for near infrared measurements. W.K. acknowledges a most generous stipend of the Karl-Winnacker Foundation (1982–1987).

Registry No. $\{(\mu\text{-phdo})[Ru(bpy)_2]_2\}(PF_6)_3$, 118494-61-4; $Ru(bpy)_2Cl_2$, 19542-80-4; $\{(\mu\text{-bppq})[Ru(bpy)_2]_2\}(PF_6)_3$, 118513-70-5; $\{(\mu\text{-phdo})[Ru(bpy)_2]_2\}^{2+}$, 118494-62-5; $\{(\mu\text{-phdo})[Ru(bpy)_2]_2\}^{4+}$, 109998-78-9; $\{(\mu\text{-bppq})[Ru(bpy)_2]_2\}^{2+}$, 118494-63-6; $\{(\mu\text{-bppq})[Ru(bpy)_2]_2\}^{4+}$, 118494-64-7.

Supplementary Material Available: A detailed description of the synthesis of the hydroquinone derivative bppqH$_2$ (1 page). Ordering information is given on any current masthead page.

Pressure-Induced Spin-State Interconversion of $[Fe(6\text{-}Me\text{-}py)_3tren](ClO_4)_2$ in Solution

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Received July 11, 1988

Abstract: The series of pseudooctahedral Fe^{II} spin-crossover complexes $[Fe(6\text{-}Me\text{-}py)_3tren](ClO_4)_2$ (**4**), $[Fe(6\text{-}Me\text{-}py)_2pytren](ClO_4)_2$ (**3**), and $[Fe(6\text{-}Me\text{-}py)py_2tren](ClO_4)_2$ (**2**) exhibit varying degrees of high- and low-spin population in solution. Specifically complex **4** is mostly high spin, while complexes **2** and **3** are of an intermediate spin state. The principal result of this paper is that with pressure the spin state of complex **4** changes from high spin ($^5T_2$) to low spin ($^1A_1$). This change is monitored by following the changes with pressure in the metal-to-ligand charge-transfer bands of the complex which are at higher energy and lower intensity for a high-spin as compared to a low-spin complex. The effect of pressure on the metal-to-ligand charge-transfer (CT) bands of complexes **2**, **3**, and **4** has been studied in acetone and dichloromethane solutions. The pressure range studied is from 0.001 kbar to 10.0 kbar (1.0 kbar = 986.92 atm = 0.1 GPa). The predominant effect of pressure, in both media for all three complexes, is a shift to lower energy and an increase in intensity of the CT bands. The difference in magnitude for these spectral changes with pressure indicate that the predominantly high-spin complex **4** is converted to a low-spin complex in solution upon the application of pressure.

Octahedral complexes of metal ions with a d^6 configuration may exist in either a high- or a low-spin electronic configuration, depending on the relative magnitude of the ligand field, 10 Dq, and the 3d-electron mean-pairing energy, P. If $|P - 10\ Dq| \cong kT$, then both the high- ($^5T_2$) and low-spin ($^1A_1$) states of the complex may be thermally populated. A spin equilibrium, $^1A_1 \rightleftarrows {}^5T_2$, arises in this case.[3-7] A compound which exhibits this phenomenon is often called a spin-crossover complex. In the solid state a number of spin-crossover complexes convert from high to low spin with decreasing temperature[3,5] or increasing pressure.[8,9] In solution spin-state interconversion has been observed with a change of temperature. The principal result presented in this paper is that the spin state of a Fe^{II} spin-crossover complex changes from high to low spin in solution with increasing pressure. This change is monitored by following the changes with pressure of the metal-to-ligand charge-transfer bands of the complex. Previously Ewald et. al[10] presented magnetic susceptibility measurements on the one compound $[Fe(S_2CN(Bu^n{}_2)_3]$ in chloroform which showed measurable spin pairing over a range of 3 kilobars. From the pressure derivative of the equilibrium constant, they extracted from their results a high-spin to low-spin volume change of −3.6 to −4.0 cc/mol.

The complexes studied in this paper are the perchlorate salts of composition $[Fe(6\text{-}Me\text{-}py)_n py_{3-n}tren](ClO_4)_2$, where the number of methyl-substituted pyridine arms of the ligand is changed to give the following complexes:

complex **1**: $n = 0$

complex **2**: $n = 1$

complex **3**: $n = 2$

complex **4**: $n = 3$

Hoselton et al.[11] have shown that the PF$_6^-$ salts of the cations of complexes **2** and **3** exhibit spin-crossover behavior in acetone and Me$_2$SO solutions. Steric interactions between the methyl groups on adjacent pyridine rings cause compound **4** to be mostly high spin in the same solvents. In addition, they have estimated the difference $|P - 10\ Dq|$ to be $\sim$200 cm^{1} for complexes **2** and **3** in solution.[12]

The laser-flash photolysis technique was employed by Xie and Hendrickson[13] to determine the $^5T_2 \rightarrow {}^1A_1$ relaxation rate of complex **3** doped in polystyrene sulfonate from 300 to 4.2 K. The temperature independence of this relaxation rate below $\sim$100 K definitively showed that complex **3** tunnels from the $^5T_2$ to the $^1A_1$ state. In a separate study it was found[14] that the apparent

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activation energy for the $^5T_2 \rightarrow {}^1A_1$ interconversion from 185–280 K Arrhenius plots is dependent on the concentration of complex **1** in the range of 0.05–0.5 mM.

Drickamer and co-workers have demonstrated that the general effect of pressure on transition-metal complexes in the solid state is to increase the ligand field and reduce the interelectronic repulsion.[8,9] These changes can result in the conversion of a high-spin material to a low-spin one.[15-18] For undoped complexes the pressure-driven transition in the solid state appears to be first order when one allows for the effects of grain boundaries, surfaces, pressure gradients, etc.

Experimental Section

Compound Preparation. Elemental analyses were performed in the Microanalytical Laboratory of the School of Chemical Sciences. Commercially available tris(2-aminoethyl)amine (tren) was purified by converting it to its hydrochloride salt, followed by recrystallization in ethanol. Anal. Calcd for $N(CH_2CH_2NH_2)_3 \cdot 3HCl$: C, 28.20; H, 8.28; N, 21.91. Found: C, 28.30; H, 8.28; N, 21.88. Other commercial reagents were used without further purification. Samples of the four Fe^{II} complexes studied in this work were prepared by a modification of the method reported by Hoselton et al.[11] All syntheses were carried out under an argon atmosphere employing Schlenkware.

[Fe(6-Me-py)$_3$tren](ClO$_4$)$_2$ (4). tren·3HCl (0.542 g, 2 mmol) and 0.726 g (6 mmol) of 6-methyl-2-pyridinecarboxaldehyde (Aldrich) were added to 60 mL of absolute methanol. NaOMe (0.34 g) was introduced to deprotonate the tren·3HCl. The yellow-–orange colored Schiff base solution was then degassed and transferred into the flask which contained a solution of 0.40 g (2 mmol) of $FeCl_2 \cdot 4H_2O$ in 30 mL of methanol under Ar. The solution color changed from yellow-orange to dark red. To this solution was added 1.3 g of $NaClO_4$ in a small amount of methanol. A microcrystalline product immediately formed, was filtered, and washed successively with oxygen-free methanol and ether. The product was then dried in an Ar stream. Anal. Calcd for $FeC_{27}H_{33}N_7O_8Cl_2$: C, 45.65; H, 4.65; N, 13.79; Fe, 7.87. Found: C, 44.82; H, 4.66; N, 13.43; Fe, 7.93.

[Fe(6-Me-py)$_2$pytren](ClO$_4$)$_2$ (3). The preparation of complex **3** is the same as for complex **4**, except the Schiff-base solution was made by first dissolving 0.542 g (2 mmol) of tren·HCl in 60 mL of absolute methanol containing 0.34 g of NaOMe and, then, adding 0.484 g (4 mmol) of 6-methylpyridinecarboxaldehyde followed after 30 min by 0.214 g (2 mmol) of 2-pyridinecarboxaldehyde. Anal. Calcd for $FeC_{26}H_{31}N_7O_8Cl_2$: C, 44.85; H, 4.49; N, 14.07; Fe, 8.02. Found: C, 43.93; H, 4.51; N, 13.74; Fe, 8.18.

[Fe(6-Me-py)py$_2$tren](ClO$_4$)$_2$ (2). The preparation of complex **2** was the same as for complex **3**, except 2-pyridinecarboxaldehyde and 6-methyl-2-pyridinecarboxaldehyde were used in the ratio of 2:1, respectively, instead of the 1:2 ratio used for complex **3**. Anal. Calcd for $FeC_{25}H_{29}N_7O_8Cl_2$: C, 44.01; H, 4.28; N, 14.36; Fe, 8.19. Found: C, 43.16; H, 4.36; N, 14.11; Fe, 8.12.

High-Pressure Measurements. Solution absorption spectra were taken by placing the acetone or dichloromethane solutions in a stainless-steel inner cell with pistons containing sapphire windows.[19] This cell was placed in a larger bomb which was filled with the pressurizing fluid, isobutyl alcohol.

Electronic absorption spectra for the polymer film were recorded with the sample loaded into an Inconel-gasketed diamond anvil cell, by using the ruby fluorescence method of pressure calibration.[20] A 100-W Oriel quartz tungsten halogen lamp with a Kratos quartermeter monochromator using a 400 blaze grating was used. Transmitted light was detected by an EMI no. 9558 PM tube. The change of density with pressure of acetone and dichloromethane are from Bridgman.[21,22]

Results and Discussion

Complexes **2**, **3**, and **4** were studied in this work. Each of these exhibit two metal-to-ligand charge-transfer (CT) bands in solution. The origin of this band is a transition from either the $^1A_1$ (low-spin)

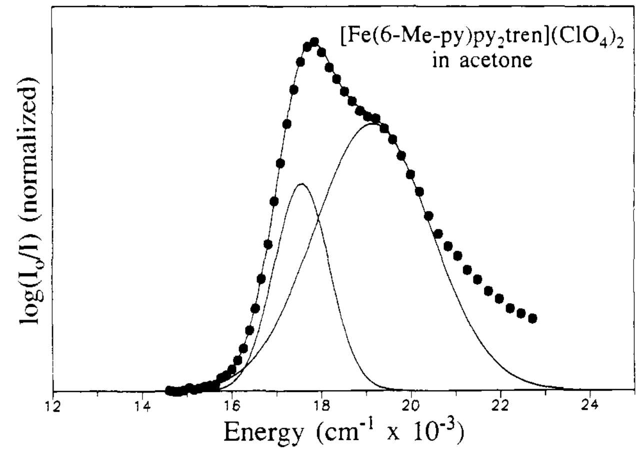

Figure 1. Metal-to-ligand charge-transfer absorption bands of [Fe(6-Me-py)py$_2$tren](ClO$_4$)$_2$ dissolved in acetone. The spin state of this complex is predominantly low spin. The tail of the CT band in the UV (not shown in figure) was subtracted in the course of fitting.

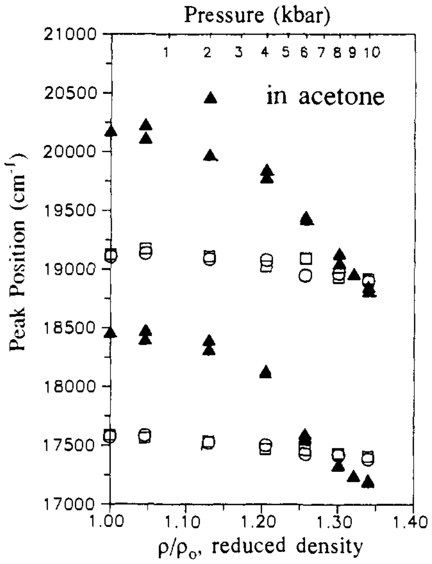

Figure 2. Shift with pressure of the charge-transfer absorption bands of [Fe(6-Me-py)$_n$py$_{3-n}$tren](ClO$_4$)$_2$ dissolved in acetone: $n = 3$ (▲), $n = 2$ (□), $n = 1$ (○).

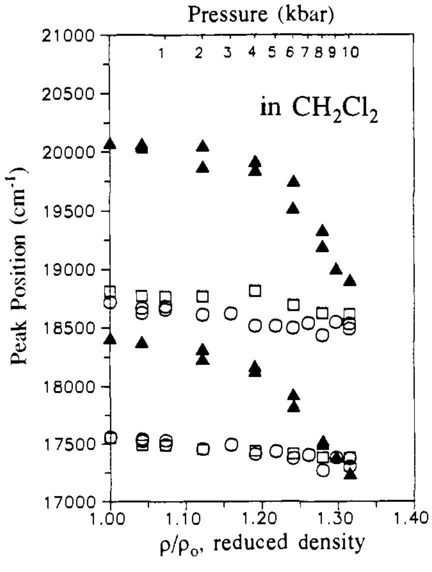

Figure 3. Shift with pressure of the charge-transfer absorption bands of [Fe(6-Me-py)$_n$py$_{3-n}$tren](ClO$_4$)$_2$ dissolved in CH$_2$Cl$_2$: $n = 3$ (▲), $n = 2$ (□), $n = 1$ (○).

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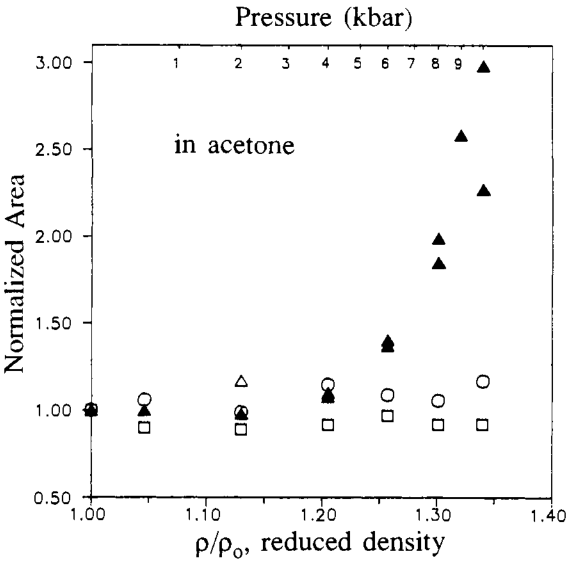

Figure 4. Change in normalized area with pressure of the charge-transfer absorption bands of [Fe(6-Me-py)$_n$py$_{3-n}$tren)(ClO$_4$)$_2$ in acetone; n = 3 (▲), n = 2 (□), n = 1 (○).

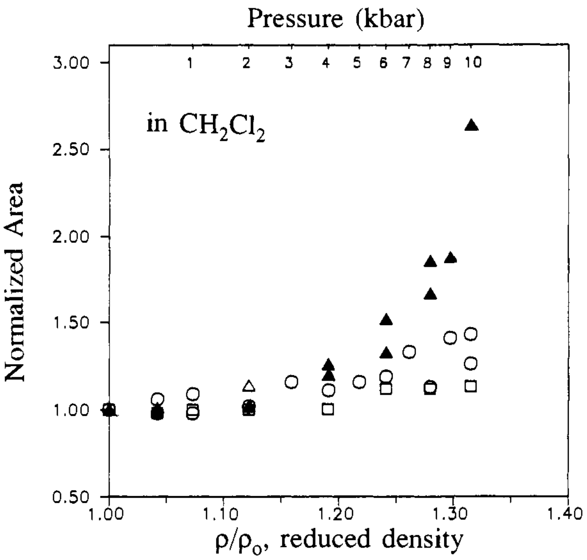

Figure 5. Change in normalized area with pressure of the charge-transfer absorption bands of [Fe(6-Me-py)$_n$py$_{3-n}$tren](ClO$_4$)$_2$ in CH$_2$Cl$_2$: n = 3 (▲), n = 2 (□), n = 1 (○).

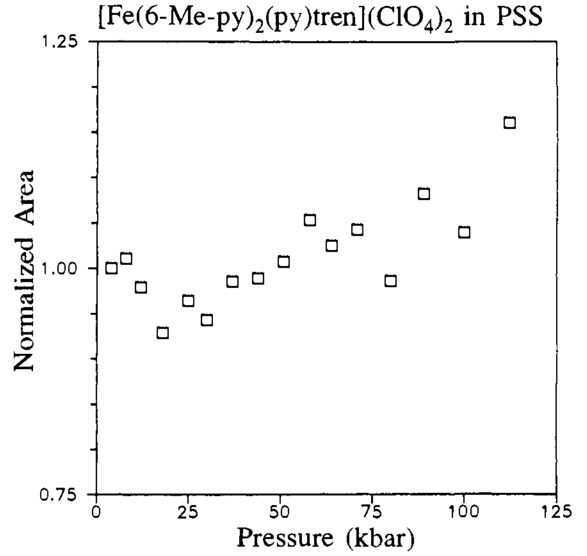

Figure 6. The change of normalized area with pressure of the charge-transfer absorption bands of [Fe(6-Me-py)$_2$(py)tren](ClO$_4$)$_2$ doped into the polyelectrolyte polystyrene sulfonate (PSS).

or $^5T_2$ (high-spin) ground state to the π^* orbitals of the pyridine moieties, since no other ligand orbitals are of the appropriate symmetry to mix with the metal orbitals.[23,24] As seen in Figure 1 (and also Figure 7) there are two peaks in both the high-spin and low-spin spectra. In each case the splitting is ~1000 cm^{-1}. It is most probable that the ligand π^* state is split in the relatively low symmetry of the molecule. There are two other general points to be made about these CT bands: (1) The high-spin CT bands lie ~1000 cm^{-1} to higher energy than the low-spin bands and (2) the high-spin CT bands are less intense than those seen for the low-spin complexes.[12,13,23] In CH$_3$CN solution the low-spin bands are more intense by a factor of ~6.[11] This increase in intensity for the low-spin CT bands could arise from a larger overlap between the t_{2g} set of orbitals (π symmetry) of the low-spin metal ion with the π^* orbitals of the pyridine ligand than for the e_g orbitals (σ symmetry) of the high-spin state with the ligand orbitals.

Specifically, our measurements indicate that in acetone the CT bands of complex **4** are located at 18.5 kK (1 kK = 1000 cm^{-1}) and 20.2 kK and at 17.6 and 19.6 kK for complexes **2** and **3**, respectively. When dissolved in dichloromethane the CT band maxima are at 18.4 and 20.1 kK for complex **4** and at 17.6 and 18.8 kK for the complexes **2** and **3**, respectively.

Figures 2 and 3 show how the maxima of the CT bands of these three complexes change with compression in acetone and dichloromethane. The pressure range studied, in both solvents, was from 0.001 to 10.0 kbar (1.0 kbar = 986.92 atm = 0.1 GPa). The shift of the CT bands is nearly identical in both media when plotted against the degree of compression of the medium, but since the compressibility of acetone and dichloromethane is different the shift with pressure is different for each solvent. The most significant feature is that, in both solvents, the shift of the complex **4** CT bands is ~1500 cm^{-1} toward lower energy, while the shifts of the CT bands of complexes **2** and **3** are <250 cm^{-1} to the red, so that by 10 kbar the CT bands of all three complexes are essentially at the same energy (see Figures 2 and 3). Figures 4 and 5 show the change in normalized area of both CT bands for the three complexes in acetone and dichloromethane as a function of the reduced density of the solvent. What is most striking is that the area of CT bands for complex **4** increases by over a factor of two, while the areas of the complex **2** and **3** CT bands increase, at most, by a factor of 1.15, so that at high pressure their areas are more nearly equal for the two different types of complexes.

In order to determine how a completely low-spin complex behaves with pressure we studied complex **3** doped into the polyelectrolyte, polystyrene sulfonate (PSS). Mössbauer data for a ^{57}Fe-enriched sample of the PSS-doped sample show that at 298 K and ambient pressure the complex is completely in the low-spin state.[13] The areas of the CT bands for this sample increase by a factor of ~1.16 over a pressure range of 125 kbar (see Figure 6). This implies that the oscillator strength for the MLCT band in a low-spin complex should change very little with pressure. The maxima for the two CT bands shifted by ~500 and ~750 cm^{-1} for the PSS-doped sample in this same pressure range. Unfortunately, complex **4** doped into PSS showed irreversible effects.

The differences in magnitude between the effect of pressure on the CT bands of complex **4** and those of complexes **2** and **3** indicate that the spin state of complex **4** is changing from mostly high spin to low spin. The evidence for this is as follows: (1) The integrated areas of the complex **4** CT bands increase with pressure more than those of complexes **2** and **3**. This reflects the increased intensity of low-spin CT bands compared to those of high-spin complexes. (2) The energies of the complex **4** peaks shift to the position of the low-spin CT bands. And (3) at 10.0 kbar the shapes

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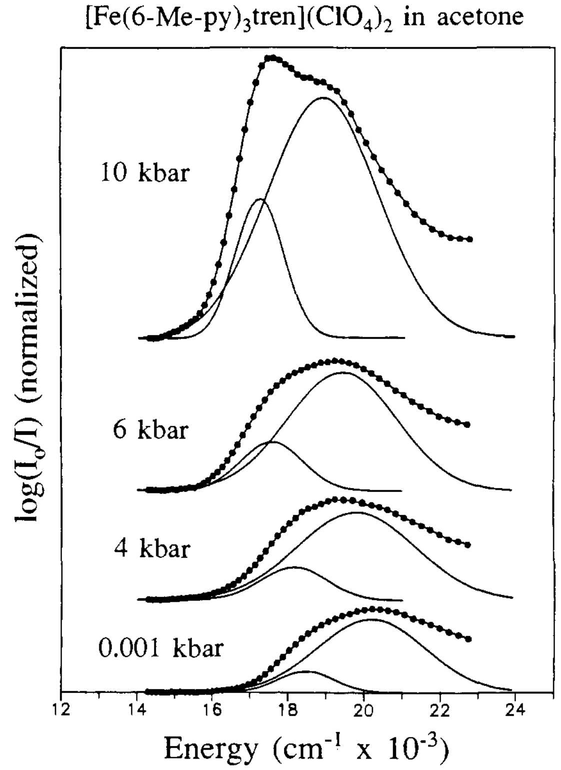

Figure 7. Changes with pressure of the charge-transfer absorption bands of [Fe(6-Me-py)$_3$tren](ClO$_4$)$_2$ in acetone. The relative heights of the absorption bands are to scale. The tail of the CT band in the UV (not shown in Figure) was subtracted in the course of fitting.

of the complex **4** spectra in the two solvent resemble those of the low-spin complexes **2** and **3**, see Figures 1 and 7.

Comments and Conclusions

The main conclusion from this study of the effect of pressure on the CT bands of a series of Fe^{II} spin-crossover complexes is that with pressure we are able to convert the spin state of [Fe(6-Me-py)$_3$tren](ClO$_4$)$_2$ from mostly high spin to low spin in solution. There have been several studies wherein spin-crossover complexes in solution have been shown to convert from high spin to low spin upon decreasing the temperature of the solution. In these cases as the temperature of the solution is decreased presumably the main effect is a depopulation of the $^5T_2$ excited state of the Fe^{II} complex, and finally all complexes are in the $^1A_1$ ground state. That is, the energy difference between the $^5T_2$ and $^1A_1$ states is not affected appreciably by temperature, and the shift from more high-spin to all low-spin complexes with temperature just reflects a Boltzmann distribution. However, in the case of the pressure-driven conversion from high to low spin in solution the increased compression on the solvent tunes the energy difference between the $^5T_2$ and $^1A_1$ states such that the $^1A_1$ state of the Fe^{II} complex is stabilized at elevated pressures. One may, in principle, use the area under the peaks as a measure of the degree of spin conversion, assuming essentially all high-spin complexes below ~5 kbar and all low-spin complexes at 10–11 kbar. This is a doubtful procedure in this case since in the intermediate pressure region there should be two pairs of peaks, one pair associated with each spin state. Nevertheless, if one proceeds in this manner it is possible to extract volume changes of −3.6 to −3.8 cc/mol in each solvent. A contributing factor to this value is certainly differences in ligand–metal bond length in the two solvents. However, there can also be differences in polarizability, dipole moment, and degree and type of solvation, and these intermolecular considerations can easily be a major consideration in the difference in volume observed.

Finally, we note that in solution this is clearly a stochastic chemical equilibrium which depends on the difference in free energy between the two states of the molecule. In the crystal the process is much more cooperative, and it is the free energy of the crystal which governs the conversion.

Acknowledgment. This work was supported in part by the Materials Science Division, Department of Energy, under Contract DE-AC02-76ER01198 and in part by NIH Grant HL13652. We acknowledge the very useful suggestions of Professor R. L. Martin.

Silsesquioxanes as Models for Silica Surfaces

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Abstract: The hydrolytic condensation of cyclohexyltrichlorosilane (CySiCl$_3$) affords [Cy$_7$Si$_7$O$_9$(OH)$_3$] (**1**), [Cy$_6$Si$_6$O$_9$] (**2**), and [Cy$_8$Si$_8$O$_{11}$(OH)$_2$] (**3a**). Trisilanol **1** and **3b**, the bis(triphenyltin) derivative of **3a**, have been structurally characterized by single-crystal X-ray diffraction studies. Trisilanol **1** undergoes corner-capping reactions with trifunctional monomers (e.g., R′SiCl$_3$, MeGeCl$_3$, MeSnCl$_3$), is selectively monosilylated to [Cy$_7$Si$_7$O$_9$(OH)$_2$OTMS] (**6a**) with chlorotrimethylsilane, and can be dehydrated to [Cy$_7$Si$_7$O$_{10}$(OH)] (**7a**). Comparison of the molecular structure of **1** with (111) β-cristobalite and (0001) β-tridymite reveals many structural similarities. Silsesquioxanes **1**, **6a**, and **7a** are discussed as models for silica surfaces.

Heterogeneous silica-supported transition-metal complexes play an important role as catalysts in the petrochemical industry.[1] Highly selective catalysts have been developed to catalyze an impressive range of chemical processes, such as hydrocarbon oxidation,[2] olefin and alkyne polymerization[3] and metathesis,[4,5]

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