Inorg. Chem. 1991, 30, 3244-3245

Synthesis of Bimetallic Barium Titanium Alkoxides as Precursors for Electrical Ceramics. Molecular Structure of the New Barium Titanium Oxide Alkoxide $Ba_4Ti_{13}(\mu_3\text{-}O)_{12}(\mu_5\text{-}O)_6(\mu_1\text{-}\eta^1\text{-}OCH_2CH_2OCH_3)_{12}(\mu_1,\mu_3\text{-}\eta^2\text{-}OCH_2CH_2OCH_3)_{12}$

Complex alkoxides are promising precursors for the preparation of fine ceramic powders, thin-layer devices, and fibers.[1] Hydrolysis and condensation of alkoxides result in the formation of oligomeric structures in solution and in the eventual formation of a gel. The formation of heterometallic species can lead to chemical homogeneity at the molecular level. Although there are numerous examples of bimetallic alkoxides in the literature,[2-4] less is known regarding the structure of partial hydrolysis products. A better understanding of the sol–gel processing of ceramics could result from a study of hydrolysis and polycondensation reactions in complex alkoxides. The investigation described herein has as its objectives the study of the synthesis and hydrolysis of heterometallic alkoxide precursors for barium titanate ceramics. For example, $BaTiO_3$ is used in high dielectric constant capacitor materials, and $Ba_4Ti_{13}O_{30}$, in high-frequency resonators.[5]

A new barium titanium oxide alkoxide was synthesized by hydrolysis of barium titanium alkoxide that was prepared by reaction of barium methoxyethoxide[6a] with titanium methoxyethoxide.[6b] Barium titanium methoxyethoxide[7] (4.99 g, 10 mmol) was dissolved in 20 mL of methoxyethanol. Deionized water (0.96 g, 60 mmol) in 20 mL of methoxyethanol was then mixed with the alkoxide solution. After 2 months at room temperature, crystals suitable for X-ray structure determination were collected. Solid analyzed as $Ba_4Ti_{13}O_{18}(OCH_2CH_2OCH_3)_{24}$[8] was isolated in 30% yield based on titanium.

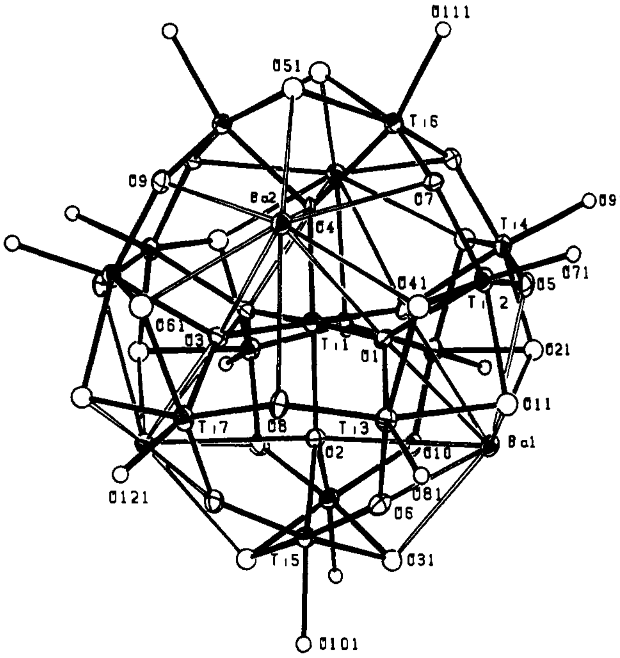

Figure 1. Perspective drawing of the Ba_4Ti_{13} cluster with 42 coordinated oxygen atoms, viewed roughly normal to the crystallographically imposed 2-fold symmetry axis which is parallel to the pseudo S_4 axis expected for the solution structure. Ba and Ti coordination spheres are distinguished by hollow and solid bonds, respectively. Oxo ligands are shown with boundary ellipsoids. Oxygen atoms of methoxyethoxide ligands are represented by unshaded spheres; oxygen atoms of dangling ligands are numbered as 071, 081, 091, 101, 111, and 121, and oxygen atoms of chelating ligands are labeled as 011, 021, 031, 041, 051, and 061. The three ether oxygen atoms that complete each Ba coordination sphere have been omitted for clarity. Selected average bond lengths (Å) and angles (deg): Ti(central)–μ_5-O, 2.020 (9); Ti(external)–μ_5-O, 2.069 (9); Ti(external)–μ_3-O, 1.832 (9); Ti(external)–OR(terminal), 1.853 (9); Ba–μ_3–O, 2.916 (9); Ba–μ_5-O, 3.080 (9), O_3–Ti_1–O_3, 180.0 (5); O_2–Ti_1–O_3, 90.0 (3); μ_3-O–Ti_2–OR(terminal), 95.9 (4); μ-O–Ti_2–μ-O, 94.2 (4); OR′(terminal)–Ti_2–OR(terminal), 85.7 (4).

X-ray structural analysis[9] of crystalline $Ba_4Ti_{13}(\mu_3\text{-}O)_{12}(\mu_5\text{-}O)_6(\mu_1\text{-}\eta^1\text{-}OCH_2CH_2OCH_3)_{12}(\mu_1,\mu_3\text{-}\eta^2\text{-}OCH_2CH_2OCH_3)_{12}$ revealed a tetrahedron of BaO_3 units superimposed on a TiO_6-$(TiO_3)_{12}$ core (see Figure 1). The $Ti_{13}O_{42}$ core resembles the $Al_{13}O_{40}$ core structure of $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{17+}$ and related ions,[10] but in the present case, the central titanium atom of the

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(6) (a) Barium methoxyethoxide was prepared according to the literature (Mazdiyasni, K. S.; Dolloff, R. T.; Smith, J. S., II. *J. Am. Ceram. Soc.* **1969**, *52*, 523). Anal. Calcd for $BaC_6O_4H_{14}$: C, 25.07; H, 4.91. Found: C, 24.83; H, 5.15. ^{13}C NMR (CD_2Cl_2): δ 71.08 (s, $OCH_2CH_2CH_3$), 61.99 (s, $OCH_2CH_2OCH_3$), 59.03 (s, $OCH_2CH_2OCH_3$). See also recent literature about the molecular structure of a barium oxide alkoxide aggregate that was prepared by reaction of Ba with $CH_3OCH_2CH_2OH$ in toluene: Caulton, K. G.; Chisholm, M. H.; Drake, S. R.; Huffman, J. C. *J. Chem. Soc., Chem. Commun.* **1990**, 1498. (b) Titanium methoxyethoxide was obtained according to the procedure of Ramamurthi (Ramamurthi, S. D.; Payne, D. A. *J. Am. Ceram. Soc.* **1990**, *73*, 2547). Anal. Calcd for $TiC_{12}O_8H_{28}$: C, 41.39; H, 8.04. Found: C, 41.29; H, 8.09. ^{13}C NMR (CD_2Cl_2): δ 75.41 (s, $OCH_2CH_2OCH_3$), 73.54 (s, $OCH_2CH_2OCH_3$), 59.33 (s, $OCH_2CH_2OCH_3$).

(7) $BaTi(OCH_2CH_2OCH_3)_6$ was synthesized as follows. A 10-mmol amount of $Ba(OCH_2CH_2OCH_3)_2$ was refluxed with an equivalent amount of $Ti(OCH_2CH_2OCH_3)_4$ in methoxyethanol (25 mL) for 1 h. Solvent was removed by evaporation to yield a white solid (yield 92%). Anal. Calcd for $BaTiC_{18}O_{12}H_{42}$: C, 34.01; H, 6.66. Found: C, 33.62; H, 6.58. IR (Nujol mull, cm^{-1}): 1353 s, 1278 m, 1264 m, 1232 s, 1197 s, 1126 s, 1076 s, 1019 s, 905 s, 838 s, 581 s, 483 s, 478 s. ^{13}C NMR (CD_2Cl_2): δ 77.38 (s, $OCH_2CH_2OCH_3$), 77.30 (s, $OC'H_2CH_2OCH_3$), 76.54 (s, $OC''H_2CH_2OCH_3$), 70.90 (s, $OCH_2CH_2OCH_3$), 68.36 (s, $OCH_2C'H_2OCH_3$), 67.98 (s, $OCH_2C''H_2OCH_3$), 58.90 (s, $OCH_2CH_2OCH_3$), 58.80 (s, $OCH_2CH_2OC'H_3$), 58.42 (s, $OCH_2CH_2OC''H_3$). CPMAS ^{13}C NMR: δ 76.5 (s, $OCH_2CH_2OCH_3$), 67.7 (s, $OCH_2CH_2OCH_3$), 60.3 (s, $OCH_2CH_2OCH_3$).

(8) Anal. Calcd for $Ba_4Ti_{13}C_{72}O_{66}H_{168}$: C, 26.51; H, 5.19; Ba, 16.84; Ti, 19.09. Found: C, 26.78; H, 5.20; Ba, 16.49; Ti, 18.69. IR (Nujol mull, cm^{-1}): 1353 m, 1260 m, 1197 m, 1152 s, 1118 s, 1059 m, 1015 m, 963 m, 930 m, 836 m, 798 s, 580 s, 507 s, 478 m, 438 m. ^1H NMR (CD_2Cl_2): δ 4.71 (t, 2 H, $OCH_2CH'_2OCH_3$, J_{H-H} = 6 Hz), 4.08 (br, 2 H, $OCH_2CH''_2OCH_3$), 3.75 (br, 2 H, $OCH''_2CH_2OCH_3$), 3.57 (t, 2 H, $OCH'_2CH_2OCH_3$, J_{H-H} = 6 Hz), 3.48 (s, 3 H, $OCH_2CH_2OCH''_3$), 3.33 (s, 3 H, $OCH_2CH_2OCH'_3$). ^{13}C NMR (CD_2Cl_2): δ 77.01 (s, $OC'H_2CH_2OCH_3$), 75.58 (s, $OCH_2CH_2OCH_3$), 73.89 (s, $OCH_2CH_2OCH_3$), 69.85 (s, $OCH_2C'H_2OCH_3$), 59.60 (s, $OCH_2CH_2OC'H_3$), 58.70 (s, $OCH_2CH_2OCH_3$). CPMAS ^{13}C NMR: δ 76.8 ($OC'H_2CH_2OCH_3$), 74.6 (s, $OCH_2CH_2OCH_3$), 72.8 (s, $OCH_2CH_2OCH_3$), 70.4 (s, $OCH_2C'H_2OCH_3$), 59.1 (s, $OCH_2CH_2OCH_3$). ^{17}O NMR (CD_2Cl_2): δ 651 (s, OTi_2Ba), 487 (s, OTi_3Ba_2).

(9) Crystallographic data for $Ba_4Ti_{13}O_{18}(OCH_2CH_2OCH_3)_{24}$ at −75 °C: colorless, transparent crystal, dimensions 0.2 × 0.2 × 0.3 mm; monoclinic, space group $C2/c$; a = 29.898 (8) Å, b = 14.604 (5) Å, c = 30.685 (7) Å, β = 118.82 (2)°; V = 11739 (11) Å^3; D_c = 1.846 g/cm^3 for Z = 4; 4187 observed reflections with $I > 2.58\sigma(I)$; $R(F_o)$ = 0.051, R_w = 0.057. Data were collected by using an Enraf-Nonius CAD4 automated κ-axis diffractometer equipped with a graphite monochromator. The structure was solved by direct methods (SHELXS-86); correct positions for the barium and titanium atoms were deduced from an E map. Subsequent least-squares refinement and difference Fourier syntheses revealed positions for the remaining non-hydrogen atoms, including disordered atomic positions for two terminal alkoxide ligands.

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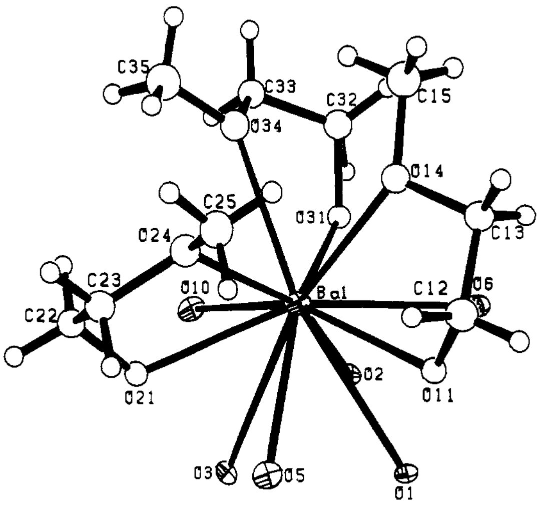

Figure 2. ORTEP plot (35% probability ellipsoids) of the barium coordination sphere showing the atom-labeling scheme. Barium and oxo oxygen atoms are represented by boundary ellipsoids, oxygen atoms of methoxyethoxide ligands are represented by large spheres, and carbon atoms are represented by small spheres. Selected average bond lengths (Å) and bond angles (deg): Ba–O(ether), 2.908 (9); Ba–OR, 2.693 (9); RO–Ba–O(ether), 60.9 (3).

$Ti_{13}O_{42}$ core is coordinated to six, not four, oxygen atoms. Each barium atom interacts with twelve oxygen atoms, six from three chelating alkoxide ether ligands and six from oxo ligands (see Figure 2). The unique central titanium atom is octahedrally coordinated to six trigonal-bipyramidal oxo ligands. Each of these internal oxo ligands is axially coordinated to two barium atoms and equatorially coordinated to the central and two external titanium atoms. External titanium atoms are coordinated to one internal (μ_5) and two bridging (μ_3) oxo ligands in addition to one terminal (μ_1-η^1) and two bridging (μ_1,μ_3-η^2) alkoxide oxygen atoms. The distorted octahedral coordination geometry of each external titanium atom is on average trigonally compressed in the direction of its three alkoxide ligands and expanded in the direction of its three oxo ligands. The chelating nature of the twelve bridging alkoxide ligands entraps the barium atoms within the cluster, in sharp contrast with the structure reported for lead(II) methoxyethoxide, which shows that methoxyethoxide ligands do not chelate through alkoxide ether oxygen atoms.[11]

$Ba_4Ti_{13}O_{18}(OCH_2CH_2OCH_3)_{24}$ was characterized by ^1H and $^{13}C\{^1H\}$ NMR spectroscopy in CD_2Cl_2 at 293 K. The ^{17}O NMR spectrum was recorded on material synthesized by hydrolysis with 10 wt % ^{17}O-enriched water. Six resonances of ^1H and $^{13}C\{^1H\}$ NMR spectra of this compound can be assigned to two types of methoxyethoxide ligands: terminal and bridging. The ^{17}O NMR spectrum of $Ba_4Ti_{13}O_{18}(OCH_2CH_2OCH_3)_{24}$ shows resonances at δ 651 and 487, which can be assigned, by analogy to other titanium oxide alkoxide systems,[12] to OTi_2Ba and OTi_3Ba_2 oxygens, respectively.

Thermal and X-ray powder diffraction analyses of the decomposition of $Ba_4Ti_{13}O_{18}(C_3O_2H_7)_{24}$ in air indicate the decomposition of alkoxide ligands between 255 and 355 °C. Crysallization of the $Ba_4Ti_{13}O_{30}$ phase occurred at 670 °C.[13a]

Preliminary results of experiments involving the partial hydrolysis of $BaTi(OCH_2CH_2OCH_3)_6$ suggest changes in powder stoichiometry at early stages of sol–gel processing. Heat treatment of gels formed by the addition of excess water to solutions of $BaTi(OCH_2CH_2OCH_3)_6$ results in the eventual formation of the perovskite structure, $BaTiO_3$, at temperatures as low as 400 °C.[13a] Both compounds, $Ba_4Ti_{13}O_{30}$ and $BaTiO_3$, have significant applications in electrical ceramics and now can be synthesized at greatly reduced temperatures compared with those for conventional mixed oxide processing (e.g. 1100 °C).[13b] The implications with respect to integration with semiconductors are profound.[14]

Acknowledgment. We acknowledge support of a Lavoisier Scholarship through the French Foreign Office and Rhone-Poulenc Chemie (J.-F.C.), Monsanto Chemical Co., and U.S. DOE Contract DMS-DEFG0291ER45439. We also acknowledge the use of facilities in the Materials Research Laboratory of the University of Illinois and are grateful to Dr. Frank S. Rosenberg and Professor Walter G. Klemperer for many helpful discussions.

Supplementary Material Available: An ORTEP diagram including all alkoxide ligands and the labeling scheme and tables of atomic coordinates, anisotropic thermal parameters, bond lengths, and bond angles (12 pages); a listing of observed and calculated structure factors (28 pages). Ordering information is given on any current masthead page.

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Received March 28, 1991

The Bis(methylcyclopentadienyl)titanium(IV) Molybdate Dimer: A Titanium(IV)–Molybdenum(VI) Eight-Membered Metal–Oxo Ring

Complexation of organometallic cations by polyoxoanions was elegantly pioneered by Klemperer.[1] We found, however, a single report on simple anions like MoO_4^{2-} or similar ones acting as ligands toward organometallic cations[2] in complexes $[(\eta^5\text{-}RC_5H_4)_2M_2O_4]$ (R = H, Me; M = Mo, W).[3] Compounds derived from such reactions may be suitable precursors of metal–oxo aggregates via the oxidation of the organic ligand under reductive coupling[4] or acid–base condensation reactions.[1] We are concerned in this paper with the high-yield synthesis of the bis(methylcyclopentadienyl)titanium(IV) molybdate dimer and its structural characterization.

An aqueous solution of $[(\eta^5\text{-}MeC_5H_4)_2TiCl_2]$ was reacted with an aqueous solution of $Na_2MoO_4\cdot 2H_2O^5$ (eq 1). The resulting

$$\underset{\mathbf{1}}{(\eta^5\text{-}MeC_5H_4)_2TiCl_2} + Na_2MoO_4\cdot 2H_2O \xrightarrow{H_2O} \underset{\mathbf{2}}{[(\eta^5\text{-}MeC_5H_4)_2Ti(\mu_2\text{-}MoO_4)]} \quad (1)$$

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