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Article

Methyltriskaidecazirconates, Molecular Forms of Zirconia

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Repeated methanolysis of $[Zr_3O](OPr^n)_{10}$ followed by extraction and crystallization from toluene yields material that is X-ray crystallographically indistinguishable from the compound previously formulated as $[Zr_{13}O_8](OMe)_{36}$. Elemental analysis and ^1H solution NMR spectroscopy strongly suggest that this material is a mixture of methyltriskaidecazirconates (MTZ) $[Zr_{13}O_8](OMe)_x(OH)_{36-x}$, $x_{av} \sim 20$, that readily cocrystallize from hydrocarbon solution. These species have the metal–oxygen framework structure reported for $[Zr_{13}O_8](OMe)_{36}$, where the 13 zirconium and 32 bridging oxygen atoms comprise a fragment of the fluorite structure adopted by ZrO_2 at elevated temperatures. Ethanolysis of $[Zr_3O](OPr^n)_{10}$ yields its ethyl analogue, $[Zr_3O](OEt)_{10}$. Both trizirconates display temperature-dependent ^1H solution NMR spectra that are interpreted mechanistically in terms of rearrangement mechanisms involving trigonal twists at the octahedral zirconium centers.

Introduction

The structures and properties of many early transition metal oxides are particle-size dependent, and although these size effects have been the subject of investigation for many years, their ultimate physical origin is unclear due to the difficulty of characterizing nanocrystalline materials on the atomic-molecular size scale.[1] This difficulty might be overcome if ensembles of stoichiometrically and structurally uniform molecular fragments of bulk oxides could be prepared, since these materials could in principle be characterized using the powerful spectroscopic and diffraction techniques associated with molecular chemistry. Unfortunately, high-nuclearity early transition metal oxide and oxoanion molecules, unlike metal cluster compounds[2] and polynuclear metal sulfides,[3] tend to adopt structures different from those adopted by bulk materials. Only one such species has been described to date, the $[Zr_{13}O_8](OMe)_{36}$ molecule reported by Morosin in 1977,[4] a molecule whose $Zr_{13}O_{32}$ core has the fluorite structure adopted by ZrO_2 at elevated temperatures[5] (see Figure 1). No further studies of this
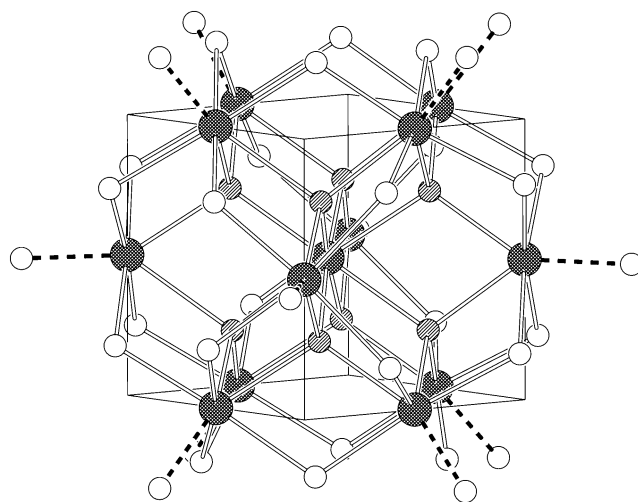

Figure 1. $Zr_{13}O_{44}$ metal–oxygen framework structure of $[Zr_{13}O_8](OMe)_{36}$ reported in ref 4. Zirconium atoms are represented by large spheres and oxygen atoms by small spheres; oxide oxygen atoms are shaded and methoxide oxygen atoms are unshaded. Metal–oxygen bonds to the μ_4-oxide and μ_2-methoxide oxygen atoms are represented by hollow bonds, and bonds to the terminal methoxide oxygen atoms are represented by filled, dashed bonds. The $Zr_{13}O_{32}$ core structure formed by the zirconium atoms, the 8 μ_4-oxide oxygen atoms, and the 24 μ_2-methoxide oxygen atoms comprise a fragment of the fluorite structure whose unit cell is included in the drawing: 1 Zr atom is at the body center of the cell and the remaining 12 Zr atoms occupy cell edge centers.

material have been reported, however, since the only sample described to date was inadvertently prepared by Dosch[6] from

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(2) Mednikov, E. G.; Ivanov, S. A.; Dahl, L. F. *Angew. Chem.* **2003**, *115*, 337−341.
(3) Dance, I. G. *Polyhedron* **1986**, *5*, 1037−1104.
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Zr(OMe)$_4$ in methanolic NaOH and the reaction conditions responsible for its formation have been impossible to replicate. In this paper, we report that methanolysis of [Zr$_3$O]-(OPr^n)$_{10}$ yields a mixture of methyltriskaidecazirconates (MTZ) [Zr$_{13}$O$_8$](OMe)$_x$(OH)$_{36-x}$, $x_{av} \sim 20$, that cocrystallize from toluene solution to yield material crystallographically indistinguishable from the material described by Morosin.

Experimental Section

Reagents, Solvents, and General Procedures. Zirconium(IV) n-propoxide, 70% solution by weight in 1-propanol, was purchased from Aldrich Chemical Co. and purified by vacuum distillation as described in ref 7. Water, 10 atom % ^{17}O isotope-enriched, was purchased from Aldrich. Reagent grade 1-propanol (Fisher Scientific) was refluxed under nitrogen over Mg(OCH$_2$CH$_2$CH$_3$)$_2$ and freshly distilled before use. Anhydrous ethanol (Aaper Alcohol and Chemical Co.) and methanol (Mallinckrodt) were refluxed under nitrogen over Mg(OCH$_2$CH$_3$)$_2$ and Mg(OCH$_3$)$_2$, respectively, and freshly distilled before use. Anhydrous methylcyclohexane (Aldrich) and toluene (Fisher Scientific) were dried over molecular sieves for at least 12 h, refluxed under nitrogen over Na, and freshly distilled prior to use. Benzene (Fisher Scientific) was dried over molecular sieves, refluxed under nitrogen over Na/benzophenone, and freshly distilled prior to use. Toluene-d_8, cyclohexane-d_{12}, methylcyclohexane-d_{14} (Cambridge Isotope Laboratories), and hexanes (Fisher Scientific) were dried over molecular sieves for approximately 24 h before use. Molecular sieves (3 Å, Linde type A, Grace Division) were activated by heating at 250 °C for at least 24 h and cooling under vacuum.

All experimental procedures were carried out under an argon or nitrogen atmosphere using standard Schlenk and drybox techniques. All glassware was washed in an ethanolic KOH bath, rinsed with dilute HCl and deionized water, and oven-dried for at least 12 h before use. Oxygen-17 NMR studies employed compounds enriched in ^{17}O. These samples were prepared following the experimental procedures described below using 10 atom % ^{17}O isotope-enriched water.

Analytical Procedures. Both 500 MHz ^{1}H and 125.7 MHz ^{13}C-{^{1}H} NMR spectra were recorded in 5 mm sample tubes on a Unity 500 or a Unity Inova 500NB spectrometer, and spectra recorded at 750 MHz (^{1}H) and 188.6 MHz (^{13}C) were measured on a Varian Unity Inova 750 spectrometer. In these spectra, chemical shifts were internally referenced to tetramethylsilane. Solution ^{17}O NMR spectra were recorded at 40.7 and 101.7 MHz in 10 mm sample tubes without sample spinning on an unlocked General Electric GN-300WB and a Varian Unity Inova 750 spectrometer, respectively. Chemical shifts were externally referenced to fresh tap water by the sample replacement method.

Elemental analysis was performed by the University of Illinois Microanalytical Service Laboratory.

Preparation of [Zr$_3$O](OPr^n)$_{10}$. A 100 mL round-bottom Schlenk flask was charged with 3.10 g (9.46 mmol) of zirconium-(IV) n-propoxide dissolved in 9.5 mL of methylcyclohexane. A solution of 60 μL (3.31 mmol) of water in 5.2 mL of 1-propanol was then added dropwise to the Zr(OPr^n)$_4$ solution via a pressure-equalizing addition funnel with vigorous stirring at a rate of approximately 1 drop per second. The reaction mixture was stirred at ambient temperature for 3.5 h, and the solvent was then removed under vacuum (10^{-2} mmHg) with slight heat (60 °C) over the course

of 3 h, yielding a white waxy solid. This solid was isolated and dried further under vacuum (10^{-2} mmHg) at 60 °C for approximately 12 h. It was extremely soluble (>1 g in 100 μL) in 1-propanol, tetrahydrofuran, heptane, cyclohexane, methylcyclohexane, toluene, and benzene. Yield: 2.09 g, 2.37 mmol, 76% based on Zr(OPr^n)$_4$. Anal. Calcd for Zr$_3$O$_{11}$C$_{30}$H$_{70}$: C, 40.92; H, 8.01. Found: C, 40.42; H, 8.07. ^{1}H NMR (500 MHz, cyclohexane-d_{12}, 22 °C): δ 4.30−3.85 (br m, −OCH$_2$CH$_2$CH$_3$), 4.01 (m, −OCH$_2$-CH$_2$CH$_3$), 3.99 (t, J = 6.8 Hz, −OCH$_2$CH$_2$CH$_3$), 1.72 (br, −OCH$_2$CH$_2$CH$_3$), 1.62 (br m, −OCH$_2$CH$_2$CH$_3$), 1.57 (sext, J = 7.3 Hz, −OCH$_2$CH$_2$CH$_3$), 1.00−0.80 (br, −OCH$_2$CH$_2$CH$_3$), 0.94 (t, J = 7.3 Hz, −OCH$_2$CH$_2$CH$_3$), 0.92 (t, J = 7.3 Hz, −OCH$_2$-CH$_2$CH$_3$). ^{1}H NMR (500 MHz, methylcyclohexane-d_{14}, −65 °C): δ 4.14 (br m, −OCH$_2$CH$_2$CH$_3$), 3.96 (br m, −OCH$_2$CH$_2$CH$_3$), 3.86 (br m, −OCH$_2$CH$_2$CH$_3$), 1.81 (br m, −OCH$_2$CH$_2$CH$_3$), 1.62 (br m, −OCH$_2$CH$_2$CH$_3$), 1.61 (m, −OCH$_2$CH$_2$CH$_3$), 1.55 (sext, J = 7.2 Hz, −OCH$_2$CH$_2$CH$_3$), 0.95 (t, J = 7.4 Hz, −OCH$_2$CH$_2$CH$_3$), 0.91 (t, J = 7.4 Hz, −OCH$_2$CH$_2$CH$_3$), 0.90−0.82 (br m, −OCH$_2$-CH$_2$CH$_3$), 0.81 (br, −OCH$_2$CH$_2$CH$_3$). ^{13}C{^{1}H} NMR (125.7 MHz, cyclohexane-d_{12}, 22 °C): δ 73.13 (−OCH$_2$CH$_2$CH$_3$), 72.31 (−OCH$_2$-CH$_2$CH$_3$), 71.08 (br, −OCH$_2$CH$_2$CH$_3$), 28.46 (−OCH$_2$CH$_2$CH$_3$), 28.05 (br, −OCH$_2$CH$_2$CH$_3$), 10.87 (−OCH$_2$CH$_2$CH$_3$), 10.83 (−OCH$_2$CH$_2$CH$_3$), 10.50 (br, −OCH$_2$CH$_2$CH$_3$). ^{13}C{^{1}H} NMR (125.7 MHz, methyl-cyclohexane-d_{14}, −65 °C): δ 72.71 (1C, −OCH$_2$CH$_2$CH$_3$), 72.55 (3C, −OCH$_2$CH$_2$CH$_3$), 71.70 (3C, −OCH$_2$CH$_2$CH$_3$), 70.28 (3C, −OCH$_2$CH$_2$CH$_3$), 28.16 (3C, −OCH$_2$CH$_2$CH$_3$), 28.14 (3C,-OCH$_2$CH$_2$CH$_3$), 27.97 (3C,-OCH$_2$CH$_2$CH$_3$), 26.91 (1C,-OCH$_2$CH$_2$-CH$_3$), 10.96 (3C, −OCH$_2$CH$_2$CH$_3$), 10.81 (3C, −OCH$_2$CH$_2$CH$_3$), 10.80 (3C, −OCH$_2$CH$_2$CH$_3$), 10.19 (1C, −OCH$_2$CH$_2$CH$_3$). ^{17}O NMR (40.7 MHz, 2:1 v/v methylcyclohexane/1-propanol, 22 °C): δ 323. ^{17}O NMR (40.7 MHz, methylcyclohexane, 22 °C): δ 276.

Preparation of [Zr$_3$O](OEt)$_{10}$. A 100 mL round-bottom Schlenk flask was charged with 4.08 g (4.63 mmol) of [Zr$_3$O](OPr^n)$_{10}$ and 40 mL of ethanol, and the resulting solution was heated to reflux in a silicone oil bath for 30 min. After the solution was allowed to cool to room temperature, the solvent was removed under vacuum (10^{-2} mmHg), yielding an oily material which was converted to a solid by further drying under vacuum (10^{-4} mmHg) for at least 2 h. This ethanolysis procedure was then repeated four additional times. After two or three treatments, not all of the solid product redissolved in ethanol at ambient temperature, but a clear solution was obtained upon heating. After the fifth and final treatment, the solid product was dried for 12 h under vacuum (10^{-4} mmHg) and purified twice by sublimation (165 °C, 10^{-4} mmHg), collecting the sublimate on a coldfinger that was cooled with dry ice; each sublimation required about 3 h. Yield: 2.01 g, 2.72 mmol, 58.7% based on Zr$_3$O(OPr^n)$_{10}$. ^{1}H NMR (750 MHz, methylcyclohexane-d_{14}, 20 °C): δ 4.15 (br, −OCH$_2$CH$_3$), 4.11 (br, −OCH$_2$CH$_3$), 1.31 (br, −OCH$_2$CH$_3$), 1.23 (br, −OCH$_2$CH$_3$). ^{1}H NMR (750 MHz, methylcyclohexane-d_{14}, −70 °C): δ 4.23 (br, −OCH$_2$CH$_3$), 4.18 (br, −OCH$_2$CH$_3$), 4.06 (br, −OCH$_2$CH$_3$), 3.98 (br, −OCH$_2$CH$_3$), 1.37 (br, −OCH$_2$CH$_3$), 1.26 (br, −OCH$_2$CH$_3$), 1.24 (t, J = 6.9 Hz, −OCH$_2$CH$_3$), 1.21 (t, J = 6.9 Hz, −OCH$_2$CH$_3$). ^{13}C{^{1}H} NMR (188.6 MHz, methylcyclohexane-d_{14}, 22 °C): δ 65.97 (br, −OCH$_2$-CH$_3$), 65.42 (−OCH$_2$CH$_3$), 64.76 (br, −OCH$_2$CH$_3$), 20.72 (−OCH$_2$CH$_3$), 20.62 (br, −OCH$_2$CH$_3$), 19.92 (br −OCH$_2$CH$_3$). ^{13}C-{^{1}H} NMR (188.6 MHz, methylcyclohexane-d_{14}, −10 °C): δ 65.91 (−OCH$_2$CH$_3$), 65.36 (−OCH$_2$CH$_3$), 65 (very br, −OCH$_2$CH$_3$), 20.75 (−OCH$_2$CH$_3$), 20.65 (−OCH$_2$CH$_3$), 19.96 (br −OCH$_2$CH$_3$). ^{13}C{^{1}H} NMR (188.6 MHz, methylcyclohexane-d_{14}, −70 °C): δ 66.29 (1C, −OCH$_2$CH$_3$), 65.74 (3C, −OCH$_2$CH$_3$), 65.18 (3C, −OCH$_2$CH$_3$), 63.80 (3C, −OCH$_2$CH$_3$), 20.77 (3C, −OCH$_2$CH$_3$),

(6) Robert Dosch, private communication.
(7) Day, V. W.; Klemperer, W. G.; Pafford, M. M. *Inorg. Chem.* **2001**, *40*, 5738−5746.

20.63 (3C, $-OCH_2CH_3$), 20.42 (3C, $-OCH_2CH_3$), 19.37 (1C, $-OCH_2CH_3$). ^{17}O NMR (40.7 MHz, ethanol, 22 °C): δ 322. ^{17}O NMR (101.7 MHz, methylcyclohexane, 22 °C): δ 278. Analytically pure product was obtained by extracting sublimed material (0.81 g, 1.09 mmol) with 4 mL of ethanol at ambient temperature. The ethanol solution was filtered through a Whatman PTFE syringe filter (25 mm diameter, 0.45 μm pore size, Fisher Scientific), the volatile materials were removed under vacuum, and the solid material remaining was dried under vacuum (10^{-2} mmHg) for 38 h. Anal. Calcd for $Zr_3O_{11}C_{20}H_{50}$: C, 32.45; H, 6.81. Found: C. 32.58; H, 6.75.

Methanolysis of $[Zr_3O](OPr^n)_{10}$. A solution of 10.9 g (12.4 mmol) of $[Zr_3O](OPr^n)_{10}$ in 100 mL of methanol was prepared in a 250 mL round-bottom Schlenk flask and heated to reflux in a silicone oil bath for 45 min. After the solution had cooled to room temperature, volatile materials were removed under vacuum (10^{-2} mmHg). This methanolysis procedure was then repeated three additional times, and the material ultimately obtained was dried under vacuum (10^{-2} mmHg) for 12 h. The product (5.5 g) was soluble in methanol and only slightly soluble (less than 1 mg/mL) in hydrocarbon solvents such as cyclohexane, methylcyclohexane, toluene, and benzene. ^1H NMR spectra (500 MHz, toluene-d_8, 22 °C) in the 5.0−3.5 ppm region displayed numerous sharp resonances plus a broad band extending from about 4.0 to 4.5 ppm (see Figure 5a).

Crystallization of $[Zr_{13}O_8](OMe)_x(OH)_{36-x}$ (MTZ) from Toluene. A slurry of the $[Zr_3O](OPr^n)_{10}$ methanolysis product (0.50 g) in 25 mL of toluene was prepared in a 100 mL round-bottom Schlenk flask. This mixture was stirred for 55 min in a silicone oil bath that had been heated to 80 °C, and the insoluble material remaining in the reaction vessel after 55 min was allowed to settle to the bottom of the flask. The warm supernatant liquid was then collected in a syringe and passed through a Whatman PTFE syringe filter (25 mm diameter, 0.45 μm pore size, Fisher Scientific) into a second 100 mL round-bottom Schlenk flask that had been placed in the heated silicone oil bath just described. The temperature of the oil bath was then reduced to room temperature at a rate of approximately 10 °C per hour, leaving the Schlenk flask undisturbed for at least 18 h. The clear, colorless, block-shaped crystals that formed were collected by cannula filtration and dried at ambient temperature for 24 h under vacuum (10^{-4} mmHg). Yield: 30 mg. This material was slightly soluble in hydrocarbon solvents such as toluene, cyclohexane, and methylcyclohexane. ^1H NMR spectra (500 MHz, toluene-d_8, 22 °C) in the 5.0−3.5 ppm region displayed a broad band extending from about 4.5 to 4.0 ppm plus sharp resonances at 4.19 and 4.16 ppm (see Figure 5b). Anal. Calcd for $Zr_{13}O_8(OH)_{12}(OCH_3)_{24}\cdot2H_2O$: C, 12.54; H, 3.86; Zr, 51.59. Found: C, 12.23; H, 3.30; Zr, 51.28.

Crystallization of MTZ from Benzene. A slurry of the $[Zr_3O]$-$(OPr^n)_{10}$ methanolysis product (0.53 g) in 26 mL of benzene was prepared in a 100 mL round-bottom Schlenk flask. The mixture was stirred for 50 min in a silicone oil bath that had been preheated to 62 °C. Clear, colorless, block-shaped crystals were obtained by following the procedure described above for the crystallization of MTZ from toluene. *c*-centered monoclinic lattice constants for MTZ were determined at −45 °C from 20 reflections aligned with graphite monochromated Mo Kα on a Siemens P4 diffractometer. They were a = 19.059(7) Å, b = 19.250(11) Å, c = 13.568(2) Å, α = 90.000°, β = 107.05(3)°, and γ = 90.000°.

Crystallization of MTZ from Methylcyclohexane. A slurry of the $[Zr_3O](OPr^n)_{10}$ methanolysis product (0.53 g) in 26 mL of methylcyclohexane was prepared in a 100 mL round-bottom Schlenk flask. Clear, colorless crystals were obtained by following

Table 1. Crystal Data and Structure Refinement for MTZ Crystallized from Toluene

chemical formula	$C_{33}H_{96}O_{44}Zr_{13}$
formula weight	2382.96
temperature	193(2) K
wavelength	0.71073 Å
crystal system	rhombohedral
space group	$R3m$-C_{3v}^5 (No. 160)
unit cell dimensions	a = 17.267(1) Å, α = 90.000°
	b = 17.267(1) Å, β = 90.000°
	c = 27.460(2) Å, γ = 120.000°
volume, Z	7090.5(6) Å^3, 3
calculated density	1.674 g/cm^3
absorption coefficient	1.438 mm^{-1}
final R indices [$I > 2\sigma(I)$]	R1^a = 0.051, wR2^b = 0.116
R indices (all data)	R1^a = 0.141, wR2^b = 0.139

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

the procedure described above for the crystallization of MTZ from toluene. These crystals were collected by cannula filtration and dried for 4 h under vacuum (10^{-2} mmHg). Yield: 25 mg. Primitive monoclinic lattice constants were determined at −75 °C as described below for MTZ crystallized from toluene: a = 13.553(1) Å, b = 20.699(1) Å, c = 17.329(1) Å; α = 90.000°, β = 99.681(2)°, γ = 90.000°.

X-ray Crystallographic Study of MTZ Crystallized from Toluene. Single crystals of MTZ were grown from toluene as described above. A full hemisphere of diffracted intensities (1365 10 s frames with an omega scan width of 0.30°) was measured using graphite-monochromated Mo Kα radiation on a Bruker SMART CCD Single-Crystal Diffraction System.[8] X-rays were provided by a normal-focus sealed X-ray tube operated at 50 kV and 40 mA. Lattice constants were determined with the Bruker SAINT software package using peak centers for 1533 reflections. A total of 14 755 integrated reflection intensities having 2θ(Mo Kα) < 53.44° were produced using the Bruker program SAINT.[9] Only 3641 of these were independent and gave R_{int} = 0.113. A face-indexed Gaussian grid absorption correction was applied to the intensity data. The structure was solved and refined using the Bruker SHELXTL-NT version 6.12 software package.[10] Structure solution was accomplished using a combination of "direct methods" and difference Fourier techniques; all stages of weighted full-matrix least-squares refinement were conducted using F_o^2 data. The crystallographic data are summarized in Table 1.

The structure was initially solved and refined in the space group $R3$-C_3^4 (No. 146). Three $Zr_{13}O_{44}$ units were found in the unit cell at the three Wyckoff *a* sites with crystallographic C_3-3 site symmetry. Although the $Zr_{13}O_{44}$ units and carbon atoms of 12 terminally bonded methoxide ligands appeared to be ordered, a difference Fourier synthesis revealed 2 low-occupancy carbon atoms bonded to each of the 24 doubly bridging oxygen atoms. Two features of the structure resulting from refinement in space group $R3$ indicated the likelihood of higher symmetry: satisfactory refinement could only be achieved for most carbon atoms when restraints were imposed on permissible values for C−O bond lengths and the refined structure possessed nearly rigorous (crystallographic) C_{3v}-3m symmetry. The space group $R3m$-C_{3v}^5 (No. 160) was therefore adopted.

(8) *SMART Software Reference Manual, Data Collection Software for CCD and Multiwire Area Detectors*; Siemens Industrial Automation, Inc.: Madison, WI, 1994.
(9) *SAINT Version 6.36a Software Reference Manual, Data Reduction Software for Single-Crystal Diffraction with an Area Detector*; Bruker AXS, Inc.: Madison, WI, 2002.
(10) *SHELXTL-NT Version 6.12 Reference Manual, Crystal Structure Solution and Refinement Software*; Bruker AXS, Inc.: Madison, WI, 2001.

The Zr and O atoms were located and refined again with anisotropic thermal parameters in space group $R3m$. Each of the three $Zr_{13}O_{44}$ units in the unit cell now occupied one out of the three Wyckoff a sites of $R3m$ with crystallographic C_{3v}-$3m$ site symmetry. This refinement gave R1 (unweighted, based on F) = 0.093 for 1612 independent absorption-corrected reflections having 2θ(Mo Kα) < 53.44° and $I > 2\sigma(I)$ and wR2 (weighted, based on F^2) = 0.291 for 3641 independent absorption-corrected reflections having 2θ(Mo Kα) < 53.44°. A difference Fourier synthesis calculated at this point contained 30 peaks with electron density in three distinct ranges: (1) the top three peaks (3.68−3.08 e$^-$/Å^3) corresponded to carbon atoms for the three crystallographically independent terminally bonded methoxide groups, (2) the next 12 peaks (2.61−1.57 e$^-$/Å^3) represented alternate methyl carbon positions for each of the six crystallographically independent doubly bridging methoxide groups, and (3) 15 peaks (1.08−0.64 e$^-$/Å^3) representing the background level near a $Zr_{13}O_{44}$ unit or disordered solvent molecules. Carbon atoms for terminal methoxide groups were incorporated in the structural model and refined with isotropic thermal parameters and full-occupancy factors; carbon atoms for bridging methoxide groups were refined with isotropic thermal parameters and occupancy factors which were half of their normal (full-occupancy) values. When the thermal parameters for three of the alternate carbon positions repeatedly refined to unrealistically high values, they were removed from the structural model. Only two peaks from additional difference Fourier syntheses refined satisfactorily, and they were treated as partial-occupancy (0.25) carbon atoms (C_{1S} and C_{2S}) with isotropic thermal parameters. These two atoms were >3.60 Å away from any atom in the $Zr_{13}O_{44}$ unit and are presumably fragments of solvent molecules occupying apparent voids in the structure.

The final structural model in the space group $R3m$ incorporated anisotropic thermal parameters for all zirconium and oxygen atoms except O_{2B} and isotropic thermal parameters for all carbon atoms and oxygen atom O_{2B}. Hydrogen atoms were not included. This model contained (full-occupancy) carbon atoms for all terminal methoxide groups, three pairs of alternate half-occupancy carbon atoms associated with three out of the six crystallographically independent doubly bridging oxygen atoms (O_{1B}, O_{3B}, and O_{5B} in Figure 4), and three half-occupancy single-position carbon atoms associated with the three remaining crystallographically independent doubly bridging oxygen atoms (O_{2B}, O_{4B}, and O_{6B} in Figure 4). The two solvent molecule atoms C_{1S} and C_{2S} were included as carbon atoms with occupancy factors of 0.25. The final agreement factors for "observed" data at convergence in space group $R3m$ were R1 (unweighted, based on F) = 0.051 and wR2 (weighted, based on F^2) = 0.116 for 1612 independent absorption-corrected reflections having 2θ(Mo Kα) < 53.44° and $I > 2\sigma(I)$. Final agreement factors for all of the data were R1 (unweighted, based on F) = 0.141 and wR2 (weighted, based on F^2) = 0.139 for all 3641 independent absorption-corrected reflections having 2θ(Mo Kα) < 53.44°. Selected bond lengths and angles from the final structure refinement in the noncentrosymmetric space group $R3m$ are given with estimated standard deviations in Table 2. Complete sets of atomic coordinates, thermal parameters, and bond lengths and angles have been included in the Supporting Information.

Morosin reported unit cell parameters of $a = 17.31(1)$ Å and $c = 27.75(2)$ Å for crystalline $[Zr_{13}O_8](OMe)_{36}$, values similar to those observed in the present study.[4] However, he assigned the centrosymmetric space group $R\bar{3}m$-D_{3d}^5 (No. 166) to the $[Zr_{13}O_8]$-$(OMe)_{36}$ structure, a space group different from the noncentrosymmetric space group assigned here. For purposes of comparison, the same space group was used to solve the structure of MTZ

Table 2. Selected Average Bond Lengths (Å) and Angles (deg) in MTZ Crystallized from Toluene[a]

| type[b]	value	type[b]	value
	Bond Lengths, Å		
Zr−O_A	2.19(2,5,13,10)	Zr−O_C	1.92(2,1,2,3)
Zr−O_B	2.17(1,3,5,8)	O_C−C_C	1.48(2,3,4,3)
	Bond Angles, deg		
Zr−O_B−Zr	111(1,2,4,6)	Zr−O_C−C_C	159(2,2,4,3)
Zr−O_B−C_B	120(1,4,8,8)	Zr−O_B−C_D	123(1,3,6,4)

[a] The first number in the parentheses following an average value of a bond length or angle is the root-mean-square estimated standard deviation of an individual datum. The second and third numbers are the average and maximum deviations from the average value, respectively. The fourth number represents the number of individual measurements which are included in the average value. [b] Atoms are labeled in agreement with Figure 4.

crystallized from toluene. This resulted in a structure where the x and y fractional coordinates for atoms in the $Zr_{13}O_{44}$ metal−oxygen core were similar to those reported by Morosin but the z fractional coordinates were inverted. Each of the three molecules in the unit cell now occupied one of the three Wyckoff a sites of $R\bar{3}m$ with crystallographic D_{3d}-$\bar{3}m$ site symmetry. Refinement of this partial model with anisotropic thermal parameters for all Zr and O atoms converged to R1 (unweighted, based on F) = 0.093 for 946 independent absorption-corrected reflections having 2θ(Mo Kα) < 53.44° and $I > 2\sigma(I)$ and wR2 (weighted, based on F^2) = 0.327 for all 1848 independent absorption-corrected reflections having 2θ(Mo Kα) < 53.44°. A difference Fourier synthesis calculated at that point contained 30 peaks with electron density in three distinct ranges: (1) the top two peaks (3.70−3.27 e$^-$/Å^3) corresponded to the carbon atoms of the two crystallographically independent terminally bonded methoxide ligands, (2) the next six peaks (2.58−1.60 e$^-$/Å^3) represented alternate methyl carbon positions for each of the three crystallographically independent doubly bridging oxygen atoms, and (3) 22 peaks (0.92−0.51 e$^-$/Å^3) which represented the background level or disordered solvent molecules. When the z coordinates for carbon atoms of the present study in space group $R\bar{3}m$ were inverted, each terminal methoxide carbon atom corresponded to one reported earlier by Morosin and the single-carbon site reported by Morosin for each of the bridging methoxide groups usually corresponded to one of the alternate sites in the present study or to a mean position for the alternate sites. Carbon atoms for both crystallographically independent terminal methoxide groups were incorporated with full-occupancy factors, and those for each (alternate) position for the three crystallographically independent bridging methoxide groups were incorporated with occupancy factors which were half of their normal (full-occupancy) value. The structural model did not include hydrogen atoms or any solvent molecule atoms. This refinement with anisotropic Zr and O atoms and isotropic C atoms in the centrosymmetric space group $R\bar{3}m$ converged to R1 (unweighted, based on F) = 0.055 for 946 independent absorption-corrected "observed" reflections having 2θ(Mo Kα) < 53.44° and $I > 2\sigma(I)$. Final agreement factors for all data were R1 (unweighted, based on F) = 0.199 and wR2 (weighted, based on F^2) = 0.200 for all 1848 independent absorption-corrected reflections having 2θ(Mo Kα) < 53.44°.

Results and Discussion

All attempts to prepare $[Zr_{13}O_8](OMe)_{36}$ by mixing dilute methanolic NaOH solutions with $Zr(OMe)_4$ as described in ref 4 were unsuccessful. An alternative strategy was therefore adopted where $Zr(OPr^n)_4$ was to be hydrolyzed according to

eq 1 and the resulting *n*-propyl triskaidecazirconate converted

$$13Zr(OR)_4 + 8H_2O \rightarrow [Zr_{13}O_8](OR)_{36} + 16ROH \quad (1)$$
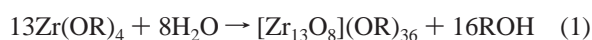
into the methyl derivative by methanolysis. Although Zr-$(OPr^n)_4$ hydrolysis at ambient temperature failed to yield the desired triskaidecazirconate, a different hydrolysis product was formed that could be converted into triskaidecazirconates by methanolysis.

Hydrolysis of $Zr(OPr^n)_4$. Oxygen-17 NMR spectroscopy proved to be a useful tool for monitoring the course of Zr-$(OPr^n)_4$ hydrolysis in methycyclohexane/1-propanol solution. Addition of up to 0.35 equiv of ^{17}O-enriched water yielded ^{17}O NMR spectra dominated by a single resonance at 323 ppm; very broad resonances appeared at ~300 and ~380 ppm upon further addition of water. If volatile materials were removed under reduced pressure following the addition of 0.35 equiv of water, a waxy solid was obtained whose CH analysis was in reasonable agreement with the formulation $[Zr_3O](OPr^n)_{10}$, a formulation consistent with the reaction stoichiometry employed:

$$3Zr(OR)_4 + H_2O \rightarrow [Zr_3O](OR)_{10} + 2ROH \quad (2)$$

This formulation was supported by $^{13}C\{^1H\}$ solution NMR spectra of methylcyclohexane-d_{14} solutions measured at −65 °C. Four resonances with relative intensities of 1:3:3:3 were observed in each of the *n*-propyl carbon regions, the pattern previously observed for several C_{3v}-$[M_3(\mu_3\text{-}O)(\mu_3\text{-}OR)(\mu_2\text{-}OR)_3(OR)_6]$ oxoalkoxides (see **a**).[11−16]

a
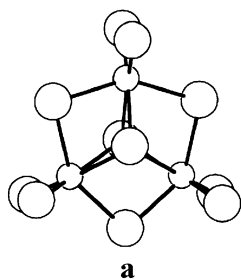
Several tetravalent metal oxoalkoxides of this type have been structurally characterized using single-crystal X-ray diffraction techniques, including those where M = Mo, R = Pr^i;[11] M = Mo, R = neopentyl;[11] M = U, R = Bu^t;[17] M = W, R = Pr^i;[12] and M = Zr, R = Bu^t.[18] Oxygen-17 NMR spectra measured in methylcyclohexane solution at 25 °C displayed a single resonance at 276 ppm, a different resonance from the resonance observed at 323 ppm in the methycyclohexane/1-propanol reaction solution. However, the 323 ppm resonance appeared after small amounts of 1-propanol were added to methylcyclohexane solutions of $[Zr_3O](OPr^n)_{10}$, and addition of increasing amounts of 1-propanol caused the intensity of the 323 ppm resonance to increase at the expense of the intensity of the 276 ppm resonance. After addition of >0.3−0.4 equiv of 1-propanol per mole of Zr, the 276 ppm resonance had disappeared completely and the intensity of the 323 ppm resonance remained constant. This transformation could also be followed by $^{13}C\{^1H\}$ NMR spectroscopy: the relatively simple $[Zr_3O](OPr^n)_{10}$ spectrum observed methylcyclohexane-d_{14} solution at −65 °C was replaced by a far more complex spectrum upon addition of >0.3−0.4 equiv of 1-propanol. These observations suggest that the initial $Zr(OPr^n)_4$ hydrolysis product observed in methycyclohexane/1-propanol solution was a 1-propanol adduct of $[Zr_3O](OPr^n)_{10}$. There is precedent for this type of behavior in hafnium(IV) oxoalkoxide chemistry, where an ethanol adduct of $[Hf_3O](OEt)_{10}$ has been isolated in crystalline form as the C_{2h} dimer $Hf_6(\mu_3\text{-}O)_2(\mu_2\text{-}OEt)_8(OEt)_{12}(EtOH)_2$,[18] but there is no compelling reason to believe that the same adduct is formed here.

Ethanolysis of $[Zr_3O](OPr^n)_{10}$. Repeated reaction of the $[Zr_3O](OPr^n)_{10}$ with neat ethanol afforded $[Zr_3O](OEt)_{10}$, which could be obtained in analytically pure form. This compound and its ethanol adduct displayed ^{17}O and ^{13}C solution NMR spectra having the same characteristics just described for their *n*-propyl analogues.

Solutions of $[Zr_3O](OEt)_{10}$ and its *n*-propyl analogue in methylcyclohexane-d_{14} both displayed temperature dependent $^{13}C\{^1H\}$ and ^1H NMR spectra characteristic of systems undergoing chemical exchange. The $^{13}C\{^1H\}$ solution NMR spectra of the ethyl derivative in the methylene region are representative. As shown in Figure 2, four resonances with relative intensities of 1:3:3:3 were observed at −70 °C, where two of the more intense resonances, those labeled b and c, had much smaller line widths than the other two resonances. The two relatively broad resonances, labeled a and d in Figure 2a, broadened with increasing temperature and coalesced at about −10 °C into a new resonance labeled a/d in Figure 2b. The chemical shift of this new resonance was 65 ppm, in good agreement with the calculated value of 64.8 ppm obtained from the weighted average of the chemical shifts for resonances a and d measured at −70 °C (64.6 ppm) after correction for the temperature dependence of chemical shifts using the dependence observed for resonances b and c (+0.2 ppm). This coalesced resonance became increasingly narrow as the temperature was increased from from −10 to +22 °C. The line widths of resonances b and c increased only slightly with increasing temperature from −70 to −10 °C, but both resonances broadened significantly between −10 and +22 °C, where the line width of resonance b increased at twice the rate observed for resonance d. Two different chemical exchange processes were therefore operative: a low-temperature process involving exclusively the unique ethyl group assigned to resonance a and the set of three equivalent ethyl groups assigned to resonance d and a high-

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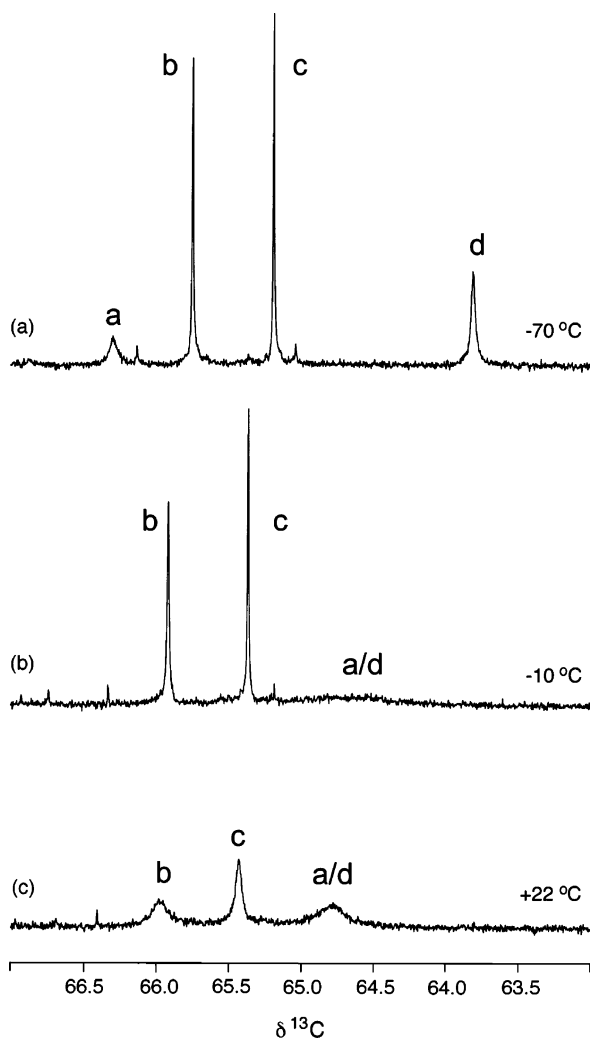
Figure 2. The 188.6 MHz $^{13}C\{^{1}H\}$ solution NMR spectrum of [Zr₃O]-(OEt)₁₀ in methylcyclohexane-d_{14} at (a) −70, (b) −10, and (c) 22 °C. Only the 63.0−67.0 ppm methylene carbon region is shown.

Figure 3. Proposed mechanisms for [Zr₃O](OEt)₁₀ rearrangements responsible for differential line broadening in solution NMR spectra measured at (a) low and (b) high temperature (see text). Only zirconium atoms (small spheres) and oxygen atoms (large spheres) are shown. The alkoxide oxygen atoms are labeled 1−10 and the oxide oxygen atom is labeled A. Arrows interconnecting oxygen atoms in **1a** and in **4a** indicate the site-exchange process implied by the low-temperature mechanism; the arrows interconnecting oxygen atoms in **1b** and in **4b** indicate the site-exchange process implied by the high-temperature mechanism.

temperature process involving the ethyl groups assigned resonances to b and c. Unlike the low temperature process, which involves mutual exchange between two and only two sites, the high-temperature process must involve more ethyl groups than those assigned to resonances b and c: there are equal numbers of ethyl groups in each set and exclusively mutual exchange would require that resonances b and c broaden at the same rate. Since differential line broadening was observed, the high-temperature process must involve other ethyl groups in addition to those assigned to resonances b and c. Given that all available evidence indicated that the sample contained one and only one species in significant concentration, the ethyl groups assigned to resonances b and c must exchange with those in the pool of ethyl groups assigned to resonance a/d.

Two closely related mechanisms are proposed in Figure 3 that can account for the temperature-dependent NMR spectra of [Zr₃O](OEt)₁₀ shown in Figure 2. Both mechanisms involve interconversion of the C_{3v} metal−oxygen framework of [Zr₃O](OEt)₁₀ observed in the ground state (**1a**, **4a**, **1b**, and **4b** in Figure 3) and an isomeric C_1 metal−oxygen framework (**2a**, **3a**, **2b**, and **3b** in Figure 3). In the
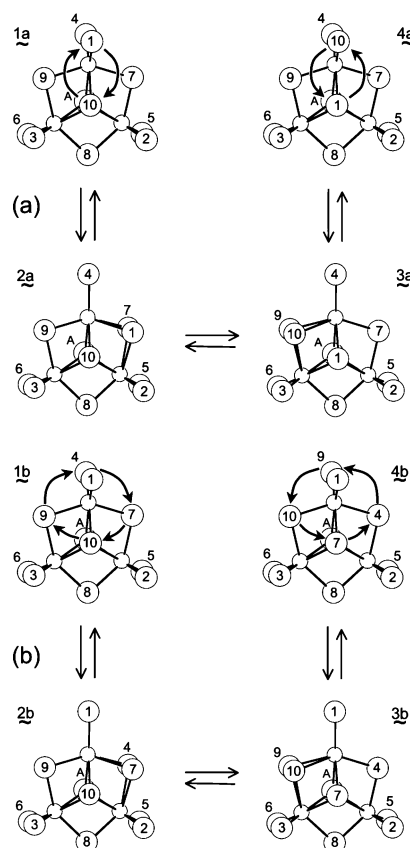
C_{3v} structure, all three metal centers are six-coordinate with (distorted) octahedral coordination geometry, but in the isomeric C_1 structure, only one metal center retains its original coordination geometry, while another remains six-coordinate but adopts (distorted) trigonal prismatic coordination geometry and the third is seven-coordinate with (distorted) capped trigonal prismatic coordination geometry. The first step of both mechanisms involves a trigonal twist at one of the metal centers. In Figure 3a, the trigonal twist is "counterclockwise," converting a terminal alkoxide ligand trans to the oxide ligand A in **1a** into a doubly bridging ligand in **2a**. In Figure 3b, the trigonal twist is "clockwise," converting a terminal alkoxide ligand trans to the triply bridging alkoxide ligand labeled 10 in **1b** into a doubly bridging ligand in **2b**. The second steps of the mechanisms shown in Figure 3 are identical and involve conversion of the chiral metal−oxygen frameworks of **2a** and **2b** into the enantiomeric metal−oxygen frameworks of **3a** and **3b**. This is achieved by sliding a pair of adjacent alkoxide ligands from one side of the framework to the other, specifically, the pair of oxygen atoms labeled 10 and 1 in **2a** and **3a** and labeled 10 and 7 in **2b** and **3b**. The third and final step in each of the mechanisms illustrated in Figure 3 is the microscopic reverse of the mirror image of the initial step.

The site-exchange schemes implied by the two mechanisms shown in Figure 3 are represented by arrows interconnecting oxygen atoms in the initial and final configurations shown in Figure 3. Comparison of configurations **1a** and **4a** shows that none of the three doubly bridging alkoxides groups and none of the terminal alkoxide groups trans to the triply bridging alkoxide group undergo site exchange but that alkoxide ligands in the triply bridging alkoxide site are exchanged with alkoxide ligands in the terminal oxygen sites trans to the oxo ligand. If the resonances labeled a and d in Figure 2a are assigned to the triply bridging alkoxide ligands and the terminal alkoxide ligands trans to the oxo ligand, respectively, the mechanism shown in Figure 3a implies the site-exchange process identified above as the low-temperature process for $[Zr_3O](OEt)_{10}$. If resonance c in Figure 2 is assigned to the terminal alkoxide ligands in $[Zr_3O](OEt)_{10}$ trans to the triply bridging alkoxide group and resonance b is assigned to the bridging alkoxide ligands, the mechanism shown in Figure 3b implies a site-exchange scheme of the type described above for the high-temperature $[Zr_3O](OEt)_{10}$ exchange process. Since the low-temperature exchange process is approaching the fast-exchange limit at temperatures where the high-temperature process is in the slow-exchange region, the influence of the high-temperature exchange process on the spectrum of $[Zr_3O](OEt)_{10}$ is most evident in the line shapes of those resonances not influenced by the low-temperature process, namely, the resonances labeled b and c in Figure 2. The mechanism proposed in Figure 3b fully accounts for the observation that the line width of resonance b increases with increasing temperature at twice the rate observed for resonance c.

Methanolysis of $[Zr_3O](OPr^n)_{10}$. Repeated reaction of the $Zr(OPr^n)_4$ hydrolysis product with methanol yielded a white powder whose ^{1}H NMR spectrum did not contain *n*-propyl resonances and showed a complex pattern of methoxide resonances in the 4.0−4.5 ppm region. This crude product could be crystallized in low yield from hydrocarbon solvents such as benzene, toluene, and methylcyclohexane, and the material crystallized from toluene proved to have unit cell parameters and crystal symmetry very similar to those reported by Morosin for $[Zr_{13}O_8](OMe)_{36}$ (see Experimental Section).[4] However, elemental analysis of material crystallized from toluene and dried under vacuum consistently showed carbon and hydrogen weight percentages of 12−13 and 3−4%, respectively, values significantly lower than those calculated for either $[Zr_3O](OMe)_{10}$ (20.02% C, 5.04% H) or $[Zr_{13}O_8](OMe)_{36}$ (17.79% C, 4.48% H). A single-crystal X-ray diffraction study was performed to resolve this apparent inconsistency.

Solid-State Structure of MTZ. A single-crystal X-ray diffraction study of the $[Zr_3O](OPr^n)_{10}$ methanolysis product crystallized from toluene yielded the $[Zr_{13}O_8](OMe)_x(OH)_{36-x}$ (MTZ) structure shown in Figure 4, the structure of a compound or mixture of compounds having the same metal−oxygen core previously reported for $[Zr_{13}O_8](OMe)_{36}$.[4] Selected bond lengths and angles are given in Table 2. The number and location of carbon atoms in this structure are ill-defined since the structure is disordered and carbon atoms

contribute little to the overall X-ray scattering. Attempts to refine the structure using $[Zr_{13}O_8](OMe)_{36}$ molecules in the structural model were unsuccessful, and satisfactory refinement was obtained only when some of the doubly bridging ligands were treated as disordered hydroxide/methoxide groups. Specifically, each carbon atom bonded to a bridging oxygen atom was included in the structural model with an occupancy factor which was 1/2 of its full-occupancy value. Thus, O1B, O3B, O5B, and their symmetry-equivalent oxygen atoms were treated as members of methoxide groups whose carbon atoms were disordered over two sites with equal probability, while O2B, O4B, O6B, and their symmetry-equivalent oxygen atoms were treated as members of hydroxide and methoxide groups occupying the same site with equal probability. This structural model therefore implied an average composition of $[Zr_{13}O_8](OMe)_x(OH)_{36-x}$ for MTZ where $x \sim 30$, a formulation consistent with the results of elemental analysis cited above.

Note that the "crystallographic disorder" manifested in the MTZ structure could reflect orientational or conformational disorder in single crystals of a pure compound and/or cocrystallization of two or more stoichiometrically distinct compounds. A distinction cannot be made between the two possibilities using single crystal X-ray diffraction techniques, since these techniques are only capable of yielding an "average" structure, and the average could be an average over different orientations or conformations of the same molecule and/or an average structure of two or more molecules having different chemical composition.

Solution ^{1}H NMR Spectra of MTZ. Solution ^{1}H NMR spectra of MTZ were not reproducible in that their precise appearance depended on reaction times, choice of solvent for extraction and crystallization, and drying conditions. Nonetheless, two characteristic features were invariably observed, features inconsistent with the $[Zr_{13}O_8](OMe)_{36}$ formulation, which implies two methyl resonances with relative intensities of 2:1. First, spectra of the crude methanolysis product always displayed several narrow methyl resonances superposed on a broad, featureless band extending from about 4.0 to 4.5 ppm (see Figure 5a). Second, spectra of crystallized material contained only two sharp methyl resonances whose relative intensities varied from sample to sample but were less than 2:1 and greater than 1:1. As illustrated in Figure 5b, these sharp resonances were superposed on a very broad resonance, and the intensity of this broad resonance also varied from sample to sample. Although none of these spectral features could be assigned with any degree of certainty, the fact that spectra of crystallized material varied from sample to sample strongly suggests that crystalline MTZ was a mixture of different species $[Zr_{13}O_8](OMe)_x(OH)_{36-x}$, where $x \sim 20$ according to elemental analysis. Elemental analysis can only place an upper limit on the number of methoxide groups present since ^{1}H NMR spectra always contained a number of weak resonances lying outside of the methoxide region, resonances that could be assigned to guest molecules in crystalline MTZ that were not removed under vacuum. Similar spectra were also observed for crystalline MTZ obtained from benzene and
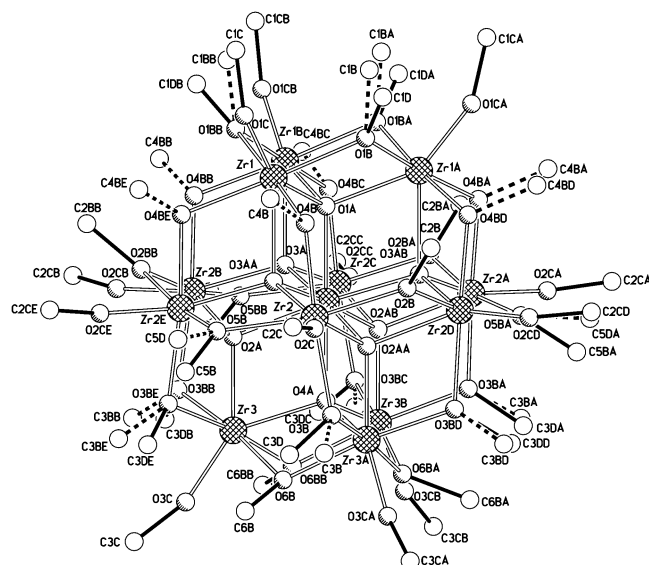
Figure 4. The C_{3v} structure of MTZ crystallized from toluene solution. Zirconium atoms are represented by large crosshatched spheres, oxygen atoms by small shaded spheres, and carbon atoms by small open spheres. Metal−oxygen bonds are represented by hollow bonds, and carbon−oxygen bonds are represented by filled bonds. The methoxy groups appear to adopt two different conformations that are distinguished through the use of dashed carbon−oxygen bonds for one conformation and solid bonds for the other. Atom labels are used to identify symmetry-equivalent sets of atoms: The 12 7-coordinate zirconium atoms fall into 3 sets of symmetry-equivalent atoms, namely, Zr1, Zr1A, and Zr1B; Zr2, Zr2A, Zr2B, Zr2C, Zr2D, and Zr2E; and Zr3, Zr3A, and Zr3B. Oxygen and carbon atoms are labeled in a similar fashion, where labels are provided for one member of each set of symmetry-equivalent atoms as follows: O1A, O2A, O3A, and O4A are each bonded to four Zr centers; O1B−O6B bridge two Zr centers; O1C−O3C are bonded to only one Zr center; C1B−C6B and C1C−C3C are bonded to oxygen atoms having the label obtained when the initial "C" in the carbon atom label is replaced by an "O"; and C1D, C3D, and C5D are alternate positions for C1B, C3B, and C5B, respectively (see text). Atom labels are not shown for the central, eight-coordinate zirconium atom Zr4 and carbon atoms C3BC, C5BB, and C5DB.

methylcyclohexane solution. Since the MTZ have cuboctahedral geometry and they pack like cubes when crystallized from toluene solution (see Table of Contents Graphic), large voids are created which are presumably occupied by solvent molecules. This material and possibly all three types of crystalline materials may therefore be clathrates whose crystal structures are determined in part by the identities of the guest molecules supplied by the crystallization solvent.

Identity of Morosin's $[Zr_{13}O_8](OMe)_{36}$. The MTZ structure obtained in space group $R\bar{3}m\text{-}D_{3d}^5$ (No. 166) with the current intensity data was quite similar to one reported in 1977 by Morosin,[4] if the z coordinates from the earlier study were inverted. In fact, inverting the published z coordinates eliminates the unusually short (<3.2 Å) intermolecular contacts between methyl groups noted by Morosin. The inverted z coordinates obtained by Morosin could be the result of an unresolved disorder in the earlier study and/or the merging of diffraction data from several different crystals to obtain the final data set used for structure determination and refinement. The similarity between the MTZ structure
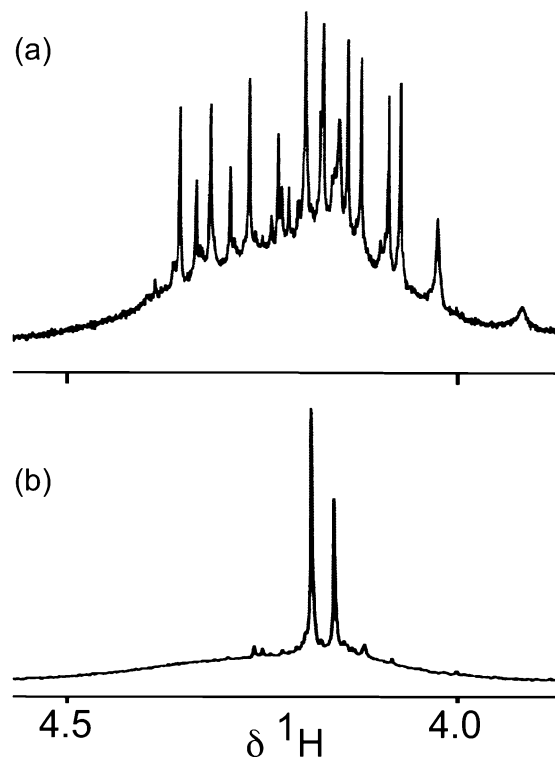

Figure 5. 500 MHz ^{1}H NMR spectra of (a) the crude product of $[Zr_3O]\text{-}(OPr^n)_{10}$ methanolysis and (b) MTZ crystallized from toluene solutions of the $[Zr_3O](OPr^n)_{10}$ methanolysis product. Both spectra were measured from toluene-d_8 solutions at 22 °C.

reported here and the $[Zr_{13}O_8](OMe)_{36}$ structure reported by Morosin does not prove that Morosin was dealing with the same type of mixture obtained in the present study, but it is strongly suggestive, given that Morosin's material was also obtained from methanol solution. The apparent reluctance of MTZ to achieve their full complement of 36 methyl groups might arise from steric crowding of the type observed in titanium oxoalkoxide chemistry.[19]

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

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