-functionalized copper−titanium heterobimetallic alkoxide $ClCu\{Ti_2(OPr^i)_9\}$ (**3**) was obtained by the equimolar reaction of anhydrous $CuCl_2$ and $KTi_2(OPr^i)_9$ in benzene−isopropyl alcohol at 40 °C. In the case of yttrium and copper derivatives, the presence of small amounts of a coordinating solvent (THF or Pr^iOH), added to solubilize the metal halides, facilitates the reaction. Also, the eliminaton of salt (KCl) in the preparation of Y and Cu compounds provides a thermodynamic assist and an increase in temperature pushes the reaction to completion. However, for the copper complex **3**, an excess of donor solvent or elevated temperatures (>50 °C) promote the formation of insoluble $Cu(OPr^i)_2$. Interestingly, the efforts made to obtain a chloride-free copper titanate by the reaction (1:2) of $CuCl_2$ and $MTi(OPr^i)_5$ (eq 6) under different conditions and in different solvents resulted in the formation of $Cu(OPr^i)_2$, MCl, and $Ti(OPr^i)_4$.

The dissolution of oligomeric metal alkoxides, $[M(OR)_n]_m$, by their reactions with early transition metal alkoxides is a convenient route to mixed-metal alkoxide precursors.[2] Such Lewis base reactions have been used for the deoligomerization of barium,[13] tin,[8] and lead[8,14] alkoxides. The investigations of barium−titanium mixed-metal alkoxides have received additional impetus due to their potential applications in ferroelectric ceramics barium titanates (e.g., $BaTiO_3$ in multilayer capacitors, $BaTi_4O_9$ as microwave dielectric resonator, $Ba_4Ti_{13}O_{30}$ in high-frequency resonators, etc.).[15] Heterometallic alkoxides offer a large flexibility in the combination and ratio of metals that can be incorporated in a single molecule[2] and in view of the large range of Ba/Ti stoichiometries present in barium titanate ceramics, we have synthesized three new heterobimetallic derivatives with Ba/Ti stoichiometries of 1:2, 1:3, and 1:4 (eqs 3−5).

The reaction of $[Ba(OPr^i)_2)]_n$ with 3 equiv of $Ti(OPr^i)_4$ in toluene−isopropyl alcohol solution produces the monomeric species $[BaTi_3(OPr^i)_{14}]$ (**5**) in almost quantitative yield. The reaction requires elevated temperatures and isopropyl alcohol and appears to be complete within several hours. Removal of solvent in vacuo leaves a viscous mass which crystallizes (−30 °C, toluene−isopropyl alcohol) as large square-shaped crystals over a period of few weeks. In an analogous manner, **4** and **6** with Ba/Ti ratios of 1:2 and 1:4, respectively, were obtained in high yields by the reaction of barium isopropoxide with appropriate quantities of $Ti(OPr^i)_4$, as outlined in eqs 3 and 5. A noteworthy aspect of the present study is the construction of heterometal alkoxide derivatives **4**−**6** with manipulable Ba/Ti stoichiometries. The neutral $Ti(OPr^i)_4$ acts as a building block and the dimeric compound **4**, with a Ba/Ti metal ratio of 1:2, reacts with a stoichiometric (1:1) amount of $Ti(OPr^i)_4$ to afford mononuclear species **5** (Ba/Ti, 1:3) which has been characterized in the solid state. Compound **5** can be converted into **6** by addition of another mole of $Ti(OPr^i)_4$ (see eq 7). The interaction of **4** with $Ti(OPr^i)_4$ is rather facile, and the reaction reaches completion within few hours of heating. However, the addition of one more $Ti(OPr^i)_4$ "brick" to **5**, in order to obtain **6**, requires drastic conditions (prolonged refluxing of the reaction mixture in toluene). Owing to the distinct spectroscopic patterns, the reaction of **5** with $Ti(OPr^i)_4$ is easily monitored by NMR spectroscopy as the educt **5** is stereochemically rigid at room temperature whereas the derivative **6** is highly fluxional at even very low temperatures. The reversibility of these conversions was not checked.

$$\underset{\mathbf{4}}{1/2\,[BaTi_2(OPr^i)_{10}]_2} \xrightarrow{Ti(OPr^i)_4} \underset{\mathbf{5}}{BaTi_3(OPr^i)_{14}} \xrightarrow{Ti(OPr^i)_4} \underset{\mathbf{6}}{BaTi_4(OPr^i)_{18}} \qquad (7)$$

In view of the suitability of alkoxide precursors for obtaining high-purity oxides, various attempted syntheses of superconducting oxide $YBa_2Cu_3O_{7-\delta}$ (YBCO) using homo- as well as heterobimetallic alkoxide derivatives are reported.[16] Although a few examples of heterobimetallic derivatives based on Y, Ba, and/or Cu are known, e.g., $BaY_2[\mu\text{-}OCH(CF_3)_2]_4(thd)_4$ (Ba:Y, 1:2),[17] $[Ba_2Cu(\mu_3,\eta^2\text{-}OCHMeCH_2NMe_2)_2(\mu,\eta^2\text{-}thd)_2(\eta^2\text{-}thd)_2(Pr^iOH)_2]$ (Y:Ba, 2:1),[18] $[Y_4Ba_2O(OEt)_8(thd)_6]$ (Y:Ba, 2:1),[19] $Ba_2Cu_4(OCEt_3)_8$ (Ba:Cu, 1:2),[20] $Ba\{Cu[OCMe(CF_3)_2]_3\}_2$

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Table 2. Selected Interatomic Distances (Å) and Angles (deg) for **1**

Y−O(7)	2.261(8)	Y−O(2)	2.308(8)
Y−O(4)	2.346(9)	Y−O(1)	2.373(8)
Y−Cl(2)	2.565(4)	Y−Cl(1)	2.566(4)
Ti(1)−O(6)	1.775(9)	Ti(1)−O(5)	1.784(9)
Ti(1)−O(4)	2.006(9)	Ti(1)−O(3)	2.019(9)
Ti(1)−O(1)	2.129(8)	Ti(1)−O(2)	2.186(7)
Ti(2)−O(9)	1.743(9)	Ti(2)−O(8)	1.769(9)
Ti(2)−O(7)	1.994(8)	Ti(2)−O(3)	2.057(8)
Ti(2)−O(1)	2.204(8)	Ti(2)−O(2)	2.207(8)
Y···Ti(1)	3.290	Ti(1)···Ti(2)	3.100
Y···Ti(2)	3.265		
O(7)−Y−O(2)	70.7(3)	O(7)−Y−O(4)	130.5(3)
O(2)−Y−O(4)	68.8(3)	O(7)−Y−O(1)	69.7(3)
O(2)−Y−O(1)	64.0(3)	O(4)−Y−O(1)	67.7(3)
O(7)−Y−Cl(2)	99.1(3)	O(2)−Y−Cl(2)	164.1(2)
O(4)−Y−Cl(2)	112.8(3)	O(1)−Y−Cl(2)	101.3(2)
O(7)−Y−Cl(1)	109.6(2)	O(2)−Y−Cl(1)	101.7(2)
O(4)−Y−Cl(1)	105.4(3)	O(1)−Y−Cl(1)	165.4(2)
Cl(2)−Y−Cl(1)	93.2(2)	O(6)−Ti(1)−O(5)	97.5(5)
O(6)-Ti(1)−O(4)	99.5(5)	O(5)−Ti(1)−O(4)	102.7(4)
O(6)−Ti(1)−O(3)	102.2(5)	O(5)−Ti(1)−O(3)	98.5(4)
O(4)−Ti(1)−O(3)	147.3(4)	O(6)−Ti(1)−O(1)	95.4(4)
O(5)−Ti(1)−O(1)	166.5(4)	O(4)−Ti(1)−O(1)	78.9(4)
O(3)−Ti(1)−O(1)	74.9(3)	O(6)−Ti(1)−O(2)	165.6(4)
O(5)−Ti(1)−O(2)	96.9(4)	O(4)−Ti(1)−O(2)	77.5(3)
O(3)−Ti(1)−O(2)	75.4(3)	O(1)−Ti(1)−O(2)	70.2(3)
O(9)−Ti(2)−O(8)	99.3(5)	O(9)−Ti(2)−O(7)	99.9(4)
O(8)−Ti(2)−O(7)	102.0(4)	O(9)−Ti(2)−O(3)	101.7(4)
O(8)−Ti(2)−O(3)	101.1(4)	O(7)−Ti(2)−O(3)	145.2(3)
O(9)−Ti(2)−O(1)	96.6(4)	O(8)−Ti(2)−O(1)	163.8(4)
O(7)−Ti(2)−O(1)	78.1(3)	O(3)−Ti(2)−O(1)	72.5(3)
O(9)−Ti(2)−O(2)	165.1(4)	O(8)−Ti(2)−O(2)	95.6(4)
O(7)−Ti(2)−O(2)	77.9(3)	O(3)−Ti(2)−O(2)	74.2(3)
O(9)−Ti(2)−O(2)	68.5(3)	Ti(1)−O(1)−Ti(2)	91.3(3)
Ti(2)−O(1)−Y	90.9(3)	Ti(1)−O(1)−Y	93.7(3)
Ti(2)−O(2)−Y	92.6(3)	Ti(1)−O(2)−Ti(2)	89.7(3)
Ti(1)−O(2)−Y	94.1(3)	Ti(1)−O(3)−Ti(2)	99.0(4)
Ti(1)−O(4)−Y	97.9(3)	Ti(2)−O(7)−Y	100.1(3)

(Ba:Cu, 1:2)[21] etc., the fixed metal stoichiometries present in these derivatives do not permit the desired metal ratios (e.g., 1(Y)/2(Ba)/3(Cu) in YBCO).[22] Further, in view of the ambiguous identity (Y) and insoluble (Ba, Cu) nature of the homometallic alkoxides of yttrium, barium, and copper, the choice left for the third component is often that of a non-alkoxide complex. Such a “heterogeneous” mixing (owing to the differential hydrolysis rates of alkoxide and non-alkoxide precursors) results in a sol or gel which is inhomogeneous with respect to the mixing of metallic constituents. In view of the above, the title derivatives with flexibility of attaining the desired metal ratio against a common heterometal partner titanium may find application in obtaining metallic constituents in a titania matrix. It is relevant to note that, using homo- and heterometal alkoxides, we have been recently successful in obtaining nanostructured metal−metal oxide composites.[23]

Solid State and Molecular Structures. Owing to the fluxional behavior of the alkoxide derivatives, the ambient-temperature ^{1}H NMR spectra of heterometal alkoxide derivatives often exhibit only one type of isopropoxide environment and are thus noninformative of the solution structures of heterometal alkoxide derivatives.[2] In order to gain insight into the coordination geometries of the metal centers, the solid state structures of **1**, **3**, and **5** were determined by single crystal X-ray crystallography.

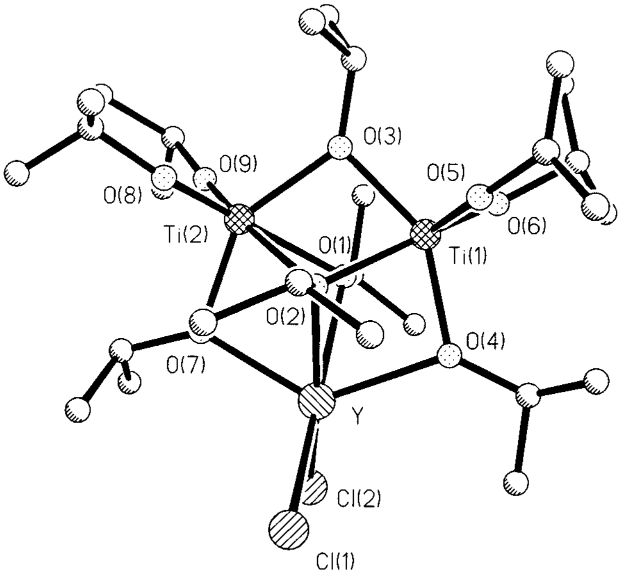

Figure 1. Ball-and-stick view of the molecular structure of $Cl_2Y\{Ti_2(OPr^i)_9\}$ (**1**) emphasizing the triangular $YTi_2(\mu_2\text{-}OPr^i)_3(\mu_3\text{-}OPr^i)_2$ framework and showing the atom numbering scheme used in the tables. Hydrogen atoms of Pr^i groups are omitted for clarity.

(a) $Cl_2Y\{Ti_2(OPr^i)_9\}$ (1). Square-shaped crystals of the (dichlorononaisopropoxodititanate)yttrium (**1**) were grown from a cold (−10 °C) isopropyl alcohol−toluene mixture and used for an X-ray structure analysis. The pertinent bond lengths and angles are listed in Table 2. The molecular structure (Figure 1) of **1** consists of a six coordinate yttrium bonded through four alkoxide oxygen atoms of the $\{Ti_2(OPr^i)_9\}^-$ unit and two chlorine atoms. The heterometallic triangle of metal atoms is bound by two capping triply bridging (μ_3-) OPr^i groups (above and below the YTi$_2$ triangle). The overall structure is a face-shared fusion of three octahedra built around a yttrium and two titanium atoms. Each metal has two terminal ligands which are chlorides in the case of yttrium. The $M_3O_9Cl_2$ framework of mononuclear **1** is a modification of the well-known M_3X_{11} core and is comparable with the structure of the trinuclear species $[La_3(O^tBu)_9\cdot(Bu^tOH)_2]$.[24] The two Y−Cl bond lengths are almost identical (2.565(4) and 2.566(4) Å) and comparatively shorter than the terminal Y−Cl distance observed in other chloro complexes of yttrium (e.g., for $ClY_2(OR)_6Na$, Y−Cl = 2.603 Å).[25] Within the $Ti_2(OPr^i)_9^-$ substructure, the titanium−oxygen bond distances are in the order commonly observed for $M'M_2(OR)_9$-type complexes of early transition metals and illustrate the stability of the $Ti_2(OPr^i)_9^-$ framework: Ti−O, terminal (average 1.767 Å) < Ti-(μ_2-O)-Ti; doubly bridged OPr^i (average 2.038 Å) < Ti$_2$-(μ_3-O)-Ti, triply bridged OPr^i (average 2.181 Å). It is noteworthy that the central metal atom yttrium is bound by the two bridging (Ti-(μ_2-OPr^i)-Y) isopropoxide oxygens (O(4) and O(7)) in an unsymmetrical fashion with a long (2.346(9) Å) and a short (2.261(8) Å) ligand bond. The average Y-μ_3-OPr^i distances in **1** are longer than Y-μ_2-OPr^i distances and follow the general trend commonly observed in heterometal complexes containing $M_2(OR)_9^-$ units (M = Sn(IV),[7b] Zr(IV),[7a] Hf(IV),[7c] U(IV),[26] Ce(IV),[27] and Th(IV)[28]), where the metal−

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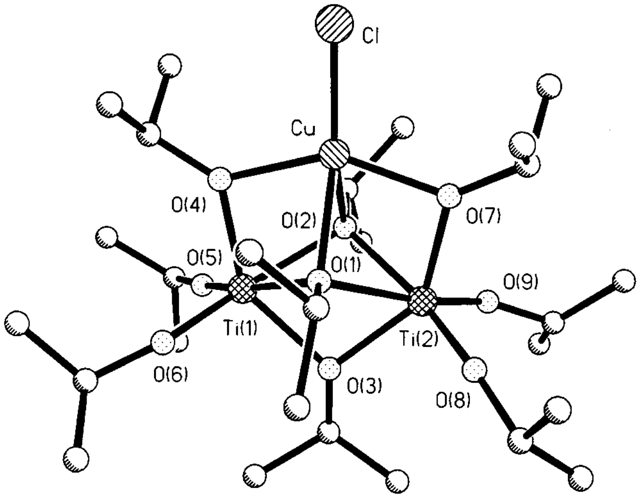

Figure 2. Ball-and-stick drawing of the molecular structure of $ClCu\{Ti_2(OPr^i)_9\}$ (**3**). Hydrogen atoms are omitted for clarity.

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

Cu−O(7)	2.007(2)	Cu−O(4)	2.008(2)
Cu−O(2)	2.149(2)	Cu−O(1)	2.157(2)
Cu−Cl	2.1720(12)	Ti(1)−O(5)	1.777(2)
Ti(1)−O(6)	1.790(2)	Ti(1)−O(4)	1.981(2)
Ti(1)−O(3)	2.066(2)	Ti(1)−O(1)	2.088(2)
Ti(1)−O(2)	2.155(2)	Ti(2)−O(8)	1.772(2)
Ti(2)−O(9)	1.783(2)	Ti(2)−O(7)	1.983(2)
Ti(2)−O(3)	2.087(2)	Ti(2)−O(2)	2.098(2)
Ti(2)−O(1)	2.155(2)	Cu···Ti(1)	2.955
Cu···Ti(2)	2.958	Ti(1)···Ti(2)	3.076
O(7)−Cu−O(4)	146.30(10)	O(7)−Cu−O(2)	76.65(10)
O(4)−Cu−O(2)	76.03(9)	O(7)−Cu−O(1)	76.12(9)
O(4)−Cu−O(1)	76.54(9)	O(2)−Cu−O(1)	70.79(8)
O(7)−Cu−Cl	107.51(8)	O(4)−Cu−Cl	106.18(8)
O(2)−Cu−Cl	145.87(7)	O(1)−Cu−Cl	143.33(8)
O(5)−Ti(1)−O(6)	98.39(12)	O(5)−Ti(1)−O(4)	100.11(11)
O(6)−Ti(1)−O(4)	100.47(11)	O(5)−Ti(1)−O(3)	101.69(11)
O(6)−Ti(1)−O(3)	104.68(10)	O(4)−Ti(1)−O(3)	143.65(9)
O(5)−Ti(1)−O(1)	166.59(10)	O(6)−Ti(1)−O(1)	94.95(10)
O(4)−Ti(1)−O(1)	78.75(9)	O(3)−Ti(1)−O(1)	73.35(9)
O(5)−Ti(1)−O(2)	94.69(10)	O(6)−Ti(1)−O(2)	166.90(10)
O(4)−Ti(1)−O(2)	76.44(9)	O(3)−Ti(1)−O(2)	73.11(8)
O(1)−Ti(1)−O(2)	71.99(8)	O(8)−Ti(2)−O(9)	98.54(12)
O(8)−Ti(2)−O(7)	100.30(12)	O(9)−Ti(2)−O(7)	101.62(12)
O(8)−Ti(2)−O(3)	101.14(11)	O(9)−Ti(2)−O(3)	104.74(11)
O(7)−Ti(2)−O(3)	142.86(9)	O(8)−Ti(2)−O(2)	166.75(10)
O(9)−Ti(2)−O(2)	94.63(10)	O(7)−Ti(2)−O(2)	78.36(10)
O(3)−Ti(2)−O(2)	73.88(9)	O(8)−Ti(2)−O(1)	95.01(11)
O(9)−Ti(2)−O(1)	166.42(10)	O(7)−Ti(2)−O(1)	76.67(9)
O(3)−Ti(2)−O(1)	71.56(8)	O(2)−Ti(2)−O(1)	71.80(8)
Ti(1)−O(1)−Ti(2)	92.90(8)	Ti(2)−O(1)−Cu	86.60(8)
Ti(1)−O(1)−Cu	88.20(8)	Cu−O(2)−Ti(1)	86.70(8)
Ti(2)−O(2)−Cu	88.28(9)	Ti(1)−O(4)−Cu	95.60(9)
Ti(2)−O(2)−Ti(1)	92.63(8)	Ti(1)−O(3)−Ti(2)	95.58(9)
Ti(2)−O(7)−Cu	95.69(10)		

oxygen contacts lengthen with increased bridging of alkoxide oxygen atoms.

(b) $ClCu\{Ti_2(OPr^i)_9\}$ (3). Single crystals of **3** suitable for an X-ray diffraction study were grown by leaving a toluene−isopropyl alcohol solution at −30 °C for two days. A ball-and-stick view of the solid state structure giving the atom numbering scheme used in the tables is shown in Figure 2. Selected bond distances and angles are summarized in Table 3. The molecular structure of **3** comprises the frequently encountered triangular "$M_3(\mu_2\text{-}OR)_3(\mu_3\text{-}OR)_2$" substructure and is strikingly similar to the solid state structures of a series of iodide heterobimetallic alkoxides of cadmium $ICd\{M_2(OPr^i)_9\}$ (M = Sn(IV), Ti(IV), Zr(IV), Hf(IV)),[7] where the formal cationic fragment CdI^+ is coordinated by the anionic $\{M_2(OPr^i)_9\}^-$ unit in a tetradentate fashion. The $MM'_2(OR)_9$ structural unit has increasingly become a common feature of the heterometal alkoxide chemistry, and structurally characterized compounds with an M_3O_5 closed triangular polyhedron are known for the metals of main group ($ICd\{Sn_2(OPr^i)_9\}$,[7b] $K_2Sb(O^tBu)_5{\cdot}$dioxane,[29] $KBa_2(OSiPh_3)_5(DME)_2$[30]), transition ($ICd\{M_2(OPr^i)_9\}$ (M = Ti, Zr, Hf),[7a,c] $[ClCd\{Zr_2(OPr^i)_9\}]_2$,[31] $(DME)KZr_2(OPr^i)_9$,[32] $ClCu\{Hf_2(OPr^i)_9\}$[33]), lanthanide ($NaCe_2(O^tBu)_9$, $(DME)_2Na_2Ce(O^tBu)_6$),[27] and actinide ($KU_2(O^tBu)_9$,[26] $NaTh_2(O^tBu)_9$[28]) elements. The triangular $CuTi_2$ frame in **3** with almost similar nonbonded Cu···Ti distances (2.955 and 2.958 Å) forms an isosceles triangle with the Ti···Ti vector (3.076 Å). The coordination environment of copper in **3** resembles a distorted trigonal bipyramid as observed in the bending of the axial O(7)−Cu−O(4) angle from the ideal 180 to 146.30°. The Cu−Cl distance of 2.1720 Å in **3** is comparable with that observed for structurally similar $ClCu\{Zr_2(OPr^i)_9\}$[34] (2.1644 Å). In contrast to the asymmetric coordination of yttrium in **1**, the copper atom in **3** is bound by the two doubly bridging OPr^i groups of $\{Ti_2(OPr^i)_9\}^-$ unit in a symmetrical fashion (Cu−O(4), 2.008(2) Å; Cu−O(7), 2.007(2) Å). Further, the copper−oxygen distances in **3** follow the expected trend (μ_3-OR > μ_2-OR), which may be explained on the basis of (i) much smaller size (Cu^{2+}, 0.72 Å; Y^{3+}, 0.95 Å)[35] and increased electrophilic behavior of copper (electronegativity, 1.90) in comparison to yttrium (electronegativity, 1.22), a combined effect of which probably results in a better fit of copper in the basket of the four oxygens of $Ti_2(OPr^i)_9^-$ unit, and (ii) the presence of two terminal chloride ligands in **1** which owing to their electron-withdrawing tendency may tend to pull the yttrium atom away from the Ti−Ti vector. Also Cu(II) is a d^9 system, and Jahn−Teller distortion induces an inherent flexibility in its coordination sphere which allows for longer semicoordinate Cu−X bonds as well as normal Cu−X bonds, where X is an anionic ligand.[36] The distances of copper to triply bridged (μ_3) oxygens (average 2.153 Å) are almost 0.15 Å longer than to the doubly bridged (μ) oxygens (average 2.007 Å) and are comparable with the distance of Cu^{2+} to the significantly larger chloride ion (2.164 Å). Furthermore, the distances of bigger Cu^{2+} to μ alkoxide oxygens (average 2.007 Å) are shorter than that of the smaller titanium ion (average 2.122 Å), which suggest that the copper coordination sphere can also be described as "3 + 2" with three strongly (O(4), O(7), Cl) and two weakly (O(1), O(2)) coordinated ligands. Each titanium is six coordinate but substantially distorted from a regular octahedron with the trans O−Ti−O angles ranging from 142.86 to 166.9° and cis angles in the range from 71.56 to 104.74° (Table 3). The three μ_2-OPr^i groups are planar at oxygen (sum of angles approaching 360°). The short terminal Ti−O bonds (average 1.780 Å) are associated with large Ti−O−C angles (average 164.7°).

(c) $\{Ti_2(OPr^i)_9\}Ba\{Ti(OPr^i)_5\}$ (5). Structural data were sought to examine the formation and existence of a dianionic

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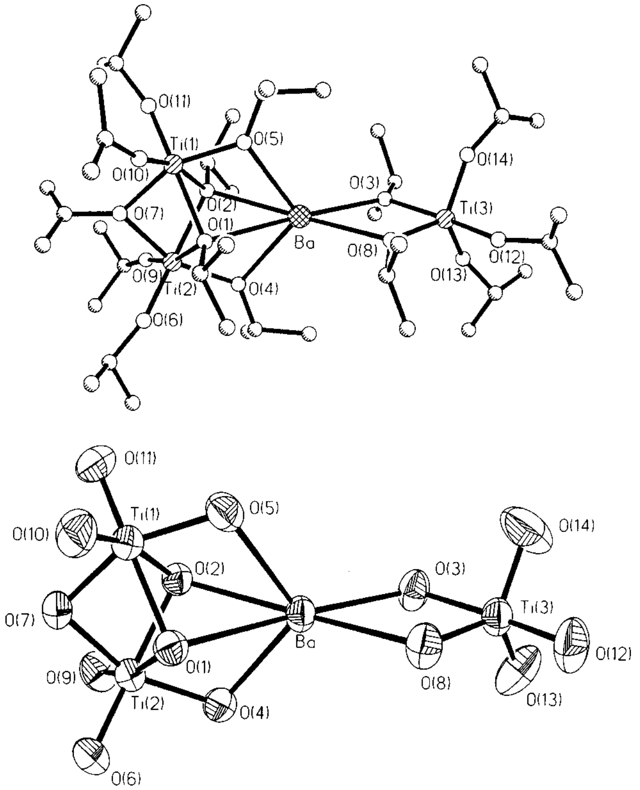

Figure 3. Representation of the molecular structure of $\{Ti_2(OPr^i)_9\}Ba\{Ti(OPr^i)_5\}$ (**5**), giving the atom numbering scheme adopted in the tables and an ORTEP plot of the $BaTi_3O_{14}$ core showing thermal ellipsoids drawn at 50% probability.

sequestering unit $\{Ti_3(OPr^i)_{14}\}^{2-}$ in the solid state. Formation of the alkali and alkaline earth metal alkoxometalates of compositions $M_2M'_3(OPr^i)_{14}$ and $M''M'_3(OPr^i)_{14}$ (M = Na, K; M′ = Zr^{IV}, Hf^{IV}; M″ = Mg, Ca, Sr, Ba), respectively, is reported and the proposed structures of these derivatives suggest a hexacoordination for the tetravalent metals.[5] However, there is no report available on the existence of a $M_3(OPr^i)_{14}^{2-}$ substructure in the solid state, although a modification of the $M_3(OR)_{14}^{2-}$ structural unit has been observed in the solid state structure of heterobimetallic acetatooxoalkoxide $PbZr_3O(OAc)_2(OPr^i)_{10}$.[37] The $\{Zr_3O(OAc)(OPr^i)_{10}\}^{2-}$ moiety binds Pb^{2+} in a pentadentate manner and can be seen as a modified $M_3(OPr^i)_{14}^{2-}$ unit where two OPr^i ligands are sacrificed at the expense of an O^{2-} ligand. In view of the observed similarity between $Ti(OPr^i)_4$ and $[M(OPr^i)_4{\cdot}Pr^iOH]_2$ (M = Zr, Hf) with respect to the formation and ligating mode of $M_2(OPr^i)_9^-$ units, we were interested in a metalloligand of the type "$Ti_3(OPr^i)_{14}^{2-}$".

Large prismatic crystals are formed over a period of a few weeks on keeping a toluene−isopropyl alcohol solution of **5** at −30 °C. Crystals suitable for diffraction studies were obtained by cleaving a well-formed crystal. The molecule of empirical formula "$Ba\{Ti_3(OPr^i)_{14}\}$" as represented in eq 4 is actually a mononuclear barium species formed by the tetra- and bidentate interaction of monoanionic $\{Ti_2(OPr^i)_9\}^-$ and $\{Ti(OPr^i)_5\}^-$ units, respectively, with Ba^{2+}. The analytical and cryoscopic data (monomer) of the product anticipated in eq 4 do indicate the presence of desired metal stoichiometry (Ba/Ti, 1:3) and possibly the $\{Ti_3(OPr^i)_{14}\}^{2-}$ structural unit, whereas the solid state structure determination reveal a different geometry and arrangement of ligands, however, with anticipated metal ratios.

The result of the X-ray structure determination of **5** is shown in Figure 3, and pertinent interatomic distances are presented in Table 4. The molecule contains a hexacoordinated barium which displays a distorted trigonal prismatic coordination geometry. A coordination figure similar to that of Ba has been observed for Er in the solid state structure of $ErAl_3(OPr^i)_{12}$.[38] An interesting aspect in the structure of **5** is the coexistence of face-sharing bioctahedral $\{Ti_2(OPr^i)_9\}^-$ and trigonal bipyramidal $\{Ti(OPr^i)_5\}^-$ units. Although five-coordinate titanium is quite common for titanium isopropoxide derivatives (e.g., $[LiTi(OPr^i)_5]_2$,[39] $[MTi(OPr^i)_5]_n$ (M = Na, K),[40] $Sm_4TiO(O^iPr)_{17}$,[41] and $[LiTiO(O^iPr)_3]_4$[42]), higher coordinated titanium centers are known only with oxo or other narrow bite angle (e.g., ethylene−glycolate ligands observed in $Ti_5(OPr^i)_9(\mu\text{-}OPr^i)(OC_2H_4O)_5$) ligands.[43]

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

Ba−O(3)	2.614(4)	Ba−O(8)	2.663(4)
Ba−O(5)	2.723(5)	Ba−O(2)	2.724(4)
Ba−O(4)	2.737(4)	Ba−O(1)	2.765(4)
Ti(1)−O(10)	1.790(5)	Ti(1)−O(11)	1.793(5)
Ti(1)−O(5)	1.937(4)	Ti(1)−O(7)	2.057(4)
Ti(1)−O(2)	2.154(4)	Ti(1)−O(1)	2.156(4)
Ti(2)−O(9)	1.786(4)	Ti(2)−O(6)	1.796(4)
Ti(2)−O(4)	1.931(4)	Ti(2)−O(7)	2.052(4)
Ti(2)−O(2)	2.148(4)	Ti(2)−O(1)	2.169(4)
Ti(3)−O(14)	1.801(6)	Ti(3)−O(13)	1.804(6)
Ti(3)−O(12)	1.824(5)	Ti(3)−O(8)	1.933(4)
Ti(3)−O(3)	2.026(4)	Ba···Ti(1)	3.652
Ba···Ti(2)	3.665	Ba···Ti(3)	3.805
Ti(1)···Ti(2)	3.079		
O(3)−Ba−O(8)	58.46(12)	O(3)−Ba−O(5)	122.94(14)
O(8)−Ba−O(5)	112.2(2)	O(3)−Ba−O(2)	127.99(11)
O(8)−Ba−O(2)	171.93(12)	O(5)−Ba−O(2)	60.76(12)
O(3)−Ba−O(4)	117.90(14)	O(8)−Ba−O(4)	123.76(14)
O(5)−Ba−O(4)	112.03(12)	O(2)−Ba−O(4)	59.41(11)
O(3)−Ba−O(1)	177.19(12)	O(8)−Ba−O(1)	120.30(12)
O(5)−Ba−O(1)	59.74(12)	O(2)−Ba−O(1)	53.51(11)
O(4)−Ba−O(1)	60.31(12)	O(10)−Ti(1)−O(11)	97.9(3)
O(10)−Ti(1)−O(5)	101.0(2)	O(11)−Ti(1)−O(5)	100.1(2)
O(10)−Ti(1)−O(7)	95.6(2)	O(11)−Ti(1)−O(7)	97.8(2)
O(5)−Ti(1)−O(7)	153.5(2)	O(10)−Ti(1)−O(2)	165.1(2)
O(11)−Ti(1)−O(2)	94.8(2)	O(5)−Ti(1)−O(2)	84.5(2)
O(7)−Ti(1)−O(2)	74.8(2)	O(10)−Ti(1)−O(1)	96.7(2)
O(11)−Ti(1)−O(1)	164.0(2)	O(5)−Ti(1)−O(1)	83.6(2)
O(7)−Ti(1)−O(1)	74.0(2)	O(2)−Ti(1)−O(1)	69.97(14)
O(9)−Ti(2)−O(6)	98.0(2)	O(9)−Ti(1)−O(4)	101.4(2)
O(6)−Ti(2)−O(4)	99.4(2)	O(9)−Ti(2)−O(7)	95.8(2)
O(6)−Ti(2)−O(7)	98.2(2)	O(4)−Ti(2)−O(7)	153.3(2)
O(9)−Ti(2)−O(2)	96.1(2)	O(6)−Ti(2)−O(2)	164.9(2)
O(4)−Ti(2)−O(2)	83.0(2)	O(7)−Ti(2)−O(2)	75.0(2)
O(9)−Ti(2)−O(1)	164.2(2)	O(6)−Ti(2)−O(1)	95.4(2)
O(4)−Ti(2)−O(1)	84.6(2)	O(7)−Ti(2)−O(1)	73.9(2)
O(2)−Ti(2)−O(1)	69.85(14)	O(14)−Ti(3)−O(13)	114.8(4)
O(14)−Ti(3)−O(12)	95.5(3)	O(13)−Ti(3)−O(12)	95.2(3)
O(14)−Ti(3)−O(8)	123.3(4)	O(13)−Ti(3)−O(8)	120.1(3)
O(12)−Ti(3)−O(8)	92.6(2)	O(14)−Ti(3)−O(3)	87.3(3)
O(13)−Ti(3)−O(3)	88.7(2)	O(12)−Ti(3)−O(3)	173.7(2)
O(8)−Ti(3)−O(3)	81.2(2)	Ti(1)−O(1)−Ti(2)	90.81(14)
Ti(2)−O(1)−Ba	95.19(13)	Ti(1)−O(1)−Ba	95.02(13)
Ti(2)−O(4)−Ba	102.1(2)	Ti(2)−O(2)−Ti(1)	91.41(14)
Ti(2)−O(2)−Ba	96.88(13)	Ti(3)−O(3)−Ba	109.5(2)
Ti(1)−O(5)−Ba	101.9(2)	Ti(3)−O(8)−Ba	110.8(2)
Ti(2)−O(7)−Ti(1)	97.1(2)		

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The Ti−O bond distances range from 1.786(4) to 2.169(4) Å, the order of variation being Ti−OPr^i < Ti-(μ_2-OPr^i) < Ti-(μ_3-OPr^i) (Table 4). Owing to the longer nonbonding Ba···Ti distances involving the $Ti_2(OPr^i)_9$ unit in **5** (cf. M···Ti distances in **1** and **3**), the Ba-μ_2-OPr^i distances span 2.730 Å and are comparable with Ba-μ_3-OPr^i distances (2.744 Å). The Ba-μ_2-OTi bond lengths involving $Ti(OPr^i)_5^-$ unit (2.638 Å) are considerably shorter than that of the $\{Ti_2(OPr^i)_9\}$ moiety (2.730 Å). The molecule can be formally viewed as a fusion of $Ba\{Ti_2(OPr^i)_9\}^+$ and $Ti(OPr^i)_5^-$ fragments; the "cationic" triangular unit "$Ba\{Ti_2(OPr^i)_9\}$" is reminiscent of the structural unit present in heterotermetallic isopropoxide $[\{Cd(OPr^i)_3\}Ba\{Ti_2(OPr^i)_9\}]_2$.[7c] Coordination at the oxygen atoms, (O(3), O(4), O(5), O(7), and O(8)) of doubly bridging isopropoxy groups is trigonal planar. The values of terminal Ti−OPr^i bond lengths (1.786−1.824 Å) are in agreement with the literature reports.[38,39,42,44] The short Ti−OR distances in **5** are associated with linearization of Ti−O−C angles; this feature as observed in the case of **1** and **3** is common among early transition metal complexes and is taken as a structural evidence for effective O pπ to metal dπ interactions.[45]

NMR Studies and Solution Structures. The room-temperature (20 °C) ^{1}H NMR spectrum of **1** exhibits signals corresponding to five different alkoxide environments in an integration ratio 2:2:1:2:2 for the *gem*-dimethyl protons of the isopropoxy groups. The methine protons are observed as two sharp septets in 4:5 intensity ratio. As found in the ambient and variable-temperature NMR studies of derivatives $ICd\{M_2(OPr^i)_9\}$ (M = Sn, Ti, Zr, Hf)[7] and other related complexes,[32] the observed spectroscopic pattern and the trend of chemical shifts (δ) vs connectivities (μ) of the isopropoxy groups is a peculiar feature of complexes based on a tetradentate $M_2(OPr^i)_9^-$ unit. Subjected to the electrophilicity of the heterometal atom (M′) the trend is: δ, μ_3-OPr^i > δ, μ_2-OPr^i (M−O−M′) > δ, μ_2-OPr^i (M−O−M) > δ, M−OR. The solution ^{13}C NMR spectrum of **1** supports the ^{1}H NMR data and displays five signals (2:2:1:2:2) in the region characteristic of methine carbons while methyl carbons are observed as four resonances. The molecular complexity from cryoscopic studies ($\eta = 1$, C_6H_6, +5 °C) in conjunction with the spectral data indicate that **1** maintains its monomeric structure (Figure 1) in solution too.

Ambient-temperature spectra of $ClY\{Ti_2(OPr^i)_9\}_2$ (**2**) in benzene-d_6 or toluene-d_8 reveals a complex pattern with a number of closely associated signals which could be properly resolved by low-temperature studies. The ^{1}H NMR spectrum at −30 °C displays eight doublets in the methyl region in an intensity ratio of 4:1:4:1:3:3:1:1. The number and relative and total intensities of the spectroscopic pattern are in agreement with a double-fold display of the signals observed for the $\{Ti_2(OPr^i)_9\}^-$ unit in **1**. The methine protons are observed as two multiplets which comprise of several overlapping septets. Attempts made to resolve the methine signals by further lowering of temperature were not successful until −90 °C. The $^{13}C\{^1H\}$ NMR spectrum of **2** at −40 °C shows six signals each for methine and methyl carbons, respectively. Molecular weight measurements using cryoscopy indicate the presence of **2** as monomeric species in solution. Although no X-ray crystallographic study has been made, a limiting structure, as inferred from low-temperature spectral data, presumably consists of two magnetically inequivalent $\{Ti_2(OPr^i)_9\}^-$ units, and a comparison with the spectroscopic pattern of **1** (if the terminal groups in each of the $Ti_2(OPr^i)_9^-$ unit are accidentally degenerate) indicates that, at lower temperatures, the site exchange of OPr^i groups takes place only among the OPr^i groups directly bound to yttrium (μ_2 and μ_3) and a site exchange in remaining OPr^i groups of the two $Ti_2(OPr^i)_9^-$ units is not observed.

Owing to the paramagnetic influence of copper(II), the room-temperature ^{1}H NMR spectrum of $ClCu\{Ti_2(OPr^i)_9\}$ (**3**) shows a very broad methyl signal with a significant (δ 2.13) downfield shift; the methine protons are not detectable. The paramagnetism of **3** makes it an interesting system for studying the Curie law, i.e., change in isotropic shift on varying the temperature. Indeed, the chemical shifts of **3** are found to be inversely proportional to the temperature in the range 0 to +100 °C. The gradual increase in temperature shows a consistent upfield shift and a noticeable sharpening in the methyl signals. The methine protons become visible as a broad peak at +85 °C. At higher (+97 °C) temperature, the methyl resonances split in two doublets of approximate intensity ratio 4:5; however, the methine signal remains a broad multiplet. The higher intensity doublet is relatively sharp and probably corresponds to the OPr^i groups not bound directly to copper center whereas the other broad doublet can be assigned to the methyl groups present on oxygen atoms (O(1), O(2), O(4), and O(7), Figure 2) bound directly to copper. The ^{13}C NMR spectrum at this temperature, however, shows only single resonances for both methyl and methine carbons.

The above studies are in agreement with simple Curie law behavior, and in view of the monomeric solid state structure (Figure 2) and the above studies being performed at elevated temperatures, the possibility of the interaction of paramagnetic centers ("$Cu(\mu\text{-}Cl)_2Cu$") in solution to form a dimeric diamagnetic system is quite low. Furthermore, the presence of monomeric species in the solution gains support from the cryoscopic studies ($\eta = 1.1$, average value of two measurement at different concentrations).

The room-temperature ^{1}H NMR spectrum of **4** is poorly resolved and shows overlapping resonances in the methyl region while the methine protons are observed as two broad multiplets. However, the resonances decoalesce on recording the spectra at low temperatures, and at −20 °C, the methyl region contains five doublets of intensity 4:6:2:4:4 whereas the methine region exhibits three overlapping multiplets in intensity ratio 2:10:8. Attempts made to use X-ray crystallography to determine the solid state structure of **4** were not successful; however, the molecular weight studies indicate the dimeric tendency of **4**. The monomeric formulation of **4** "$BaTi_2(OPr^i)_{10}$" is actually a ligand-deficient derivative of the M_3X_{11} structural unit, frequently observed in the heterometal alkoxide chemistry,[2] where each of the metal atoms has an octahedral coordination figure. In the case of **4**, the simplest structural change to achieve a M_3X_{11} motif involves the dimerization of **4** via "terminal" OPr^i groups present on barium. Such an association would be facilitated by the tendency of barium to achieve a higher coordination number. In view of the known X-ray structures of other "$M'M_2X_{10}$" systems which support the proposed dimerization, e.g., $[ClCd\{Zr_2(OPr^i)_9\}]_2$[30] and $[BaZr_2(OPr^i)_{10}]_2$,[46] a tentative structure (**I**) of **4** is proposed.

The spectral (^{1}H and ^{13}C) data of **5** are not structurally diagnostic due to the overlapping nature of the signals. However, on lowering the temperature, the resonances corresponding to different ligand environments separate out and the

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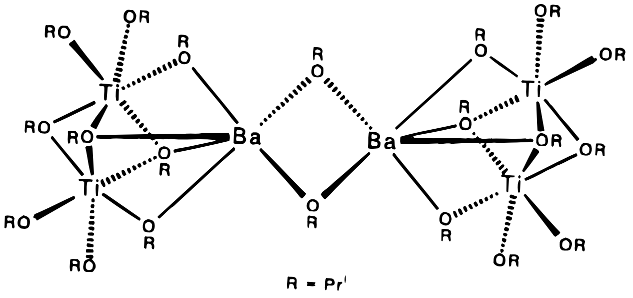
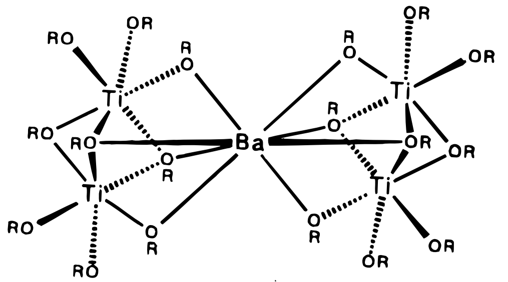


R = Pr^i

I



R = Pr^i

II

best resolved spectra (^{1}H and ^{13}C) are observed at −53 °C. The ^{1}H NMR spectrum exhibits seven sets of methyl resonances in an integration ratio of 1:1:2:1:2:5:2 whereas the methine region displays two distinct septets and a multiplet (two overlapping septets are seen) which integrate approximately 3:6:5. The ^{1}H NMR observations are corroborated by the ^{13}C NMR spectrum, which shows seven signals each for methyl and methine carbons. Fourteen signals are expected for the solid state structure of **5**; however, the relative and total intensities of ^{1}H and ^{13}C NMR spectra support the solid state structure of **5**, if some of the resonances are accidentally equivalent or equilibrated via some fluxional process. The solid state ^{13}C CP MAS NMR spectrum corroborates the solution observations and exhibits seven signals each for methyl and methine carbon atoms (see Experimental Section). The cryoscopic data indicating the monomeric tendency of **5** and the analysis of spectral data plausibly suggest the retention of the molecular framework (Figure 3) of **5** in solution too.

In contrast to **4** and **5**, the ^{1}H and ^{13}C NMR spectra of **6** reveal only one time-averaged isopropoxide resonance and are noninformative of the structural pattern existing in the solution. Attempts made to freeze the fluxional behavior of **6** in the temperature range +20 to −70 °C were not successful. A similar spectroscopic pattern was observed for ^{13}C NMR which shows single resonance for methyl and methine carbons. Molecular weight studies correspond to the monomeric behavior of **6** in freezing benzene. In view of the known X-ray structure of $Ba\{Zr_2(OPr^i)_9\}_2$[46] and the observed similarity in the bonding mode (tetradentate) of $Ti_2(OPr^i)_9^-$ and $Zr_2(OPr^i)_9^-$ units, we anticipate **6** to adopt a similar structure (**II**), where two equivalent $\{Ti_2(OPr^i)_9\}^-$ fragments are bound to the central atom barium in a spiro configuration. Although in analogy to zirconium derivative $Ba\{Zr_2(OPr^i)_9\}_2$[46], the tentatively proposed structure (**II**) of **6** shows Ba^{2+} to be eight coordinate, the possibility of barium being present in the preferred hexacoordination cannot be ruled out.

Conclusion

The present study describes the solution and solid state characterization of new alkoxotitanates of Y, Ba, and Cu, which besides constituting the 1:2:3 superconductor ($YBa_2Cu_3O_{7-\delta}$), are ubiquitous components of various other advanced ceramics. The solid state structures of **1**, **3**, and **5**, based on the interaction of the confacial bioctahedral $Ti_2(OPr^i)_9^-$ unit with the Y, Ba, or Cu atom, demonstrates the facile formation of sequestering anion $\{Ti_2(OPr^i)_9\}^-$ in both anion transfer (**1**−**3**) and Lewis acid−base (**4**−**6**) reactions that supports the stability of a confacial bioctahedral framework based on the small titanium atom.

Acknowledgment. We thank the Deutsche Forschungsgemeinschaft for financial support in the framework of program SFB 277 and Dr. Michael Zimmer for recording the solid state NMR spectra. S.M. gratefully acknowledges the Alexander von Humboldt-Stiftung, Bonn, Germany for the award of a research fellowship.

Supporting Information Available: X-ray crystallographic files in CIF format for **1**, **3**, and **5** are available on the Internet only. Access information is given on any current masthead page.

IC9613218