Ti^{4+} and Zr^{4+} inside Aluminosilicate and Borosilicate Cages: A Computational Study

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Ab initio Hartree−Fock SCF calculations on the compounds $Si_4Al_4O_{12}H_8M$ and $Si_4B_4O_{12}H_8M$, where M = Ti, Zr, indicate that *endohedral* complexes, in which the M cation occupies the center of the aluminosilicate or borosilicate cage, will be stable compared to their Na complexes and the M cation in aqueous solution. The $Si_4Al_4O_{12}H_8^{4-}$ cage is strongly disorted by the Ti cation, but the calculated cage distortions in the other compounds are much smaller, consistent with a better match between the interior dimensions of the cage and the size of the cation. Incorporation of Ti or Zr in the center of the $Si_4Al_4O_{12}H_8^{4-}$ cage substantially reduces the NMR shieldings of the Si, Al, and O, providing spectral signatures for the formation of such compounds. For $Si_4Al_4O_{12}H_8Ti$ the S_4 symmetry equilibrium structure has a local geometry about the Ti and calculated UV excitation energies very close to those in $Ti(OH_2)_4^{4+}$, but for the other endohedral complexes, i.e., $Si_4Al_4O_{12}H_8Zr$, $Si_4B_4O_{12}H_8Ti$, and $Si_4B_4O_{12}H_8Zr$, the calculated excitation energies are considerably smaller than those for the hydrated M cations, consistent with their longer nearest-neighbor M−O distances. Thus, such endohedral complexes provide new spectral environments for the Ti^{4+} and Zr^{4+} cations.

Introduction

Recently there has been considerable interest[1] in T_8 or double-4-ring (D4R) compounds, such as $Si_8O_{12}R_8$, which contain eight tetrahedrally coordinated atoms at the corners of a cube, with bridging O atoms along each edge. Each T atom is coordinated to three O's and one R group (usually alkyl or H). H atoms can be trapped inside the T_8 cage,[2] presumably in their centers. Such T_8 cages are also secondary building units for zeolites,[3] a class of materials which can incorporate many different cations within their larger cage sites.[4] T_8 anionic cages, such as $Si_4Al_4O_{12}R_8^{4-}$, can also be prepared and can be crystallized as their Na salts.[5] The Na^+ ions occupy sites on four of the outside faces of the T_8 D4R, so we might call such compounds *exohedral*. The question arises whether small highly charged cations might form *endohedral* complexes with $Si_4Al_4O_{12}R_8^{4-}$, with the cation in the center of the T_8 cage. This would certainly modify the properties of the Si_4Al_4... cage. More importantly, the cation environment within the cage might well be unusual.

To test the possibile existence and properties of such compounds, we have carried out ab initio Hartree−Fock quantum mechanical calculations of structures, energetics, and NMR and visible−UV spectral properties for the Ti^{4+} and Zr^{4+} endohedral complexes of $Si_4Al_4O_{12}H_8^{4-}$ and its smaller analogue $Si_4B_4O_{12}H_8^{4-}$.

Recently George and Catlow[6a] studied the incorporation of Na^+, F^-, and OH^- into the center of a neutral T_8 compound, $Si_8O_{12}(OH)_8$, focusing upon charge distribution changes and incorporation energies. They found that the Na^+ endohedral compound was unstable compared to $Si_8O_{12}(OH)_8$ and free Na^+. In an earlier study[6b] using empirical force-field techniques the same group found a large relaxation of the cage geometry when Ni^{2+} was enclosed within a T_{12} D6R aluminosilicate cage.

Computational Methods

We employ standard molecular orbital methods,[7] as in our previous studies on T_8 compounds.[8] Specifically, we use Hartree−Fock SCF theory with the relativistic polarized effective core potential basis sets of Stevens et al. (SBK)[9] to evaluate the structures and energetics. NMR shieldings are evaluated using the GIAO SCF method,[10] and visible−UV excitation energies are evaluated using the configuration interaction singles (CIS) method[11] both with the 3-21G* basis set.[7] The geometry optimizations were done with the program GAMESS[12] and the GIAO NMR and CIS calculations with the program GAUSSIAN94.[13]

Results

We first calculated the equilibrium structures for the endohedral forms of $Si_4Al_4O_{12}H_8Ti$, $Si_4Al_4O_{12}H_8Zr$, $Si_4B_4O_{12}H_8Ti$, and $Si_4B_4O_{12}H_8Zr$ at the polarized SBK SCF level. For each endohedral complex we initially assumed S_4 symmetry. Structures for the S_4 symmetry forms of $Si_4Al_4O_{12}H_8Ti$, $Si_4Al_4O_{12}H_8Zr$, and $Si_4B_4O_{12}H_8Ti$ are shown in Figure 1. NMR shieldings calculated for the various compounds are collected in Table 1, and calculated M−O distances and UV excitation energies calculated using the CIS method are collected in Table 2.

Figure 1 shows clearly that the T_8 cage in $Si_4Al_4O_{12}H_8Ti$ has "collapsed" around the Ti, giving an approximately tetrahedral local environment (see also Table 2). We also found another S_4 symmetry structure with a less distorted cage which was *almost* a local minimum. Starting from the equilibrium geometry for free $Si_4Al_4O_{12}H_8^{4-}$ with Ti^{4+} placed at its center, the optimization run had lowered the energy by about 300 kcal/mol and converged to better than 0.10 kcal/mol for a structure in which Ti was essentially 12-coordinate before dropping by an additional 100 kcal/mol to reach the collapsed equilibrium S_4 structure, shown in Figure 1. The Ti−O distances in this equilibrium strucure are 1.871 (×4), 2.571 (×4), and 3.202 Å (×4), so that the Ti is essentially 4-coordinate. It seems reasonable to compare the environments of the M cations at the centers of the Si_4Al_4... or Si_4B_4... cages with those expected in acidic or basic aqueous solution. The smaller Ti^{4+} would be 4- or 6-coordinated by water while the larger Zr^{4+} would be

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TABLE 1: Calculated NMR Shieldings (in ppm) for Endohedral Complexes and for Reference Compounds, Obtained Using the GIAO Method and the 3-21G* Basis Set at the Polarized SBK Equilibrium Geometries

molecule	σ^{Si}	σ^{Al}	σ^{B}	σ^{O}	σ^{Ti}	σ^{Zr}
$Si_4Al_4O_{12}H_8^{4-}$	588.1	620.0		297.4		
$Si_4Al_4O_{12}H_8Na_4$	580.2	621.1		285.8−288.8		
$Si_4B_4O_{12}H_8^{4-}$	576.2		134.7			
$Ti(OH)_4$				132.7	541.2	
$Ti(H_2O)_4^{4+}$				86.5−123.1	583.8	
$Zr(OH)_4$				202.7		2402.1
$Zr(H_{2O)4}^{4+}$				198.8−206.8		2555.8
$Zr(H_2O)_8^{4+}$				305.9		2935.5
$Si_4Al_4O_{12}H_8Ti$, intermediate geometry	583.2	601.9		213.7−215.6	478.0	
$Si_4Al_4O_{12}H_8Ti$, collapsed, S_4 minimum	553.3	592.4		25.7−287.5	421.5	
$Si_4Al_4O_{12}H_8Ti$, C_1 local minimum	563.0 × 2, 546.9, 582.1	604.2 × 2, 602.8, 600.8		56.0−290.6	536.4	
$Si_4Al_4O_{12}H_8Zr$	557.3	601.0		199.7−253.7		2484.4
$Si_4B_4O_{12}H_8Ti$	549.7		129.0	134.6−267.4	604.6	
$Si_4B_4O_{12}H_8Zr$	549.3		128.2	205.5−249.1		2544.6

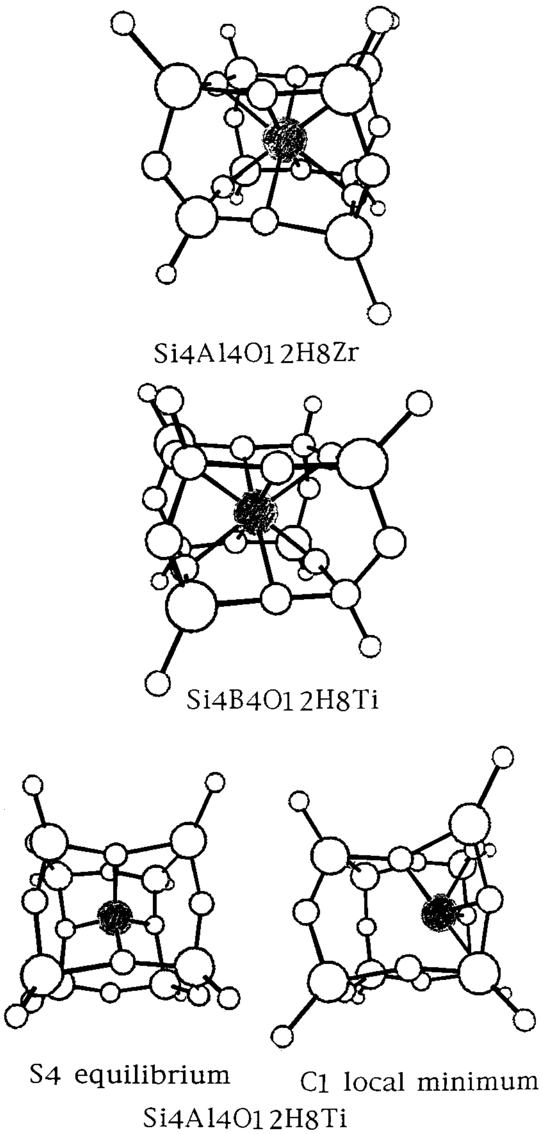

Figure 1. Plots of the geometries of the S_4 and C_1 symmetry isomers of $Si_4Al_4O_{12}H_8Ti$ and of the S_4 isomers of $Si_4Al_4O_{12}H_8Zr$ and $Si_4B_4O_{12}H_8Ti$. The Ti or Zr atoms are represented by solid circles. The other atoms are represented by empty circles, with Si, Al, O, and H in order of decreasing size

TABLE 2: Calculated Lowest Three Singlet Excitation Energies for Ti^{4+} and Zr^{4+} Complexes Using CI-Singles (CIS) Method the 3-21G* Basis and Polarized SBK Geometries

molecule	R(M−O), Å	ΔE, eV
$Ti(OH)_4$	1.806 × 4	8.01, 8.31, 8.31 (8.15, 8.54, 8.54[a])
$Ti(OH_{2)4}^{4+}$	1.913−1.921	6.87, 7.01, 7.07
$Si_4Al_4O_{12}H_8Ti$ uncollapsed	2.528 × 4, 2.495 × 8	4.01, 4.03, 4.06
$Si_4Al_4O_{12}H_8Ti$, equilib collapsed S_4 struct	1.871 × 4, 2.571 × 4, 3.202 × 4	6.76, 7.09, 7.09
$Si_4Al_4O_{12}H_8Ti$ C_1 local minimum	1.91, 1.94, 2.01, 2.07, 2.09, 2.22, 2.85, 2.98, 3.30, 3.47, 3.49, 3.49	5.64, 5.94, 5.97
$Si_4B_4O_{12}H_8Ti$	2.004 × 4, 2.162 × 4, 2.987 × 4	5.77, 5.95, 5.95
$Zr(OH)_4$	1.959 × 4	8.40, 8.55, 8.70
$Zr(OH_{2)4}^{4+}$	2.106−2.110	7.96, 8.15, 8.25
$Zr(OH_{2)8}^{4+}$	2.327	7.46, 7.77, 7.77
$Si_4A_{14}O_{12}H_8Zr$	2.244 × 4, 2.249 × 4, 3.171 × 4	6.63, 6.91, 7.30
$Si_4B_4O_{12}H_8Zr$	2.18 × 4, 2.24 × 4, 2.89 × 4	6.52, 6.76, 6.91
$Si_4Al_4O_{12}H_8^{4-}$		9.73, 10.14, 10.14
$TiCl_4$		6.26, 6.26, 6.31 (exp 4.4, 5.3)

[a] 6-311+G* basis.

6- or 8-coordinate[14] (although both cations would hydrolyze extensively). In the molecules $Ti(OH)_4$ and $Ti(OH_2)_4^{4+}$ the optimized Ti−O distances are 1.806 Å and 1.913−1.921 Å, respectively. Thus, the nearest-neighbor environment of Ti is not too much different in the endohedral T_8 complex than in a typical 4-coordinate aqueous environment.

The calculated distortion of the Si_4Al_4... cage is much smaller if we replace Ti by Zr. The calculated Zr−O distances in $Si_4Al_4O_{12}H_8Zr$ are 2.249 (×4), 2.244 (×4), and 3.171 Å (×4), while the Zr−O distances in $Zr(H_2O)_4^{4+}$ and $Zr(H_2O)_8^{4+}$ are 2.106−2.110 and 2.327 Å, respectively. Thus, the larger Zr^{4+} cation distorts the T_8 cage much less, and its environment within the T_8 cage is quite unique, with eight nearest neighbors closer than they would be in aqueous solution. In the same way, the cage distortion is much smaller for $Si_4B_4O_{12}H_8Ti$, since the Si_4B_4... cage and the Ti^{4+} cation are apparently better matched in size.

Evaluation of the Hessian matrix for $Si_4Al_4O_{12}H_8Ti$ showed three imaginary frquencies, indicating that the S_4 structure was a saddlepoint on the energy surface. We then moved the Ti away from the cube center along a body diagonal and found a local energy minimum of C_1 symmetry, which was however higher in energy than the S_4 symmetry isomer. We were not able to locate a C_1 symmetry isomer lower in energy than the S_4, perhaps because of insufficient computer time to search various possible starting geometries. When the S_4 symmetry form of $Si_4B_4O_{12}H_8Ti$ was distorted in the same way, the optimization procedure lead back to the S_4 symmetry isomer.

For $Si_4Al_4O_{12}H_8Ti$ we also obtained an optimized geometry of C_1 symmetry in which the Ti^{4+} was *exohedral*, located on the *outside* of one of the faces on the T_8 cube. This structure was found to be *higher* in energy than the S_4 endohedral structure by about 0.14 hartree.

We then evaluated energies at the polarized SBK SCF level for the reactions:

$$Si_4Al_4O_{12}H_8Na_4 + M(OH)_4 \rightarrow Si_4Al_4O_{12}H_8M + 4NaOH \quad (1)$$

and

$$Si_4Al_4O_{12}H_8Na_4 + M(H_2O)_4{}^{4+} \rightarrow Si_4Al_4O_{12}H_8M + 4NaH_2O^+ \quad (2)$$

where M = Ti, Zr. The reactant molecule $Si_4Al_4O_{12}H_8Na_4$ is of C_{4v} symmetry with the Na^+ ions on the outsides of four faces of the T_8 cube. This molecule is shown in Figure 1 of ref 8 (identified as $Si_4Al_4O_{12}H_8Na_4$, Al···Si···Al···Si), and its structure agrees well with experiment, as discussed in ref 8.

In the first reaction the M^{4+} cation is initially in the very strongly coordinating environment of four OH^- ions, while in the second it is initially in aqueous solution, coordinated by the weaker base H_2O. The formation of the T_8 endohedral complex could be made even more favorable by using a less strongly coordinating solvent than water. Note that for the second reaction we must evaluate the hydration energy of the metal−water cations. We utilize the approach of Rashin and Honig[15] to estimate these energies. We evaluate the Born radius for the ion by adding the Rashin and Honig value of 1.49 Å for the O−H radius to our calculated M−O distance. The Born energy is then given as the square of the charge on the ion divided by this radius and multiplied by 0.266, to give the hydration enthalpy in hartrees. The hydration enthalpy so obtained for $Ti(H_2O)_4{}^{4+}$ is −1.244 hartrees, and that for NaH_2O^+ is −0.118 hartree. Although this approach is quite approximate, it has yielded reasonable values in our recent studies of ions in solution.[16]

Reaction 1 is found to be highly endoergic ($\Delta E = +352$ kcal/mol for Ti and +334 kcal/mol for Zr). This is a simple consequence of the strong interaction of the M^{4+} cation with OH^-. By contrast, the ΔE values obtained for reaction 2 (after inclusion of the hydration energy terms) are −159 kcal/mol for Ti and −147 kcal/mol for Zr. Thus, reaction 2 is exoergic even though the hydration energy for the $M(OH_2)_4{}^{4+}$ species using the Rashin and Honig approach has a magnitude larger than 700 kcal/mol. However, if reaction 2 is modified for the Zr case so that $Zr(H_2O)_8{}^{4+}$ rather than $Zr(H_2O)_4{}^{4+}$ is chosen as the source of Zr, the reaction becomes endoergic by 39 kcal/mol. This clearly raises some ambiguity in terms of the energetics in solution.

We have considered one additional energetic term for reaction 2: the hydration energy of the Na's on the exterior of neutral $Si_4Al_4O_{12}H_8Na_4$. One might expect these electropositive atoms on the exterior to be hydrated fairly strongly, while the Ti or Zr in the interior of the T_8 cube would not be. This would stabilize the reactant side in reaction 2 and therefore reduce the magnitude of the exoergicity. Polarized SBK calculations on $Si_4Al_4O_{12}H_8Na_4(H_2O)_4$ indicate a stabilization energy of about 56 kcal/mol for attachment of the four H_2O molecules (giving a 5-coordinate Na in the "supermolecule"). Of course, this correction would increase in magnitude if we considered more H_2O molecules coordinating to the exohedral Na^+ ions. At the same time, even $Si_4Al_4O_{12}H_8Ti$ would be stabilized to some extent by hydration, an energetic effect we have completely ignored. In any case, we can always "drive" reaction 2 toward products by using less strongly coordinating solvents, thus reducing the solvation energy of M^{4+}.

Our results indicate very similar energetics for the $Si_4B_4O_{12}H_8M$ compounds, whose energies of formation from $Si_4B_4O_{12}H_8{}^{4-}$ and M^{4+} are slightly more exothermic than those for the Si_4Al_4... cage (by about 24 and 9 kcal/mol for Ti and Zr, respectively). We also examined the energetics for formation of $Si_8O_{12}H_8Ti^{4+}$ from $Si_8O_{12}H_8$ and $Ti(H_2O)_4{}^{4+}$, the analogue of reaction 2, and found it to be *endoergic* by 121 kcal/mol. Therefore, incorporation of Ti^{4+} into neutral $Si_8O_{12}H_8$ will not be favorable in aqueous solution.

The NMR shieldings shown in Table 1 indicate that the Si, Al, and B are all strongly deshielded by the incorporation of Ti^{4+} or Zr^{4+} at the center of the T_8 cube. The magnitude of the deshielding is about 30, 20, and 6 ppm for Si, Al, and B, respectively. This strong deshielding, coupled with the presence of only one Si, Al, or B signal (at least for the S_4 symmetry structure), could be a powerful diagnostic for the existence of such compounds. For the intermediate S_4 symmetry structure of $Si_4Al_4O_{12}H_8Ti$, before the strong distortion has occurred, the deshielding is much smaller. In all the structures the O atoms closest to the M cations are strongly deshielded, while those farther away are little changed from their values in the empty T_8 anion. This is seen dramatically in the C_1 local minimum geometry of $Si_4Al_4O_{12}H_8Ti$, where the smallest O shielding is 56.0 ppm while the largest is 290.6, almost unchanged from the $Si_4Al_4O_{12}H_8{}^{4-}$ value. The change in Ti shielding depends on the size of the T_8 cage—it is deshielded for the Si_4Al_4... case, but its shielding is increased compared to $Ti(H_2O)_4{}^{4+}$ when it is incorporated in the Si_4B_4... cage. This is consistent with the presence of eight O's fairly near the Ti in $Si_4B_4O_{12}H_8Ti$, an effective coordination number of 8. For Zr the calculated shielding is somewhat larger in the Si_4B_4... cage than in the Si_4Al_4... cage, but the change is not so dramatic as for Ti. Both endohedral compounds show Zr shieldings fairly close to that in the tetraaquo cation.

The calculated UV absorption energies in Table 2 are probably the most interesting results since they address the possibility of designing materials that have Ti or Zr in unique spectral environments. The lowest energy transitions in such componds are basically ligand-to-metal charge-transfer transitions, from a nonbonding p orbital on the ligand to the metal−ligand antibonding orbital of e symmetry. From the results for the $M(OH)_4$ and $M(OH_2)_4{}^{4+}$ complexes in Table 2, it is clear that the more strongly coordinating ligand, OH^-, gives both shorter M−O distances and larger UV excitation energies. A reduction in the bond distances thus destabilizes the antibonding e orbital and increases the CT energy. Comparing $Zr(H_2O)_4{}^{4+}$ and $Zr(H_2O)_8{}^{4+}$, we see little change in the CT energy, since the larger bond distance in the 8-coordinate complex is compensated by the larger number of nearest neighbors.

In the endohedral Si_4Al_4... and Si_4B_4... compounds, the distances to the four nearest O atoms are generally larger than in $M(OH)_4$ or $M(OH_2)_4{}^{4+}$ (with the exception of $Si_4Al_4O_{12}H_8Ti$) , but there are additional O neighbors at longer distances.

For the intermediate uncollapsed geometry of $Si_4Al_4O_{12}H_8Ti$ the Ti−O distances are still quite long and the spectral energies are about 3 eV smaller than in $Ti(OH_2)_4{}^{4+}$, but for the collapsed S_4 symmetry equilibrium geometry the M−O distances and CT energies are comparable to those in the tetraaquo complex. For $Si_4B_4O_{12}H_8Ti$ the Ti−O distances remain longer than in the aquo complex, and the CT energies are consequently smaller. For the Zr case both the Si_4Al_4... and Si_4B_4... endohedral complexes give longer Zr−O distances and lower CT energies than in $Zr(OH_2)_4{}^{4+}$.

Note that the CT energies calculated at the CIS 3-21G* level are seriously overestimated compared to those from experiment. For example, such calculations give a lowest CT energy of 6.26 eV for $TiCl_4$ (as shown in Table 2), while the experimental value is about 4.4 eV[17] and large basis set multireference CI calculations[18] give agreement with most experimental features to within a few tenths of an electronvolt. We established that expanding the bais set from 3-21G* to 6-311+G* had little effect on the CIS energies, at least for the case of $Ti(OH)_4$. Better results would require a more sophisticated method than CIS (such as the multireference CI approach employed for $TiCl_4$ in ref 18), but such methods are not yet practical for compounds the size of $Si_4Al_4O_{12}H_8Ti$. We anticipate that the CIS calculations reproduce correctly the trends in UV energies if not their absolute values.

Conclusions

The aluminosilicate cage anion $Si_4Al4O_{12}H_8{}^{4-}$ is large enough to accommodate highly charged cations such as Ti^{4+} or Zr^{4+}. The aluminosilicate cage actually collapses around the Ti^{4+}, giving a local tetrahedral coordination environment not much different from that in $Ti(OH_2)_4{}^{4+}$. When Zr^{4+} is substituted for Ti^{4+}, the aluminosilicate cage is much less distorted. For the smaller borosilicate T_8 cage, $Si_4B_4O_{12}H_8{}^{4-}$, the cage distortion is smaller for both Ti^{4+} and Zr^{4+}. The formation of such endohedral complexes from the Na T_8 compounds and M^{4+} in aqueous solution is calculated to be exoergic. In $Si_4Al_4O_{12}H_8$-Ti the Si, Al, and O all show a strong NMR deshielding relative to their values in $Si_4A_4O_{12}H_8Na_4$, which should prove useful in identifying them. Similar shielding trends are seen for the Si_4B_4... endohedral compounds. Reductions in the UV CT energies, compared to the aquo species, are seen for $Si_4B_4O_{12}H_8$-Ti and for both Si_4Al_4...and Si_4B_4... endohedral complexes of Zr.

These results support the concept that endohedral complexes of the T_8 anions with polyvalent cations such as Ti^{4+} or Zr^{4+} will be stable and that at least some of them will have unusual NMR and spectral properties. In particular, when the polyvalent cation is fairly large compared to the dimensions of the T_8 cube, the cube distortion is small and the cation−oxygen distances remain fairly long, leading to unusually low charge-transfer transition energies.

Methods have already been developed to synthesize soluble aluminosilicates[5] like $Si_4Al_4O_{12}H_8{}^{4-}$ and to form various molecular titanosilicates and zirconosilicates.[19] Based on the present results, solution hydrolysis of Si, Al, and Zr precursors together (e.g., $RSi(OH)_3$, $AlMe_3$, and $ZrCl_4$) might well produce the compound $Si_4Al_4O_{12}H_8Zr$ with an endohedral geometry and a unique Zr spectral environment.

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