Rational Design of Two-Dimensional Layered Aluminophosphates with $[Al_3P_4O_{16}]^{3-}$ Stoichiometry

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Topological analysis elucidates some general features of two dimensional (2D) 3.4-connected nets of aluminophosphates with $Al_3P_4O_{16}^{3-}$ stoichiometry. It proves that four-membered rings (4MRs) are essential for the construction of their networks. The distinct 2D sheets of $Al_3P_4O_{16}^{3-}$ layers, including both known and hypothetical nets, are systematically generated by computer. Calculation results show that a large number of 2D nets are energetically feasible compared to the known 2D nets. This suggests that they are likely to be synthesized under certain conditions. The secondary building units (SBUs) constructing the 2D networks of $Al_3P_4O_{16}^{3-}$ layers are commonly found as capped 6MRs (SBU1), double-diamond rings (SBU2), branched edge-sharing double 4MRs (SBU3), and double intergrown-capped 6MRs (SBU4). Some typically hypothetical 2D nets including novel 4.6, 4.6.8, 4.6.8.12, 4.8, and 4.6.10 nets, which have lower energies, are described in this paper. The calculated bond lengths and bond angles are in agreement with those of the existing AlPOs. This work represents a rational way to design the 2D layered materials.

Introduction

Since 1982, a series of microporous aluminophosphates ($AlPO_4$-*n*, Al/P = 1) have been synthesized hydrothermally in the presence of various organic templates.[1−5] These materials, like aluminosilicate zeolites, have great potential in applications of adsorption and catalysis. Their frameworks are typically built up from alternating vertex-sharing tetrahedral AlO_4 and PO_4 units. Recently, through utilization of a nonaqueous synthesis technique,[6] a large number of aluminophosphates with an Al/P ratio of nonunity have been continuously reported by our lab and others, of which the two-dimensional (2D) layered materials constitute an important area of chemistry materials.[6,7] These materials exclusively contain tetrahedral phosphate groups with terminal oxygens (−OH/or =O), which render them potentially useful in the self-assembly process to build up three-dimensional (3D) frameworks. The study of 2D layered AlPOs supplies important information on the formation models of one-dimensional (1D) chains and 3D microporous materials.[8] In addition, it appears that to investigate the templating effect from a 2D layer system is much easier than from 3D microporous system because there are much stronger interactions (i.e., H-bondings) between the templates and the host inorganic networks in 2D layered compounds.

So far, three distinct stoichiometries have been found in the organically templated aluminophosphate layer family (i.e., $Al_3P_4O_{16}^{3-}$,[9−23] $Al_2P_3O_{12}^{3-}$,[24,25] and $AlP_2O_8^{3-}$).[19] The $Al_3P_4O_{16}^{3-}$ layers exhibit rich structural

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diversity. Except for $Al_3P_4O_{16}H{\cdot}2C_3H_5$,[19] an unusual layered compound which contains AlO_5, the 2D networks of $Al_3P_4O_{16}^{3-}$ are all built up from alternating AlO_4 and $PO_3(=O)$ units. All Al tetrahedra share four oxygens with adjacent P atoms, whereas phosphates share only three oxygens with adjacent Al atoms, leaving one oxygen atom terminal. The inorganic layers are held together through extensive H-bonding systems between the P=O groups and the protonated organic amines located in the interlayer region. Of the known $Al_3P_4O_{16}^{3-}$ layers, five are with unique inorganic networks. They are $[Al_3P_4O_{16}][Co(en)_3]3H_2O$ (4.6 net),[13] $[Al_3P_4O_{16}]1.5[NH_3CHMeCH_2NH_3]$ (4.6 net),[15] $[Al_6P_8O_{32}]$-$4[C_6NH_9]2[H_3O]$ (4.6-net),[21] $[Al_3P_4O_{16}]3[CH_3CH_2NH_3]$ (4.6.8 net)[18], and $[Al_3P_4O_{16}]1.5[NH_3(CH_2)_4NH_3]$ (4.6.12 net).[10] It is interesting to find that the 4.6.8 and 4.6.12 nets are resemblant to the 3-connected 2D nets in 3D $AlPO_4$-21 and $AlPO_4$-5, respectively.[26] It is believed that, by judicious selection of the synthesis conditions, such as the type of templates, the P/Al ratios, and the type of solvents, many more interesting structures will be synthesized. However, so far it is still unlikely to predict the final products from the reaction conditions. This problem is due to the fact that the formation mechanism of zeolite and zeolite-related materials is still unclear. Therefore, it is important to find a way to rationally design and synthesize target materials. In this work, we use a computational method to systematically enumerate the 2D 3.4-connected $Al_3P_4O_{16}^{3-}$ nets that are likely to be synthesized, and further discuss their topological and structural features. Further work is being focused on the investigation of possible templates that can direct the formation of those hypothetical 2D layers in terms of host−template interactions.[27]

Some Topological Features of 2D 3.4-Connected $Al_3P_4O_{16}^{3-}$ Nets. The $Al_3P_4O_{16}^{3-}$ anionic sheets are constructed from alternating AlO_4 and $PO_3(=O)$ units. Therefore, their 2D networks can be considered as 2D 3.4-connected planar nets. Following some rules proposed by Grünbaum, Shepherd,[28] and Wells,[29,30] we describe some general features about the 2D 3.4-connected nets of $Al_3P_4O_{16}^{3-}$.

Considering a periodic 2D 3.4-connected net having N nodes and P_n polygons of n sides ($n = 3, 4, 5, ...$) in the unit cell, some topological features are as follows:

(1) There are only even-sided polygons in the net.

There are two types of nodes, representing the Al atom and P atom, respectively. Since they are connected alternatively in a polygon, the number of sides of a polygon must be even.

$$\sum_{n=4,6,8,\ldots} nP_n = \frac{24}{7}N \qquad (1)$$

The total number of edges is $1/2\sum_n nP_n$. Equation 1 means that 2 times of the total number of edges is 24/7 times of the total number of nodes in the unit cell. Therefore, the total number of the nodes in the unit cell must be the multiple of seven, for example, 7, 14, 21, etc.

$$\sum_{n=4,6,8,\ldots} P_n = \frac{5}{7}N \qquad (2)$$

The equation describes that the total number of polygons is 5/7 times of the total number of nodes in the unit cell. Therefore, the total number of polygons must be the multiple of five, for example, 5, 10, 15, etc.

$$F + V - E = 0 \qquad (3)$$

By using the above equations, (1) and (2), we can get the relationship of the total number of polygons ($F = \sum_n P_n$), the total number of vertexes ($V = N$), and the total number of edges ($E = 1/2\sum_n nP_n$). Their relationship is equivalent to the well-known Euler relationship.

(5) The number of quadrangles is no less than two-thirds of the total number of polygons.

Supposing there is no quadrangle in the net, then the least number of edges of a polygon is 6. Since the average number of sides of each polygon is 4.8 according to the above equations, (1) and (2), there must exist some quadrangles in the net.

$$4P_4 + 6P_6 + 8P_8 + \ldots + 2nP_{2n} = 24N/7 \qquad (4)$$

$$P_4 + P_6 + P_8 + \ldots + P_{2n} = 5N/7 \qquad (5)$$

Now, we investigate the least number of quadrangles in the unit cell. If we enumerate the possible numbers and type of polygons that meet the above equations, (4) and (5), we can get a table of the possible numbers and types of polygons. From the table, it is found that the number of quadrangles at least takes up two-thirds of the total number of polygons in the unit cell. Therefore, it is concluded that four-membered rings are essential for the construction of 2D 3.4-connected nets.

Methods of Generation of the Periodic 2D 3.4-Connected Nets. *Generation of the Meshes.* Wood and Prize had described a procedure to investigate the possible new 2D 3-connected meshes of the zeolitic framework.[31] Here we use a method similar to generate 2D 3.4-connected meshes of $Al_3P_4O_{16}^{3-}$ layers. The meshes are generated in a hexagonal array of nodes, and each node can be connected with its six nearest neighbors (Figure 1a). Different from Wood's method, the generation of 2D 3.4-connected meshes must obey the following rules in topology: (i) There are two types of points: 3-connected point (P atom) and 4-connected point (Al atom); (ii) the same type of points cannot directly be connected according to Lowenstein's rule; (iii) the mesh must be expanded into a periodic 2D net.

In the 2D 3.4-connected nets, each node has three kinds of possible linkages, that is, connecting with three neighboring nodes (represent 3-connected point), connecting with four neighboring nodes (represent 4-connected point), and connecting with no neighboring

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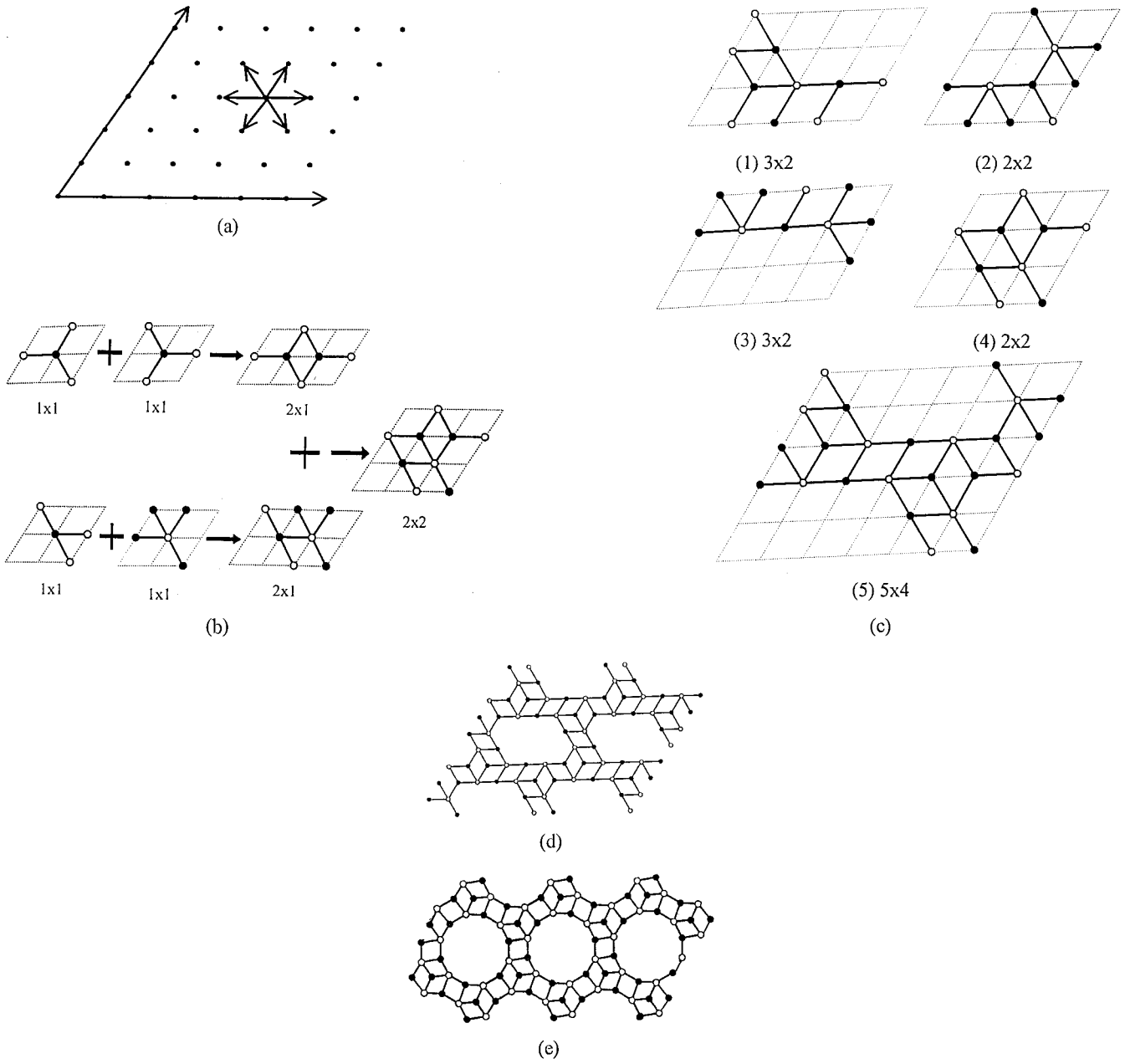

Figure 1. (a) Axial system and unit cell of nodes in mesh generation; (b) the generation of a 2 × 2 mesh; (c) the generation of a 5 × 4 mesh by combining four child meshes (1) 3 × 2, (2) 2 × 2, (3) 3 × 2, (4) 2 × 2 (in b); (d) the 4.6.12 net which is expanded from the 5 × 4 mesh in (c); (e) the relaxed 4.6.12 net.

nodes. Thus, each node may have $C_6^3 + C_6^4 + 1 = 36$ possible configurations.

To avoid repeatedly enumerating and reduce the exponential time complexity, we adopt the divide-and-conquer algorithm[32,33] to reduce the degree of combination explosion. Therefore, we could generate large sizes of meshes on the personal computer in reasonable time. The largest meshes we generated is a 8 × 8 mesh, which contains about 200 atoms including briding and terminal oxygen atoms.

In the first step, we generate the child meshes based on rules 1 and 2. The primary child meshes are 1 × 1 meshes with a total amount of 36. Bigger size child meshes can be derived from these primary child meshes. However, the two child meshes that must have self-consistent linkages can be incorporated to a bigger size child mesh. It needs to determine which two child meshes can be incorporated. We save the arrangement of the new generated child mesh for future incorporation. Figure 1b illustrates the generation of a 2 × 2 mesh.

In the second step, we incorporate the generated child meshes into a bigger periodic mesh. We divide a mesh into four parts; each part can be chosen from the corresponding child mesh sets. Each child mesh must have consistent node type and linkage in their bounds with its peripheral mesh, and the final mesh must become a periodic net. Figure 1c shows the generation of the known 4.6.12 net. By combining four child meshes, (1) 3 × 2 mesh, (2) 2 × 2 mesh, (3) 3 × 2 mesh,

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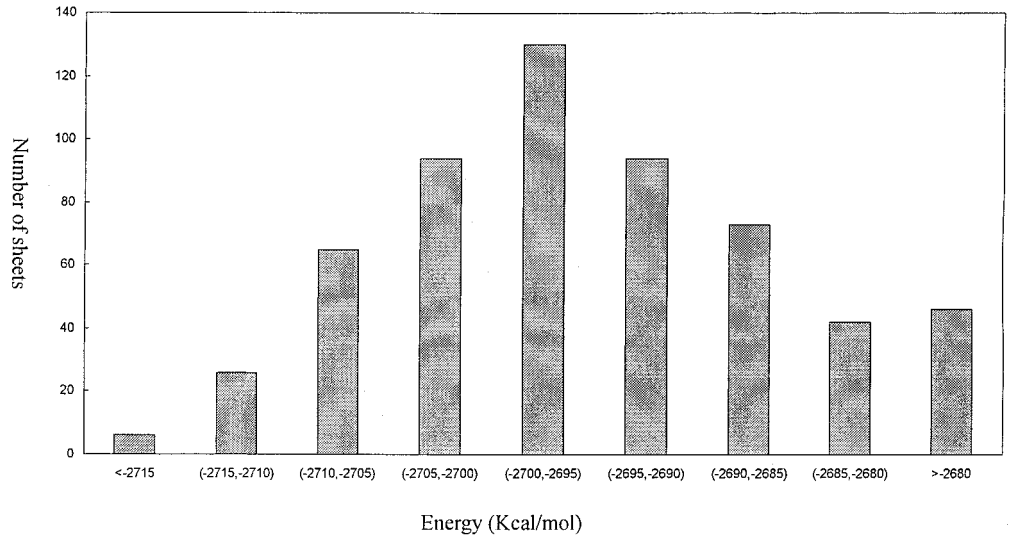

Figure 2. Energy distribution of generated 2D $Al_3P_4O_{16}^{3-}$ sheets.

and (4) 2 × 2 mesh, we get a final 5 × 4 mesh (5), which can be further expanded into the mesh of a 4.6.12 net (Figure 1d).

Identify the Same Topological Mesh. It is found that some different meshes may be chosen from the same topological sheet, even if their node configurations are different. Among the abundant meshes generated by our generation procedure, there are in fact only a few distinct topological sheets. To identify the same sheets, we adopt coordination sequences (CSQ), which is used to investigate the topological identity of frameworks and of atomic positions within a framework.[34,35] CSQ is a number sequence in which the *k*th term is the number of atoms in "shell" *k* that are bonded to atoms in "shell" $k - 1$. Shell 0 consists of a single atom, and the number of atoms in the first shell is the conventional coordination number. Coordination sequences can easily be computed by simply counting.

According to the concept of CSQ, the same topological mesh must have the same CSQ. Therefore, we can delete other meshes with the same CSQ to keep the distinct sheets. It is found that using 10 shells are enough to identify all the meshes correctly.

It is known that the CSQ can help to recognize the topological equivalent points.[35] The points having the same CSQ are the topological equivalent points. The higher symmetry a mesh has, the more nodes in the mesh that have the same CSQ. We estimate the average number of the kinds of CSQ and delete the low symmetrical meshes whose average number is close to 1.5. In this way we can delete the disordered and irregular meshes that are not likely to be synthesized.

Relax the Meshes by a Genetic Algorithm. The position of each node in the generated mesh is fixed at the lattice point, so it is difficult to recognize the polygons in the mesh. To relax the meshes, there are two kinds of parameters to be changed: one is the coordinate of all points in the meshes; another is the size and inclination of the mesh. Because these parameters may be far away from the ideal value, there are a lot of local minimums due to large ranges of parameter variation. Since conventional algorithms (i.e., gradient algorithm) often fall into the local minimum, we adopt the genetic algorithm (GA),[36−38] which provides a robust mechanism for finding the global minimum, to alter the coordinates of the points in the mesh and the shape of the mesh. GA involves the following cycles: (i) evaluate the fitness of all of the individuals in the population; (ii) create a new population by performing operations, such as crossover, fitness-proportionate reproduction, and mutation on the individuals whose fitness has just been measured; (iii) discard the old population and iterate using the new population. We combine these parameters into a string as an individual of GA, and in terms of a generated mesh we randomly generate a set of possible solutions as the initial generation. The fitness of an individual is defined as "Energy" *E*. *E* indicates the deviation between the current mesh and an ideal mesh, in which the distance of two connected points is similar in length, the angle whose vertex is the 3-connected point comes close to 120°, and the angle whose vertex is the 4-connected point comes close to 90°. Through minimizing *E*, the meshes are relaxed well so that we can investigate them conveniently. Figure 1e shows the relaxed 4.6.12 net.

Results and Discussion

After a series of computer procedures mentioned above were performed, over 500 distinct 3.4-connected meshes with periodic arrangements are generated. The 2D $Al_3P_4O_{16}^{3-}$ nets are obtained by substituting the 3- and 4-connected points in the meshes with P and Al atoms, respectively. Bridging oxygens are added between P and Al atoms, and one terminal oxygen is attached to each P atom. It is found that all the 2D nets are constructed from almost arbitrary combination of four-, six-, eight-, ten-, or twelve-membered rings.

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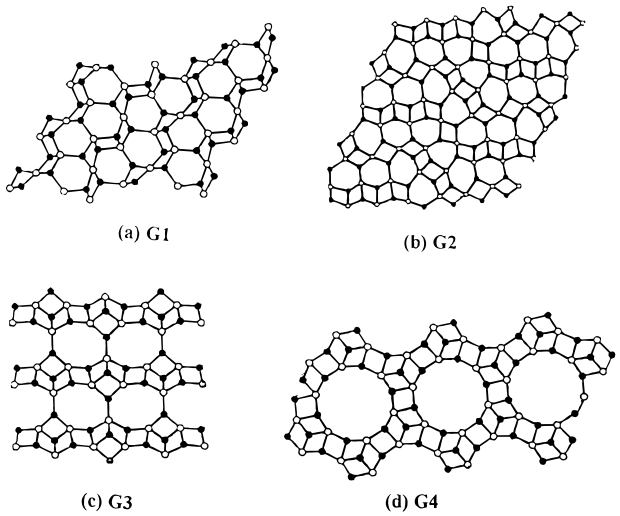

Figure 3. Generated known 2D $Al_3P_4O_{16}^{3-}$ sheets (a) G1, 4.6 net(a); (b) G2, 4.6 net; (c) G3, 4.6.8 net; (d) G4, 4.6.12 net.

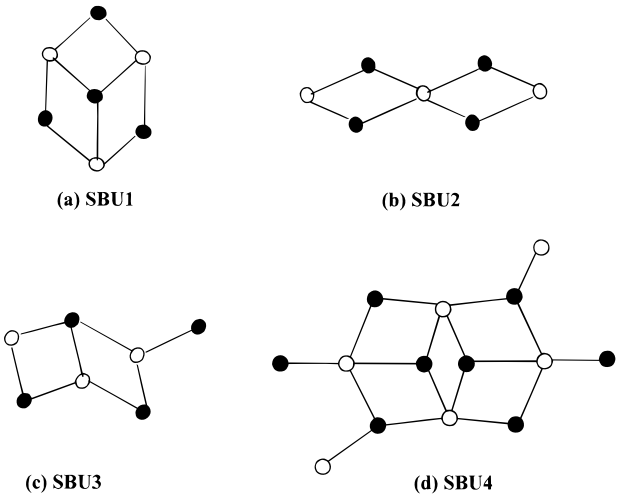

Figure 4. Some main secondary building units (SBUs) for the construction of 2D $Al_3P_4O_{16}^{3-}$ sheets (a) capped 6MR (SBU1); (b) double-diamond (SBU2); (c) branched edge-sharing double 4MR (SBU3); (d) double intergrown-capped 6MR (SBU4).

However, four-membered rings are found essential for the construction of 2D $Al_3P_4O_{16}^{3-}$ nets, as proved by previous topological analysis. To obtain energetically feasible 2D sheets, we minimize the energies of these 2D nets by calculation using the Cerius package[39] with a Burchart 1.01 force-field[40,41] (the double-bonding character of P═O is ignored here). The energy distribution is shown in Figure 2. It is found that the generated known $Al_3P_4O_{16}^{3-}$ sheets, including 4.6(a), 4.6(b), 4.6.8, and 4.6.12 nets (Figure 3a−d), possess lower energy varying from −2719 to −2705 kcal/mol. This suggests that some hypothetical nets with energy close to and lower than −2705 kcal/mol are most likely to be synthesized under certain conditions.

The hypothetical layers with lower energy are mainly classified as 4.6, 4.6.8, 4.6.10, 4.6.12, 4.6.8.12, and 4.8 nets. Some common secondary building units (SBUs) for the construction of these hypothetical 2D nets are shown in Figure 4. Figure 4a is a capped 6MR (SBU1), which has been found in the known 4.6.8[18] and 4.6.12[10] nets. The double-diamond SBU in Figure 4b (SBU2) has also been found in the known 4.6(a) net.[15] Figure 4c is a branched edge-sharing double 4MR (SBU3), which has been found in our newly synthesized 4.6(b) net.[21] Figure 4d is a double intergrown-capped 6MR (SBU4). A similar SBU has been found in a known 2D layer with $Al_2P_3O_{12}^{3-}$ stoichiometry.[25]

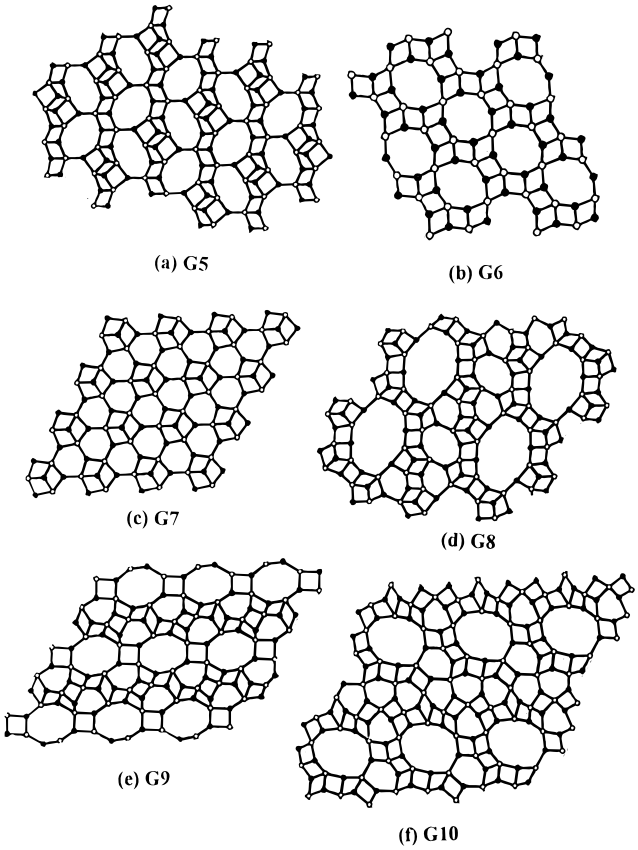

Figure 5. Some typically hypothetical 2D $Al_3P_4O_{16}^{3-}$ nets: (a) G5; (b) G6; (c) G7; (d) G8; (e) G9; (f) G10.

Table 1. Energies and Their Components of Some Generated Sheets (kcal/Mol $Al_3P_4O_{16}$)

sheet no.	bonds energy	van der Waals energy	electrostatic energy	Urey−Bradley energy	total energy	note
G1	−2672.350	−13.636	−39.027	12.277	−2712.736	4.6a[15]
G2	−2672.350	−14.819	−39.231	21.427	−2704.973	4.6b[21]
G3	−2672.875	−13.234	−38.845	11.021	−2713.933	4.6.8[18]
G4	−2673.160	−12.238	−39.566	6.286	−2718.678	4.6.12[10]
G5	−2673.565	−15.364	−37.529	2.920	−2723.538	4.6.8
G6	−2670.225	−14.090	−39.753	20.447	−2703.621	4.8
G7	−2672.500	−13.059	−39.603	11.008	−2714.154	4.6
G8	−2673.175	−14.479	−39.764	6.667	−2720.751	4.6.8.12
G9	−2672.500	−12.892	−38.461	15.644	−2708.209	4.6.8
G10	−2672.475	−14.240	−38.613	14.144	−2711.184	4.6.10

Figure 5 shows some typically hypothetical 2D $Al_3P_4O_{16}^{3-}$ nets with minimized energy similar to or lower than the known 2D nets. The calculated energies and their components are listed in Table 1. The calculated T−O bond lengths and O−T−O bond angles are listed in Table 2 (the P═O double-bonding character is ignored in the calculation). It should be noted that the calculated energy and bond lengths and bond angles of generated known 2D nets are in agreement with those

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Table 2. Calculated Bond Length and Bond Angle Range of Some Generated 2D Sheets

sheet no.	bond length range (Å)		angle degree range (deg)		
	Al−O	P−O	T−O−T	O−P−O	O−Al−O
G1	(1.712,1.763)	(1.517,1.536)	(138.809,154.213)	(105.380,110.179)	(106.212,114.914)
G2	(1.727,1.756)	(1.519,1.532)	(134.590,153.697)	(107.352,110.693)	(104.325,110.830)
G3	(1.722,1.773)	(1.514,1.544)	(134.932,151.936)	(105.836,112.316)	(106.085,112.190)
G4	(1.729,1.752)	(1.524,1.536)	(138.853,144.466)	(106.777,109.450)	(107.493,111.170)
G5	(1.717,1.742)	(1.519,1.532)	(138.146,156.505)	(105.502,111.821)	(106.739,110.431)
G6	(1.714,1.750)	(1.516,1.542)	(139.100,160.875)	(105.048,109.759)	(104.778,112.872)
G7	(1.728,1.774)	(1.527,1.534)	(136.068,156.796)	(104.616,112.121)	(104.212,110.644)
G8	(1.719,1.761)	(1.511,1.531)	(133.473,154.590)	(106.412,113.015)	(105.122,111.918)
G9	(1.716,1.760)	(1.516,1.528)	(138.371,157.578)	(105.922,110.814)	(102.166,112.357)
G10	(1.713,1.765)	(1.516,1.549)	(136.287,156.519)	(106.474,111.888)	(103.988,111.735)

of known 2D nets from experimental structural data. This further proves that our generated $Al_3P_4O_{16}^{3-}$ networks are reasonable structures.

G5 is a 4.8 net with the lowest energy (−2723 kcal/mol) among the generated 2D nets. Its structure is constructed from double intergrown-capped 6MR SBUs (SBU4). The 2D network contains two types of orientated 8MRs both elliptical and circular in shape (Figure 5a). The Al−O bond lengths are in the range of 1.717−1.742 Å and the O−Al−O bond angles are in the range of 106.7−110.4°. The P−O bond lengths vary from 1.519 to 1.532 Å and the O−P−O bond angles vary from 105.5 to 111.8°. These bond lengths and bond angles are typical for the aluminophosphate materials.

G6 (Figure 5b) belongs to the 4.8 net, which is constructed from double-diamond SBUs (SBU1). Its structure contains regular 8MRs, which are wrapped by a series of undulating edge-sharing four-ring chains. This type of chains has been observed in 3D JDF-20: $Al_5P_6O_{24}H^{2-}$ (an AlPO with 20MR channels)[42] and AlPO−HAD: $Al_4P_5O_{20}H^{2-}$ (an AlPO with intersecting 12- and 8MR channels).[43] The calculated bond lengths of Al−O and P−O are in the range of 1.714−1.750 and 1.516−1.542 Å, respectively. The O−Al−O and O−P−O bond angles are in the range of 104.8−112.9°and 105.0−109.8°, respectively.

G7 is featured by a series of capped 6MR chains (Figure 5c). They are further connected to form 6MRs in the sheet. Removing the capped phosphate groups, the 2D net of G7 is resemblant to the 6^3 net of 3-connected 2D net proposed by J. V. Smith.[44] Its bond lengths and bond angles are listed in Tables 1 and 2, which are normal for AlPO materials.

G8 contains four-, six-, eight-, and twelve-membered rings in the 2D net (Figure 5d). The capped 6MRs connected through four rings form a series of chains. These chains are further connected with each other to form six-, eight-, and twelve-membered rings. The bond lengths and bond angles of G8 are typical for AlPO materials.

G9 (Figure 5e) is a 4.6.8 net constructed from the branched double four-ring SBUs (SBU3). The 2D net contains regular eight-membered ring systems connected through four rings, and a series of undulating edge-sharing four-ring chains. Calculation results show that G9 also has reasonable T−O bond lengths and O−T-O bond angles as compared to existing AlPOs.

G10 is a 4.6.10 net (Figure 5f). Until now, no 2D AlPO sheets containing ten rings are reported. G10 contains a regular ten-membered ring system. Branched double edge-sharing four rings (SBU3) are found as SBUs. The calculated energy of G10 is similar to that of the known 2D sheets, and the calculated bond lengths and bond angles also are in good agreement with the known AlPO compounds. This suggests that this type of 2D net is possible to be synthesized.

Above we have shown some hypothetical 2D $Al_3P_4O_{16}^{3-}$ nets that are possible to be synthesized. Our further work is being focused on how to select the synthesis conditions, especially on how to choose the template agents directing the assembly of the inorganic layers. We have summarized some regularities of the interaction, that is, H-bonding characters, between the template agents and inorganic layers. On the basis of the discovered rules, we are focusing on rationalization of the synthesis work.[27]

Conclusion

This work provides a rational way to systematically enumerate the 2D layered aluminophosphates with $Al_3P_4O_{16}^{3-}$ stoichiometry. Energy calculation indicates that many more hypothetical 2D nets may yet be synthesized. We further discussed the fundamental structural features of 2D $Al_3P_4O_{16}^{3-}$ nets. This will further assist us in the design of synthesis routes through choosing suitable template agents for the specific materials.

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