Precursors to Ultrathin Films of ZrO₂
Design on a Molecular Level

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Final Seminar

April 27, 2000

Sol-gel derived thin films (<1 μm) are the oldest and most widely used commercial application of sol-gel technology. Films prepared by traditional sol-gel processing techniques have been utilized mainly for optical and electronic purposes. Recently, submicron device miniaturization has created a demand for ultrathin (<100 Å) oxide films. However, sol-gel chemistry involves the hydrolysis and condensation of molecular precursors to form polymeric intermediates having dimensions greater than 100 Å, making the traditional sol-gel approach unsuitable for the preparation of ultrathin films. The research presented in this seminar is concerned with the isolation, synthesis, and characterization of zirconium(IV) n-alkoxides and oxoalkoxides designed to serve as suitable molecular precursors for the preparation of zirconia films with thicknesses <100 Å.

Tetra-n-propyl orthozirconate (1) was purified by vacuum distillation and isolated as a moisture sensitive, crystalline solid. According to a single crystal X-ray diffraction study, compound 1 has the same tetrameric structure observed previously for n-alkyl orthoaluminates (Figure 1a). According to 13C and 1H NMR spectroscopy, the Zr₄O₁₆ core structure was retained in hydrocarbon solution. A variable temperature 13C NMR study of Zr₄(OPr₆)₁₆ in methycyclohexane-d₄ revealed an intramolecular dynamic process for 1 between -30 and +5 °C involving a twisting motion whereby two of the four octahedrally coordinated zirconium centers undergo degenerate exchange through a trigonal prismatic intermediate (Figure 1b).
Hydrolysis of tetra-n-propyl orthozirconate with 1.5 equiv of water in n-propanol under reflux yielded a new polyoxozirconate complex, n-propyl triskaidecazirconate, $[\text{Zr}_{13}\text{O}_{38}]_{2}[(\text{OH})_{2}]_{12}(\text{OPr}^{+})_{24}$ (2). A single crystal X-ray diffraction study of 2 revealed a Zr$_{13}$O$_{44}$ metal-oxygen framework (Figure 2) having a structure similar to that reported for the methyl-triskaidecazirconate, $[\text{Zr}_{13}\text{O}_{38}](\text{OMe})_{24}$,10. Here alkoxide oxygens are represented by large open circles and the two types of oxide oxygens are represented by large circles that are uniquely shaded. The central zirconium atom of 2 is tetrahedrally distorted from an octahedral cubic environment, and the Zr$_{13}$O$_{32}$ core structure of 2 (Figure 3a) is a fragment of tetragonal zirconia (Figure 3b). The twelve zirconium atoms in $[\text{Zr}_{13}\text{O}_{38}]_{2}[(\text{OH})_{2}]_{12}(\text{OPr}^{+})_{24}$ which surround the ZrO$_{8}$ oxide core are seven-coordinate and have a coordination environment analogous to that found in monoclinic zirconia. Hydrolysis of tetra-n-butyl orthozirconate under the same conditions yielded the n-butyl analog of n-propyl triskaidecazirconate.

Figure 2

(a) (b)

Figure 3

Ultrathin films of zirconia were obtained after the chemisorption and subsequent hydrolysis of Zr$_{4}$(OPr$^{+}$)$_{6}$ on the surface of YBa$_2$Cu$_3$O$_{7}$ (YBCO). An increase in surface zirconium was observed by XPS upon repeated cycles of adsorption and hydrolysis of the alkoxide. The zirconia films were shown to be chemically stable tunneling barriers between YBCO and a metal electrode and are currently being used to probe the superconducting mechanism of YBCO.11

References


Hydrolysis of tetra-n-propyl orthozirconate with 1.5 equiv of water in n-propanol under reflux yielded a new polyoxozirconate complex, n-propyl triskaidecazirconate, \([\text{Zr}_{11} \text{O}_{38}](\text{OH})_{12}(\text{OPr}^+)_2\) \((\text{a})\). A single crystal X-ray diffraction study of \((\text{a})\) revealed a \(\text{Zr}_{11}\text{O}_{34}\) metal-oxygen framework (Figure 2) having a structure similar to that reported for the methyl-triskaidecazirconate, \([\text{Zr}_{11} \text{O}_{38}](\text{OMe})_{26}\) \((\text{b})\). Here alkoxide oxygens are represented by large open circles and the two types of oxide oxygens are represented by large circles that are uniquely shaded. The central zirconium atom of \((\text{a})\) is tetrahedrally distorted from an octahedral cubic environment, and the \(\text{Zr}_{11}\text{O}_{32}\) core structure of \((\text{a})\) is a fragment of tetragonal zirconia (Figure 3b). The twelve zirconium atoms in \([\text{Zr}_{11} \text{O}_{38}](\text{OH})_{12}(\text{OPr}^+)_2\) which surround the \(\text{ZrO}_8\) oxide core are seven-coordinate and have a coordination environment analogous to that found in monoclinic zirconia. Hydrolysis of tetra-n-butyl orthozirconate under the same conditions yielded the \(n\)-butyl analog of \(n\)-propyl triskaidecazirconate.

![Figure 2](image)

![Figure 3](image)

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References


METALLOPROTEIN DESIGN

Jeffrey A. Sigman

Final Seminar

May 2, 2000

Design and construction of metal-binding sites in proteins is an attractive approach toward the elucidation of the structure and function relationships in metalloenzymes. Metal centers in proteins are important for both stability and enzymatic activity, however, the principles required to engineer and control the properties of metal-binding sites are not yet fully understood. The design or re-design of metal-binding sites in proteins is in some respects similar to de novo design of proteins. The goal of both approaches is to engineer a protein with new or enhanced properties. Whereas de novo design involves creation of both the protein and the binding site for the metal co-factor, our approach focuses on just the metal site by building on a pre-existing protein scaffold. This is in fact similar to the approach used in nature in which a limited number of thermodynamically stable protein folds are used but diversity in function is still obtained by altering the protein active site.

The protein scaffolds we have chosen to upon are yeast cytochrome c peroxidase (CcP) and and sperm whale myoglobin (swMb). CcP is a 34kDa heme protein that utilizes oxidizing equivalents derived from hydrogen peroxide to oxidize two molecules of ferrous cytochrome c.

\[
\text{CcP-Fe(III)} + \text{H}_2\text{O}_2 \rightarrow \text{CcP-Fe(IV)=O, Trp191}^+ + \text{H}_2\text{O} \\
\text{CcP-Fe(IV)=O, Trp191}^+ + 2\text{Cytc-Fe(II)} \rightarrow \text{CcP-Fe(III)} + 2\text{Cytc-Fe(III)}
\]

Mb is a small, 17 kDa molecular weight, protein that reversibly binds dioxygen. These proteins are ideal templates for protein model studies because both have recombinant expression systems that have been optimized and have been extensively characterized by various spectroscopic techniques. Furthermore, X-ray crystal structures have been solved for both the native and several mutant forms of the proteins. CcP and swMb have been used as templates for the purpose of engineering metal binding sites characteristic of cytochrome P450 (cyt P450) and cytochrome c oxidase (CcO), respectively.

The cyt P450 class of enzymes are known to perform a variety of reactions including hydroxylations, epoxidations, dealkylations, and sulfoxidations. Thiolate ligation from an axial cysteine residue has been shown to be essential for the interesting spectroscopic properties and activity of this enzyme. For instance, replacement of the axial histidine residue in myoglobin with cysteine resulted in an enzyme with similar spectroscopic properties to high-spin ferric cyt P450. In previous work, a proximal His175Cys mutant in CcP was constructed and demonstrated that the sulfur of cysteine did not ligate to the heme. The authors concluded that the cysteine was too far from the heme to bind and X-ray crystal structure refinement of this mutant showed that the cysteine was instead oxidized to cysteic acid. Clearly, other structural elements may be important in facilitating ligation of a proximal cysteine in this protein. Crystallographic studies of cyt P450 show that a conserved non-polar phenylalanine residue and the protein backbone form an enclosure around the proximal cysteine ligand. In CcP the amino acid at the analogous position to this non-polar amino acid is Asp235 (see figure 1). Therefore, the mutation of Asp235 to Leu, which is similar in shape.