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Structures and Stabilities of Titanium Silsesquioxanes

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The structures and stabilities of the titanium analogues of fully condensed silsesquioxanes, $[HTiO_{1.5}]_n$, $n = 4-12$, are investigated with ab initio electronic structure theory including electron correlation effects. In addition, the distribution of Ti atoms in T_8, $H_8Ti_pSi_{8-p}O_{12}$; $p = 1-7$, are compared with the Al distribution in zeolites. The fully substituted POSS are found to have similar structures to the silicon analogues though the titanium compounds seem to be more stable for all cage sizes than the silicon compounds.

Introduction

For many years, polyhedral oligomeric silsesquioxanes (POSS) have attracted considerable experimental and theoretical interest because of their wide variety of practical uses.[1] Recently, metal-substituted POSS have generated interest, not only because they can be considered as model compounds for metal-doped zeolites but also because they have demonstrated catalytic ability themselves.[2] In particular, titanosilsesquioxanes (Ti-POSS) and related compounds have attracted attention as good catalysts for alkene epoxidation.[3] There have been several experimental and theoretical studies of the mechanism of alkene epoxidation on titanium silicate and selective oxidations in titanium-containing zeolites, using simple model systems.[4] However, very little experimental or theoretical information is available about Ti-POSS compounds themselves.

The present paper presents results of electronic structure calculations on Ti-POSS in order to understand the molecular and electronic structure and properties of these important and novel compounds. Following a discussion of the structures and properties of the smallest titanium−oxo compounds, dititanoxanes, and small ring compounds of titanoxanes, the fully-Ti-substituted-POSS are considered. In addition, the Ti distribution in POSS compounds that are only partially substituted with Ti atoms is investigated, to compare this distribution with analogous Al distributions in zeolites.[5]

Computational Methods

The geometries of all molecules of interest have been fully optimized at the restricted Hartree−Fock (RHF) level of theory using the SBK effective core potential[6] and the valence triple-ζ plus polarization (TZVP) basis sets developed by Wachters[7] and Goddard.[8] For $[HTiO_{1.5}]_n$, geometry optimizations have also been carried out using SBK augmented by a set of six d-type polarization functions on oxygen atoms (d exponent = 1.280, the same as in TZVP), referred to as HF/SBK+d(O). For dititanoxane and some Ti−Si-mixed-POSS, geometry optimizations were also carried out using second-order perturbation theory (MP2)[9] with the TZVP basis set (MP2/TZVP). All compounds were characterized as minima or transition states by calculating and diagonalizing the Hessian matrix of energy second derivatives at the MP2/TZVP level for dititanoxane and HF/SBK level for the cage compounds. For some of the larger compounds, a single point MP2 energy calculation was carried out to obtain more reliable energetics. Corresponding calculations have been performed for selected silicon analogues with the same TZVP basis set for comparison purposes. All calculations were performed with the GAMESS electronic structure code.[10]

Results and Discussion

A. Dititanoxane. First, consider the smallest type of compound that contains a −Ti−O−Ti− unit, the dititanoxane shown in Figure 1. This molecule may be considered to be a building block for Ti-POSS or mixed Ti/Si-POSS. Two, nearly isoenergetic, local minima (gauche 2 and trans) have been found at the HF/SBK level of theory. Both conformers were optimized in C_2 symmetry, but the trans isomer attains nearly C_{2h} symmetry, as shown in Figure 1. However, at higher levels of theory the trans isomer disappears, and only the gauche isomer appears to be a minimum on the potential energy surface (PES). A second gauche isomer (gauche 1) on the MP2/TZVP PES has a geometry that is quite similar to gauche 2 except for the Ti−O−Ti angle. This conformation is found to be more stable than gauche 2 by only 0.5 (0.4 with the zero point correction) kcal/mol at the MP2/TZVP level, suggesting the Ti−O−Ti bend potential is very floppy.

In the all-silicon analogue, intramolecular hydrogen bonding between the −OH groups was observed.[1p] This stabilization through hydrogen bonding is not found in this titanium compound, perhaps because the TiO bond is about 0.15 Å longer than a typical SiO distance.[1] It is interesting to compare the present results with recent B3LYP/6-311G + d(Ti) calculations on $(HO)_3TiOTi(OH)_3$.[11] As in the present case, two isomers, one gauche and one trans, were located. There are two apparent hydrogen bonds in the B3LYP trans isomer, but this structure is less stable by 4 kcal/mol. All attempts to find such a hydrogen-bonded isomer on the PES of $H(HO)_2TiOTi(OH)_2H$ were unsuccessful. This suggests hydrogen bonding is not important for the stabilization of titanoxane units.

The HF/SBK Ti−O bond lengths for the gauche2 isomer in Figure 1 are longer than those obtained with all electron HF/

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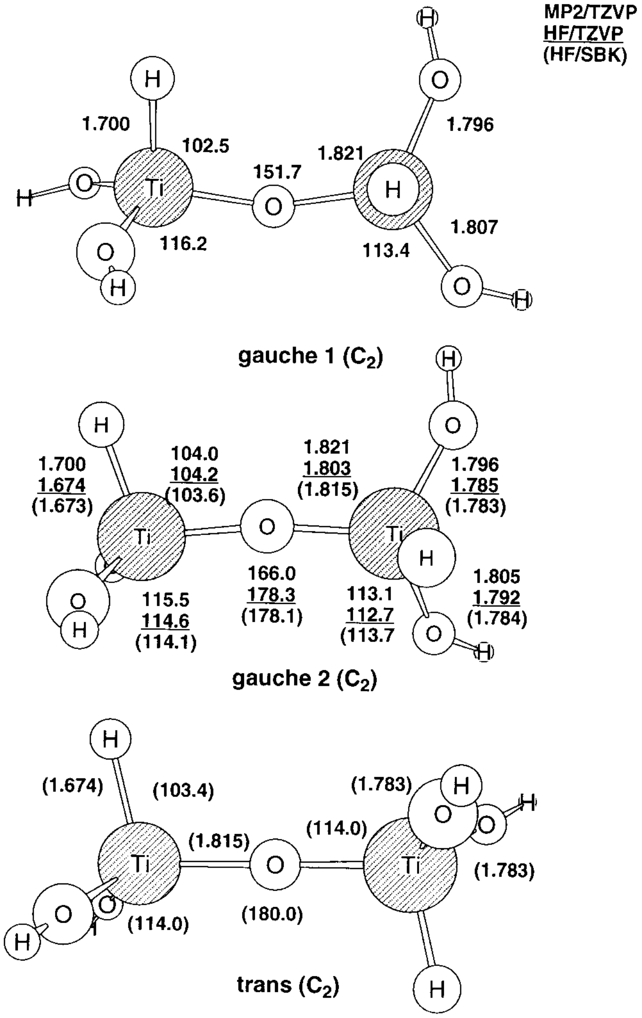


Figure 1. Optimized structures for three isomers of $H(OH)_2TiOTi(OH)_2H$ at three levels of theory in angstroms and degrees.

TZVP calculations, but the addition of electron correlation lengthens this bond. The Ti−O(−H) bond length is 0.02−0.03 Å longer than that of H_3TiOH at the same level of theory.[12] As for the Si−O−Si angle in the silicon analogues,[1b,p] the addition of electron correlation decreases the Ti−O−Ti angle from linear to 151.7° and 166.0° for gauche1 and gauche2, respectively. This latter angle (gauche2) is very close to the experimental value (169.3°) in $[(C_5Me_4Ph)TiCl_2]_2(\mu\text{-}O)$ with C_2 symmetry.[13] The MP2/TZVP Ti−O−Ti bending frequencies in gauche1 and -2 are only 43.7 and 33 cm^{-1}, respectively, suggesting the potential energy surface is quite flat.

B. Cyclotitanoxanes. Next, consider the structures of the cyclotitanoxanes, $[H(OH)TiO]_n$, $n = 3-6$. These are larger, two-dimensional components of Ti-POSS. The optimized structures of two isomers of tri- and tetracyclotitanoxanes are shown in Figure 2. They are quite similar to each other except for the orientations of OH and H groups. For simplicity, a notation for these compounds is adopted that is analogous to that used for the corresponding silicon species: cyclic $[H(OH)TiO]_n$, is referred to as Ti-D_n.

As discussed for dititanoxane, little hydrogen bonding is observed in the all-cis isomers of these ring compounds (Figure 2). The Ti−O−H angles are nearly linear (>170°), so the OH groups do not bend toward the neighboring Ti atom. The linearity of the Ti−O−H linkage has been discussed previously in terms of back-bonding from O into the empty Ti d orbitals.[12] Therefore, the trans isomer is slightly more stable than the second isomer both for Ti-D_3 and Ti-D_4, by 1.0 and 1.7 kcal/mol, respectively at the MP2/TZVP//HF/TZVP level, in contrast with cyclosiloxanes in which the all-cis isomer is the most stable.[1p]

The structures of two isomers of Ti-D_5 and Ti-D_6 are shown in Figure 3. Note that the Ti−O−Ti angles bend to the inside of the ring in both isomers of Ti-D_6 at the HF/TZVP level. As for Ti-D_3 and Ti-D_4, the Ti-D_5 trans isomer is 3.2 kcal/mol more stable than the second isomer at the MP2/TZVP//HF/TZVP level, while the stability of the all-trans isomer relative to all-cis is quite small (0.02 kcal/mol) for Ti-D_6 at the same level of theory.

Analysis of Figures 2 and 3 suggests that the ring Ti−O bond length shortens slightly and the Ti−O−Ti bond angle increases as n increases from 3 to 5. The bond angle increase reflects the release of strain as n increases. For $[H(OH)TiO]_6$, there are two kinds of Ti−O bond, and the Ti−O−H angle is much smaller than in the other ring structures.

There have been some experimental studies of titanium−oxo compounds with ring or cage structures, Ti_3O_3,[14] Ti_4O_6,[13] Ti_5O_6,[15] Ti_6O_6,[16] and Ti_6O_8.[17] All of these have cyclopentadienyl groups (Cp) attached to each titanium atom. The Ti_3O_3 ring in $[\{Ti(\eta^5\text{-}C_5Me_5)(\mu\text{-}O)\}_3(\sigma\text{-}CH_2CH{=}CHMe)_3]$[14] is nearly planar with the following X-ray parameters: $d(Ti{-}O) = 1.824-1.854$ Å, $\angle(O{-}Ti{-}O) = 104.2-106.1°$, $\angle(Ti{-}O{-}Ti) = 132.7-133.4°$. Our Ti−O distance is a little shorter and the calculated O−Ti−O angle is smaller than the experimental values, probably because of the bulky ligands, C_5Me_5 and $CH_2CH{=}CHMe$, in the experimental system. The experimental structure is more similar to our trans isomer. The Ti_4O_4 ring in the trigonal bipyramidal oxygen bridged Ti_5O_6 cluster is rather distorted.[15] This molecule has a complicated structure with the Ti−O bond length in the range 1.806−1.829 Å. These are longer than those of our simple ring structures.

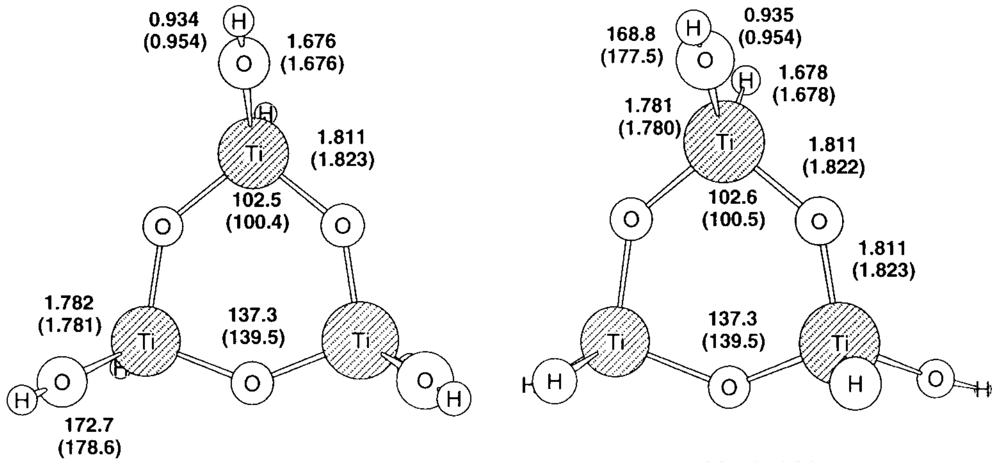
C. Fully Substituted POSS. Now consider the structures and stabilities of pertitanosilsesquioxanes, $[HTiO_{1.5}]_n$, $n = 4$, 6, 8, 10, and 12 (see Figure 4), with all silicon atoms replaced by titanium atoms in fully condensed POSS. These species are referred to as Ti-T_n. The optimized geometric parameters are shown in Table 1. In general, the three basis sets predict similar geometries. The Ti−O bond distance decreases slightly, and the Ti−O−Ti bond angle increases as n increases. There is no obvious trend for the O−Ti−O bond angle. These trends are similar to those found for the silicon analogues.[18] As mentioned above, the titanium−oxygen compound with an adamantane-like Ti_4O_6 cage structure has been synthesized.[13] The Ti_4O_6 cage corresponds to $[HTiO_{1.5}]_4$ in Figure 4 and Table 1, so it is interesting to compare these structures. The cage in $[(C_5Me_4Ph)Ti]_4(\mu\text{-}O)_6$ has nearly T_d symmetry with the following X-ray data: $d(Ti{-}O) = 1.824-1.847$ Å, $\angle(O{-}Ti{-}O) = 100.6-102.3°$, and $\angle(Ti{-}O{-}Ti) = 122.9-124.1°$. Our calculated values are in good agreement with these X-ray parameters, except for a slightly shorter calculated Ti−O bond length. In contrast to the compounds discussed in the previous section, the existence of the bulky ligands do not seem to have as serious an effect on the Ti_4O_6 framework in this case.

The thermodynamic stability of these Ti-POSS may be assessed by calculating the energetics of their hydrolysis to the monomer (1) and ring compounds (2):

$$[HTiO_{1.5}]_n + 1.5nH_2O = nHTi(OH)_3 \qquad (1)$$

$$[HTiO_{1.5}]_n + 0.5nH_2O = 2[H(OH)TiO]_{0.5n} \qquad (2a)$$

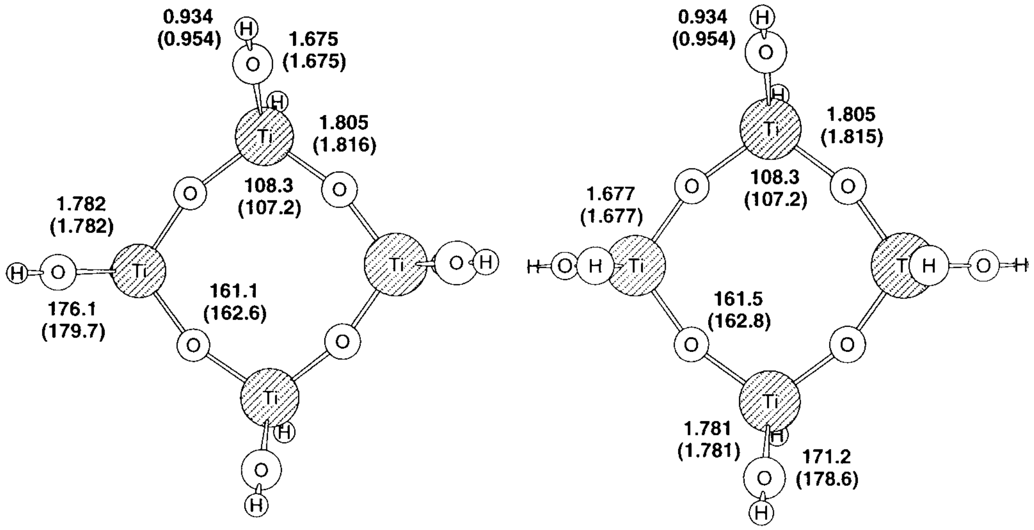
$$[HTiO_{1.5}]_n + 3H_2O = [H(OH)TiO]_3 + HTi(OH)_3 \qquad (2b)$$



[H(OH)TiO]$_3$ all cis (C_{3v})

[H(OH)TiO]$_3$ t-c-t (C_{2v})

HF/TZVP (HF/SBK)



[H(OH)TiO]$_4$ all cis (C_{4v})

[H(OH)TiO]$_4$ all trans (D_{2d})

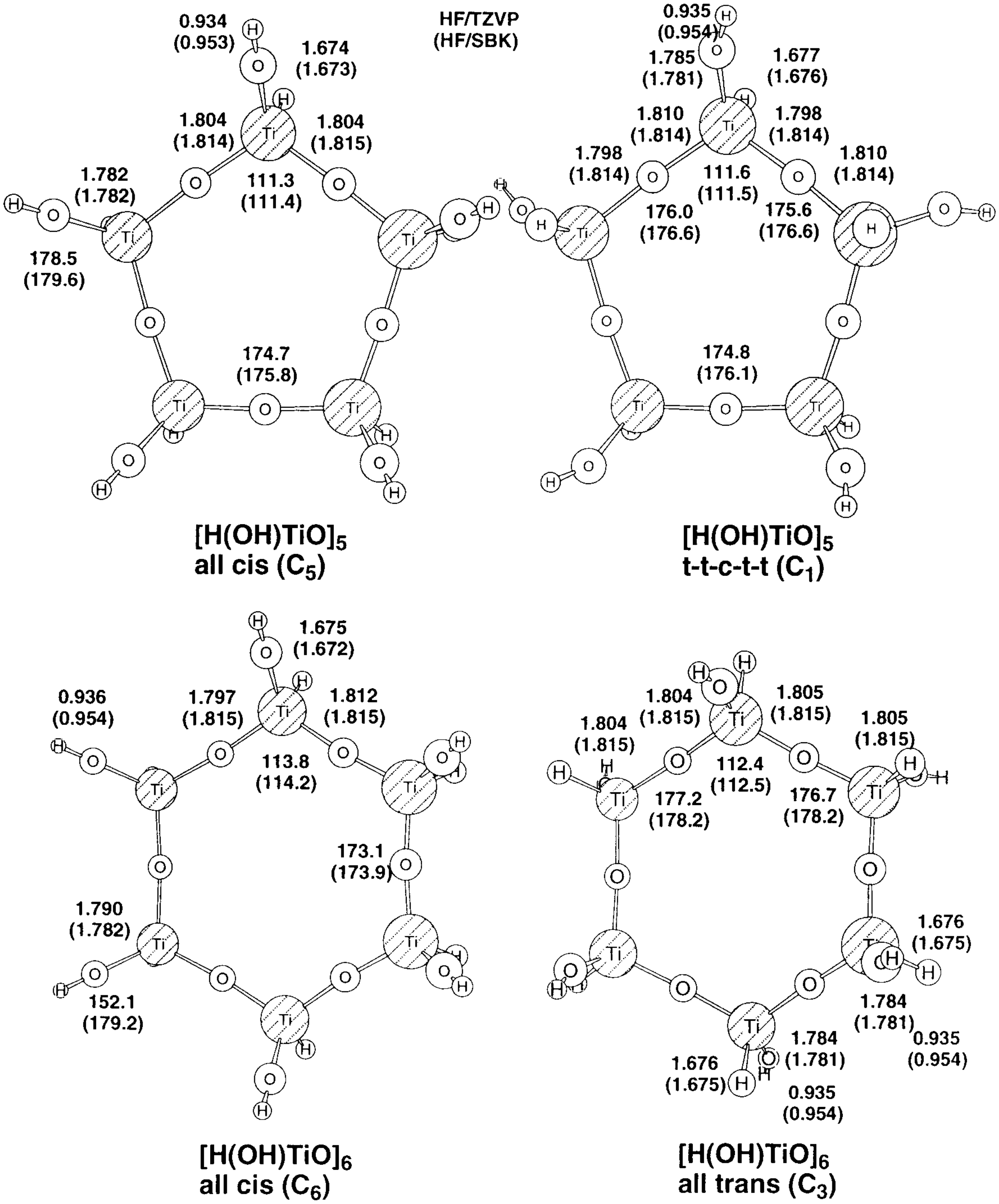
Figure 2. Optimized structures for two isomers of [H(OH)TiO]$_n$, $n = 3$ and 4, at two levels of theory in angstroms and degrees.

Reactions 2a and 2b have been used for $n = 6-12$ and $n = 4$, respectively.

The energetics for the hydrolysis reactions (1) are compared with those for the corresponding silicon compounds in Table 2. A negative ΔH (exothermic) means the cage structure is less stable than the hydrolysis product, HTi(OH)$_3$; $\Delta H/n$ is the reaction energy per Ti unit while $\Delta\Delta H/n$ is the $\Delta H/n$ relative to that of $n = 4$. The larger cage structures are more stable than the smaller ones for both Ti- and Si-POSS. Furthermore, Ti-POSS are more stable than Si-POSS for all sizes of the cage compounds. This may be explained by the flexibility of the Ti−O−Ti bond, as already mentioned.

Reaction energies for hydrolysis reactions (2a,b) are compared with the corresponding silicon reactions in Table 3. An interesting difference between Ti and Si is that a minimum in the exothermicity occurs for $n = 10$ in the case of Si, whereas there is a monotonic increase in exothermicity (in the direction of T$_n$) even for $n = 12$ in the case of Ti. It is well-known experimentally that T$_8$ is the most stable and well characterized fully condensed Si-POSS.[19] However, the present results for the hydrolysis reaction energies suggest T$_{10}$ is more stable than T$_8$. On the other hand, the calculated Ti reaction energies suggest that it might be possible to make Ti cage structures that are larger than T$_8$ or T$_{10}$. Furthermore, it is expected that Ti-POSS are more stable than the analogous Si-POSS not only for the larger cages but also for the smaller cage structures, based on the reaction energies in Tables 2 and 3. Therefore, it is not surprising that a Ti$_4$O$_6$ cage structure has already been synthesized experimentally.[13] With regard to structure, it is well-known from experimental[20] and theoretical results[1c,18] that in [HSiO$_{1.5}$]$_{12}$ the most stable isomer has D_{2d}, rather than D_{6h}, symmetry. For the Ti-POSS, we also have located two isomers, D_{6h} and D_{2d} structuresm as shown in Figure 5, and the D_{2d} structure is still more stable than the D_{6h} structure by 3.6 (6.4 at HF/TZVP) kcal/mol at the MP2/TZVP level.

The energy levels of the highest occupied (HOMO) and lowest unoccupied (LUMO) orbitals of Ti-POSS are displayed in Table 4. There are many orbitals with nearly the same energy near these HOMO(s) and LUMO(s). The energy gaps are consistently ~3 eV smaller than those for the Si-POSS. In particular, the LUMO(s) are much lower in energy in the titanium compounds. This suggests the existence of lower-lying



$[H(OH)TiO]_5$ all cis (C_5)

$[H(OH)TiO]_5$ t-t-c-t-t (C_1)

$[H(OH)TiO]_6$ all cis (C_6)

$[H(OH)TiO]_6$ all trans (C_3)

Figure 3. Optimized structures for two isomer of $[H(OH)TiO]_n$, $n = 5$ and 6, at two levels of theory in angstroms and degrees.

excited electronic states in the Ti compounds. One also would expect these Ti-POSS compounds to be more reactive than their Si analogues. There are also interesting differences between the Ti-POSS and Si-POSS "frontier" orbitals. The HOMO of all Si-POSS is an oxygen lone-pair orbital[18] and the LUMO has Si−O antibonding character. For Ti-POSS the HOMO is primarily Ti−H bonding, while the LUMO is Ti−H antibonding with significant d orbital contribution.

D. Partially Substituted POSS. There are two well-known rules, Lowenstein's rule[21] and Dempsey's rule,[22] that are taken to govern the distribution of Al atoms within zeolite frameworks. Lowenstein's rule forbids Al atoms from occupying neighboring tetrahedral framework sites, while Dempsey's rule suggests that the number of Al−O−Si−O−Al linkages is minimized for a given Si/Al ratio. These rules are primarily based on experimental observation for some kinds of zeolites, but there have been attempts to explain them theoretically.[5] It is interesting to explore the possibility that these rules might also apply for mixed Si/Ti-POSS compounds. This was investigated using the T_8 species $H_8Ti_pSi_{8-p}O_{12}$ as model compounds, as illustrated in Scheme 1, and compared with the theoretical results for the aluminum compounds.[5a,d] The structures of all of these isomers were optimized at the HF/SBK level of theory; Hessians obtained at the same level of theory confirmed that all structures are minima on their respective potential energy surfaces. These structures were then re-optimized with HF/TZVP. A MP2/TZVP single point energy calculation was carried out only for $p = 2$, because the relative stability is different for the HF/SBK and HF/TZVP results.

The titanosilsesquioxanes corresponding to $p = 1^{3e,h,j,n}$ and $4f^{3a,d}$ (Scheme 1) have been synthesized with substituents such as a cyclopentadienyl group and bulky alkoxy groups on the

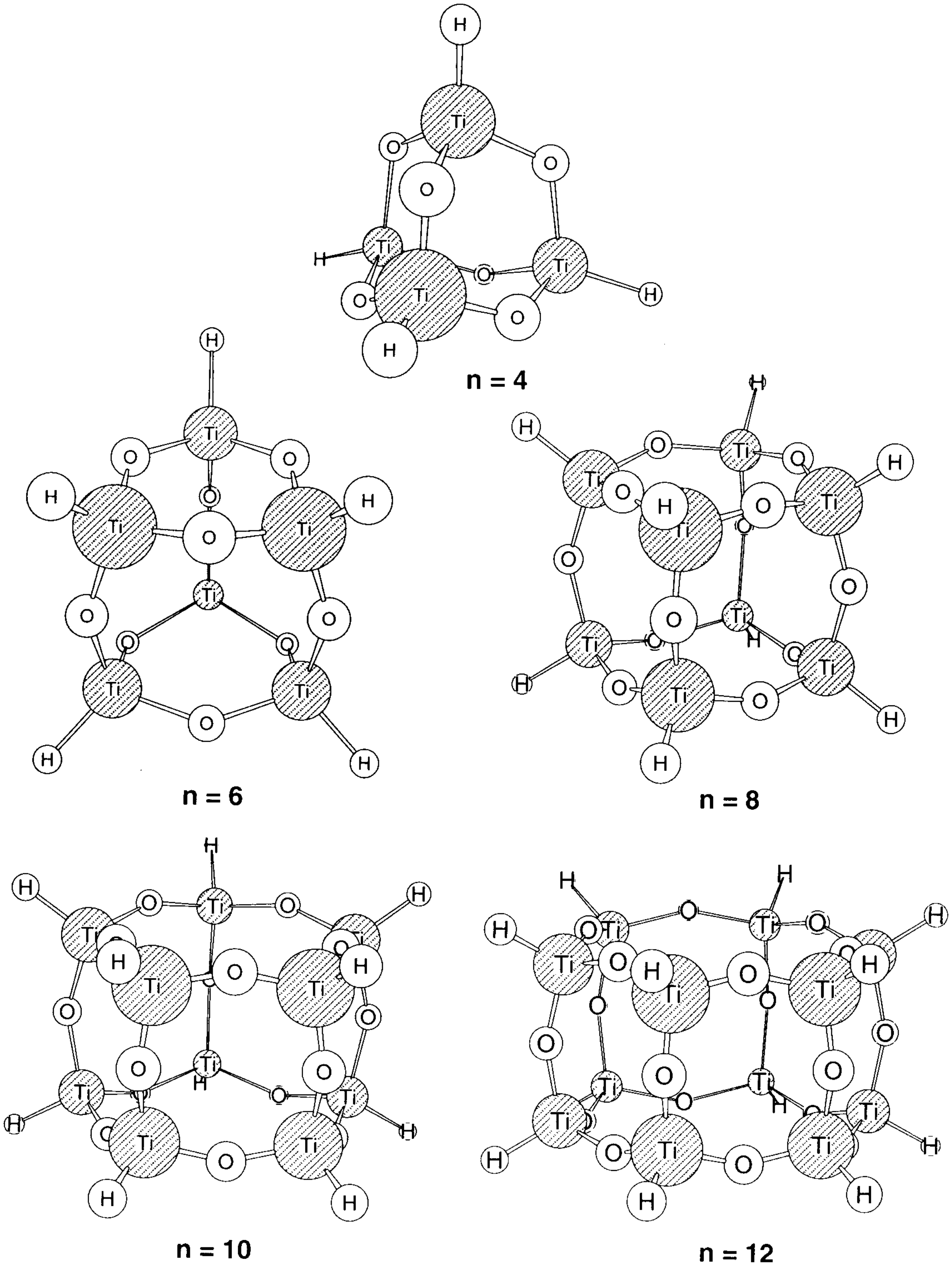


Figure 4. HF/TZVP optimized structures of $[HTiO_{1.5}]_n$, $n = 4$, 6, 8, 10, and 12.

titanium atoms. X-ray data are available for both compounds. A theoretical HF/SVP study has been carried out on $H_8Ti_4Si_4O_{12}$.[3b] The HF/TZVP optimized structures for $p = 1$ and 4f are shown in Figure 6. X-ray data are available for both species, so the averaged experimental values are included in the figure. The deviation of the calculated Ti−O distance from the experimental value is unusually large in the case of $p = 1$. However, for 4f, the calculated parameters are in good agreement with the X-ray structure, even though the experimental structures have bulky substituents.

Table 5 shows the relative stabilities of the $H_8Ti_pSi_{8-p}O_{12}$ species at various levels of theory. The data for the ring structure, $H_8Ti_2Si_2O_4$, are also shown for comparison. For the ring system, the isomer with nearest neighbor Ti atoms is less stable by 1.8 kcal/mol (see Figure 7). The corresponding energy difference for the aluminum analogue, $H_8Al_2Si_2O_4{}^{2-}$, is calculated to be a much larger, 17.0 kcal/mol (71 kJ/mol), at the HF/6-31G* level.[5d] This means that Ti does not have a strong tendency to take a particular position in mixed Ti/Si compounds, in contrast to the Al analogues. For the titanium cage structures the energy differences are much smaller at all levels of theory and the HF/TZVP values are smaller than those obtained using HF/SBK. Tossell[5d] has investigated the relative stabilities of three isomers of $H_8Al_2Si_6O_{12}{}^{2-}$ that are comparable with 2a−c in the present system and $H_8Al_4Si_4O_{12}{}^{2-}$ corresponding to 4a,e,f in this work. The HF/6-31G* relative energies of the former

TABLE 1: Geometries (Å and deg) of $[HTiO_{1.5}]_n$ (n = 4, 6, 8, 10, and 12) at HF/SBK,[a] HF/SBK+d(O),[b] and HF/TZVP[c] Levels of Theory

n	sym	rings[a]	Ti−O	Ti−H	Ti−O−Ti	O−Ti−O
4	T_d	3R	1.815[c]	1.696	122.9	102.0
			⟨1.819⟩[b]	⟨1.697⟩	⟨123.0⟩	⟨101.9⟩
			(1.826)[a]	(1.694)	(125.2)	(100.6)
6	D_{3h}	3R	1.811	1.688	133.8	102.0
			⟨1.815⟩	⟨1.689⟩	⟨134.0⟩	⟨101.8⟩
			(1.821)	(1.688)	(135.9)	(99.8)
		4R	1.808		143.5	108.5
			⟨1.811⟩		⟨144.6⟩	⟨108.6⟩
			(1.815)		(148.2)	(107.9)
8	O_h	4R	1.807	1.685	151.0	108.2
			⟨1.810⟩	⟨1.686⟩	⟨151.0⟩	⟨108.2⟩
			(1.814)	(1.686)	(152.8)	(107.2)
10	D_{5h}	4R	1.806	1.683	154.9	108.0
			⟨1.809⟩	⟨1.684⟩	⟨155.2⟩	⟨108.0⟩
			(1.813)	(1.684)	(156.3)	(107.0)
		5R	1.806		155.6	111.5
			⟨1.809⟩		⟨155.4⟩	⟨111.7⟩
			(1.813)		(157.3)	(111.7)
12	D_{6h}	4R	1.805	1.681	157.4	108.0
			⟨1.809⟩	⟨1.683⟩	⟨158.0⟩	⟨108.0⟩
			(1.813)	(1.682)	(159.1)	(106.9)
		6R	1.807		154.8	113.8
			⟨1.810⟩		⟨154.6⟩	⟨114.2⟩
			(1.814)		(156.4)	(114.9)

[a] This column refers to the rings whose geometric parameters are specified. For example, 3R refers to a three-membered ring.

(2a = 0, 2b = −17, 2c = −23 kcal/mol) and the latter (4a = 0, 4e = −40, 4f = −57 kcal/mol) are much larger than those of the titanium analogues at all levels of theory. Note that the energy difference between the titanium single ring system (1.8 kcal/mol) and the double ring system (4e − 4f = 1.9 kcal/mol) is very similar, in analogy with the aluminum compounds.[5d] For the Ti/Si system, most of the energy differences are less than 1 kcal/mol and are sensitive to the inclusion of polarization functions. Interestingly, the isomers with nearest neighbor Ti atoms are not found to be particularly unstable, as seen for p = 2 and 3. Even at the MP2/TZVP level of theory, the p = 2 isomer with the largest distance between two titanium atoms is least stable, although the energy differences are too small to be meaningful. So, neither of the zeolite rules appear to apply for this system.

TABLE 2: MP2/TZVP Hydrolysis Reaction Energies (Eq 1, kcal/mol) for $[HTiO_{1.5}]_n$

n	symmetry	ΔH	ΔH/n	ΔΔH/n
4	T_d	3.6	0.9	0.0
		(−14.4)	(−3.6)	(0.0)
6	D_{3h}	42.0	7.0	6.1
		(21.2)	(3.5)	(7.1)
8	O_h	81.2	10.2	9.3
		(48.6)	(6.1)	(9.7)
10	D_{5h}	109.4	10.9	10.0
		(65.6)	(6.6)	(10.2)
12	D_{6h}	133.4	11.1	10.2
		(79.9)	(6.7)	(10.3)

[a] The values in parentheses are the MP2/TZVP energies for the silicon analogues, $[HSiO_{1.5}]_n$.

TABLE 3: MP2/TZVP Hydrolysis Reaction Energies (Eqs 2a,b, kcal/mol) for $[HTiO_{1.5}]_n$

n	symmetry	ΔH[a]
4	T_d	−11.1
		(−21.4)
6	D_{3h}	12.8
		(7.2)
8	O_h	21.9
		(11.3)
10	D_{5h}	32.1
		(19.1)
12	D_{6h}	32.8
		(−1.7)

[a] The values in parentheses are the MP2/TZVP energies of the silicon analogues, $[HSiO_{1.5}]_n$.

The thermodynamic stabilities of the mixed-POSS T_8 compounds have been estimated using the hydrolysis reaction 3.

$$H_8Ti_pSi_{8-p}O_{12} + 12H_2O = pHTi(OH)_3 + (8 - p)HSi(OH)_3 \quad (3)$$

The reaction enthalpies ΔH and ΔH/8 and the average Ti−Ti distance in the cage structures are given in Table 6. The reaction enthalpy differences among the isomers are quite small, and there is no obvious general relation between ΔH and the Ti−Ti distance.

There is an apparent discrepancy in the theoretical calculations for Al/Si systems, which have much larger energy differences than the Ti/Si system. Schroder and Sauer[5a] studied double-

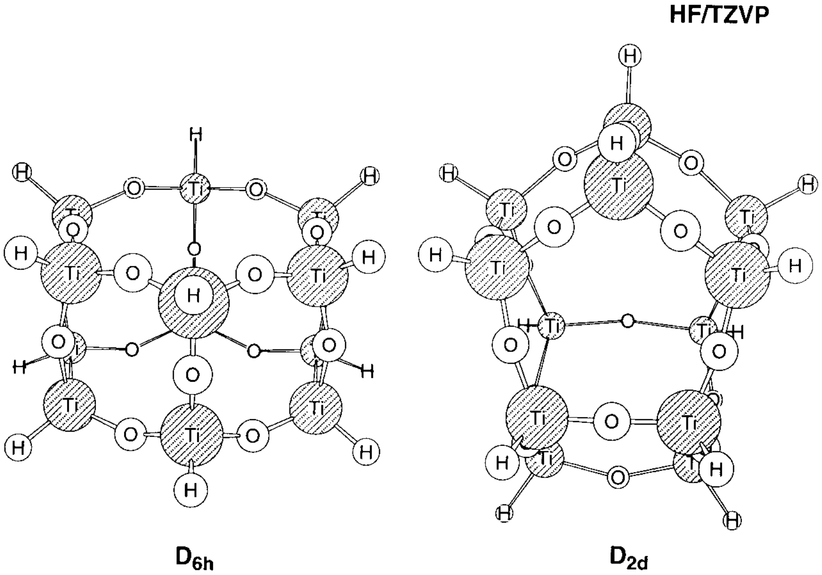


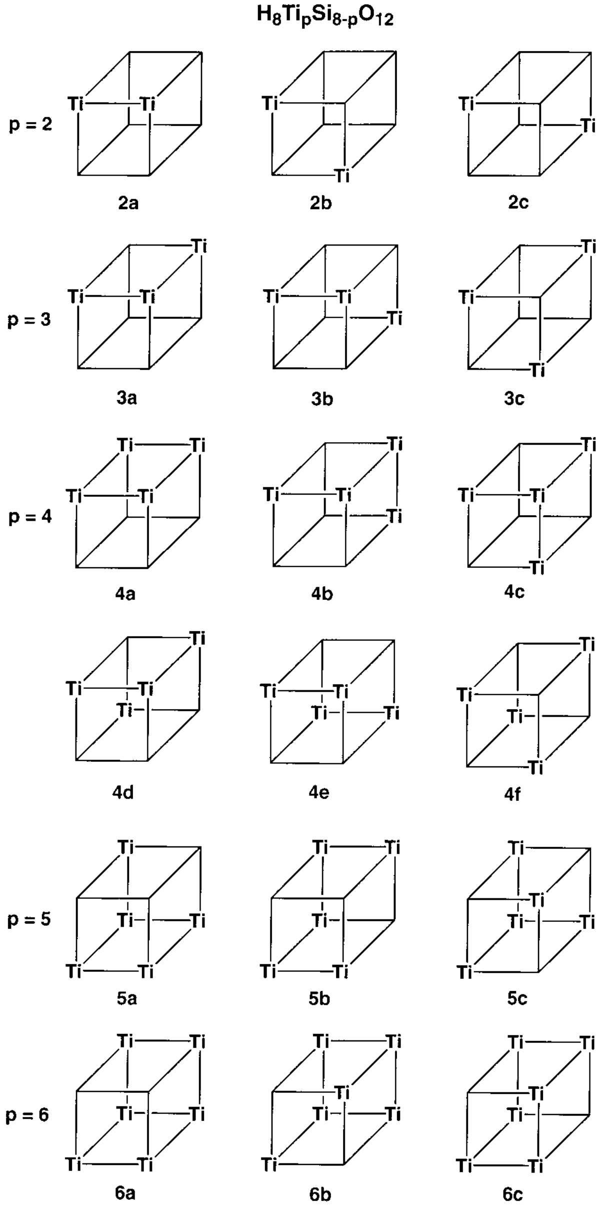
Figure 5. HF/TZVP optimized structures of two isomers of $[HTiO_{1.5}]_{12}$.

TABLE 4: HOMO and LUMO HF/TZVP Energies (eV) of $[HTiO_{1.5}]_n$, n = 4, 6, 8, 10, and 12[a]

N	symmetry	HOMO	LUMO
4	T_d	−12.5 (−13.7)	1.1 (3.6)
6	D_{3h}	−12.7 (−13.7)	1.1 (3.5)
8	O_h	−12.7 (−13.1)	1.2 (3.6)
10	D_{5h}	−12.7 (−13.1)	1.2 (3.7)
12	D_{6h}	−12.7 (−13.2)	1.2 (3.3)

[a] The values in parentheses are the HF/TZVP energies of the silicon analogues, $[HSiO_{1.5}]_n$.

SCHEME 1



six-ring compounds and found HF/3-21G energy differences that are inconsistent with Dempsey's rule. On the other hand, Tossell's[5d] HF/6-31G* calculations are consistent with Dempsey's rule for some isomers of double-four-ring compounds (T_8). It is not clear whether this difference is due to the different systems investigated by these two groups or to the computational levels. The energy differences for the isomers and reaction enthalpies of eq 3 are too small to make any conclusions regarding the two rules in the present system. However, one can tentatively conclude from Tables 5 and 6 that 4f and 5c are particularly stable, as observed by Tossell for the Al analogues.[5d] This suggests particular stability for those structures in which Si and Ti atoms are distributed equally in the cage. Note that 4f and 5c have, respectively, six and three four-membered rings with the Ti−O−Si−O−Ti linkage, respectively. Structure 3c also has three such rings. So, it may be that a Ti−O−Si−O−Ti is related to the stability of the Ti/Si molecules, even though this is not consistent with Dempsey's rule for the Al containing zeolites.

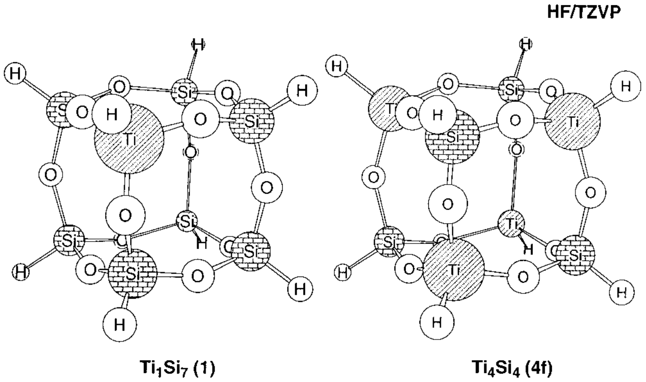
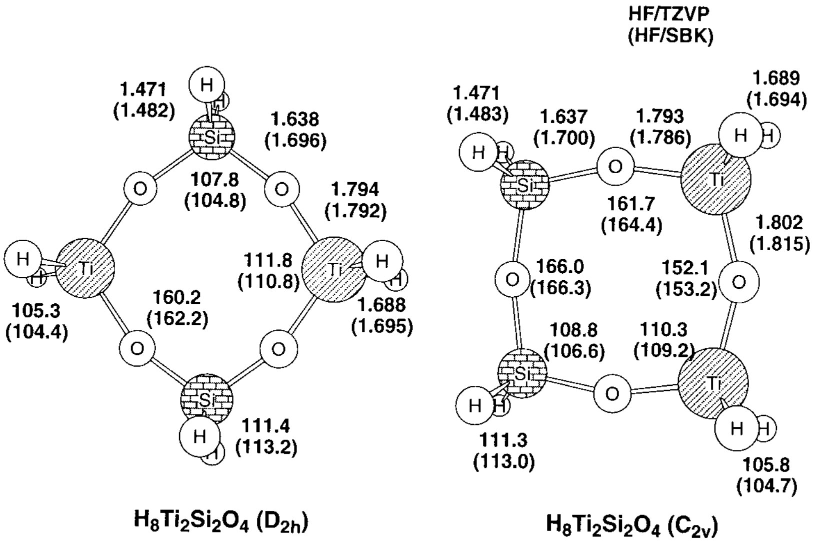


Figure 6. HF/TZVP optimized structures of p = 1 (left) and p = 4f (right) of $H_8Ti_pSi_{8-p}O_{12}$. The values in parentheses are the X-ray data. p = 1: r(Ti−O) = 1.798 (1.658[3n]), r(Si−O(Ti)) = 1.631 (1.625[3n]), r(Si−O(Si)) = 1.625 (1.641[3n]), r(Ti−H) = 1.686, r(Si−H) = 1.457, ∠Ti−O−Si = 148.0 (151.0[3n]), ∠O−Ti−O = 107.2 (111.4[3n]), ∠Si−O−Si = 152.4, ∠O−Si−O(Ti) = 108.0, ∠O−Si−O(Si) = 108.9; p = 4f: r(Ti−O) = 1.800 (1.794[3a], 1.795[3d]), r(Si−O) = 1.633 (1.616[3a], 1.632[3d]), r(Ti−H) = 1.683, r(Si−H) = 1.459, ∠Ti−O−Si = 151.3 (153.9[3a], 153.6[3d]), ∠O−Ti−O = 108.3 (109.5[3d]), ∠O−Si−O = 107.7 (108.6[3d]), r(Ti- - -Ti) = 4.644 (4.806[3a]), r(Si- - -Si) = 4.762 (4.581[3a]), r(Ti- - -Si) = 3.326 (3.321[3a]).

TABLE 5: Relative (kcal/mol) Energies of $H_8Ti_pSi_{8-p}O_{12}$ (p = 2−6) and $H_8Ti_2Si_2O_4$ at Various Levels of Theory

P	isomer	HF/SBK	HF/TZVP//HF/SBK	HF/TZVP	MP2/TZVP//HF/TZVP
			$H_8Ti_pSi_{8-p}O_{12}$		
2	a	0.0	0.0	0.0	0.0
	b	−1.0	−0.01	−0.4	−0.1
	c	−0.9	0.3	0.1	0.3
3	a	0.0	0.0	0.0	
	b	−1.1	0.2	−0.0	
	c	−2.2	−0.1	−0.9	
4	a	0.0	0.0	0.0	
	b	−0.5	−0.2	−0.4	
	c	−0.4	−0.4	−0.7	
	d	−1.8	−0.2	−0.9	
	e	−2.1	0.1	−0.4	
	f	−4.1	−0.7	−2.3	
5	a	0.0	0.0	0.0	
	b	−0.9	−0.2	−0.4	
	c	−2.1	−0.5	−1.3	
6	a	0.0	0.0	0.0	
	b	−0.8	−0.4	−0.8	
	c	−0.5	−0.5	−0.7	
			$H_8Ti_2Si_2O_4$		
C_{2v}	0.0	0.0			
D_{2h}	−3.5	−1.8			

The net Mulliken atomic charges and the HOMO and LUMO energy levels for $H_8Ti_pSi_{8-p}O_{12}$ are given in Table 7. For all compounds, Ti atoms have considerably larger positive charges



$H_8Ti_2Si_2O_4$ (D_{2h}) $H_8Ti_2Si_2O_4$ (C_{2v})

Figure 7. Optimized structures of two isomers of $H_8Ti_2Si_2O_4$ in angstroms and degrees.

TABLE 6: HF/TZVP Hydrolysis Reaction Energies (Eq 3, kcal/mol) and Average Ti−Ti Distance (Å) for $H_8Ti_pSi_{8-p}O_{12}$ ($p = 1-7$)

P		Δ*H*	Δ*H*/8	*d*(Ti- - -Ti)
1		55.1	6.9	
2	a	55.4	6.9	3.4
	b	55.8	7.0	4.7
	c	55.4	6.9	5.7
3	a	56.0	7.0	3.9
	b	56.0	7.0	4.6
	c	56.9	7.1	4.7
4	a	56.1	7.0	3.9
	b	56.5	7.1	4.3
	c	56.8	7.1	4.1
	d	56.9	7.1	4.5
	e	56.5	7.1	4.6
	f	58.4	7.3	4.6
5	a	56.8	7.1	4.3
	b	57.3	7.2	4.5
	c	58.2	7.3	4.4
6	a	57.1	7.1	4.4
	b	57.9	7.2	4.4
	c	57.9	7.2	4.5
7		57.7	7.2	4.4

TABLE 7: Average HF/TZVP Mulliken Net Atomic Charges and HOMO and LUMO Energy Levels (eV) of $H_8Ti_pSi_{8-p}O_{12}$ ($p = 1-7$)

		net atomic charge						orbital energy level	
P		Ti	Si	O(Ti)	O(Si)[a]	H(Ti)	H(Si)	HOMO	LUMO
1		1.563	1.178	−0.830	−0.703	−0.154	−0.120	−12.6	2.1
2	a	1.574	1.175	−0.855	−0.702	−0.149	−0.119	−12.6	1.5
	b	1.573	1.174	−0.831	−0.701	−0.151	−0.116	−12.6	2.0
	c	1.564	1.173	−0.830	−0.699	−0.153	−0.114	−12.6	2.1
3	a	1.575	1.172	−0.867	−0.702	−0.146	−0.115	−12.6	1.4
	b	1.575	1.169	−0.846	−0.699	−0.149	−0.112	−12.6	1.5
	c	1.583	1.168	−0.833	−0.700	−0.149	−0.110	−12.6	1.9
4	a	1.590	1.166	−0.895	−0.700	−0.148	−0.118	−12.6	1.3
	b	1.574	1.171	−0.874	−0.700	−0.145	−0.109	−12.6	1.3
	c	1.574	1.176	−0.875	−0.703	−0.144	−0.104	−12.6	1.3
	d	1.583	1.163	−0.857	−0.698	−0.147	−0.108	−12.6	1.4
	e	1.591	1.155	−0.856	−0.692	−0.150	−0.110	−12.6	1.4
	f	1.593	1.153	−0.833	−0.833	−0.146	−0.100	−12.7	1.8
5	a	1.584	1.167	−0.897	−0.699	−0.145	−0.109	−12.6	1.3
	b	1.587	1.157	−0.879	−0.696	−0.146	−0.106	−12.6	1.3
	c	1.592	1.152	−0.865		−0.146	−0.101	−12.6	1.3
6	a	1.589	1.161	−0.916	−0.697	−0.145	−0.107	−12.6	1.2
	b	1.591	1.153	−0.899		−0.145	−0.100	−12.6	1.3
	c	1.590	1.152	−0.897		−0.145	−0.101	−12.7	1.3
7		1.591	1.161	−0.933		−0.143	−0.098	−12.7	1.2

[a] Net atomic charge of oxygen atoms connected to only silicon atoms.

than Si atoms. In contrast, in zeolites Al atoms have smaller positive charges than Si atoms.[23] Consequently, the O and H atoms that are directly bonded to Ti are more negative than are those bonded to Si. So, the electron density distribution in the mixed Ti/Si compounds is rather different from that in zeolites. The LUMO energy decreases as the number of Ti atoms increases, while the HOMO is nearly constant, as noted above for the pure Ti compounds.

Concluding Remarks

We have systematically investigated the structures and properties of various titanium analogues of POSS. The fully substituted POSS, $[HTiO_{1.5}]_n$, $n = 4-12$, are found to have similar structures to the silicon analogues, though the titanium compounds seem to be more stable for all sizes of the cage in this study than the silicon compounds. So, it may be possible that Ti-POSS have rather different structures containing larger rings.

With regard to the distribution of Ti atoms in T_8, $H_8Ti_pSi_{8-p}O_{12}$, $p = 1-7$, the energy differences among the isomers are so small that no clear trend is apparent at the present level of theory. Lowenstein's rule seems to apply for the compounds involving more than three titanium atoms, with the structure having silicon and titanium atoms distributed equally predicted to be most stable. On the other hand, Dempsey's rule does not appear to apply, since the Ti−O−Si−O−Ti sequence seems to stabilize these compounds. Therefore, unlike the case for zeolites, the present results suggest that Ti can take any position without any significant preference.

Tossell[24] has noted that adherence to Lowenstein's rule can be attributed to a difference in the valence of the two metals (e.g., Al vs Si) and to differences in metal oxygen differences. Since the "rule" is followed for the C,Si pair, for which the valence is the same, the differential in metal−oxygen distances appears to be the more important factor. In the present case Ti and Si have the same valence, while the SiO and TiO distances differ by about the same amount as AlO vs SiO in zeolite cages. So, it appears that these factors are not sufficient to account for the very small energy differences in the Si,Ti case.

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