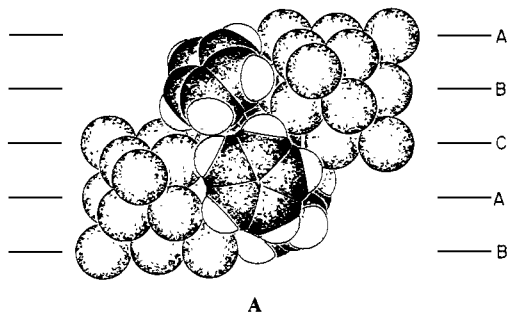


Figure 2. SCHAKAL drawings of (a) anion **4** as observed in the solid-state X-ray crystallographically and (b) anion **4** in the coordinatively unsaturated configuration proposed as an intermediate during rearrangement (see text). Oxygen atoms are represented by large open circles, uranium atoms by large filled circles, carbon atoms by large shaded circles, titanium atoms by small open circles, tungsten atoms by small filled circles, and hydrogen atoms by small shaded circles. One member of each symmetry-equivalent set of oxygen atoms is labeled in (a). Variable-temperature 33.9-MHz ^{17}O NMR spectra of anion **4** as a $(n\text{-C}_4\text{H}_9)_4\text{N}^+$ salt in CH_3CN are shown in (c)–(g). Only the 375–875 ppm region is included; i.e., the O_A resonance is not shown.

of the U(IV) coordination sphere. The space-filling model of anion **4** shown in A illustrates the nonbonding interactions contributing



to this stability. The four C_5H_5 rings are packed tightly around a cubic-close-packed array of 38 oxygens, protecting the uranium centers from the anion's environment. Bonding interactions also play a key role in stabilizing the U(IV) coordination sphere in **4**. Specifically, the stability of anion **4** relative to $[(\eta^5\text{-C}_5\text{H}_5)_3\text{U}(\kappa^1\text{O-NbW}_5\text{O}_{19})_2]^{5-}$ (**1**) and $[(\eta^5\text{-C}_5\text{H}_5)_3\text{U}(\kappa^1\text{O-NbW}_5\text{O}_{19})]^{2-}$ (**2**) can be explained in terms of the chelate effect in **4** and the greater basicity of an OTi^{IV} terminal oxygen in $\text{TiW}_5\text{O}_{19}^{4-}$ relative to an ONb^{V} terminal oxygen in $\text{NbW}_5\text{O}_{19}^{3-}$.

The title anion, although relatively inert toward electrophiles and weak nucleophiles,⁵ is rapidly degraded by strong nucleophiles such as OH^- and $(\text{C}_2\text{H}_5)_2\text{NH}$. Since $\text{TiW}_5\text{O}_{19}^{4-}$ is stable toward these reagents under the same conditions, the site of attack is most likely the uranium center. The avenue of approach to uranium in **4** (see A) is too restricted, however, and nucleophilic attack must therefore be accompanied by structural rearrangement. A plausible mode of rearrangement can be derived from variable-temperature ^{17}O NMR spectra shown in Figure 2c–g. At low

temperatures, ^{17}O NMR resonances can be assigned to oxygens in **4** by using well-established chemical shift scales,¹¹ assuming that resonances from oxygens bonded to uranium are too broad to be observed, as is the case with **1**² and **2**.³ Spectra measured at elevated temperatures are relatively simple and correspond to the resonances expected for a $\text{C}_{4v}\text{TiW}_5\text{O}_{19}^{4-}$ ligand. Such effective ligand symmetry can be obtained for $\text{TiW}_5\text{O}_{19}^{4-}$ in **4** by cleaving both¹² U– O_{g1} bonds (U– O_{g1} in Figure 1a), and symmetrizing the entire structure to the D_{2h} configuration shown in Figure 2b. Assuming rapid rotation about the Ti– O_{u2} bond in this coordinatively unsaturated intermediate configuration, the $\text{TiW}_5\text{O}_{19}^{4-}$ ligand achieves effective C_{4v} symmetry on the NMR time scale.

Acknowledgment. We acknowledge the National Science Foundation for support of this research and are grateful to Dr. Egbert Keller for providing a copy of his SCHAKAL program.

Registry No. **2**, 99127-88-5; **3**, 99127-89-6; **4**, 99112-31-9; $4\text{-}4\text{CH}_3\text{CN}$, 99127-87-4; TiCl_4 , 7550-45-0; WO_4^{2-} , 14311-52-5; $(\text{C}_5\text{H}_5)_3\text{VCl}$, 1284-81-7.

Supplementary Material Available: Crystal structure analysis report, Table I (fractional atomic coordinates and isotropic thermal parameters for non-hydrogen atoms), Table II (anisotropic thermal parameters), Table III (fractional coordinates for hydrogen atoms), Table IV (bond lengths for the anion), Table V (bond angles for the anion), Table VI (bond lengths and angles for the cations), Table VII (bond lengths and angles for CH_3CN molecules of crystallization), Figure 3 (perspective drawings of cations), Figure 4 (perspective drawings of CH_3CN molecules of crystallization), and structure factor tables for the crystal structure analysis of $\{[(\eta^5\text{-C}_5\text{H}_5)_2\text{U}]_2(\mu\text{-}\kappa^2\text{O-TiW}_5\text{O}_{19})_2\}[(n\text{-C}_4\text{H}_9)_4\text{N}]_4\cdot 4\text{CH}_3\text{CN}$ (53 pages). Ordering information is given on any current masthead page.

(11) (a) Filowitz, M.; Ho, R. K. C.; Shum, W. *Inorg. Chem.* **1979**, *18*, 93. (b) Che, T. M.; Day, V. W.; Francesconi, L. C.; Fredrich, M. F.; Klemperer, W. G.; Shum, W. *Inorg. Chem.*, in press.

(12) Although cleavage of a single U– O_{WTi} bond is a reasonable alternative, we consider it less likely than a concerted process since it leads to short $\text{C}_5\text{H}_5\cdots\text{OTiW}$ contacts. Specifically, the $\text{TiW}_5\text{O}_{19}^{4-}$ reorientation accompanying U– O_{g1} cleavage (see Figure 1a) implies close $\text{C}_5\text{H}_5\cdots\text{O}_{g3}$ contacts at the other uranium center.

Molecular Building Blocks for the Synthesis of Ceramic Materials: $[\text{Si}_8\text{O}_{12}](\text{OCH}_3)_8$

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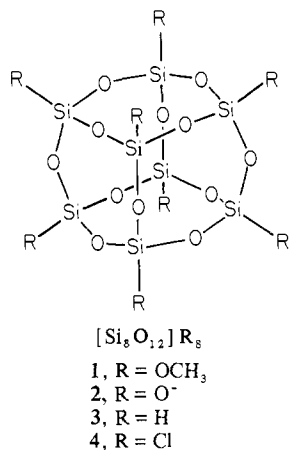
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Received June 24, 1985

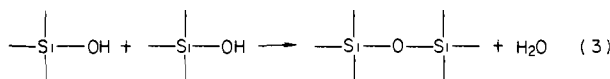
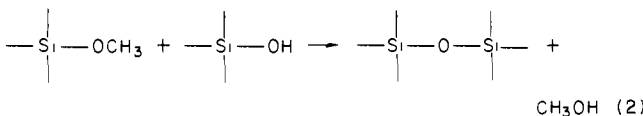
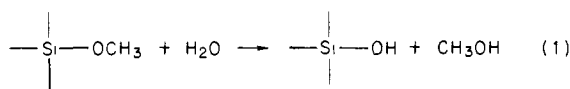
Ceramic materials have traditionally been prepared from structurally simple starting materials. As a result, their structural features are relatively difficult to control or modify in a systematic fashion. Many polymeric organic and organometallic materials, on the other hand, can be designed and synthesized in a more controlled fashion by proceeding in a stepwise manner, i.e., by first preparing tailor-made molecular building blocks and then polymerizing these monomers in a subsequent reaction step. Any attempt to extend this building-block approach to the synthesis of ceramic materials must begin with the preparation of suitable

(1) (a) Crystalytics Co. and University of Nebraska. (b) University of Illinois.

molecular building blocks. We describe here the synthesis, structure, and hydrolysis of the polysilicic acid ester $[\text{Si}_8\text{O}_{12}](\text{O}-\text{CH}_3)_8$ (**1**). This molecule is designed to serve as a building block

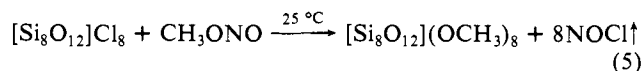
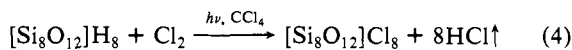


for the synthesis of silicas based on $[\text{Si}_8\text{O}_{12}]\text{O}_{8/2}$ subunits by hydrolysis according to eq 1 followed by condensation according



to eq 2 and/or 3.² The rigid cubic $[\text{Si}_8\text{O}_{12}]$ core offers the possibility of generating porous yet rigid materials due to geometric factors limiting the density with which corner-linked cubes can fill space.

Attempts to prepare the title compound in one step by alkylating the known $\text{Si}_8\text{O}_{20}^{8-}$ ion³ (**2**) were frustrated by an inability to prepare a salt of **2** soluble in an anhydrous, aprotic solvent. This difficulty has been avoided by following the two-step reaction sequence given in eq 4 and 5. Photochemical chlorination of



$[\text{Si}_8\text{O}_{12}]\text{H}_8$ (**3**) followed by sublimation of the product yields $[\text{Si}_8\text{O}_{12}]\text{Cl}_8$ (**4**) in >95% yield. Reaction of **4** with neat methyl nitrite in a sealed tube⁶ followed by sublimation and crystallization from toluene yields $[\text{Si}_8\text{O}_{12}](\text{OCH}_3)_8$ (**1**) in 45% yield. In contrast

(2) For a review of ceramic oxide preparations from alkoxide precursors, see: Sakka, S. *Treatise Mater. Sci. Technol.* **1982**, 22, 129.

(3) (a) Glixielli, S.; Krokowski, T. *Rocz. Chem.* **1937**, 17, 309. (b) Smolin, Yu. I.; Shepelev, Yu. F.; Pomes, R.; Hoebbel, D.; Wieker, W. *Kristallografiya* **1979**, 24, 38.

(4) (a) Müller, R.; Köhne, R.; Sliwinski, S. *J. Prakt. Chem.* **1959**, 9, 71. (b) Larsson, K. *Ark. Kemi* **1960**, 16, 215. (c) Frye, C. L.; Collins, W. T. *J. Am. Chem. Soc.* **1970**, 92, 5586.

(5) Anal. Calcd for $\text{Si}_8\text{O}_{12}\text{Cl}_8$: Si, 32.09; Cl, 40.50. Found: Si, 31.74; Cl, 40.75. IR (Nujol, 1400–250 cm^{-1}) 1142 (s), 1090 (sh), 795 (vw), 712 (s), 515 (s), 450 (m), 335 (m); the very weak band at 795 cm^{-1} is assigned to $\text{Si}_8\text{O}_{12}\text{H}_8\text{Cl}_8$ impurities (<3%); ^{29}Si NMR (CCl_4 , $\text{Me}_4\text{Si} = 0$, 49.7 MHz, 0.015 M $\text{Cr}(\text{acac})_3$) δ -91.16 (s); sublimation temperature 130 °C (0.5 torr); MS, m/z 665 ($\text{M}^+ - \text{Cl}$).

(6) Caution: Methyl nitrite is toxic (Slovak, A. J. M.; Hill, R. N. *JOM, J. Occup. Med.* **1981**, 23, 857) and explosive under pressure (Selle, H. Z. *Elektrochem.* **1957**, 61, 672. Shaw, R. *Combust. Flame* **1973**, 21, 127).

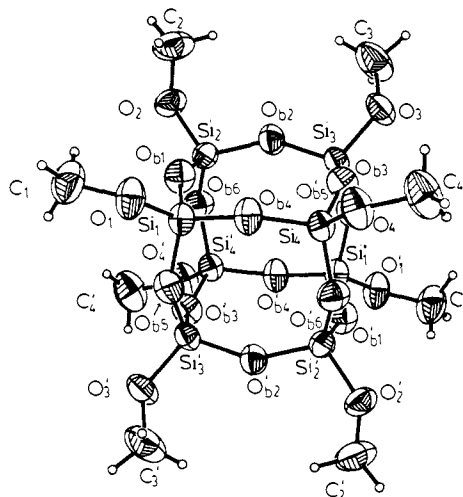


Figure 1. Perspective ORTEP drawing of the centrosymmetric $[\text{Si}_8\text{O}_{12}](\text{OCH}_3)_8$ molecule with Si, C, and O atoms represented by thermal vibration ellipsoids drawn to encompass 50% of the electron density; hydrogen atoms are not labeled in this drawing and are represented by arbitrarily-sized spheres for purposes of clarity. Atoms labeled with a prime are related to those labeled without a prime by the crystallographic inversion center at (0,1,0). Average values¹⁰ for structurally equivalent bond lengths and angles of interest: Si-O_b, 1.604 (2,2,5,12) Å; S-O (methoxy), 1.596 (3,2,4,4) Å; C-O, 1.399 (5,10,19,4) Å; O-Si-O, 109.5 (1,11,32,24)°; Si-O_b-Si, 148.2 (2,22,37,6)°; and Si-O-C, 126.7 (2,12,21,4)°.

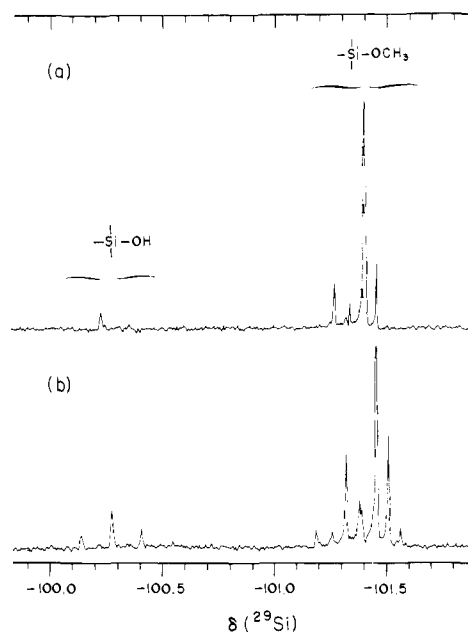


Figure 2. $^{29}\text{Si}\{^1\text{H}\}$ 49.7-MHz FT NMR spectra¹² of 0.1 M $[\text{Si}_8\text{O}_{12}](\text{O}-\text{CH}_3)_8$ in CH_3CN measured (a) 7–8 h and (b) 58–59 h after hydrolysis with four equivalents H_2O . The chemical shift scale shown is externally referenced to SiMe_4 at 0 ppm.

with ionic reagents such as CH_3OLi or CH_3ONa that attack **4** with degradation of the $[\text{Si}_8\text{O}_{12}]$ core, CH_3ONO displaces chloride from **4** with retention of stereochemical configuration at silicon. The integrity of the $[\text{Si}_8\text{O}_{12}]$ core in **1** was established by a single-crystal X-ray diffraction study⁸ (see Figure 1). Structural

(7) Anal. Calcd for $\text{Si}_8\text{O}_{26}\text{C}_8\text{H}_{24}$: C, 14.45; H, 3.64; Si, 33.80. Found: C, 14.37; H, 3.61; Si, 34.19. IR (Nujol, 1400–250 cm^{-1}) 1155 (s), 1090 (vs), 848 (m), 795 (w), 720 (w), 570 (vs), 470 (w), 395 (m), 360 (m), the weak band at 720 cm^{-1} is assigned to Nujol; $^{29}\text{Si}\{^1\text{H}\}$ NMR (CH_3CN , $\text{Me}_4\text{Si} = 0$, 49.7 MHz, 0.015 M $\text{Cr}(\text{acac})_3$) δ -101.40 (s); $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , $\text{Me}_4\text{Si} = 0$, 90.5 MHz) δ 51.30 (s); ^1H NMR (C_6D_6 , $\text{Me}_4\text{Si} = 0$, 360 MHz) δ 3.36 (s); sublimation temperature 135 °C (0.5 torr); MS, m/z 664 (M^+); capillary GC on a 10-m bonded DB-1 column at 190 °C exhibits one component at 3.41 min.

parameters for **1** given in the Figure 1 caption are in good agreement with corresponding parameters for related silsesquioxanes (RSiO_{1.5})₈.¹¹

Hydrolysis of **1** in CH₃CN with 4–20 equiv of water produces a clear, colorless gel that dries to a transparent, monolithic glass. Solution ²⁹Si{¹H} NMR spectra¹² measured prior to gelation display resonances in the –101 to –102 ppm region arising from (≡SiO)₃SiOCH₃ centers¹³ and resonances in the –99.5 to –100.5 ppm region arising from (≡SiO)₃SiOH centers¹⁴ but no resonances in the –90 to –95 region arising from (≡SiO)₂Si(OR)₂ centers, R = CH₃ or H.^{13,14} A ²⁹Si NMR spectrum measured after partial hydrolysis of **1** is shown in Figure 2a. The five largest resonances observed are assigned to [Si₈O₁₂](OCH₃)₈ (δ –101.41) and [Si₈O₁₂](OCH₃)₇(OH) (≡SiOH at δ –100.17, ortho and meta ≡SiOCH₃ at δ –101.27 and –101.46, para ≡SiOCH₃ at δ –101.35). The smaller –101.33 ppm resonance is assigned to the four equivalent ≡SiOCH₃ silicons in *o*-[Si₈O₁₂](OCH₃)₆(OH)₂ since its intensity relative to the intensities of the [Si₈O₁₂](OCH₃)₈ and [Si₈O₁₂](OCH₃)₇(OH) resonances is in good agreement with the value predicted by a random hydrolysis model where all ≡SiOCH₃ groups in the [Si₈O₁₂](OCH₃)_{8–*n*}(OH)_{*n*} system hydrolyze at the same rate.¹⁵ Spectra measured after further hydrolysis (see Figure 2b) are also consistent with this model but are more difficult to interpret since several resonances are unresolved and additive chemical shift parameters must be invoked to provide unambiguous assignments.}

We plan to remeasure ²⁹Si{¹H} NMR spectra of hydrolyzed **1** at higher magnetic field strengths in order to obtain higher spectral dispersion and reinforce the conclusion that hydrolysis proceeds without degradation of the [Si₈O₁₂] core structure and are currently investigating the course of condensation reactions (2) and (3) in solutions, gels, and glasses using ²⁹Si FT NMR and CP MAS NMR techniques.

Note Added in Proof. Preliminary results indicate that **4** can be converted into **1** with HC(OCH₃)₃.

(8) Large well-shaped colorless single crystals of [Si₈O₁₂](OCH₃)₈ suitable for X-ray diffraction studies, obtained by sublimation, are at 20 ± 1 °C, triclinic, space group P $\bar{1}$ -C₁¹ (No. 2), with *a* = 9.046 (4) Å, *b* = 8.990 (4) Å, *c* = 8.546 (4) Å, α = 99.93 (3)°, β = 101.24 (3)°, γ = 99.42 (3)°, and *Z* = 1 [μ₀(Mo K_α) = 0.5 mm⁻¹, ρ_{calc} = 1.68 g cm⁻³]. Three-dimensional diffraction data (a total of 3010 independent reflections having 2θ_{Mo K_α} < 55°) were collected on a computer-controlled Nicolet autodiffractometer using graphite-monochromated Mo K_α radiation and full 1.0° wide ω scans. The structure was solved by "direct methods" techniques (SHELXTL) and the resulting structural parameters have been refined to convergence⁹ [R(unweighted, based on *F*) = 0.038 for 2164 reflections having *I* > 3σ(*I*)] using counting-statistics weighted cascade block diagonal least-squares techniques and a structural model which incorporated anisotropic thermal parameters for all Si, C, and O atoms and isotropic thermal parameters for all hydrogen atoms.

(9) See paragraph at end of paper regarding supplementary material.

(10) The first number in parentheses following an averaged value of a bond length or angle is the root-mean-square estimated standard deviation of an individual datum. The second and third numbers, when given, are the average and maximum deviations from the averaged value, respectively. The fourth number represents the number of individual measurements which are included in the average value.

(11) (a) [Si₈O₁₂](CH₃)₈: Larsson, K. *Ark. Kemi* **1960**, *16*, 203. (b) [Si₈O₁₂](C₆H₅)₈: Shklover, V. E.; Struchkov, Yu. T.; Makarova, N. N.; Andrianov, K. A. *Zh. Strukt. Khim.* **1978**, *19*, 1107. Hossain, M. A.; Hursthouse, M. B.; Malik, K. M. A. *Acta Cryst., Sect. B* **1979**, *B35*, 2258. (c) [Si₈O₁₂](C₂H₅)₈: Baidina, I. A.; Podbenezhskaya, N. V.; Alekseev, V. I.; Martynova, T. N.; Borisov, S. V.; Kanev, A. N. *Zh. Strukt. Khim.* **1979**, *20*, 648. (d) [Si₈O₁₂][OSi(CH₃)₃]₈: Smolin, Yu. I.; Shepelev, Yu. F.; Pomes, R. *Khimiya Silik. Oksidov* **1982**, 68.

(12) All ²⁹Si{¹H} FT NMR spectra were measured under gated decoupling conditions. In order to reduce *T*₁'s to ca. 2 s, all solutions contained 0.015 M Cr(acac)₃. The Cr(acac)₃ did not affect the rate or course of the reactions studied. To ensure accurate integrated intensities, three *T*₁'s were allowed to elapse between observe pulses.

(13) Marsmann, H. C.; Meyer, E.; Vongehr, M.; Weber, E. F. *Makromol. Chem.* **1983**, *184*, 1817.

(14) Klemperer, W. G.; Mainz, V. V.; Millar, D. M., manuscript in preparation.

(15) If α is the overall fraction of methoxy groups hydrolyzed, the relative abundance of [Si₈O₁₂](OCH₃)_{8–*n*}(OH)_{*n*} is 8!/[*n*!(8–*n*)!α^{*n*}(1–α)^{8–*n*}]. The relative abundance of isomers is determined statistically by symmetry numbers.}

Acknowledgment. This work was supported at the University of Illinois by the U.S. Department of Energy, Division of Material Science, under Contract DE-AC02-76ER01198. We are grateful to Dr. Cecil Frye for useful comments on the preparation of **3** and to Dr. Peter Wolynes for helpful discussions. Kurt Rothenberger played a key role in early stages of the work. Acknowledgment is also made to Dr. Egbert Keller for providing a copy of his SCHAKAL program.

Registry No. **1**, 98922-99-7; **3**, 281-50-5.

Supplementary Material Available: Crystal structure analysis report, Table I (fractional atomic coordinates for non-hydrogen atoms), Table II (anisotropic thermal parameters for non-hydrogen atoms), Table III (fractional atomic coordinates for hydrogen atoms), Table IV (bond lengths involving non-hydrogen atoms), Table V (bond angles involving non-hydrogen atoms), and structure factor amplitude tables for the X-ray structural analysis of [Si₈O₁₂](OCH₃)₈ (21 pages). Ordering information is given on any current masthead page.

Interaction of a Hydrogen Molecule with Palladium

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Received April 29, 1985

Electronic processes in chemisorption and catalytic action on a metal surface play fundamental roles in chemistry and chemical industry but are still hidden in a veil theoretically. We study theoretically the interaction of a hydrogen molecule with palladium as a model of chemisorption and catalytic action of a metal surface. We use sophisticated ab initio theories explained below. The basic assumption is the local nature of the interaction between hydrogen and palladium.^{1–3} We will show that even the Pd₂ fragment shows chemisorptive and catalytic activities for the hydrogen molecule. The H₂ molecule is adsorbed and dissociated very smoothly on the Pd₂ "surface" with almost no barrier and shows an equilibrium with the two atomic hydrogen radicals. The Pd–Pd bond is not weakened in this process, which is related to the stability of the catalytic surface. The mechanism of the catalytic activity is different from the one proposed for a nickel surface.⁴ It is a bond alternation mechanism in which the dangling bond of the Pd surface plays an essential role.

We consider first the interaction of a hydrogen molecule with a Pd atom.^{5,6} It was shown that the Pd atom in the ¹S(d¹⁰) ground state shows an affinity to the H₂ molecule but does not work to cleave the H–H bond. A long equilateral triangle is a stable form in which the hydrogen molecule is attached weakly to the Pd atom. On the other hand, the excited states of the Pd atom, the ^{1,3}D(d⁹s¹) states, are repulsive.

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