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Ab Initio Molecular Orbital Study on the Ge-, Sn-, Zr- and Si/Ge-Mixed Silsesquioxanes

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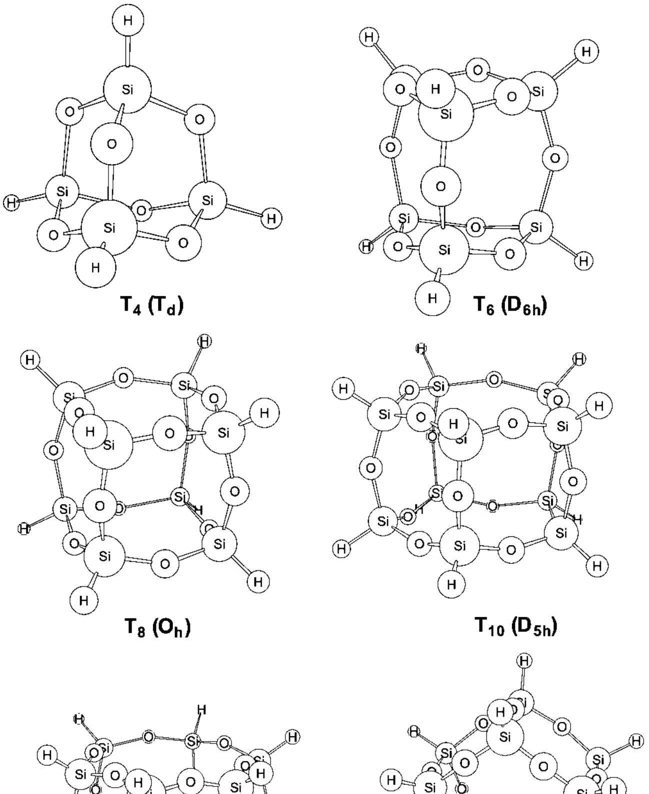
For the purpose of designing new functional silsesquioxanes (POSS), the structure and stability of the analogous compounds of the heavier group 14 and 4 elements such as germanium (Ge-POSS), tin (Sn-POSS) and zirconium (Zr-POSS) analogues of POSS were investigated and compared with those of the parent POSS and the titanium analogue (Ti-POSS) with electronic structure theory calculations, including electron correlation effects. In order to obtain information about the metalloxane (−X−O−X−) linkage, the structures and properties of the building blocks of metallasilsesquioxanes, such as dimetalloxanes, $H(OH)_2XOX(OH)_2H$, X = Ge, Sn and Zr, and cyclometalloxanes, $[H(OH)XO]_n$, $n = 3-6$, X = Ge, Sn and Zr, were examined. The stability of the Si/Ge-mixed POSS were also studied in comparison with POSS and the completely germanium-substituted POSS.

Introduction

For many years, polyhedral oligomeric silsesquioxanes (POSS), $[RSiO_{1.5}]_n$, $n = 4, 6, 8, 10, 12$ . . . (some examples of the fully condensed POSS are shown in Scheme 1), have been the focus of considerable experimental and theoretical interest because of their wide variety of practical uses, for example, as materials with good thermal resistance, permeability, permittivity, and photochemical properties.[1] As easily seen from Scheme 1, they have beautiful highly symmetric structures and the potential to employ various organic−inorganic hybrid materials by introducing many kinds of organic functional groups on the silicon atoms of the framework. This means that the design of new materials that are based on these species is of considerable interest and relatively straightforward. Interest in POSS generally stems from (i) the properties and reactions of POSS themselves and related polymeric species that are based on POSS[2] and (ii) modeling of catalytic reactions on silica surfaces or organic polymers.[3] In the latter, various metals attached to incompletely condensed POSS play an important role. On the other hand, the chemistry of the fully condensed POSS in which silicon atoms are replaced by other metals is not well-known, probably due to experimental difficulties. Interest in these species arises because the metallasilsesquioxanes (fully or partially metal substituted POSS) may have the potential to be new functional materials or building blocks of useful polymers or nanocomposites; theoretical study of such compounds is expected to provide valuable information to experimental chemists.

SCHEME 1



T_4 (T_d) T_6 (D_{6h}) T_8 (O_h) T_{10} (D_{5h}) T_{12} (D_{6h}) T_{12} (D_{2d})

In recent years, the authors have explored various aspects of the chemistry of POSS and POSS-related compounds, such as the mechanism of the formation of T_8, $[HSiO_{1.5}]_8$,[4] structures and catalytic ability of the fully and partially titanium substituted POSS, $[HTiO_{1.5}]_n$, and $H_8Ti_pSi_{8-p}O_{12}$,[5] and the insertion of H_2 into various POSS species.[6] The present work continues these investigations of POSS and POSS-related compounds, in order to develop a deeper understanding of these compounds and their properties and reactivity, with a specific focus on the metallasilsesquioxanes mentioned above. In the present work, the structure and stability of the Ge, Sn and Zr analogues of POSS and the Si/Ge-mixed POSS are predicted based on ab initio electronic structure theory calculations.

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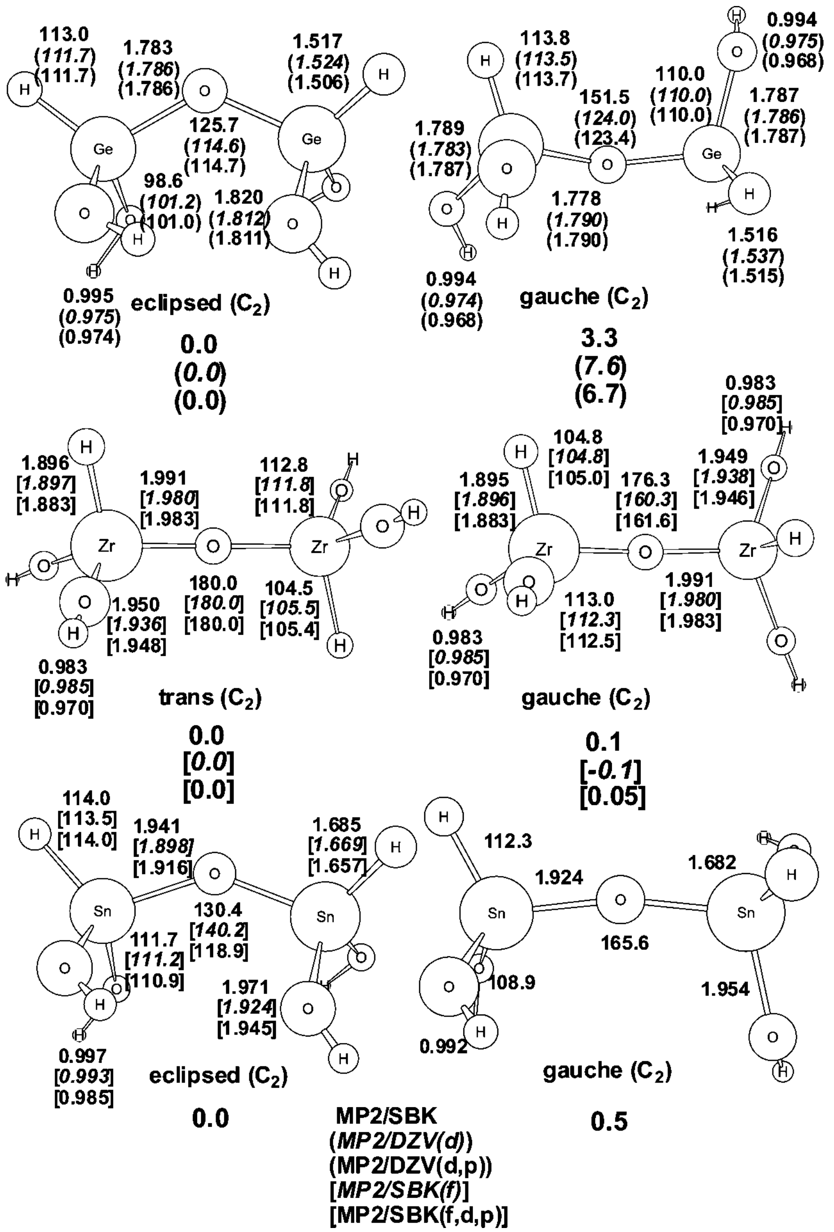


Figure 1. Optimized structures (angstroms and degrees) and relative energies (kcal/mol) of the two isomers of $H(OH)_2GeOGe(OH)_2H$, $H(OH)_2ZrOZr(OH)_2H$ and $H(OH)_2SnOSn(OH)_2H$ at various levels of theory. Note that the MP2/SBK, MP2/DZV(d) and MP2/DZV(d,p) levels of theory were employed for $H(OH)_2GeOGe(OH)_2H$ while MP2/SBK, MP2/SBK(f) and MP2/SBK(f,d,p) were used for the other compounds. Overall, five levels of theory were employed, as noted at the bottom of the figure.

Computational Methods. The geometries of all molecules of interest have been fully optimized at the Hartree−Fock and MP2[7] levels of theory, using the SBKJC effective core potential (ECP),[8] in order to compare all metallaoxanes considered here at the same levels of theory. In addition, a set of f polarization functions was added to the Zr (exponent = 0.300731) and Sn (exponent = 0.552585) SBKJC basis sets for some energy comparisons. So, the highest level of theory used in the calculations with SBK is MP2/SBK(f,d,p) for the small Sn and Zr compounds. The all-electron double-ζ plus polarization DZV(d) or DZV(d,p)[9] basis sets were used for some of the Ge compounds, while the triple-ζ plus polarization TZV(d,p)[10] basis set was employed for the silicon compounds. All compounds were characterized as minima or transition states by calculating and diagonalizing the Hessian matrix of energy second derivatives at the optimized geometries. All calculations were performed with the GAMESS electronic structure codes.[11]

Result and Discussion

I. Fully Substituted Silsesquioxanes. ***A. Dimetallaoxanes.*** First, consider the structures and properties of the reference molecules that contain the basic X−O−X (X = Ge, Sn and Zr) units, digermanoxanes ($H(OH)_2GeOGe(OH)_2H$), distannoxanes ($H(OH)_2SnOSn(OH)_2H$) and dizirconoxanes ($H(OH)_2ZrOZr(OH)_2H$), compared with those of the parent disiloxanes and dititanoxanes examined in earlier work. The optimized geometries of the X−O−X species are depicted in Figure 1. Two isomers are located as minima on the respective potential energy surfaces for each compound at all levels of theory, except distannoxane, for which the gauche isomer is found only at the MP2/SBK level of theory.

For the Ge and Sn compounds, the eclipsed form is more stable than gauche as predicted previously[4a] for the Si analogue. As noted for the Si system, this is likely due to the intramo-

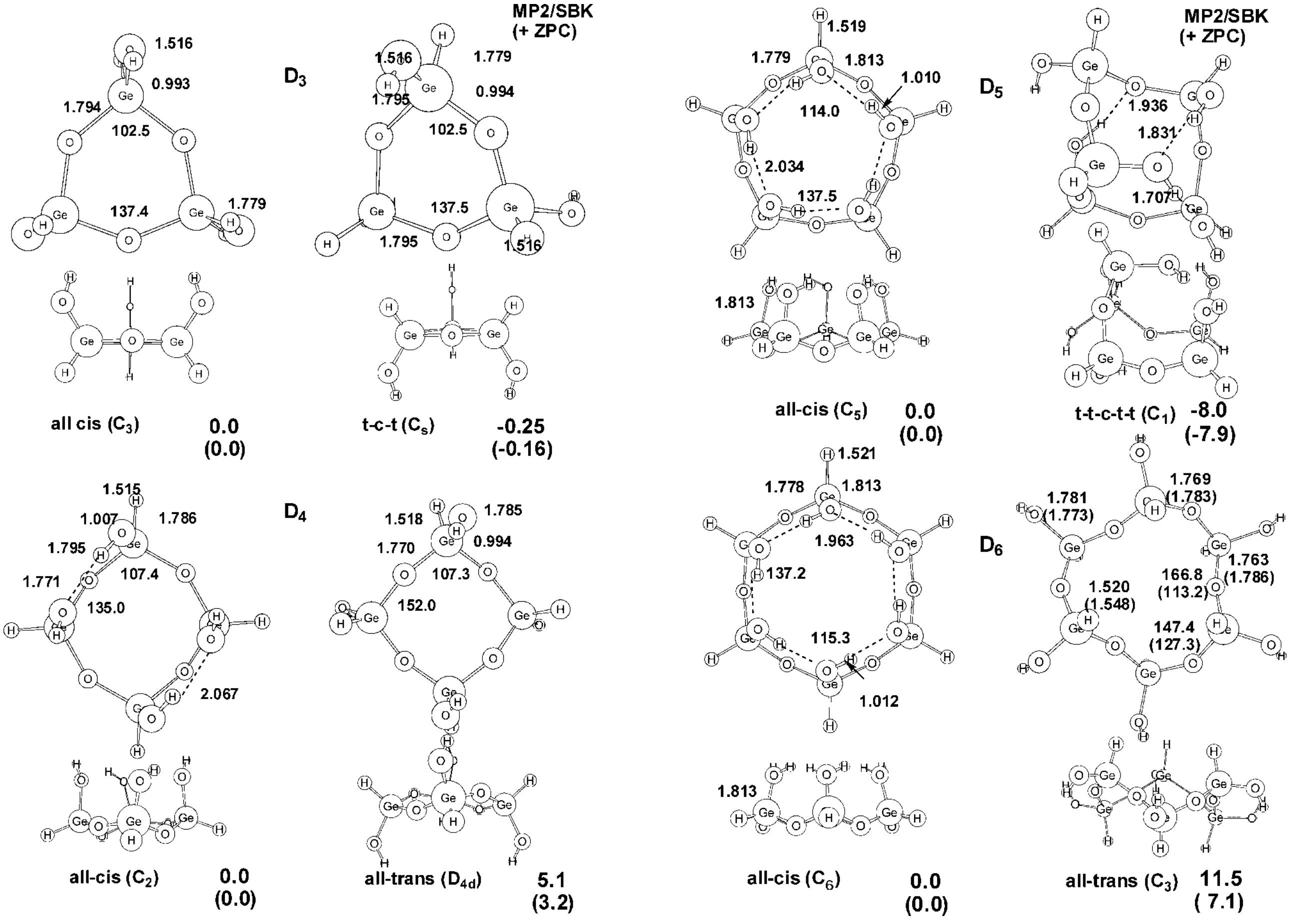


Figure 2. MP2/SBK optimized structures (angstroms and degrees) and the MP2/SBK and the zero-point-energy corrected relative energies (kcal/mol) of the two isomers of Ge-D_n, $[H(OH)GeO]_n$, $n = 3-6$. Shown below each structure is a side view of the ring. The notation "t" and "c" refers to trans and cis, respectively, so t-c-t means trans−cis−trans. The point group symmetry is given in parentheses.

TABLE 1: The MP2/SBK Geometries (Å and deg), Net Atomic Charges of X (q_X) and O (q_O) Atoms in $H(OH)_2XOX(OH)_2H$ (X = Si, Ti, Ge, Sn and Zr), and Heats of Reaction (kcal/mol) for the Condensation Reaction, $2HX(OH)_3 = H(OH)_2XOX(OH)_2H + H_2O$

X	X−O	X−O−X	q_X	q_O	ΔH (kcal/mol)[a]
Si					
eclipsed	1.688	150.7	1.242	−0.906	−11.0
gauche	1.697	169.4	1.240	−0.928	
Ti					
trans	1.836	180.0	0.884	−0.685	
gauche	1.835	168.8	0.874	−0.681	−2.6
Ge					
eclipsed	1.783	125.7	1.108	−0.809	−10.3
gauche	1.778	151.5	1.121	−0.884	
Sn					
eclipsed	1.941	130.4	1.518	−0.979	−9.5
gauche	1.924	165.6	1.548	−1.048	
Zr					
trans	1.991	180.0	1.497	−0.970	−1.7
gauche	1.991	176.3	1.494	−0.970	

[a] These values are based on the MP2/SBK + ZPC energies.

lecular hydrogen bonds that are formed between the OH groups in the eclipsed form. However, it is apparent that the effect of the hydrogen bonds decreases as one proceeds down group 14, since the X−O distance increases, thereby diminishing the possibility of hydrogen bond formation. This explains why the energy difference between the two conformers of the Sn compound is an order of magnitude smaller than that in the Ge species. The MP2/SBK Ge−O−Ge (125.7°) and Sn−O−Sn (130.4°) bond angle in the eclipsed form is smaller than the disiloxane Si−O−Si angle (150.7°). As the figure shows, the MP2 optimization with all-electron basis sets, such as DZV(d) and DZV(d,p), predict a much smaller Ge−O−Ge angle compared to the MP2/SBK values. The same tendency was found for the Si analogue.[12] Otherwise, the SBK and DZV(d) basis sets predict similar geometries. SBK augmented with polarization functions (SBK(f,d,p)) has an effect on the geometry optimizations that is similar to that of the all-electron basis set, shortening bond distances and decreasing the Sn−O−Sn bond angle.

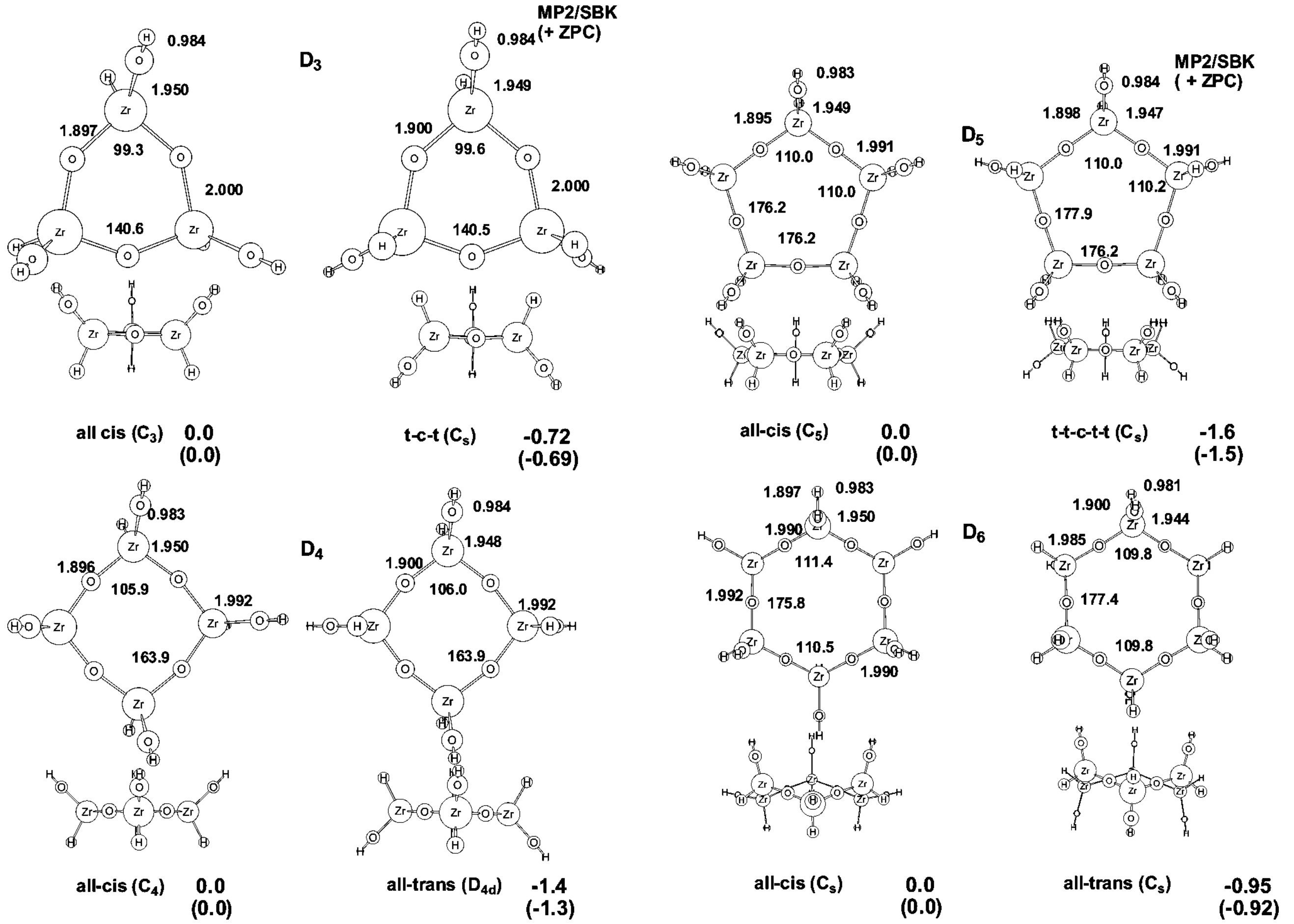


Figure 3. MP2/SBK optimized structures (angstroms and degrees) and the MP2/SBK and the zero-point-energy corrected relative energies (kcal/mol) of the two isomers of Zr-D_n, $[H(OH)ZrO]_n$, $n = 3-6$. Shown below each structure is a side view of the ring. The notation "t" and "c" refers to trans and cis, respectively, so t-c-t means trans—cis—trans. The point group symmetry is given in parentheses.

Contrary to the group 14 compounds, hydrogen bonding does not seem to be important in dizirconoxanes, similar to the Ti analogues, and the relative energies of the two isomers (trans and gauche) are almost equal. In these Zr—O—Zr compounds, hydrogen bonding is essentially impossible, as the Zr—O bond length is longer than the Ge—O and Si—O bonds, and the Zr—O—H angle is almost linear. The almost linear X—O—X or X—O—R angles have also been observed experimentally in the sterically crowded Zr[13] and Ti compounds.[14] This is most likely due to the efficient interaction between the orthogonal pπ-orbitals of the oxygen atoms and d-orbitals of the metal atoms.> Adding polarization functions makes the Zr—O bond length slightly longer and the Zr—O—Zr angles smaller compared to the MP2/SBK values.

Table 1 summarizes some geometric parameters, net atomic charges and dimerization (condensation) energies of two $HX(OH)_3$ (X = Si, Ge, Sn, Ti and Zr) to dimetalloxanes of interest. As this table shows, the extent of charge separation in the X—O bond decreases in the order Sn $\sim$ Zr > Si $\sim$ Ge > Ti, while the exothermicities of the condensation reaction decrease in the order Si $\sim$ Ge $\sim$ Sn $\gg$ Ti $\sim$ Zr. So, the dizirconoxanes and dititanoxanes are less stable than the other compounds from this thermodynamic perspective.

B. Cyclometallaoxanes. The optimized geometries of two isomers (all-cis in which all the OH groups exist on the same side of the ring plane and a second isomer) of $[H(OH)XO]_n$ (referred to as D_n), $n = 3-6$, X = Ge, Sn, Zr, are shown in Figures 2, 3, 4, and 5. The Ge species are shown in both Figures 2 and 5 to emphasize the similarity of the second all-trans isomers in the Ge and Sn compounds in the latter figure.

The Zr-D_n compounds (Figure 3) all have quasi-planar structures, and the all-cis isomer is always slightly higher in energy, probably due to steric effects. As for the Ti analogues,[5a] hydrogen bonding seems to be less important.

Factors such as hydrogen bonding and the "floppiness" of the X—O—X linkage make the situation in Ge-D_n (Figure 2) and Sn-D_n (Figure 4) more complicated. In these species, the Ge-D_4 and Ge- and Sn-D_6 all-cis isomer is slightly lower in energy, because hydrogen bonding makes a contribution. However, for Sn-D_4, the relative stabilities are reversed by the zero-point-energy (ZPE) correction, because of the very small energy differences and the rather small contribution of hydrogen bonding in the all-cis isomer. Because of the very small energy differences, the relative energies could also change if larger basis sets or higher levels of theory (e.g., CSD(T)) were used. The relative energies are similar to the previously observed behavior of cyclosiloxanes, $[H(OH)SiO]_n$, $n = 3-6$.[4b] However, as seen in Figures 2 and 4, the t-t-c-t-t isomers of Ge-D_5 and Sn-D_5 are not planar ring structures; rather, they look like incomplete cage structures that may be stabilized by strong hydrogen bonds that are enabled by floppy X—O—X linkages. Furthermore, another all-trans type D_6 isomer has been located for both Ge and Sn, as depicted in Figure 5. As seen from the side view and the cube in the middle of the figure, they look like an incomplete T_8. They are much lower in energy than the all-cis isomer, which is slightly stabilized with rather long hydrogen bonds. In other

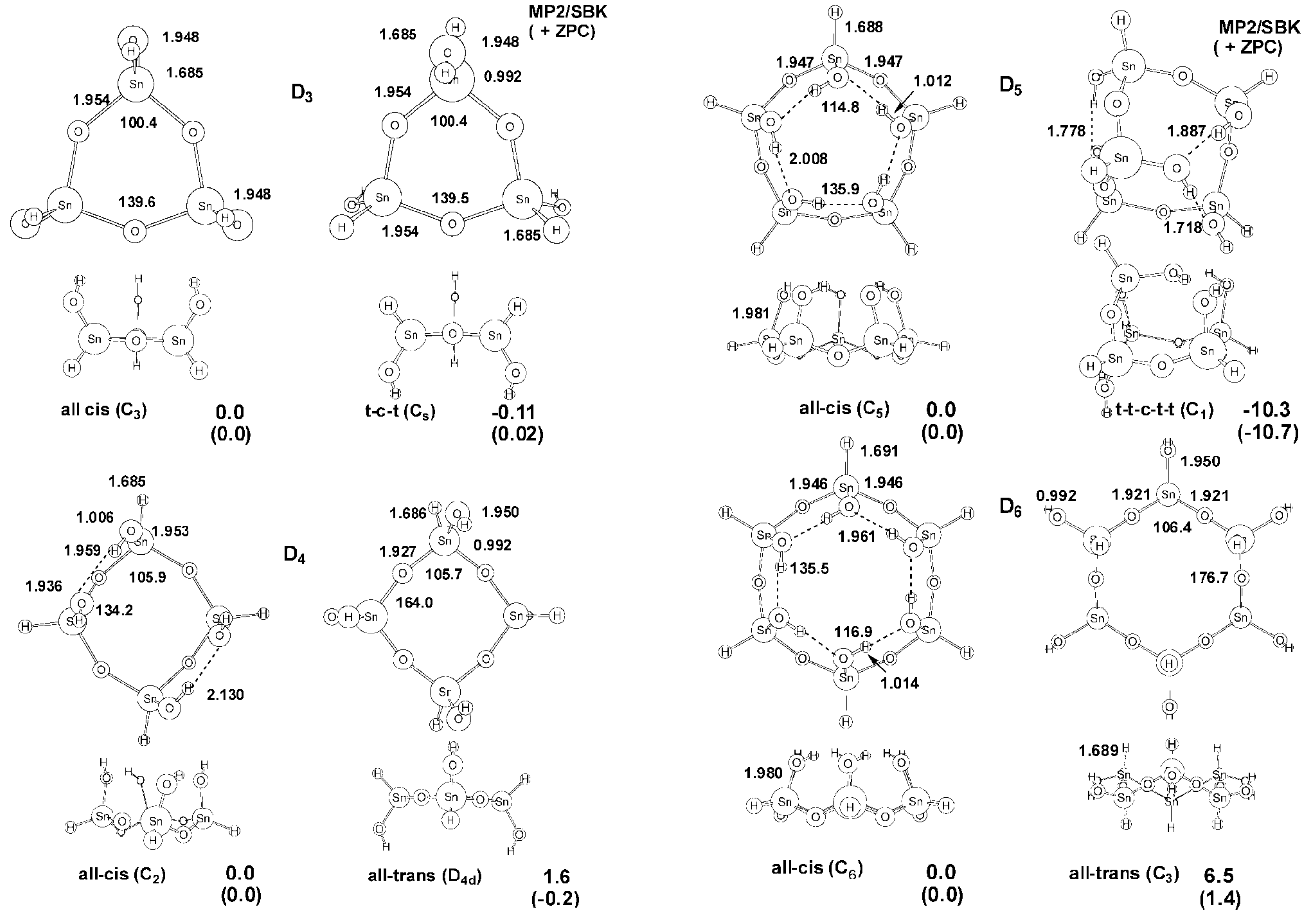


Figure 4. MP2/SBK optimized structures (angstroms and degrees) and the MP2/SBK and the zero-point-energy corrected relative energies (kcal/mol) of the two isomers of Sn-D_n, $[H(OH)SnO]_n$, $n = 3-6$. Shown below each structure is a side view of the ring. The notation "t" and "c" refers to trans and cis, respectively, so t-c-t means trans−cis−trans. The point group symmetry is given in parentheses.

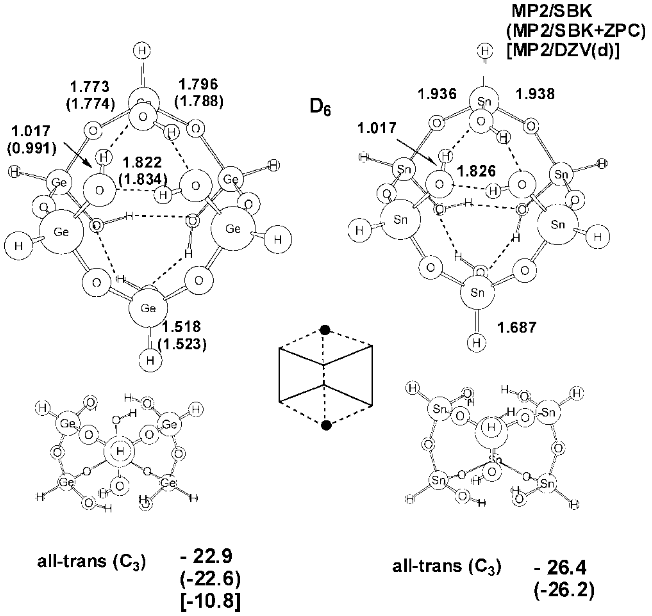


Figure 5. MP2/SBK and MP2/DZV(d) optimized structures (angstroms and degrees) and the MP2/SBK, the zero-point-energy corrected MP2/SBK and MP2/DZV(d) energies (kcal/mol) relative to the all-cis isomer of the second all-trans isomer of Ge-D_6 and Sn-D_6. Shown below each structure is a side view of the ring. The point group symmetry is given in parentheses. The cube in the center of this figure illustrates the similarity of the structures to an incompletely condensed cubic structure. The black circles correspond to the missing corners.

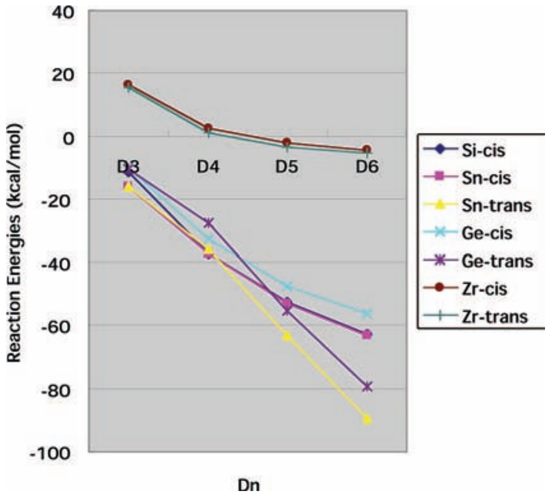


Figure 6. MP2/SBK heats of reaction (kcal/mol) of condensation for $[H(OH)XO]_n$, $n = 3-6$, X = Si, Ge, Sn and Zr.

words, the shorter (stronger) hydrogen bonding as well as the floppy X−O−X linkages causes the second all-trans isomer to be more stable than the all-cis isomer. Based on these results, it can be concluded that hydrogen bonding plays a very important role in the structure of the cyclic germanoxanes and stannoxanes considered here.

The thermodynamic stabilities of the cyclic metallaoxanes can be estimated by the heats of reaction for their condensation

TABLE 2: MP2/SBK and MP2/SBK(f)[a] Geometries (Å and deg) of $[HSnO_{1.5}]_n$ (n = 4, 6, 8, 10 and 12)

		X–O	X–H	X–O–X	O–X–O
T_4		<1.940>[a] 1.981	<1.661> 1.680	<123.5> 122.9	<101.6> 102.0
T_6	R_3[b]	<1.924> 1.960	<1.668> 1.685	<134.8> 134.4	<100.9> 101.2
	R_4	<1.905> 1.930		<149.8> 148.6	<107.3> 107.8
T_8		<1.904> 1.935	<1.672> 1.688	<153.5> 152.8	<106.8> 107.2
T_{10}	R_4	<1.904> 1.934	<1.676> 1.691	<154.6> 154.2	<106.7> 107.0
	R_5	<1.897> 1.927		<160.0> 159.0	<109.6> 110.0
T_{12}-D_{6h}	R_4	1.934	1.694	154.8	107.0
	R_6	1.926		158.3	111.6
T_{12}-D_{2d}	R_4	<1.904> 1.935	<1.676> 1.694	<153.6> 153.0	<106.8> 107.2
	R_5	<1.890> 1.918		<173.3> 172.3	<109.4> 109.5

[a] The values in brackets are the MP2/SBK(f) geometries. [b] R_n means the face consisted of the D_n ring.

from the monomer (see eq 1 below). As seen in Figure 6, the heats of the condensation reaction to produce cyclozirconoxanes in both isomers are much less exothermic than those of the group 14 analogues, suggesting that the cyclic zirconoxanes are less stable thermodynamically than the group 14 analogues.

$$nHX(OH)_3 = [H(OH)XO]_n + nH_2O$$
$$X = \text{Si, Ge, Sn and Zr} \qquad (1)$$

C. Metallasilsesquioxanes. The optimized geometries of the cage species $[HSnO_{1.5}]_n$ (Sn-T_n), n = 4, 6, 8, 10 and 12, are shown in Table 2 (see also Scheme 1 for the general structures). The geometries of the Ge and Zr analogues, $[HGeO_{1.5}]_n$ (Ge-T_n) and $[HZrO_{1.5}]_n$ (Zr-T_n), have been reported previously.[6] As in the other metallasilsesquioxanes, there are two Sn-T_{12} isomers (D_{6h} and D_{2d}) (see Scheme 1), with the D_{2d} isomer being lower in energy by 11.7 (HF/SBK) and 8.7 (MP2/SBK) kcal/mol. Furthermore, the MP2/SBK D_{6h} structure has four imaginary frequencies. A similar prediction was made for the Ge analogue. Therefore, only the D_{2d} T_{12} structures are likely to be observed for the heavier group 14 elements such as Ge-T_{12} and Sn-T_{12}.

The thermodynamic stabilities of these cage compounds are estimated here using the condensation reaction:

$$nHX(OH)_3 = [HXO_{1.5}]_n + 1.5nH_2O$$
$$X = \text{Si, Ge, Sn, Ti and Zr} \qquad (2)$$

As shown in Figure 7, based on this measure, the Zr cage structures are thermodynamically least stable among the metallasilsesquioxanes considered here. This is consistent with the corresponding predictions for the smaller building blocks discussed above.

II. Si/Ge Mixed Silsesquioxanes. As seen in the preceding section, metalloxanes containing elements from the same group are predicted to have similar structures and stabilities. So, Ge-substituted compounds are expected to have stabilities that are similar to those of the corresponding Si compounds, and therefore may be promising candidates for new functional POSS. This may also be relevant to understanding the character and behavior of Ge atoms in zeolites as impurities.[6]

The structures and relative stabilities of two isomers of some Si/Ge mixed cyclic compounds, $H_8Si_2Ge_2O_4$, are shown in

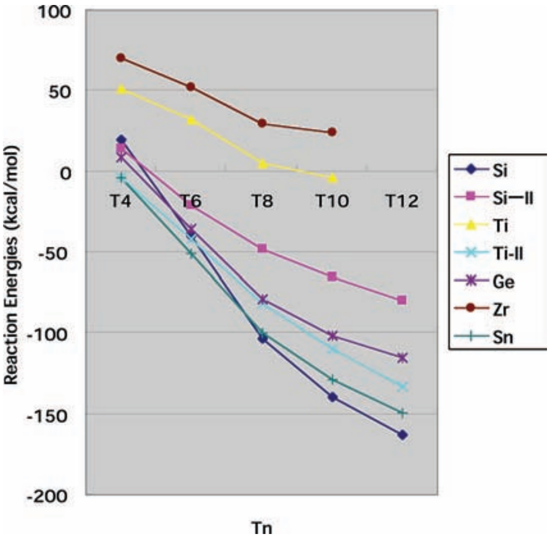


Figure 7. MP2/SBK and MP2/TZV(d,p) (X = Si and Ti only) heats of condensation reaction (kcal/mol) for $[HXO_{1.5}]_n$, n = 4, 6, 8, 10 and 12, X = Si, Ge, Sn, Ti and Zr. Si−II and Ti−II correspond to the MP2/TZV(d,p) values.

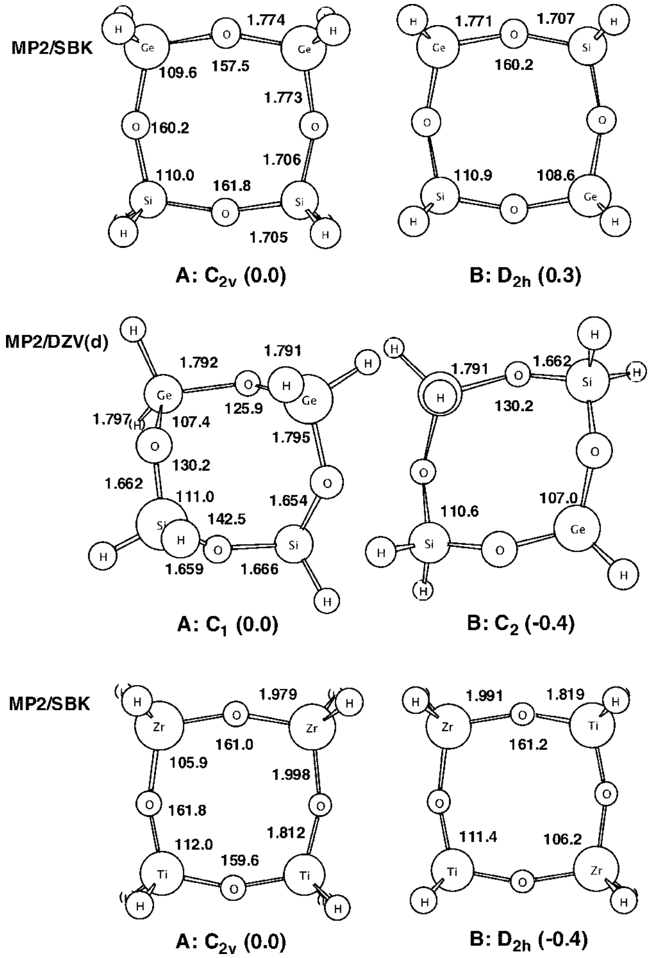


Figure 8. MP2/SBK optimized structures of two isomers of $H_8Ge_2Si_2O_4$ (top), the MP2/DZV(d) optimized structures of two isomers of $H_8Ge_2Si_2O_4$ (middle) and the MP2/SBK optimized structures of two isomers of $H_8Zr_2Ti_2O_4$ (bottom) in angstroms and degrees.

TABLE 3: MP2/SBK and MP2/DZV(d)[a] Relative (ΔE, kcal/mol) Energies and Condensation Reaction Energies (ΔH, kcal/mol)[b] of Various Isomers of $H_8Ge_pSi_{8-p}O_{12}$

isomer[c]	ΔE[d]	ΔH
p=0		−103.5
p=1		−100.2
p=2		
a	0.0 (0.0)[b]	−97.1
b	0.4 (1.5)	−96.8
c	0.3(1.4)	−96.9
p=3		
a	0.0	−94.0
b	0.3	−93.7
c	0.4	−93.3
p=4		
a	0.0 (0.0)	−91.1
b	0.3	−90.8
c	0.4	−90.7
d	0.6	−90.5
e	0.5	−90.6
f	1.4 (7.1)	−89.7
p=5		
a	0.0	−87.8
b	0.3	−87.6
c	0.7	−87.1
p=6		
a	0.0	−84.9
b	0.4	−84.5
c	0.2	−84.6
p=7		−81.8
p=8		−79.0

[a] Values in parentheses. [b] See eq 3 in the text. [c] See Scheme 2. [d] The energies relative to isomer "a" in each case; a, b, c, . . . refer to various isomers.

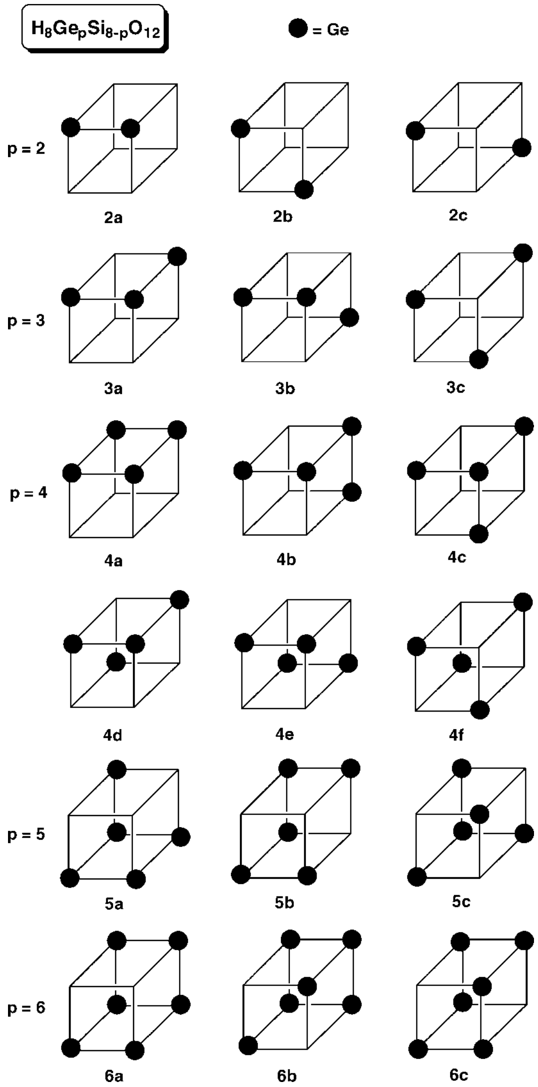
Figure 8. It has been shown previously that in Si/Ti mixed compounds, the isomer (B) in which the positions of Ti and Si atoms alternate is slightly lower in energy than the isomer (A) in which the two Ti atoms are on the same side of the ring.[5a] For the mixed Si/Ge compounds in Figure 8, MP2/SBK and MP2/DZV(d) predict these two isomers to be essentially isoenergetic. The Ti/Zr mixed four membered ring, $H_8Ti_2Zr_2O_4$, isomers are also shown in Figure 8. Here again the two isomers are essentially isoenergetic. Therefore, the distribution of the two elements in these compounds is not expected to have a serious effect on their stabilities, in contrast to the Al atoms in zeolites in which, according to Lowenstein's rule and Dempsey's rule, the Al atoms tend to assume positions as far from each other as possible.[5a] Table 3 shows the MP2/SBK and MP2/DZV(d) relative energies of the $H_8Ge_pSi_{8-p}O_{12}$ (p = 2−6) isomers (see Scheme 2). The MP2/SBK relative energies follow those of the Si/Ge-mixed D_4 ring structure, $H_8Si_2Ge_2O_4$; the isomer in which the Ge atoms are localized in the same part of the cage is (slightly) lowest in energy for p = 2−6. This is in sharp contrast with the Si/Ti mixed T_8 species.[5a] To examine basis set effects, the structures of all p = 2 isomers and two (a and f) p = 4 isomers were reoptimized with MP2/DZV(d). The order of the relative energies is the same as that obtained with the smaller basis set, and the energy differences increase.

The reaction energies for the condensation reactions (eq 3)

$$p\mathrm{HGe(OH)_3} + (8-p)\mathrm{HSi(OH)_3} = \mathrm{H_8Ge_pSi_{8-p}O_{12}} + 12\mathrm{H_2O} \quad (3)$$

for the Si/Ge mixed T_8 are also summarized in Table 3. Using this definition, Si-T_8 (p = 0) is thermodynamically more stable than Ge-T_8 (p = 8). The reaction energy monotonically increases as the number of Ge atoms increases, suggesting that the thermodynamic stability of the Si/Ge-mixed POSS primarily depends on the ratio of the number of the Si and Ge atoms.

SCHEME 2



Concluding Remarks. In an attempt to design new functional POSS using reliable computations, structures and stabilities for various sizes of Ge, Sn, Zr, and the Si/Ge-mixed POSS and their building blocks have been studied.

It is not surprising that properties of metallasilsesquioxanes can be predicted from those of the building blocks: linear and cyclic metalloxanes. Germanoxanes and stannoxanes with linear, ring and cage structures are found to have similar structures and stabilities, although the relative thermodynamic stabilities are small compared to the silicon analogues. Furthermore, the structures and properties of the Si/Ge-mixed POSS are predicted to be intermediate between those of POSS and Ge-POSS. On the other hand, the structure and properties of zirconoxanes are similar to those of the titanoxanes. The thermodynamic stability of the Zr-POSS, estimated from the heats of the condensation reaction, is the smallest of all of the metals studied here. Therefore, it may be difficult to synthesize this species experimentally.

Based on the present study of fully metal substituted POSS, the Si-based POSS is found to be the most stable compared to the other heavier group 14 or group 4 analogues, probably because the significant oxophilicity of silicon makes a strong framework.

For the heavier 14 group elements, the M−O−M bending motion may be too floppy to form stable large polyhedral structures but the low frequency/large amplitude vibrations may be favorable for the formation of more strained small cage structures, such as T_4. In addition, the Si−O−H linkage can make hydrogen bonds that are favorable for building a cage structure in condensation reactions. The Zr-POSS is predicted to be thermodynamically less stable, but the large cavity compared to the other POSS analogues is worth noting.

For the partially metal substituted POSS, one might be able to control their properties by changing the number of metal atoms for mixed group 14 elements. However, more studies of these mixed group 14 species are needed to develop a complete understanding of their properties.

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