Chemical Bonding and Reactivity of the Octahydridosilsesquioxane

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The chemical bonding and reactivity of $Si_8H_8O_{12}$ and $Ge_8H_8O_{12}$, and the symmetry breaking of the octahedral $Ge_8H_8O_{12}$, $Si_8O_{12}(C(CH_3)_3)_8^+$ and $Si_8O_{12}Cl_8^+$ are studied by means of *ab initio* quantum chemistry methods, Bader topological theory and group theory. The Fukui function and the molecular electrostatic potential are both used as DFT-based reactivity descriptors. The stability of the octa-substituted POSS, $Si_8R_8O_{12}$, and the effect of the functional group R on Si-O and Si-R bonds are also discussed and the thermochemical parameters of $Si_8H_8O_{12}$, $Si_8Li_8O_{12}$ and $Si_8F_8O_{12}$ are determined using G3B3 method. This study shows that $Si_8H_8O_{12}$ and $Ge_8H_8O_{12}$ are both isoelectronic and hard amphoteric molecules characterized by an acid hollow and an outer cage of base character. These molecules contain same number of valence molecular orbitals spanning same symmetry representations with similar shapes. Further, they have similar chemical reactivity behavior toward electrophilic and nucleophilic reagents. While $Si_8H_8O_{12}$ is stable in O_h, the $Ge_8H_8O_{12}$ undergoes a geometry distortion from O_h to T_h due to Pseudo-Jahn Teller effect. The stabilization energy gains from this PJT distortion is nearly 6.14 kcal/mol at MP2/6-311+G(d). The substitutional JT analysis reveals that the substitution of O by some group X = {S, Se, NH}, can form viable T_h $Ge_8H_8X_{12}$. The replacement of hydrogen by functional group in $Si_8H_8O_{12}$ shows that the Si-O bond lengths in $Si_8R_8O_{12}$ are correlated inversely with the electronegativity of the substituents. The calculated enthalpies of formation predict $Si_8H_8O_{12}$ to be 809 kcal/mol less stable than $Si_8F_8O_{12}$ and 316 kcal/mol more stable than $Si_8Li_8O_{12}$. The study of the JT instability in O_h $Si_8O_{12}(C(CH_3)_3)_8^+$ and $Si_8O_{12}(C(CH_3)_3)_8^+$ reveals that the ground states of these ions belong to C_{3V} and D_{4h} point groups and are characterized at B3LYP/def-SVP by the JT stabilization energies of 3858 cm^{-1} and 1376 cm^{-1}, respectively.