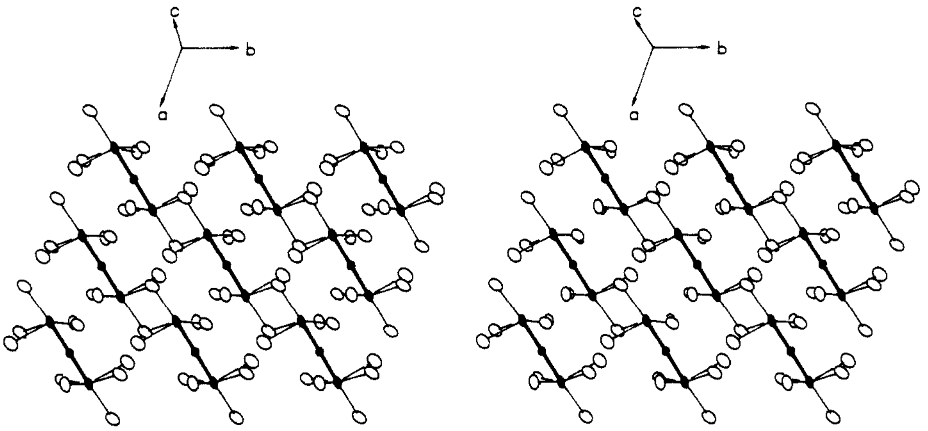

Figure 1. A stereoview of the *ab* plane of β-(ET)$_2$AuI$_2$ at 20 K shows the AuI$_2^-$ anions and the numerous short H···I contacts (thin lines) with distances less than the van der Waals radii sum of 3.3 Å. The environment about each terminal I atom of the anions is nearly an octahedron of atoms. Thermal ellipsoids are known very precisely and are drawn at the 99% probability level.[16]

materials, there is a nearly octahedral environment of atoms about the terminal halogen atoms of the anion (see Figure 1). The shortest H···X distances and their corresponding C–H···X angles for several β-(ET)$_2$X salts with X$^-$ = linear anion are given in Table I. Although the most precise geometries in Table I are those obtained from neutron diffraction data, the low-temperature X-ray results agree surprisingly well, by comparison. Thus, the neutron diffraction experiments *verify* previous assumptions concerning the H···X geometries based upon low-temperature X-ray diffraction data. The H atom geometries that were calculated for the completely ordered structures of β-(ET)$_2$IBr$_2$[11] and β-(ET)$_2$ICl$_2$[12] from low-temperature X-ray data are also expected to be accurate (by comparison) and these parameters are included in Table I. The differences in the H···X interactions of the β-(ET)$_2$X salts with X$^-$ = AuI$_2^-$, IBr$_2^-$, and ICl$_2^-$ are summarized as follows: (i) for the shortest H···X contacts in the above three salts, the angles about the H atoms, namely C–H···I, C–H···Br, and C–H···Cl, are largest for β-(ET)$_2$ICl$_2$ (approaching 180°) and are smallest for β-(ET)$_2$AuI$_2$; (ii) for longer contact distances in each of the above salts, the corresponding C–H···X angles are much smaller (i.e., approaching 120°); (iii) the H···Br, and H···Cl contact distances are as much as 0.38, 0.26, and 0.41 Å *shorter* than their respective van der Waals radii sums,[10] which is significant in comparison to the estimated errors for the values of the H···X distances derived from X-ray data (±0.1 Å or less). The above structural results confirm that the closest H···X contacts in the β-(ET)$_2$X salts are the main contributors to the cohesive forces between the 2D ET molecule networks and the anions in these crystals and that these H···X interactions are similar to H-bonding interactions in other organic compounds.[13,14] The discovery of the very short H···I contacts in β-(ET)$_2$AuI$_2$ is surprising because such interactions are generally assumed to be weak.[13,14] In summary, there are important implications for the design and synthesis of new β-(ET)$_2$X systems where the X$_n^-$ anions contain halide (I, Br, Cl, F) atoms, namely, that H-bonding interactions of the type H···X play a major role in determing the crystal cohesive forces between donors and anions thereby controlling compound formation.

Acknowledgment. Work was carried out at Argonne National Laboratory under Contract W-31-109-ENG-38 and at the High Flux Beam Reactor (HFBR), Brookhaven National Laboratory, under Contract DE-AC02-76CH00016 and is supported by the U.S. Department of Energy. T.J.E. is a research collaborator with the Chemistry Department, Brookhaven National Laboratory. K.S.W. is an undergraduate research participant sponsored by the Argonne Division of Educational Programs from St. Michael's College, Winooski, VT. We thank J. Henriques for his expert technical assistance and T. F. Koetzle and R. K. McMullan for their assistance and helpful discussions.

Supplementary Material Available: Table S1, neutron data collection and refinement parameters; Table S2, atomic positional and thermal parameters for β-(ET)$_2$AuI$_2$ at 20 (neutron data) and 120 K (X-ray data); Table S3, atomic positional and thermal parameters for β-(ET)$_2$I$_3$ at 20 (neutron data) and 9 K (X-ray data); Table S4, atomic positional and thermal parameters for β-(ET)$_2$IBr$_2$ at 9 K (X-ray data) (6 pages). Ordering information is given on any current masthead page.

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Polyhedral Oligometallasilsesquioxanes (POMSS) as Models for Silica-Supported Transiton-Metal Catalysts: Synthesis and Characterization of (C$_5$Me$_5$)Zr[(Si$_7$O$_{12}$)(c-C$_6$H$_{11}$)$_7$]

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Heterogeneous silica-supported transition-metal compounds play an increasingly important role as catalysts in the petrochemical industry.[1] The commerical importance of such catalysts has stimulated an intense interest in the chemical processes which occur on the surface of heterogeneous catalysts. Although recent

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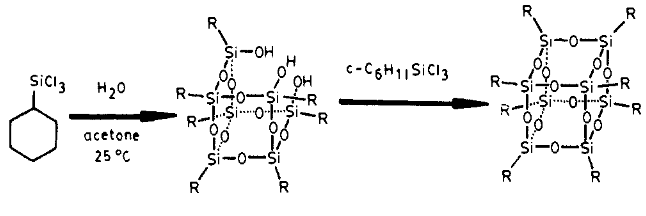
advances[2] in physiochemical and spectroscopic techniques have allowed great strides toward understanding the reaction chemistry that occurs on surfaces, detailed mechanistic studies are still inherently difficult due to the very complicated atomic structure of the surface. In some cases, serious doubts exist as to whether or not the "observed" surface species are in fact responsible for the observed chemistry.

This paper outlines our efforts toward developing a suitable model system which can be used to simplify the study of silica surface complexes. In this report we describe the synthesis and structural characterization of the first example from a new class of transition-metal-containing siloxane macromolecules which are designed to mimic surface sites possessing three hydroxyl groups bonded to a single transition-metal atom. These new compounds, called polyhedral oligometallasilsesquioxanes (POMSS), are formally derived from the substitution of transition-metal atoms into the silicon–oxygen frameworks of polyhedral oligosilsesquioxanes (POSS).[3] The general approach that is described here has the potential of providing many homogeneous analogues of silica-supported complexes for both spectroscopic comparison and mechanistic chemical studies.

Compound **1** can be prepared in surprisingly good yields by the hydrolytic condensation of $C_6H_{11}SiCl_3$ in aqueous acetone.[4] The compound exists as a strongly hydrogen bonded dimer in both the solid state[5] and in relatively nonpolar solvents such as $CHCl_3$ and CS_2 but as the monomeric form in CS_2/pyridine.[4] The original structural assignment[4] of **1** was based on its dimeric tendencies and the fact that octamer **2** ($R = C_6H_{11}$) is formed upon treatment with additional $C_6H_{11}SiCl_3$. We have recently confirmed the fact that all three hydroxyl groups point toward a single vertex by ^{13}C and ^{29}Si NMR spectroscopy,[6,7] as well as a single-crystal X-ray diffraction study.[5]



1 R= c-C₆H₁₁ **2**

Compound **1** is very reactive toward early transition-metal halide and alkyl complexes. The reaction of a 0.01 M CH_2Cl_2 solution of **1** with 1 equiv of yellow $(C_5Me_5)Zr(CH_2C_6H_5)_3$[8] proceeds instantaneously to afford 3 equiv of toluene and a quantitative yield of **3** as colorless orthorhombic crystals after slow evaporation of the solvent. Compound **3** can also be prepared in nearly quantitative yield by the reaction of $(C_5Me_5)ZrCl_3$[8] and **1** in CH_2Cl_2/pyridine.

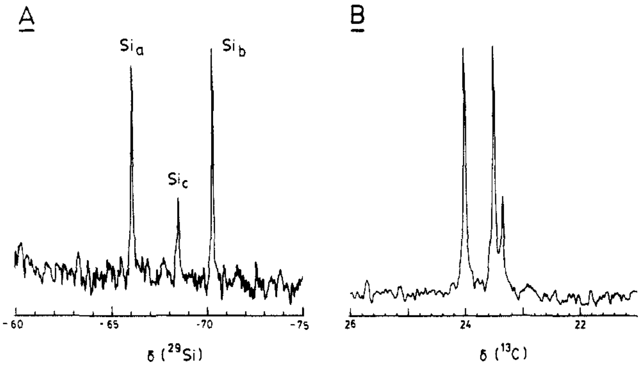


Figure 1. (A) $^{29}Si\{^1H\}$ NMR of 3. (B) $^{13}C\{^1H\}$ NMR of 3. Region between 20–25 ppm shows C_{3v} symmetry of C attached to Si.

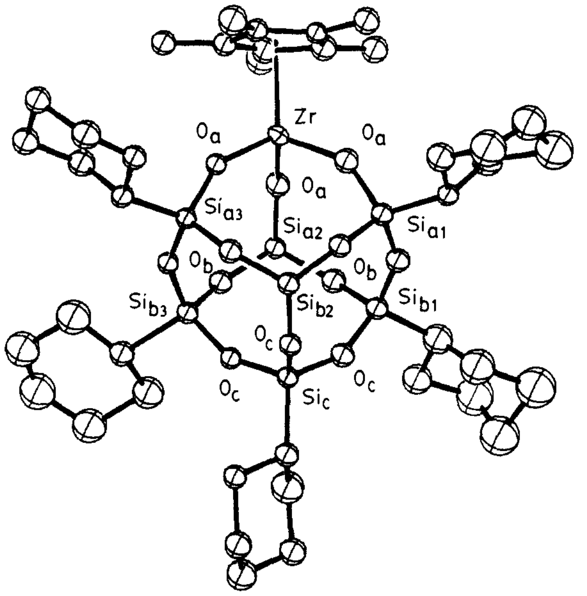
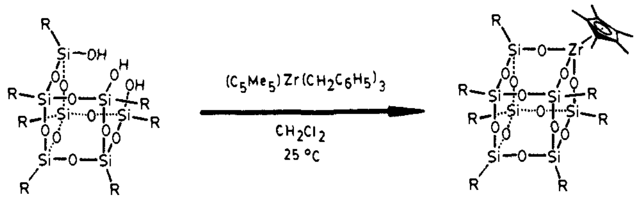


Figure 2. Perspective ORTEP plot of 3 showing 20% thermal ellipsoids for non-hydrogen atoms. Cyclohexyl rings on Si_{a2} and Si_{b2} have been omitted for clarity. Selected bond distances and angles are collected in Table I.



1 R= c-C₆H₁₁ **3**

Despite its large size and apparent complexity, the structure of **3** can be assigned by using conventional spectroscopic techniques. The stoichiometry was ascertained from ^1H NMR and mass spectral data.[9] ^{13}C and ^{29}Si NMR data[10] conclusively demonstrate that the molecule possesses the expected local C_{3v} symmetry about the zirconium atom. The ^{29}Si NMR spectrum (Figure 1A) consists of three singlets in a 3:3:1 ratio for the silicon atoms located two (Si_a), four (Si_b), and six (Si_c) atoms away from

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[5] F. J. Feher, unpublished results. The compound crystallizes from $CHCl_3$ as a hydrogen-bonded dimer in the monoclinic space group $P2_1/m$ with a cell volume of 3027 $Å^3$ ($a = 10.34$ Å, $b = 21.61$ Å, $c = 14.45$ Å, $\beta = 110.4°$, $Z = 2$). The two molecules which comprise the dimer are crystallographically related by the inversion center. Each molecule also incorporates a crystallographic mirror plane of symmetry. Poor diffraction and severe disordering of the cyclohexyl rings prevented a satisfactory solution of the structure.

[6] For **1**: $^{13}C\{^1H\}$ NMR (62.5 MHz, $CDCl_3$, 25 °C) δ 27.554 br s, 26.886 br s, 26.656 br s (2:1:2 for CH_2); 23.881 s, 23.542 s, 23.112 s (3:3:1 for SiCH). $^{29}S\{^1H\}$ NMR (49.7 MHz, $CDCl_3$, 25 °C, 0.02 M $Cr(acac)_3$) δ −60.159 s, −67.993 s, −69.544 s (3:1:3).

[7] All ^{13}C and ^{29}Si NMR spectra were recorded using inverse-gated proton decoupling in order to minimize nuclear Overhauser enhancement effects. For ^{29}Si NMR spectra, all samples contained 0.02 M $Cr(acac)_3$ in order to reduce T_1's to <2 s. To ensure accurate integrated intensities, at least three T_1's were allowed to elapse between observation pulses.

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[9] For **3**: ^1H NMR (250.1 MHz, $CDCl_3$, 25 °C) δ 2.072 (s, 15 H), 1.722 (v br m, 35 H), 1.226 (v br m, 35 H), 0.678 (v br m, 7 H, SiCH). Mass spectrum (70 eV, 200 °C), *m/e* (relative intensity) 1196 (M^+, 100%), 1113 ($M^+ - 83$, 24%). No other peaks larger than 7% of the base peak.

[10] For **3**: $^{13}C\{^1H\}$ NMR (62.5 MHz, $CDCl_3$, 25 °C) δ 121.094 (s, Cp); 27.782, 27.653, 27.600, 27.015, 26.864, 26.750 (s, CH_2); 24.006, 23.501, 23.350 (s, 3:3:1, SiCH); 10.630 (s, CH_3). $^{29}Si\{^1H\}$ NMR (49.7 MHz, $CDCl_3$, 25 °C, 0.02 M $Cr(acac)_3$) δ −66.058 s, −68.486, −70.286 s (3:1:3).

Table I. Selected Average Bond Distances and Angles for Chemically Equivalent Atoms[a]

bond dist/Å		bond angles/deg	
$Zr–O_a$	1.958 (32, 6)	$O_a–Zr–O_a$	103.4 (12, 6)
$Si_a–O_a$	1.610 (36, 6)	$Zr–O_a–Si_a$	145.8 (14, 6)
$Si_a–O_b$	1.620 (29, 12)	$O_a–Si_a–O_b$	110.2 (13, 12)
$Si_b–O_b$	1.620 (24, 12)	$O_b–Si_a–O_b$	108.4 (13, 6)
$Si_b–O_c$	1.600 (46, 6)	$Si_a–O_b–Si_b$	151 (4, 12)
$Si_c–O_c$	1.619 (30, 6)	$O_b–Si_b–O_b$	110.6 (27, 6)
		$O_b–Si_b–O_c$	108.2 (17, 12)
		$Si_b–O_c–Si_c$	151 (5, 6)
		$O_c–Si_c–O_c$	108.0 (11, 6)

[a] The first numbers in parentheses are the root-mean-square deviations of chemically equivalent bonds or angles. The second numbers are the number of independent measurements used in the calculations.

the zirconium atom. The ^{13}C NMR spectrum also exhibits a 3:3:1 ratio of resonances for the cyclohexyl carbons attached to silicon (Figure 1B).[7]

We have also conducted a single-crystal X-ray diffraction study[11] on **3** in order to gain insight into the specific bonding capabilities of **1**. An ORTEP plot of **3** (Figure 2) shows that **1** can easily accommodate a large transition-metal atom without any unusual distortions to the siloxane framework. The Si–O bond distances, as well as the Si–O–Si and O–Si–O bond angles, are within the ranges observed[12] for structurally analogous POSS octamers **2**. The Zr–O bond distances and angles are also within the ranges expected for three-legged piano stool complexes of this type[13] (Table I).

In summary, we have described the synthesis and characterization of the first example from a new class of silicon–oxygen-based macromolecules which incorporate transition-metal atoms into a "cubelike" silsesquioxane framework (POMSS). We have demonstrated that such molecules can be easily synthesized and structurally characterized by using conventional spectroscopic techniques. The ease with which zirconium (one of the larger transition metals)[14] can be incorporated into the siloxane framework suggests that it will be possible to synthesize POMSS that contain a wide variety of different metals. Since the short-range (two–six atoms) molecular structure of **3** in the vicinity of the metal atom is very similar to those observed or proposed for some silica-supported transition-metal catalysts,[1] we believe that POMSS complexes such as **3** can be used to model reaction chemistry that occurs on a silica surface. We are currently synthesizing other related POMSS complexes which will allow us to test this hypothesis.

Acknowledgment. I thank my colleagues for their enthusiastic support and, in particular, Professor Robert J. Doedens for his assistance with the X-ray crystallographic study.

Note Added in Proof. The X-ray crystal structure of **1**, obtained by recrystallization from pyridine/hexane, has been successfully solved. Details will be published in a subsequent article.

Supplementary Material Available: X-ray crystal data for **3** including experimental procedures, tables of crystal data, and perspective ORTEP plots (36 pages). Ordering information is given on any current masthead page.

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(11) See the supplementary material for details regarding the X-ray crystal structure.

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DNA Strand Scission by Bleomycin: Catalytic Cleavage and Strand Selectivity

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The bleomycins (BLM's) are structurally related antitumor antibiotics that are now used routinely for the treatment of certain malignancies; the biochemical locus of action of bleomycin is thought to be DNA.[2] Oxidative DNA strand scission by bleomycin has been demonstrated in the presence of several metal ions, and the mechanism of DNA cleavage by these metallobleomycins has been studied extensively.[3] Of particular interest is the selectivity of bleomycin for certain sequences, notably G·pyrimidine sites,[4] and the ability of bleomycin to mediate double-strand breaks.[5]

Recently, we reported on $d(CGCT_3A_3GCG)$, a self-complementary dodecanucleotide that acts as an efficient substrate for cleavage by Fe^{II}·BLM + O_2; not surprisingly, most cleavage occurred at the (double-stranded) GC recognition site. By the use of this oligomer, we were able to identify and quantify all significant degradation products produced.[6] Analysis of the data suggested that each BLM-mediated DNA "event" required two electrons, consistent with earlier proposals for O_2 activation by BLM.[7] Presently, we extend our earlier observations concerning Fe·BLM–dodecanucleotide interaction and demonstrate that (i) bleomycin can act *catalytically* in DNA degradation, (ii) both ends of the BLM molecule participate in determining DNA binding specificity, (iii) BLM and decarbamoyl-BLM have different coordination geometries when bound to Fe, and (iv) BLM can probably assume two different orientations at double-strand cleavage sites.

Although numerous studies have dealt with DNA cleavage by bleomycin, in virtually all cases the number of DNA lesions produced has failed to exceed the number of bleomycin molecules employed.[8] This observation and the mechanistic analogy between bleomycin and cytochrome P-450[9] have tended to support the

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