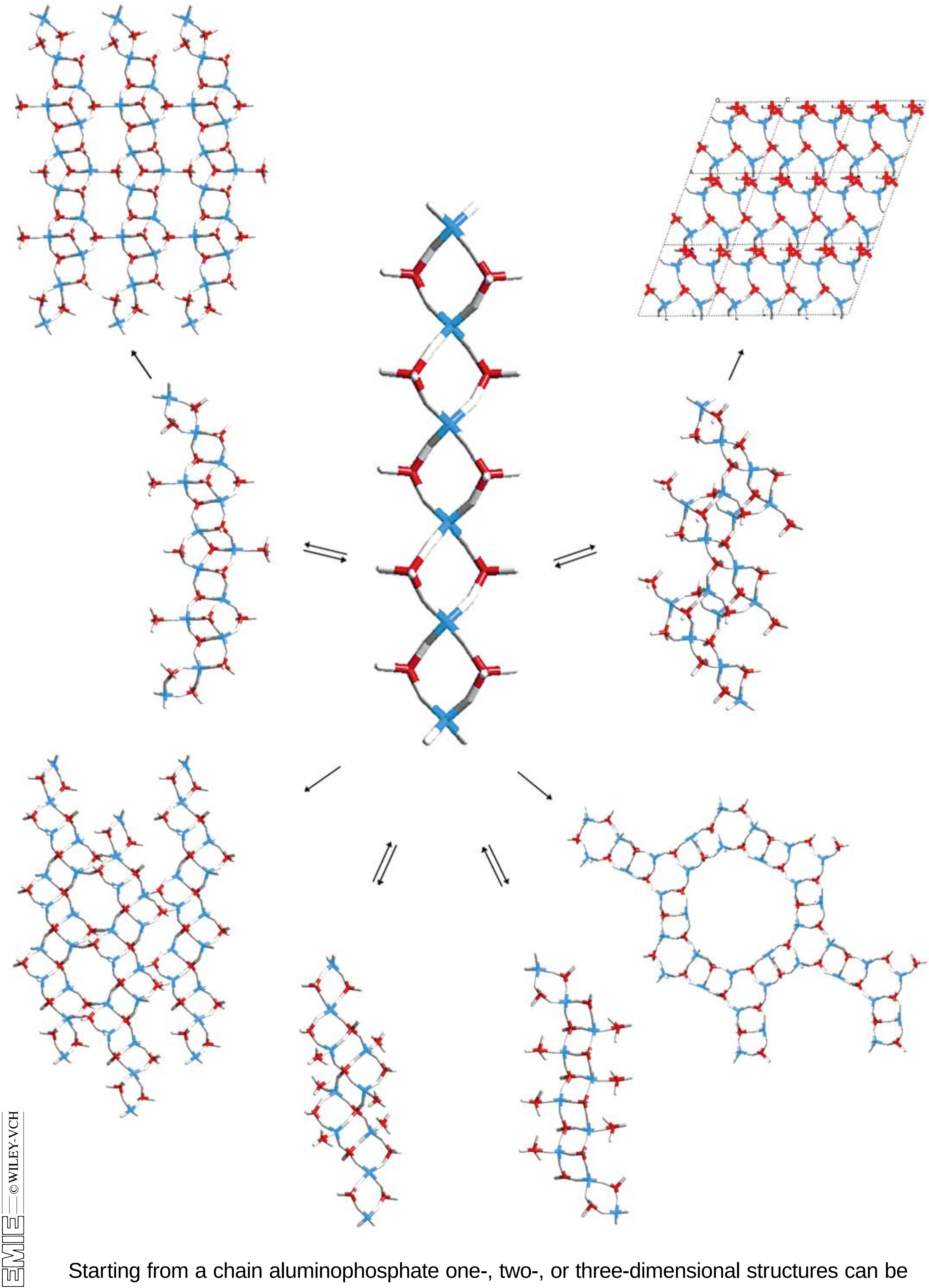

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Starting from a chain aluminophosphate one-, two-, or three-dimensional structures can be formed by a hydrolysis-condensation self-assembly pathway (oxygen: white, phosphorus: red, aluminum: blue).

A New Model for Aluminophosphate Formation: Transformation of a Linear Chain Aluminophosphate to Chain, Layer, and Framework Structures

Scott Oliver, Alex Kuperman, and Geoffrey A. Ozin*

Self-assembly pathways of inorganic compounds to form microporous framework materials continues to be a topic under intense debate. The current view of the mode of formation of this class of materials is constantly evolving, and is in many cases different for each framework composition, which now spans most of the periodic table. For aluminophosphates, several models have been proposed, some of which are closely related to those of the aluminosilicates. In this review we discuss the contemporary models for the formation of aluminophosphates and a new model, developed in our laboratory, which accounts for the formation and structures of a family of one-dimensional (1D) chain, two-dimensional (2D) porous layer, and three-dimensional (3D) open-framework aluminophosphate materials. The building block for this model is a linear chain aluminophosphate, which is the first species to crystallize from the synthesis system. Structural, stereochemical, charge, and chemical information present in the chain precursor can be transcribed, under a particular set of experimental conditions, to allow the formation of other chain types through a hydrolysis–condensation self-assembly pathway. The sibling aluminophosphate chains can be crystallized from the system or condense further to more complex porous layer or open-framework aluminophosphate structures. Other solute species, such as aluminum oxide double octahedra or fluorinated aluminum species, can be incorporated into the final structures by a chain-encapsulation process. This construction paradigm represents a new way of rationalizing aluminophosphate structures and their formation.

Keywords: aluminum · phosphorus · solid-state chemistry · zeolite analogues

1. Introduction

The large number of synthetic and naturally-occurring inorganic layered and open-framework materials constitutes an important area of materials chemistry.[1–3] Within the domain of aluminophosphate compositions, a large number of synthetic microporous framework materials have been documented since their initial discovery by Flanigen et al.[4, 5] A series of aluminofluorophosphate layers[6, 7] and frameworks[8–12] has also been discovered in the last several years.

Aluminophosphate frameworks are built of alternating, corner-sharing phosphorus(V) oxide and aluminum(III) oxide tetrahedra. In some materials aluminum can be four-, five-, and/or six-coordinate. While a number of dense-phase and small-pore aluminophosphates occur as natural minerals, the majority of known structure types are synthetic. Their preparation typically entails hydrothermal treatment of an aqueous gel containing templating amine or quaternary ammonium species. Some structures can only be obtained with a specific template, such as JDF-20,[13] which can only be synthesized with triethylamine as template. In contrast, others such as $AlPO_4$-5[14] can be made in the presence of any of more than twenty-three amines ($AlPO_4$-n denotes a porous aluminum phosphate framework). Many of the frameworks contain a single channel system, in which the walls of the channel comprise six-rings of T atoms (T = alternating Al and P centers, bridged by oxygen), analogous to the double-pyroxene chains of $AlPO_4$-tridymite.

Recently the number of reports on new chain[15–20] and layer[19–29] aluminophosphate structures has increased steadily. Many of these materials, including those obtained in our laboratory, are prepared by nonaqueous synthesis procedures.[15, 17–19, 21–23, 27] The discovery of these new materials has been attributed to the drastically different properties of a nonaqueous system compared to an aqueous system.[24, 30, 31] In spite of the large number of organic templates that may be employed in the synthesis of these new chain and layer aluminophosphates, the only established compositions for

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layered structures to date are either $[Al_3P_4O_{16}]^{3-}$ or $Al_2P_3O_{12}H_x]^{(3-x)-}$ ($x = 1-2$), where many of these inorganic layers possess the same architecture.

Similarly, there are only four known chain aluminophosphate structures containing tetrahedrally coordinated aluminum centers. Two are isostructural and of stoichiometry $[AlP_2O_8H_x]^{(3-x)-}$ ($x = 1$, 2),[15,16] while the remaining two, UT-2[19] and UT-7[20] (University of Toronto, structure numbers 2 and 7), are isostructural and have the same formula, $[Al_3P_5O_{20}H]^{5-}$. The latter differ in their organic template species, namely cyclopentylammonium for UT-2 and cycloheptylammonium for UT-7. Two chain aluminophosphates are also known that contain exclusively octahedrally coordinated aluminum centers. The compound with a $[Al(H_2PO_4)_3]$ chain structure described by Kniep et al. was prepared by the evaporation of a concentrated, viscous solution,[17] while, more recently, Attfield et al. achieved the hydrothermal synthesis of an $[Al(PO_4)_2(OH)]^{4-}$ chain.[18]

A number of soluble aluminophosphate and aluminophosphonate monomeric complexes have also been reported; for instance, the tetramethylammonium salt of the trimeric diphosphatoaluminate complex was reported in 1969.[32] Cassidy et al. later isolated an $[Al_4(PO_4)_4]$ cubic complex from ethanol, in which each aluminum atom resides in an octahedral environment, connected to three phosphate ions of the cube corners and three ethoxy groups.[33] Kniep et al. also isolated a pentameric $[Al_2(H_2PO_4)_3](PO_4)$ cluster from a concentrated, viscous solution.[34] In 1996 Mason et al. prepared two different alkylaluminophosphate complexes, one of which contains a $Al_2O_4P_2$ four-ring. The other complex has a cubic $Al_4O_{12}P_4$ inorganic core, in which the nonbridging vertices of the aluminum and phosphorus tetrahedra are capped by *tert*-butyl and trimethylsiloxy groups, respectively.[35] Yang et al. also prepared a related cubic aluminophosphonate complex, in which the phosphorus centers carry terminal *tert*-butyl groups.[36] This research has also led to the discovery of related soluble phosphates and phosphonates containing boron[37,38] and gallium[39,40] centers.

In recent years significant progress has been made towards the development of mechanisms of formation of zeolites and aluminophosphate molecular sieves. Some models account for the final framework structures by postulating various building blocks, such as four-rings, six-rings, and other small secondary building units (SBUs; the primary building units are the simple monomeric polyhedra), similar to those believed to be involved in zeolite formation.[3a, 10] More recently, the role of the organic template has been discussed by Lewis et al.[41, 42] Their calculations were performed on aluminophosphate, metal-substituted aluminophosphate, and zeolite frameworks. Davis et al. have also made thermochemical calculations of both microporous and dense-phase aluminophosphates.[43] These results have led to a better understanding of the synthesis of aluminophosphate framework structures.

Other, older models are based on chain species that run through the structure parallel to the main channel system, such as the narsarsukite, double-crankshaft[44, 45] and triple-crankshaft chains.[46] Although these species can be identified in the frameworks, there is no direct evidence that they participate in the assembly process. Furthermore, double- or triple-crankshafts are rather complex and are difficult to envisage as stable species in solution. It has also been argued that pseudoboehmite is intercalated by polyphosphate, which forms an amorphous aluminophosphate layer either directly[47, 48] or via molecular species that are present in the aluminophosphate solution.[49, 50] The disordered layered material is proposed to undergo a solid-state transformation to give the crystalline framework. Chain tectons and models dealing with their transformation to give more complex chains or layers have not been reported. Only the mode of formation of 3D frameworks has been discussed previously.


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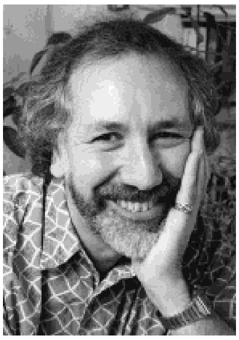
G. A. Ozin

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The starting materials generally employed in the synthesis of aluminophosphates are phosphoric acid and an aluminum oxide in the form of pseudoboehmite or alkoxide.[3a] The mineralization of alumina by phosphoric acid is a well-documented process because of its relevance to soil science.[51, 52] Generally, phosphate ions form covalent bonds through bridging oxygen atoms to aluminum atoms by replacing hydroxide ions and breaking Al-O-Al linkages in the mineral. Through dissolution of the mineral structure, aluminophosphate molecular species are leached into the supernatant. Such species have been detected experimentally and their structure has been modeled.[53–58]

The next step in the formation of aluminophosphates is less clear. There is evidence that "aggregation polymers" exist for metal phosphates; the most studied are the aluminophosphate polymers in viscous gels.[59–63] These aggregation polymers are stable in acidic medium, and precipitate on rendering the medium alkaline.[60] The materials were found to be amorphous upon precipitation. The aggregation polymers have also been suggested as a "transition between the heteropoly acids and soluble complexes."[61] Chain species tend to form as the Al:P ratio of the solution is raised above 1:1;[61–63] for instance, Kniep et al. isolated large crystals of the $Al(H_2PO_4)_3$ chain structure by evaporation of a concentrated (Al:P = 1:5) solution.[17]

The stability of an unbranched chain aluminophosphate is also supported by the well-known fact that polyphosphates and ring metaphosphates avoid branching owing to the reduced negative charge of branching $PO_{2.5}$ groups over that of the negative PO_3^- groups of the chain, rendering branching points highly susceptible to removal by hydrolysis.[64] A similar tendency to avoid chain branching may occur for the aluminophosphates; thus, all higher molecular weight solution species may exist as nonbranched, 1D chains prior to their precipitation. This would also prevent the formation of condensed phosphates instead of aluminophosphate species. It is important to note that acidic starting conditions are also required for the synthesis of aluminophosphate molecular sieves; the pH value shifts into the range for alkaline compounds as the synthesis proceeds. Based on these observations, one can conclude that in the synthesis of aluminophosphates, it is initially necessary to build a concentration of aluminophosphate polymeric species in solution, which then self-assemble into various structures. Certainly, the work on aggregated aluminophosphate polymers clearly indicates that a polymeric aluminophosphate chain should be considered as the precursor in the formation of chain, layer, and framework aluminophosphates.

Here, we propose a new self-assembly model for the formation of aluminophosphates, in which a progenitor chain is introduced, which can account for the structures of 1D to 3D aluminophosphates and whose existence is supported by direct experimental evidence. Examples are given of the hydrolysis–condensation processes that can occur on the parent chain. These are only a few of the possible chain types that may be constructed in this way. We have also proposed a nomenclature scheme to denote a particular chain type, and it is hoped that this model will contribute to a greater understanding of the mode of formation of chain, layer, and framework aluminophosphates.

2. Discussion

2.1. The Parent Chain

The first structure that we obtained in our synthetic work using the tetraethylene glycol (TEG) solvent system was that of a 1D chain compound containing charge-balancing triethylammonium ions. This structure proved to be identical to that reported by Jones et al. when they used 2-butanol as solvent.[15] From the same TEG system we also obtained the anionic framework structure JDF-20, which contains triethylammonium ions in its channels; this had also been previously reported by Jones et al.[13] Inspection of the JDF-20 framework showed it to be composed of linear chains, which are linked to chains of a different type.[31] We proposed that the latter chain type was derived from hydrolysis and condensation of the linear aluminophosphate chain.[65] Arguably, the chain and JDF-20 structures co-crystallize and one phase grows in at the expense of the other.

Many other structures crystallize in the TEG–triethylamine system when water is used as an additive reagent.[24, 31] These new structures were also envisaged to be built of chain-building blocks derived from the parent chain. Structural studies of aluminophosphates prepared in other systems allow their architectures to be rationalized by similar chain-building blocks derived from the parent chain. We developed a scheme according to which many different types of chains can be formed by performing hydrolysis and condensation reactions on the parent chain.[65] However, the existence of this parent chain remained nebulous until one of the hypothetical crystal structures of this model was confirmed experimentally.[19, 20] Significantly, this 1D chain structure thermally transforms to give a 2D porous layer structure that we had previously isolated in the same synthesis system.[19] This appears to be one of the hitherto unrecognized assembly pathways for aluminophosphate layers and frameworks.

The parent chain is therefore the linear chain structure that crystallizes in the TEG–triethylamine system.[15] It consists of corner-sharing Al_2P_2 four-rings bridged at the aluminum(III) centers; two doubly bridging phosphates occur in each four-ring (Figure 1a). The parent chain only crystallizes for a specific set of templates, reagent concentrations, and reaction conditions, which explain its absence in other systems. The linear chain is likely the most stable polymeric aluminophosphate species. It has a simple structure, and contains only one type of aluminum(III) and phosphorus(V) site. The identical arrangement of orthogonally organized four-rings exists in other mixed oxides, such as the borosilicate chains of the mineral garrelsite,[3] and a zinc phosphate chain structure.[66] Importantly, the parent chain structure has also been isolated in an aqueous system, in which ethylenediamine was used as template.[16] This shows that the structure can also form in aqueous systems, which is an essential ingredient of the present model.

The tetrahedrally coordinated aluminum centers of the parent chain are fully coordinated to phosphate groups. This arrangement is similar to that found in homopolyoxo ions and heteropolyoxo ions. For example, the central aluminum atom in the Keggin ion is tetrahedrally coordinated, while the outer

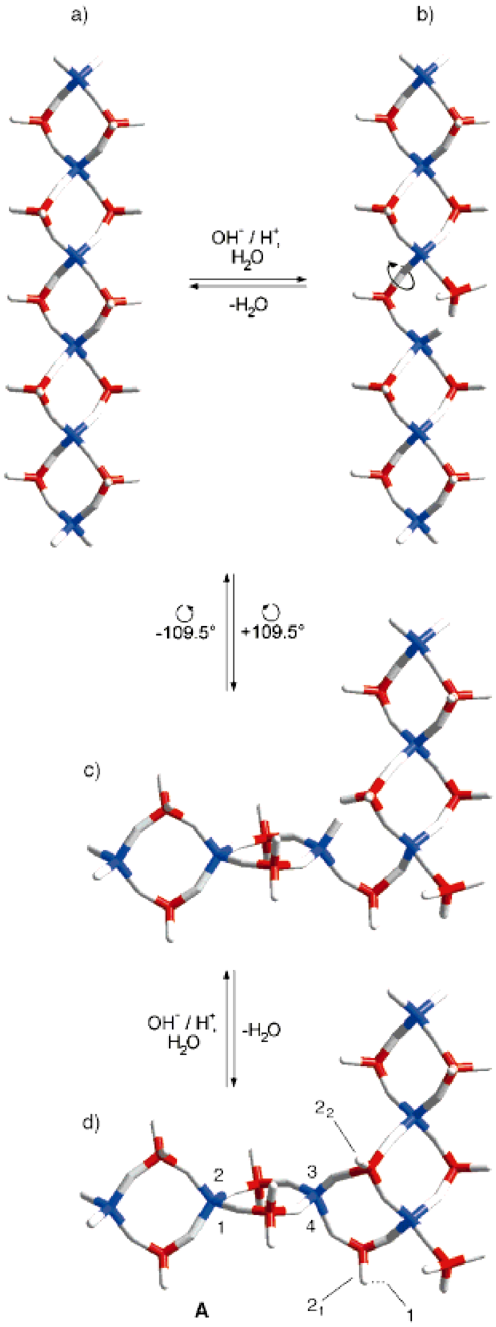

Figure 1. The transformation of the parent chain to give edge-sharing four-rings and terminal $P(O_{Al})(O)_3$ phosphate groups. All steps are reversible, as indicated by the equilibrium arrows. a) Parent chain. b) Ring-opening hydrolysis results in an AlOH group and a terminal phosphate group. c) Rotation about the remaining Al-O-P linkage of the chain brings the AlOH group in the vicinity of a POH group on the adjacent four-ring of the chain. d) Condensation and regeneration of the catalytic water molecule to define two edge-sharing four-rings (structure **A**; for numbering see text). Color scheme (same for all figures): Oxygen: white; phosphorus: red; aluminum: blue.

aluminum atoms are all octahedrally coordinated.[67] Similarly, phosphate groups display a tendency to doubly or triply bridge metal centers in inorganic chain structures, such as molybdenum phosphates[68–70] and vanadium phosphates[71] as well as in chain-building units of higher dimensionality structures.[72] The same is true for vanadium arsenates.[73] The preference of Al^{III} to be surrounded by four phosphate groups is also seen in molecular aluminophosphate complexes, in which one aluminum atom is coordinated to four phosphates groups.[74] It is possible that this type of monomeric unit is the precursor to the parent chain and is the species that is first mineralized from the starting materials.[74]

2.2. Chain-to-Chain Transformations

The parent linear chain is a metastable product that in solution can undergo dynamic hydrolysis of the Al–O and P–O bonds.[60–63] Even under predominantly nonaqueous conditions this will occur, as water will always be present in sufficient amounts. Depending on the pH, acid or base hydrolysis is expected to cleave the Al–O and P–O bonds, and terminal AlOH and POH groups are thereby formed (Figure 1b). Since polymeric aluminophosphate chains in solution are expected to be highly flexible, particularly at the elevated synthesis temperatures, rapid rotation and bending motions occur about the unhydrolyzed Al-O-P linkage (Figure 1b). Rotation would bring the AlOH and POH groups closer together (Figure 1c), allowing intra-chain condensation to occur with the loss of water (Figure 1d). In this way, two corner-sharing four-rings are transformed into two edge-sharing four-rings. Note that the reverse process is also likely, and is indicated by the equilibrium arrows for each step. A terminal phosphate group that is located at the aluminum atom common to the edge-sharing four-rings can remain on, or be cleaved off the chain by hydrolysis, allowing another degree of freedom for possible transformation pathways.

If the process shown in Figure 1 proceeds in the forward direction, the transformation is expected to continue down the chain backbone, for example, to the next four-ring of the parent chain. There are now several choices for the third four-ring to connect to the first two (Figure 2). Each Al-O-P linkage in the next four-ring, labeled 1 through 4 (see Figure 1d), has an equal chance of becoming hydrolyzed. Hydrolysis at sites 3 or 4 simply leads to an open-chain type (see below). If the ring is opened at site 1, rotation around the remaining oxygen bridge will bring the resulting AlOH group only within the proximity of the POH group also labeled 1. (Note that in Figure 1d, the POH group 1 is hidden behind the POH group 2_1.) The third four-ring thereby connects to form a new section in which the three edge-sharing four-rings define a "*cis*" conformation (Figure 2a).

Alternatively, for hydrolysis at site 2, rotation can bring the AlOH group close to one of two hydroxy groups, labeled 2_1 and 2_2 (Figure 2b and 2c, respectively). Rotation in one direction (i.e., +109.5°) connects the chain onto phosphate group 2_1, and a section in which all the edge-sharing four-rings are "*trans*" to each other is formed (Figure 2b). Rotation in the other direction (i.e., –109.5°) results in condensation to phosphate group 2_2, and gives a "zigzag" chain section (Figure 2c). Subsequent four-ring "foldings" can be envisaged to continue down the chain, leading to an infinite chain with a new connectivity. For the "*trans*" chain, the process can continue down the chain without hindrance (Figure 3a). Similarly, the zigzag chain can readily be formed (Figure 3b). In the case of the "*cis*" chain, however, the chain must bend

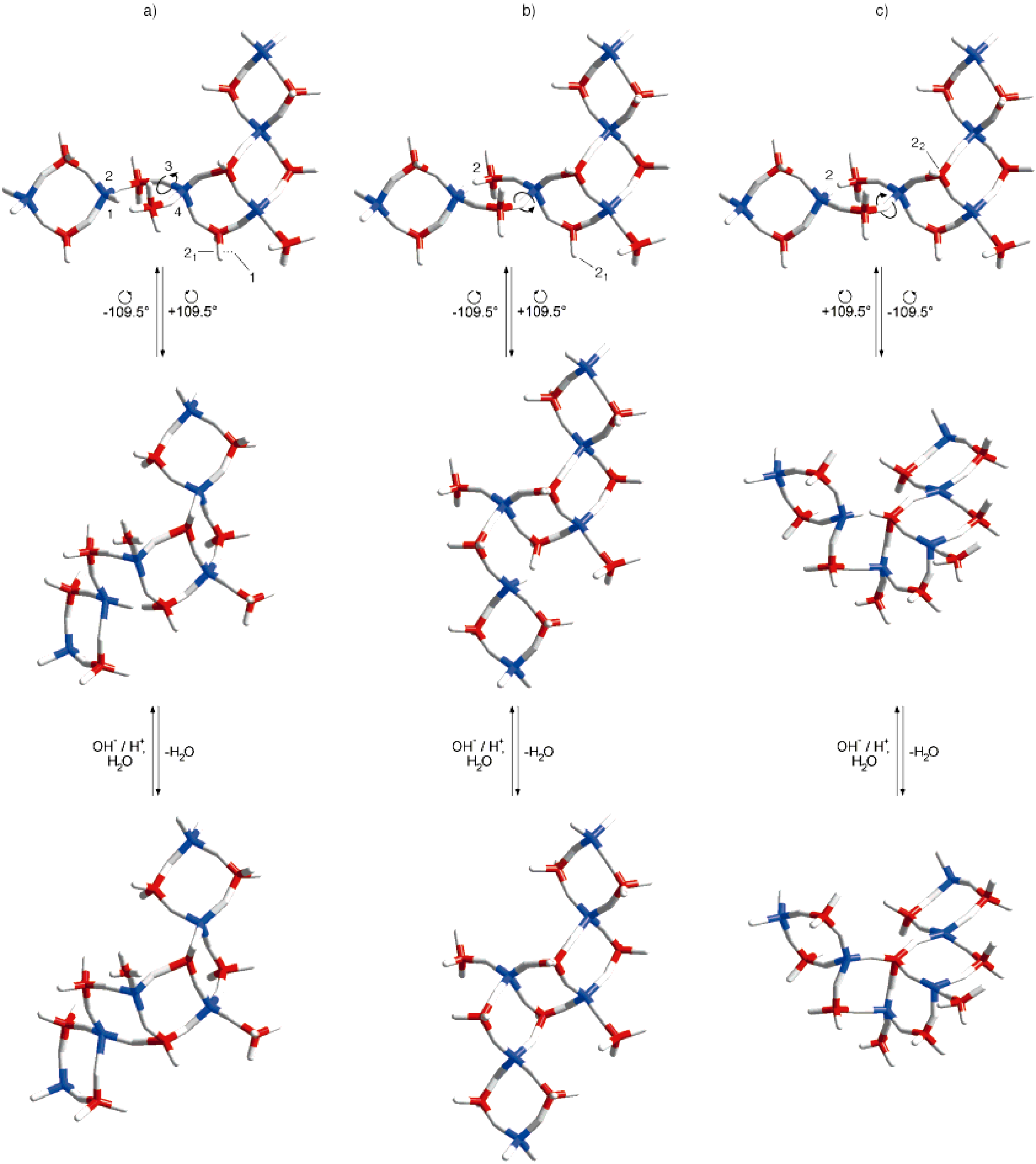

Figure 2. The next step in the transformation of the parent chain (after the formation of **A**) to form three edge-sharing four-rings. In each case the hydrolysis is followed by a rotation and a condensation. a) Formation of a "*cis*" section: ring-opening at position 1 and connection of the resulting AlOH group to the POH group 1. b) Formation of a "*trans*" section: ring-opening at position 2 and connection to the POH group 2_1. c) Formation of a "zigzag" section: ring-opening at position 2 and ring-closure at the POH group 2_2.

back in the opposite direction to avoid folding back onto itself. This leads to a chain with an alternating "*cis*–*trans*" arrangement (Figure 3c). An infinite connectivity scheme of this type would be equivalent to the double-crankshaft chain that has been previously described,[44, 45] except that in the present case, terminal phosphate groups are present on each aluminum atom. However, as will be seen, only small sections of the "*cis*–*trans*" chain type are necessary to rationalize aluminophosphate formation. With careful consideration of the means by which the ring-opening and ring-closing process propa-

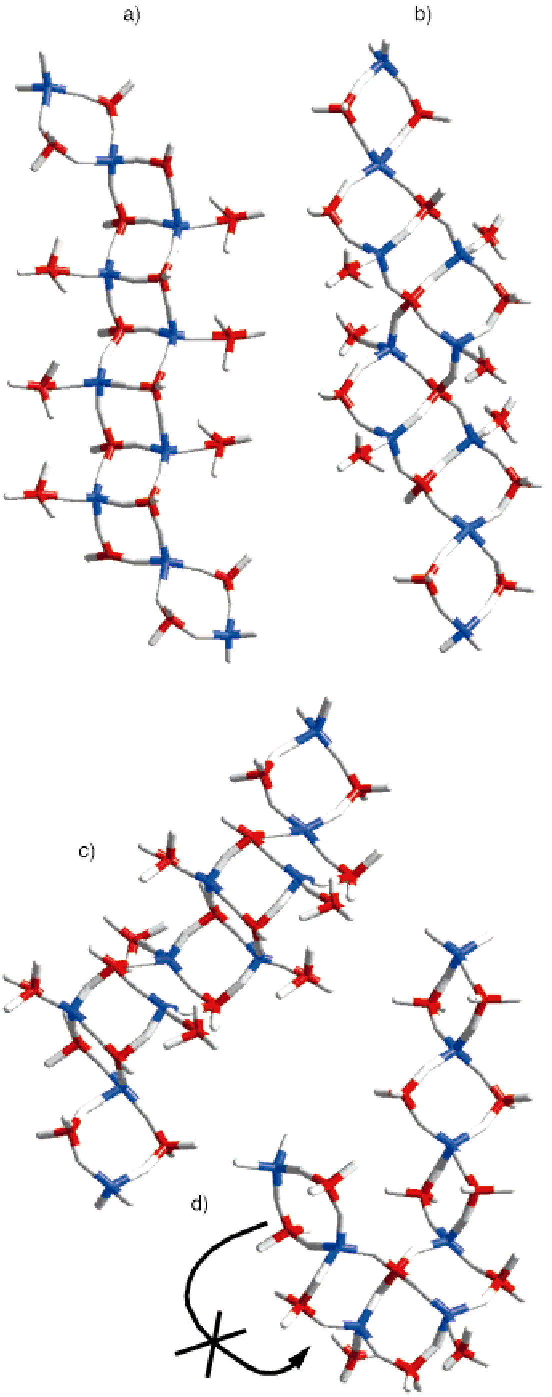

Figure 3. Extended sections of the chain types given in Figure 2. The terminal phosphate groups have been retained on each aluminum atom in these examples. The original connectivity on the end of the sections to the parent chain has also been shown for emphasis (as has been done for all the figures). a) A *trans* chain section, $(T_P)_7$; b) a zigzag chain section, $[Z(3,3)_P]_7$; c) an alternating *cis – trans* chain section, $(C_P)_7$; d) the zigzag chain given in Figure 2c. Hydrolysis of the next four-ring would not allow connection to the side necessary for a zigzag chain with two four-rings per leg. For nomenclature see Table 1.

gates down the axis of the parent chain, it becomes evident that for the zigzag chain, there must be an odd number of four-rings per leg (Figure 3d).

There are many other degrees of freedom for transformations of the parent chain by this process. For example, corner-sharing four-rings can be skipped in the process and remain intact (Figure 4a – e). Another example involves only ring-opening of the four-rings, resulting in an "open" chain intermediate as previously mentioned (Figure 4a). Further, each resulting chain type in principle represents an infinite family, since the different chain sections can be of any length, such as those shown in Figures 4b and 4c. Combinations of these processes can also occur on a single chain, allowing an unlimited number of mixed chain types; one example is shown in Figure 4e. The chains displayed in Figure 4 are but a few examples of the large number of possibilities. Additional intrachain condensation of a transformed chain can also occur, which results in, for example, phosphate-capped six-rings connected through four-rings (Figure 4f), or the connection of sections of five edge-sharing four-rings to sections of three corner-sharing four-rings (Figure 4g; this example will be important later). We will show that intrachain condensation and the formation of a chain with capped six-rings leads to many layer and framework aluminophosphates. Computer modeling studies show all chain types have high conformational stability. All tetrahedra remain only slightly distorted, as found in aluminophosphates, and bond angles and lengths need not be changed beyond their energetically accessible limits.[75]

With such a large number of possible chain types, we have introduced a nomenclature scheme, which is summarized in Table 1. Only the repeat unit of a particular chain need be described, and each section of the repeat unit is given a specific label for chain type, and a subscript for its length in terms of the number of aluminum atoms or four-rings. In this way, any chain type may be labeled. Examples of this nomenclature scheme are given throughout the figure captions.

Although the chain transformations can be viewed as a chain "zipping" process, it is more likely that they occur simultaneously or in short succession, along the entire length of the chain. It is possible that they happen during the short synthesis time scales that are sufficient for many aluminophosphate materials; for instance, the high-temperature or microwave synthesis of $AlPO_4$-5 only requires a few seconds.[76, 77] It should also be kept in mind that although chain transformations, such as those shown in Figures 1 – 4, seem complex, they only involve a very small number of operations per asymmetric unit.

The structure of polymeric UT-2, which we characterized in the TEG – cyclopentylamine system,[19] is in fact the chain structure shown in Figure 4g right. This is significant because we had previously hypothesized this chain to exist, and have now isolated what appears to be a "missing link" in the chain mechanism. As expected, the singly bridging, triply terminal $P(O_{Al})O_3$ phosphate groups reside on the edge-sharing four-rings of the *cis – trans* chain sections. The only other aluminophosphate crystal structure containing a singly bridging phosphate group is that of the monomeric $Al(PO_4)_4$ cluster previously mentioned.[74] It seems that a kinetic product has been trapped, in which the typically unstable terminal phosphate groups interact with those of other chains, thereby locking in the metastable structure. Even more surprising is that this structure, in which the chains are arranged into layers, undergoes a thermally induced solid-state transforma-

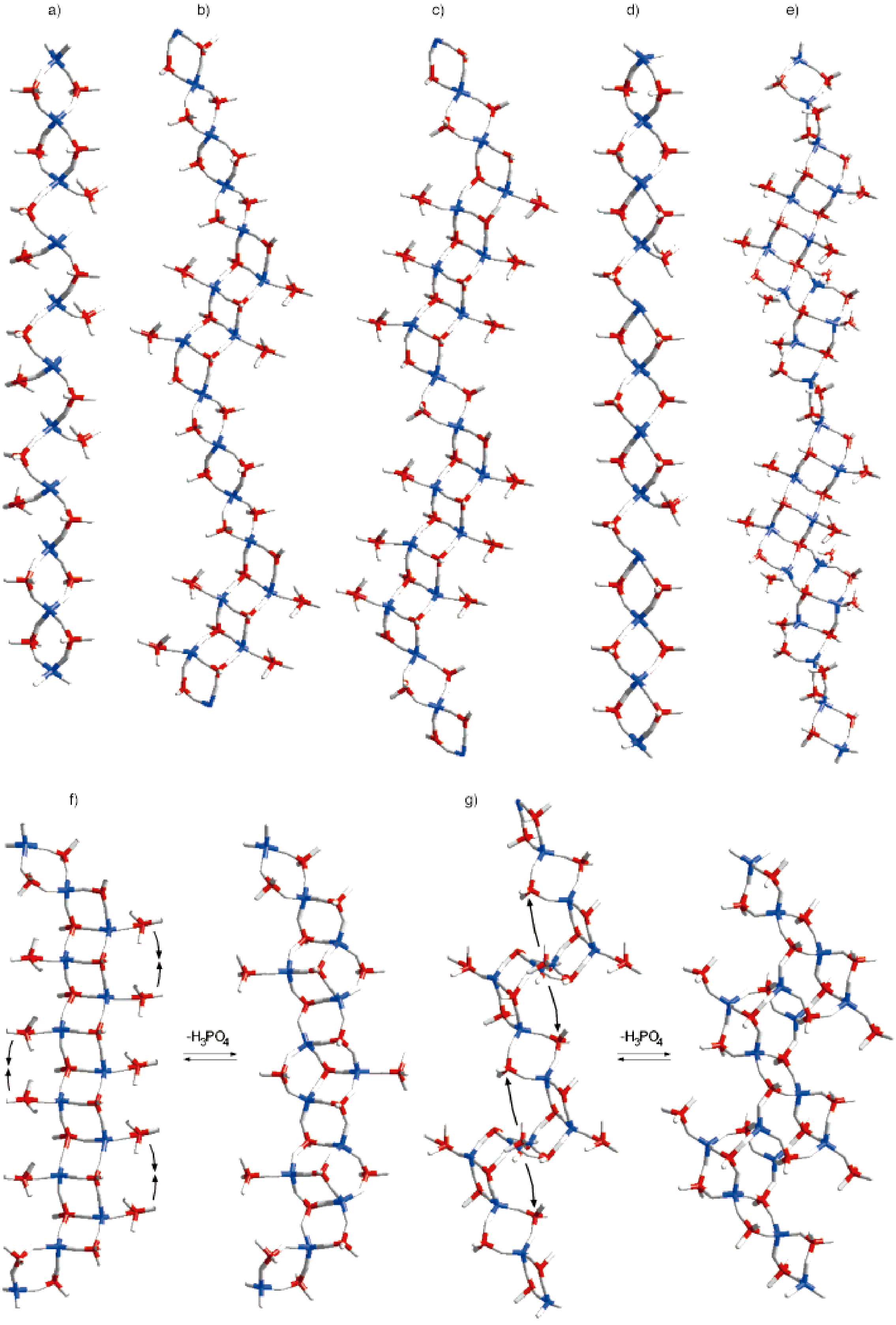

Figure 4. More examples of possible chain types; sections of varying length are displayed. a) A partially opened chain, $\diamond_2(O_P)_2$. b) A partial *trans* chain, $\diamond_5(T_P)_5$. c) Same as in b) but with sections of different length, $\diamond_3(T_P)_7$. d) Another partially opened chain, $\diamond_3(O_P)_1$. e) A chain containing three different sections, $\diamond_3(T_P)_5[Z(3,3)_P]_5$; f) Intrachain condensation of the *trans* chain ,$(T_P)_{10}$, results in a chain with edge-sharing four- and six-rings, in which the six-rings are capped by triply bridging phosphate groups alternating above and below the plane of the chain. g) Intrachain condensation of the C_p section of a partial *cis–trans* chain, $\diamond_3(C_P)_5$, with the parent chain section results in a new chain type, which we have characterized by X-ray crystallography.[19, 20] For nomenclature see Table 1.

Table 1. Nomenclature scheme for the description of the repeat units in aluminophosphate chains.

$\diamond_n$	Section of *n* corner-sharing four-rings of the unhydrolyzed parent chain
T_n	Section of *n* edge-sharing four-rings in a *trans* conformation
$(T_P)_n$	Section of *n* edge-sharing four-rings in a *trans* conformation, with terminal phosphate groups remaining on the aluminum centers
C_n	Section of *n* edge-sharing four-rings in a *cis–trans* conformation
$(C_P)_n$	Section of *n* edge-sharing four-rings in a *cis–trans* conformation, with terminal phosphates remaining on the aluminum centers
O_n	Section of *n* corner-sharing four-rings that have been ring-opened (and have lost their terminal phosphate groups)
$(O_P)_n$	Section of *n* corner-sharing four-rings that have been ring-opened, with terminal phosphate groups remaining on the aluminum centers
$[Z(a,b)]_n$	Section of *n* edge-sharing four-rings in a zigzag conformation; subsections of *a* and *b* four-rings per leg, respectively
$[Z(a,b)_P]_n$	Section of *n* edge-sharing four-rings in a zigzag conformation; subsections of *a* and *b* four-rings per leg, respectively, with terminal phosphate groups remaining on the aluminum centers

tion to the layered structure UT-3.[19] We had previously obtained UT-3 directly in the same synthetic system (i.e., in the presence of small amounts of water, which evidently catalyzed the transformation) and determined its structure by single-crystal X-ray diffraction.

We consider this unprecedented chain-to-layer transformation to be fundamentally important for comprehending the formation of aluminophosphates. The parent chain is initially hydrolyzed in solution, leading to the formation of other chain structure types. These chains are solvated and interact with alkylammonium ions, which keeps them apart in solution. The cationic templates reduce the chain–chain electrostatic repulsion, allowing them to crystallize from solution. Simple aggregation of the chains through ionic bonds to the template[15, 16, 18] or interchain hydrogen bonds[17, 19, 20] results in a chain structure, while chain condensation causes cross-linking and leads to a porous layer or open-framework structure. Rapid precipitation of the chains would result in an amorphous material that would appear to be layered by various experimental probes, but in reality contains layers of poorly arranged chains. Further heating of this phase would allow the chains to reconstruct, cross-link, and organize to form the final, crystalline structure. This would be consistent with, and account for, the various results and the typically fast precipitation rate of aluminophosphates that have been reported to date.[59–64] In the reconstruction process, the final structure is controlled by both the chain type and properties of the organic template. The templates are therefore only partly responsible for the resulting structure. This serves to elucidate the often unclear role of the template,[3a] and the template-dependent and template-independent trends that are observed for aluminophosphates.

The known solid-state transformations of aluminophosphate frameworks, such as that of VPI-5 to AlPO$_4$-8,[78, 79] AlPO$_4$-21 to AlPO$_4$-25,[44] and AlPO$_4$-C to AlPO$_4$-D,[45] as well as aluminophosphate minerals obtained through the solid-state transformation of other phases[80] provide supporting evidence for the present model. These transformations also involve hydrolysis–restructuring–condensation processes, and have been referred to as chain-to-chain transformations. Furthermore, they are chemically equivalent to the processes we propose, as well as to the UT-2 to UT-3 chain-to-layer transformation discussed above. In fact, solid-state transformations play a vital role in the formation of many chain, layered, and framework structures, as will be described in more detail below.

The chain model is also consistent with the P:Al ratios in aluminophosphates, which lie between 2.0 and 1.0 for most extended aluminophosphate structures. The largest value of 2 is only present in the parent linear chain. By hydrolytically cleaving the terminal phosphate groups from transformed chains (see Figures 4–10), the P:Al ratio is gradually reduced. The greater the degree of hydrolysis, the more phosphate groups that are removed, particularly in condensing to layers and frameworks. This accounts for the generally lower P:Al ratios in the higher dimensionality aluminophosphates.

Similarly, this accounts for the invariant, P:Al ratio of 1.0 for aluminophosphate frameworks. All aluminophosphates avoid direct Al-O-Al linkages between tetrahedral AlO$_4$ units; for zeolites this is known as Lowenstein's rule.[3] Recent calculations on the energy of formation of aluminophosphates show this rule to be both valid and strictly obeyed.[81] There are consequently no P-O-P linkages between the tetrahedral units in the nonmetal-substituted, aluminophosphate frameworks, and the P:Al ratio is 1.0. These rules are obeyed by the parent chain, which initiates the alternating Al and P centers. The maximum number of phosphate groups that may be removed from the chain by hydrolysis, while still maintaining an extended chain structure, is one of the two phosphate groups on each four-ring, thereby defining a minimum P:Al ratio of 1.0. Interestingly, in this respect the aggregation polymers of aluminophosphates prefer to form in solutions in which the P:Al ratio lies between 1 and 2.[61–63, 80] These also happen to be the ratios used for the synthesis of chain, layer, and framework aluminophosphates.

2.3. Chain-to-Layer and Chain-to-Layer-to-Framework Transformations

Having introduced the various chain types and the mode by which they form, we will now proceed to show structural examples of chain types and how they can account for the various architectures of aluminophosphate materials. The first example is that of the porous layer AlPO$_4$-5-like structure $[Al_3P_4O_{16}]^{3-}\cdot 3[R^+]$[22, 24, 27] (Figure 5). Intrachain condensation of $[Al_3P_4O_{16}]^{3-}$ chains of the type shown in Figure 5a forms a chain containing capped six-rings (Figure 5b), which snap together to create the two-dimensional net[82] (Figure 5c). The resemblance of the layer structure to AlPO$_4$-5 itself is not likely a coincidence. Removal of the caps and interlayer condensation would result in the AlPO$_4$-5 framework. However, the pathway given in Figure 5 does not necessarily have to be followed to obtain AlPO$_4$-5. Instead, the chains given in Figure 5a responsible for the AlPO$_4$-5 layer could bypass the layer "intermediate" and undergo

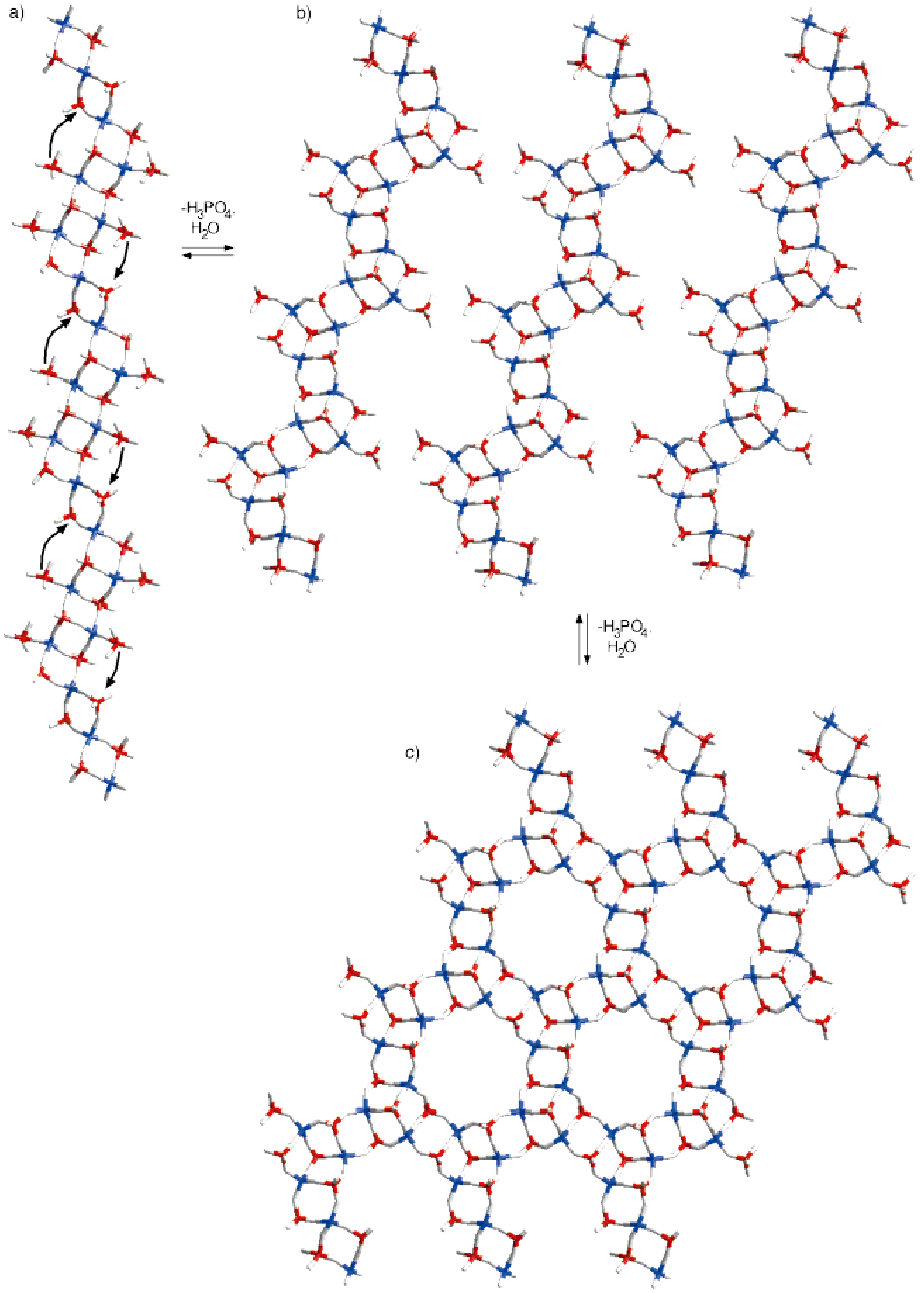

Figure 5. Formation of the capped $AlPO_4$-5-like layered structure. a) The partial *trans* chain, $\diamond_3(T_P)_7$. b) Intrachain condensation creates an array of edge-sharing four- and six-rings; phosphate caps on the six-rings alternate above and below the plane of the chain. c) Condensation of the chains to form the two-dimensional structure containing twelve-rings.

simultaneous chain-to-framework connection to create the framework, as will be shown for several frameworks below. The choice of the $AlPO_4$-5 layer or $AlPO_4$-5 framework as the end product is determined by parameters such as the synthesis conditions and template properties. Thermodynamically, the framework represents the more stable structure and is thus easy to isolate.[14] By contrast, the layer requires less vigorous reaction conditions to restrict hydrolysis and cross-linking processes.

In the context of the porous layer $AlPO_4$-5 structure (Figure 5c), two metal-substituted MAPO-*n* frameworks are worthy of mention.[14] The structure of MAPO-46 may be considered as two such capped layers arranged back-to-back, with the caps pointing in opposite directions. One layer is the layered $AlPO_4$-5 structure, while the other contains six-rings in which, instead, the phosphorus centers of the six-rings are bound through their terminal oxygens to a capping metal atom. This "double-layer" in turn connects to its two neighboring double-layers through the respective phosphate and metal caps, to define the overall framework. The CoAPO-50 framework may also be considered to be constructed exclusively of layers with the $AlPO_4$-5 structure. In this case, the cobalt atoms cap the opposite side of the phosphate-capped six-rings, and connect to the phosphate caps of the next layer. While the predominance of the $AlPO_4$-5 framework architecture has been previously noted,[3, 41] it has not been pointed out that the capped $AlPO_4$-5 layer structure is also a predominant architecture among the $AlPO_4$-*n* structures. This underscores the importance of the chain shown in Figure 5a in the formation of $AlPO_4$-5 and related MAPO-*n* structures.

The result of another chain-to-layer transformation is the $[Al_3P_4O_{16}]^{3-}$ layer structure, which has been isolated in several nonaqueous systems.[20, 21, 25, 28] The $[Al_3P_4O_{16}]^{3-}$ chain, as was shown in Figure 4 f right, is formed from an "all-*trans*" chain by loss of terminal phosphate groups and intrachain condensation. Connection of the chains by further loss of phosphate groups forms the layered architecture, depicted in Figure 6. Interestingly, the layer arrangement of four-, six- and eight-rings is the same as that which occurs in the projection of the $AlPO_4$-12 structure along the *a* axis, with the exception that the the six-rings of the present layer are also capped by a triply bridging phosphate group.[14] As for the $AlPO_4$-5 layer, these layers can cross-link to form the $AlPO_4$-12 framework by removing the capping phosphate groups, or the starting chains (see Figure 4 f right) could by-pass the layer to directly form $AlPO_4$-12.

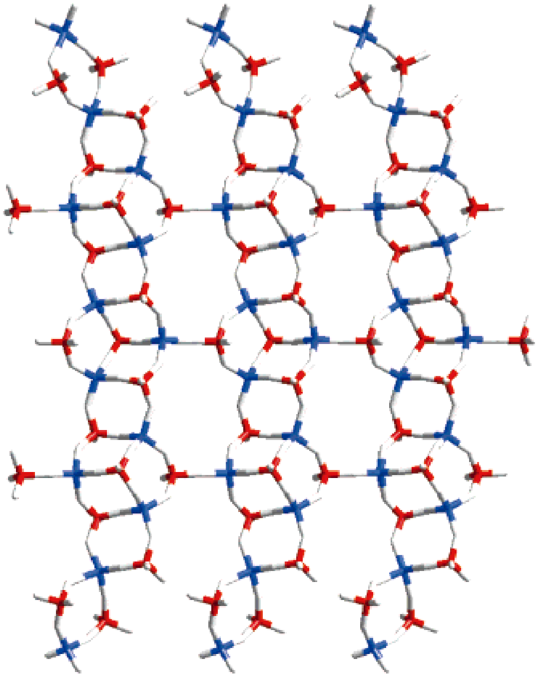

Figure 6. The $[Al_3P_4O_{16}]^{3-}$ layer from capped six-rings. Condensation of the chain given in Figure 4 f left with loss of terminal phosphate groups and water leads to the formation of a layer containing eight-rings.

2.4. Chain-to-Framework Transformations

An example of the connection of chains directly to a framework is shown in Figure 7. The formation of JDF-20 can be explained by the fusion of two simple types of chains,[31, 65] the parent chain (Figure 1 a), and the $[Al_4P_4O_{17}]^{2-}$ zigzag chain (Figure 3 b). The parent chain connects to two zigzag chains through six-rings (Figure 7 a). This building unit is arranged in a hexagonal array in the *ab* plane and thus defines the elliptical unidimensional channels of the framework, in which the units are connected through zigzag chains. Two sets of eight-ring channels perpendicular to the main channel are thereby created (Figure 7 b). The presence of parent and zigzag chains requires hydrolysis conditions that are less severe. This accounts for the fact that this material was only recently discovered in a predominantly nonaqueous triethylene glycol system. The ratio of parent $[AlP_2O_8H_2]^-$ chains to $[Al_2P_2O_{8.5}]^{2-}$ chains (the zigzag chains are one-half the length of the parent chain per asymmetric unit) in the structure is 1:2; their condensation affords a framework of the observed composition $[Al_5P_6O_{24}H]^{2-}$.

2.5. Chain Encapsulation

As two or more chain types can construct a new structure, it is expected that they can condense with other alumina or aluminophosphate solute species that coexist in the system. The coordination and aggregation state of aluminum(III) is known to be highly dependent on the pH value,[83, 84] as are those of the molecular aluminophosphates[57, 58] and aggregation polymers.[60–63] Such species might be incorporated between the chains under a particular set of synthesis conditions. This represents another degree of freedom for the chain model, and accounts for a number of other structure types.

One example is the aluminophosphate framework of tinsleyite (Figure 8 right). $AlPO_4$-tinsleyite[85] is exclusively built of octahedral AlO_6 and tetrahedral PO_4 units. Four vertices of the aluminum octahedra are occupied by the oxygen atoms of the neighboring phosphate groups. One third of the aluminum atoms have their coordination sphere completed by two terminal oxygen atoms (OH^-, H_2O), while the remaining two thirds achieve this as doubly oxygen-bridged pairs (Al-(μ_2-O)$_2$-Al). The structure of tinsleyite can be derived from the open chain given in Figure 8 left, which connects to aluminum(III)-based double octahedra (shown in the center of Figure 8) on either side of the chain. Octahedral coordination is favored for aluminum(III) under more acidic conditions.[83, 84] Thus, it is possible that under these conditions a chain aluminophosphate species contains octahedrally coordinated aluminum centers, as for the $[Al(H_2PO_4)_3]$ chain of Kniep et al.,[17] or that the aluminum coordination sphere changes from tetrahedral to octahedral by simply increasing its coordination with terminal water molecules. Aluminum(III) is known to partially exist as condensed oxo polyhedra, such as Al_2O_{10} dimers, in solution under acidic conditions.[83, 84] $AlPO_4$-tinsleyite therefore represents a chain-to-framework condensation in which a second species, in this case an alumina dimer, participates in the chain connection process.

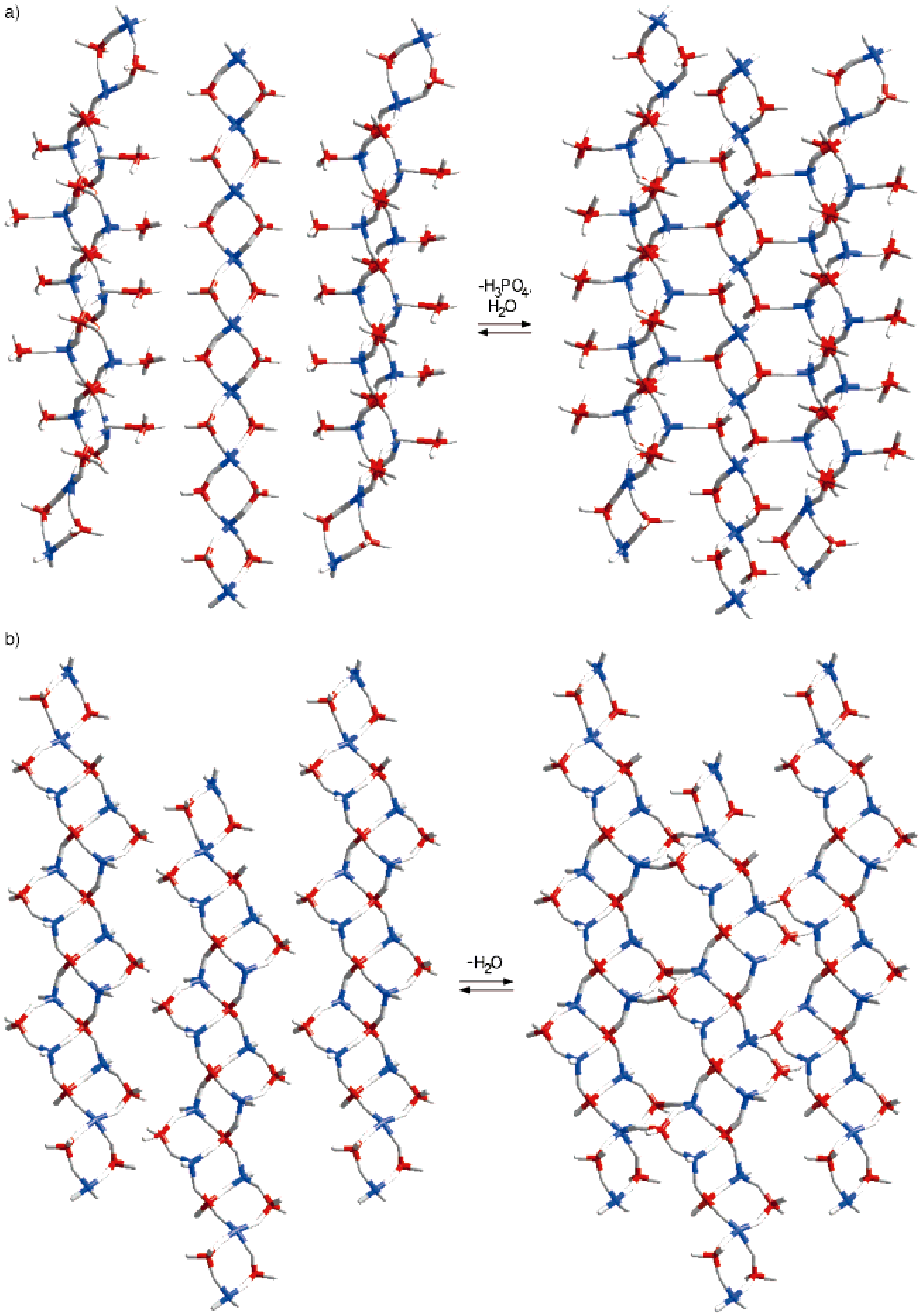

Figure 7. Chain condensation that leads to the framework topology of JDF-20. a) Two zigzag chains, $[Z(3,3)_P]_\infty$, connect to a parent chain, $\diamond_\infty$ and condense with formation of six-rings to give the building-block of the framework. Four such building blocks are arranged around the main channel of the structure: one on the top, one on the bottom, and one each side. b) The end-on view of three units from a), and the $[Z(3,3)]_\infty$ zigzag chains that reside on them; condensation of three of the zigzag chains leads to the formation of two independent eight-ring channels that intersect the main channels.

Another example of this kind of chain encapsulation is the recently reported framework of the aluminofluorophosphate UT-6.[12] This chabazite-like structure is related to $AlPO_4$-CHA (such as the $AlPO_4$-34, MAPO-34, MAPO-44 and MAPO-47 frameworks), in which one aluminum atom in each six-ring of the hexagonal prisms is replaced by an octahedrally coordinated aluminum atom, which connects to an octahedrally coordinated aluminum atom of an adjacent hexagonal prism through two bridging fluorine atoms. The UT-6 structure can be derived from the chain given in Figure 9a.

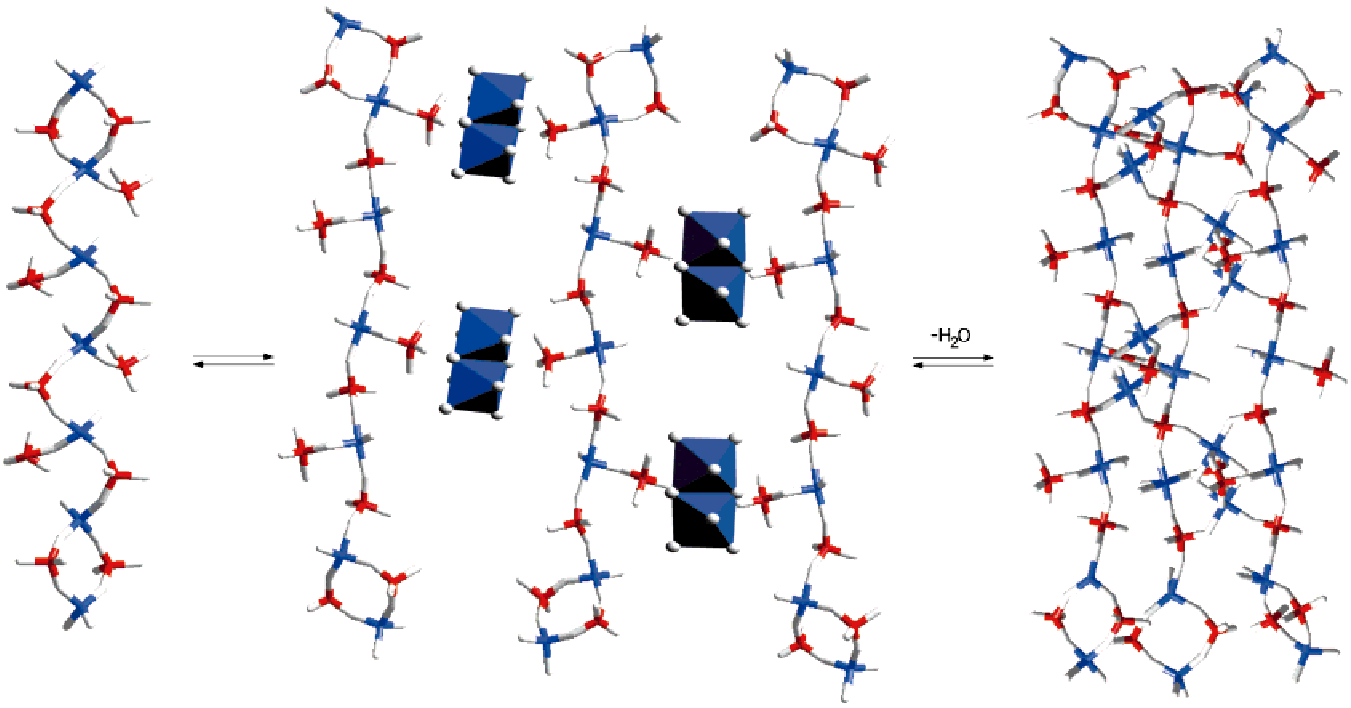

Figure 8. Model for the formation of the tinsleyite framework with its distorted eight-rings (right) from the open chain type, $(O_P)_\infty$ (left). The terminal phosphate groups extend outwards and reach above (center left) and below (center right) the Al_2O_{10} double-octahedra.

A plane of these chains surround one aluminum center of an adjacent plane of partially fluorinated (Al-(μ_2-F)$_2$-Al) double octahedra, to form the bottom six-ring of the hexagonal prism (depicted in yellow in Figure 9b). The other aluminum center of these double octahedra connects to the next layer of chains. Likewise, a plane of double octahedra above completes the upper six-ring of the hexagonal prism (not shown, but the second six-ring is depicted in pink, Figure 9c). In this way, a primitive array of hexagonal prisms is constructed that defines the framework of UT-6.

Significantly, the UT-6 structure thermally transforms in the solid state to $AlPO_4$-CHA, by removal of the bridging fluorine atoms and extra-framework template cations.[12] This is likely the mode by which the various polytypes of $AlPO_4$-CHA frameworks are formed. Initial condensation of the chains (Figure 9a) and Al_2O_{10} double-octahedra, followed by separation and dehydration of the double-octahedra to give tetrahedral centers, builds up the $AlPO_4$-CHA framework. Only with this knowledge of the UT-6 structure and its transformation is it possible to understand the origin of this framework. Similarly, it becomes possible to rationalize the formation of other aluminophosphate structures that would otherwise be very difficult to explain.

The final example, which also involves chain encapsulation of aluminum double-octahedra, is VPI-5. The chain proposed to be responsible for the formation of VPI-5 connects through aluminum double-octahedra to build up the structure of VPI-5, which contains 18-membered rings (Figure 10; the second octahedron of the dimer is not shown, but resides in the next layer). In this case, the alumina dimers separate but the octahedral coordination is retained; the fifth and sixth coordination sites of aluminum are occupied by terminal water molecules that reside in the main channel.[46] This mode of formation would account for the difficulty in synthesizing VPI-5,[49, 50] as one must first age the gel, and carefully control the pH. For the process given in Figure 10 to occur, one must first build up the more complex chain type given in Figure 10 left, as well as leach aluminum double-octahedra into the gel and encapsulate them with relatively labile terminal phosphate groups of the chain. Once this is achieved, nucleation of the material can begin.

The chain-assembly model has been developed by considering the relationships between crystal structures of various new aluminophosphate materials, which have been isolated by reaction profiling of nonaqueous synthesis systems. In many cases, the chain-to-layer and chain-to-framework transformations obscure the presence of the parent chain in the final structure of the product. This is evident in the UT-2 chain to UT-3 layer transformation.[19] Additionally, the chains responsible for the structures in most cases span the layer planes, which is also unique to the chain model. In this way, the complex arrangements of rings and channel systems of aluminophosphate frameworks can readily be understood. The dominance of particular chain precursors, such as that for $AlPO_4$-5 (Figure 5a), accounts for the large degree of template-independence observed for many aluminophosphate structures. The chain model only requires that the transformed sections of edge-sharing four-rings be three-to-five units long. This minimizes the number of chain hydrolysis steps of the parent linear chain.

2.6. Inorgano-Gene: The Progenitor Chain

Finally, it is interesting to consider that the paradigm shift presented in this review is in the same spirit as the emerging

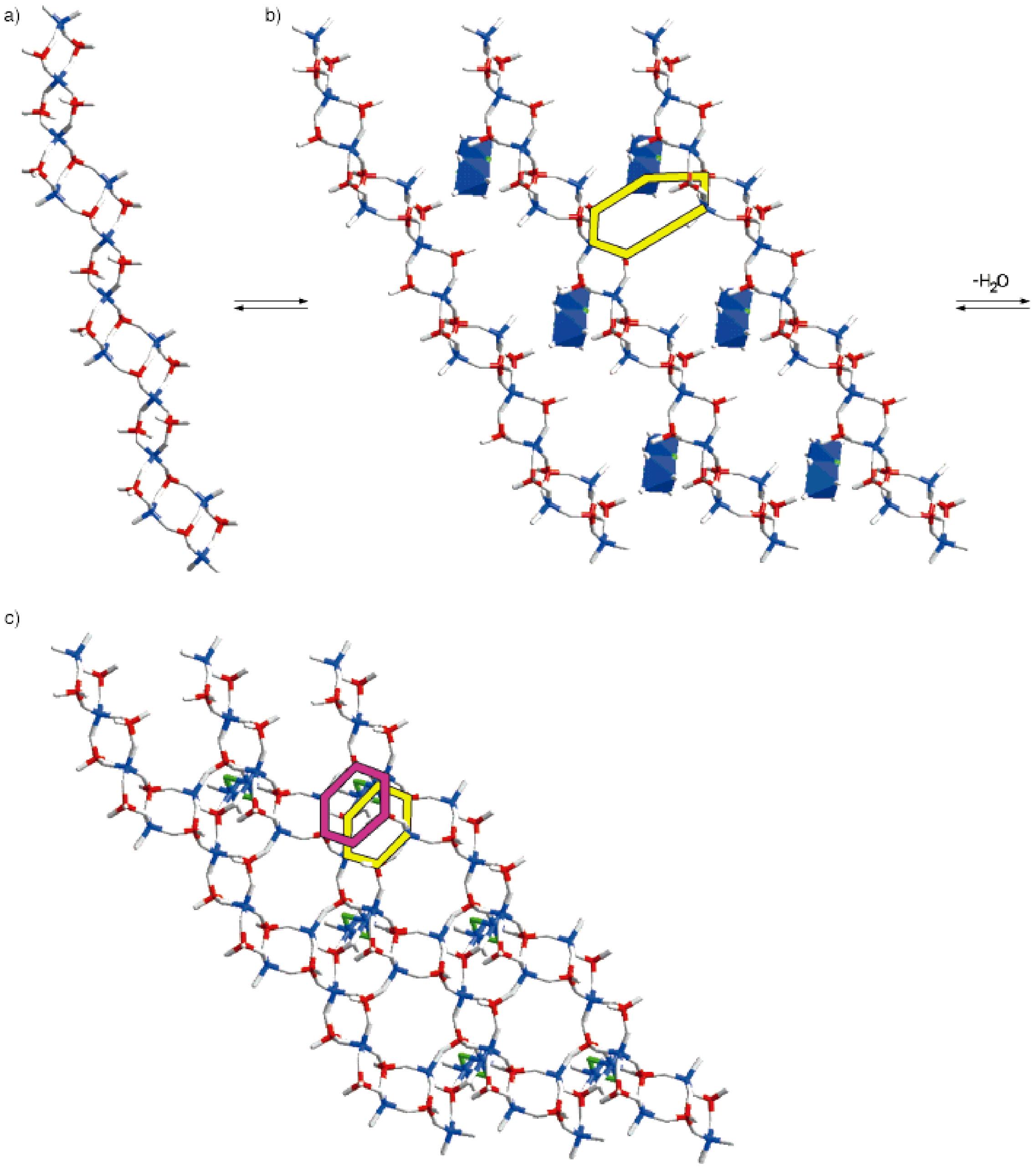

Figure 9. The build up of the UT-6 framework. a) $\Diamond_3(\mathrm{T})_3$ chain. b) The chains surround the closer octahedron of the $\mathrm{O_5Al\text{-}(\mu_2\text{-}F)_2\text{-}AlO_5}$ dimeric units to form the bottom six-ring of the hexagonal prisms (yellow). (The $\Diamond_3(\mathrm{T})_3$ chain has been slightly rotated to emphasize the shape that will become the hexagonal prisms). c) Condensation to the aluminum octahedra forms the bottom six-ring (yellow) and will connect in a like manner to the aluminum octahedra above the plane of the layer to form the other six-ring of the hexagonal prisms (pink). Fluorine atoms for UT-6 are shown in green.

biological view of materials chemistry and the description of inorganic materials with complex form.[86] The idea that inorganic materials have the capacity to store vast amounts of information is not new.[87] The thinking goes back to Schrödinger's aperiodic crystal description of the information-carrying genetic apparatus, and subsequently in another expression as the crystal abacus. In its more contemporary guise, the idea abounds in information storage materials found in, for example, records, tapes and discs. In the context of crystallography, Mackay first forwarded the proposal of an "inorganic gene" as a genetic algorithm in the search for the lowest energy configuration of a system of *N* atoms.[87]

In such a departure from the usual view of the aluminophosphate system, the structural, stereochemical, charge, and chemical information that is encoded in the chain can be transcribed to tectons based on an organic template and an aluminophosphate. In a synergistic co-assembly process these tectons will generate new and more complex structures, or "inorgano-phenotypes". Their survival in a particular synthesis is determined by the interplay of kinetic and thermodynamic factors, so that kinetic products are generated in local energy minima. Various hydrolysis "editing operations" of the parent linear chain can permute and alter the structure-directing information in the chain to produce

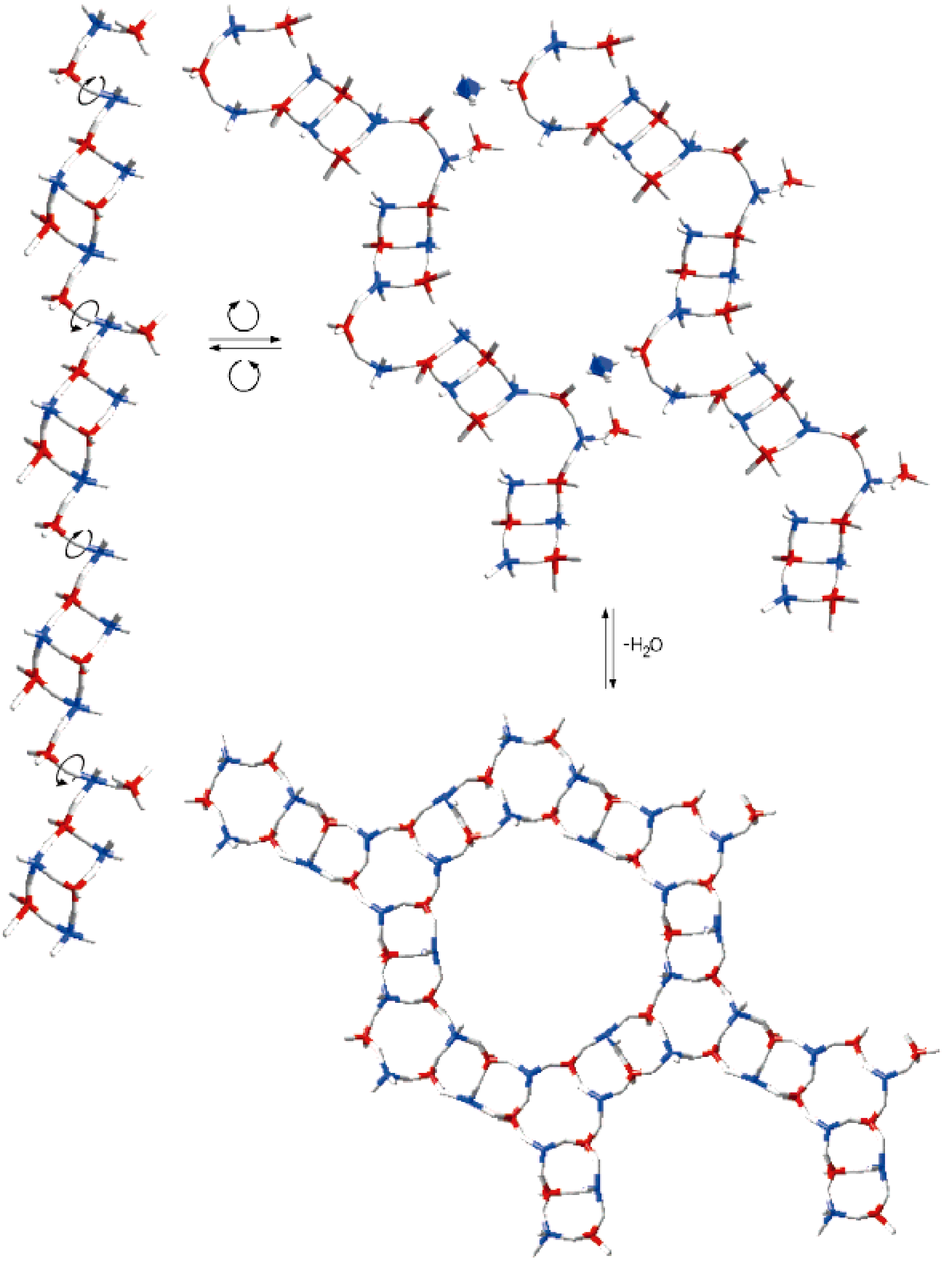

Figure 10. Direct formation of the VPI-5 framework, in which a capped VPI-5 layered "intermediate" of the type shown for $AlPO_4$-5 (Figure 5) is bypassed. Loss of phosphate groups from a chain type $(O_P)_2(T)_2$ gives the less symmetric chain type $(O)_2(T)_2(O)_1(O_P)_1(T)_2$ (left). Simple rotation around the linkages surround monomeric aluminum species with POH groups (center), and subsequent condensation leads to the framework topology.

condensed structures of varying dimensionality and degrees of "fitness."[87]

3. Summary and Outlook

The chain self-assembly model invokes a facile hydrolysis–condensation process of a metastable species that can be crystallized from the aluminophosphate synthesis system. Simple transformations of the parent chain can explain the wide variety of chain, porous layer, and open-framework structures found for aluminophosphates. Coupled hydrolysis and condensation reactions of the linear chain can produce a large number of other more complex chain structure types. Only a few selected examples of these are described herein. The amount of catalytic water in the system, which determines the amount of chain hydrolysis and thereby the resulting structure types. It should be possible to probe the aluminophosphate system and its structures in greater detail to further elucidate the chain self-assembly model. It is likely that new chain structures will be discovered that fit into the chain scheme presented. We hope that this chain model will allow for the rational design of new chain, layer, and framework structure types.

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