Energy-Preeminent Isomer of the $Ca_3(PO_4)_2$ Cluster

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The potential energy surface associated with the $Ca_3(PO_4)_2$ cluster has been systematically studied through ab initio calculations. An isomer with D_{3h} symmetry was found to have the lowest energy. It has the distinct feature that each calcium atom is surrounded by four oxygen atoms. The energy separation between this isomer and the closest local minimum is 82 Kcal/mol.

Introduction

Calcium phosphate clustering with a Ca/P molar ratio of 1.50 is extremely important from the viewpoint of vertebrate biomineralization because clustering is implicated in the formation process of hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$), which has a chemical and structural resemblance to bone and tooth minerals.[1−3] In vitro, an amorphous calcium phosphate was shown to be formed with a Ca/P molar ratio of 1.45 ± 0.05 as a precursor in the crystal growth process of hydroxyapatite in a solution supersaturated as highly as a physiological solution.[4] Despite its biological interest, few calculations of calcium phosphate clusters have been reported to date.[5,6] We have therefore initiated a series of works for studying the stability of calcium phosphate clusters with a Ca/P molar ratio of 1.50 through ab initio calculations. Our focus, in the present article, is on the results of geometry optimizations for a set of $Ca_3(PO_4)_2$ isomers.

Computational Method

The wave functions have been calculated within the restricted Hartree−Fock (RHF) scheme using a split valence plus polarization (SVP) basis set quality.[7,8] For each isomer, the calculation has been restricted to a singlet-state configuration. Nevertheless, we have ensured that the ground state of the isomer associated with the lowest energy corresponds to a closed-shell configuration. In a mathematical sense, no criterion guarantees that the global minimum has been found on a potential energy surface (PES). Nonetheless, using the chemical restriction that any of the considered isomers conserves the two PO_4 groups in which each phosphorus atom is surrounded by four oxygen atoms, we can perform a systematic search on the PES by enumerating all of the different topologies, that is, the different ways of connecting the calcium and oxygen atoms, encountered in the $Ca_3(PO_4)_2$ cluster. All of the different topologies have been constructed according to the following process which is composed of three stages.

(1) First, all of the possible $Ca-PO_4$ fragments have been constructed from the calculation results of the singlet-state PES associated with the $CaPO_4H$ molecule. Within the RHF scheme, the calculations have shown the existence of three distinct energy minima (Figure 1) on the PES of the $CaPO_4H$ molecule. The isomer corresponding to Figure 1a is more stable than that corresponding to Figure 1b by 2 kcal/mol and that corresponding to Figure 1c by 122 kcal/mol.

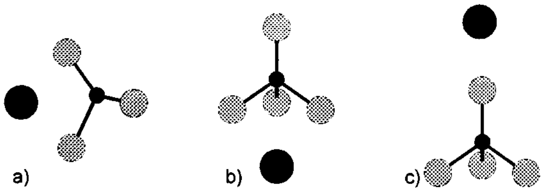

Figure 1. : Bonding sites for one calcium atom located (a) on the edge, (b) on the face, and (c) at the top of a PO_4 tetrahedron. Phosphorus, oxygen, and calcium atoms are represented as black spheres, large gray spheres, and large black spheres, respectively.

The high energy associated with the isomer represented in Figure 1c results from the fact that the calcium atom at the top of a PO_4 tetrahedron is no longer a cation but appears as a neutral atom. The neutrality of the calcium atom arises because its single neighboring oxygen, being bonded to a phosphorus atom, cannot reach an O^{2-} state. The calcium ion is, therefore, not chemically bonded to the oxygen atom and only a weak interaction takes place.

(2) Second, all of the possible $Ca-PO_4-Ca$ fragments are constructed by superimposing the PO_4 groups of two $Ca-PO_4$ fragments (Figure 2). Among the nine possible $Ca-PO_4-Ca$ fragments, we disregard two fragments, corresponding to Figure 2h,i, because the two calcium atoms are too close to each other.

(3) Lastly, all of the possible $Ca_3(PO_4)_2$ topologies are constructed by superimposing a calcium atom of two $Ca-PO_4-Ca$ fragments (Figure 3). The total number of possible $Ca_3(PO_4)_2$ topologies is 89. Note that we therefore disregard the situations in which the Ca_2PO_4 and $CaPO_4$ fragments are separated.

Based on the 89 topologies, we have defined 89 different $Ca_3(PO_4)_2$ initial geometries. Each initial geometry has been obtained by treating the PO_4 as a regular tetrahedron, while the calcium atoms have been located on the top, edge, or face sites, using the bond lengths calculated on the $CaPO_4H$ molecule. The initial geometries have subsequently been optimized.

Results and Discussion

On many occasions, following the geometry optimization, we obtained an isomer with a topology different from the initial one. Two different causes contribute to these changes in topology. The first one is the displacement of calcium atoms from the top of a PO_4 tetrahedron. This displacement is in agreement with the calculation performed on the $CaPO_4H$ isomer

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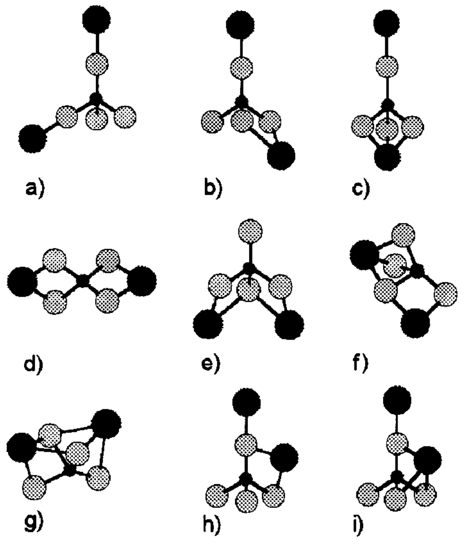

Figure 2. Nine topologies in a system composed of two calcium atoms connecting a PO_4 tetrahedron obtained by superimposing the PO_4 groups of any of the two $Ca{-}PO_4$ fragments in Figure 1.

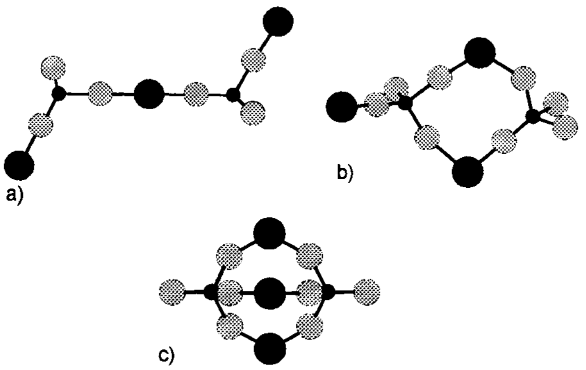

Figure 3. Three topologies corresponding to the $Ca_3(PO_4)_2$ cluster obtained by superimposing a calcium atom of two identical $Ca{-}PO_4{-}Ca$ fragments in Figure 2a. The topologies represented in a−c have one, two, and three calcium atoms, respectively, connecting the two PO_4 tetrahedrons.

having a calcium atom on top of the PO_4 tetrahedron. Although this isomer is a local minimum on $CaPO_4H$ PES, it has two vibrational modes with frequencies of 33 and 39 cm^{-1}, respectively. Any slight displacement of the calcium atom from the top of the PO_4 tetrahedron leads to the escape of the calcium atom from this energy minimum position to reach the lower energy minimum position located on the edge of the PO_4 tetrahedron shown in Figure 1a. A similar effect occurs on $Ca_3(PO_4)_2$ PES, and all of the geometries in which there are one or two calcium atoms on the top of a PO_4 tetrahedron convert to other geometries belonging to different topologies, after geometry optimization. The second cause is that two calcium atoms are too close to each other in the initial geometry in some topologies. In this case, either no stationary point or a stationary point other than a local minimum is found on the PES.

Following the geometry optimization of all 89 initial geometries, 19 different isomers were obtained, each corresponding to an energy minimum on the PES. Their energies are shown in Figure 4 (top). The number of initial geometries converted into each isomer is given in Figure 4 (bottom).

It should be noted, however, that there exists supplemental local minima on the PES for some topologies. For instance, two distinct local minima of symmetry D_{2d} and D_{2h} exist for a topology having a symmetry rotational axis obtained from the two $Ca{-}PO_4{-}Ca$ fragments represented in Figure 2d. Likewise, nine such topologies have more than one isomer each. In such cases, the isomer with the lowest energy has been used in Figure 4 (top) for each topology.

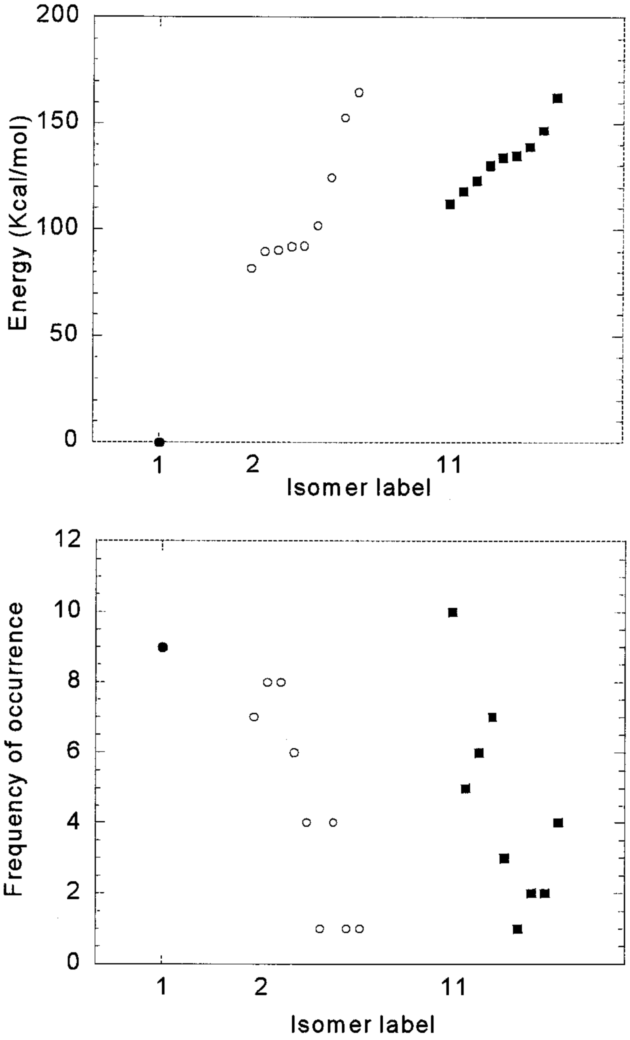

Figure 4. (Top) energy of the different isomers on the $Ca_3(PO_4)_2$ PES. The 19 local minima associated with the lowest energies are considered. The isomers where three, two, and one calcium atoms bridge two PO_4 tetrahedrons are labeled in the range [1−2], [2−10], and [11−19], respectively, and their energies are plotted as dots, open circles, and squares, respectively. (Bottom) frequency of occurrence of each isomer after the geometry optimization of 89 initial geometries.

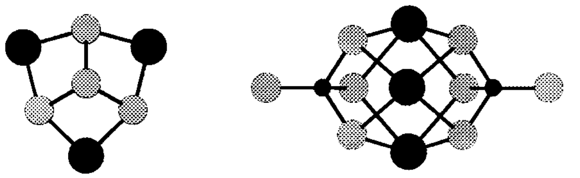

Figure 5. Top and side views of the D_{3h} isomer of the $Ca_3(PO_4)_2$ cluster associated with the lowest energy.

An significant feature of the local minima is that a specific isomer, labeled 1 in Figure 4, is preeminent in its stability. This isomer, which is associated with the lowest energy minimum, is the only one in which any of the calcium atoms reach four neighboring oxygen atoms. This isomer has a D_{3h} symmetry with all three calcium atoms bridging the two PO_4 groups, as shown in Figure 5.

We analyzed a situation where one calcium atom is located between two faces of two PO_4 tetrahedrons forming six CaO

TABLE 1: Bond Lengths in Ångstroms Calculated with the SVP and 6-311G(2d,f) Basis sets for the $Ca_3(PO_4)_2$ Isomers Represented in Figure 5 (Isomer A) and in Figure 1c (Isomer B)[a]

	SVP	6-311G(2d,f)
	Isomer A	
CaO	2.34	2.30
PO_b	1.59	1.57
PO	1.46	1.44
	Isomer B	
CaO	2.13	2.06
PO_b	1.58	1.56
PO	1.47	1.45

[a] O_b indicates the oxygen atoms bonded simultaneously to a phosphorus and a calcium atom.

bonds. The situation involves three isomers in total. All three isomers were higher in energy than the corresponding isomers with the central calcium atom located on an edge site of two PO_4 tetrahedrons forming four CaO bonds.

For verification of the accuracy of the calculations performed using the SVP basis sets, comparative geometry optimizations using the 6-311G(2d,f) basis sets[9−11] have been performed for the two structures in which three calcium atoms bridge two PO_4 groups, i.e., the isomer shown in Figure 5 associated with the lowest energy minimum and the isomer shown in Figure 3c. The energy difference between the two structures calculated with SVP and 6-311G(2d,f) basis sets is 112 and 96 kcal/mol, respectively. The corresponding geometrical parameters are given in Table 1.

These results are in agreement with considerations reported in ref 7 by the authors of the SVP basis sets. Therefore, the energy difference among many of the present isomers should be considered as indicative only. Nonetheless, the large energy difference between the isomer shown in Figure 5 and the other isomers is undoubtedly valid. The use of the SVP basis set permits us to reach the above conclusion with limited computer resources. The existence of a large energy difference between isomers, together with the size of the basis sets required, permit us to consider the study of larger calcium phosphate clusters with a Ca/P molar ratio of 1.50, such as $[Ca_3(PO_4)_2]_2$ and $[Ca_3(PO_4)_2]_3$. The latter is of greater interest due to the presumed role of a cluster of the formula $Ca_9(PO_4)_6$ in the biomineralization process.[1−3]

Conclusions

The present systematic study on the PES associated with the $Ca_3(PO_4)_2$ cluster has revealed that the isomer associated with the lowest energy minimum has a D_{3h} symmetry. This isomer has the notable feature that each calcium atom is surrounded by four oxygen atoms from PO_4 groups.

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