Review

Rings, chains and cages in metal phosphate chemistry: The interdependence and possible interconversion between various structural forms ☆

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ABSTRACT

Our endeavour to build soluble model compounds of basic building blocks in zeolite structures have resulted in a plethora of main group and transition metal phosphate complexes. Many of these complexes show highly intriguing and novel structural features. Careful examination of the core structures allowed us to rationalize the interdependence between the different structural types and visualize their plausible pathway of formation. Due to the high reactivity and short life span of the intermediates it has not been possible to characterize many intermediates. However, the common structural features present in the isolated products drive us to arrive at a plausible mechanism. Further investigation and isolation of other structural types will definitely provide more credential to these hypotheses and help us to solve the zeolite jigsaw.

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Contents

1. Introduction

The chemistry of metal phosphates is being pursued by chemists for a long time due to their relevance in many biological systems. Phosphates are available in the human body as hydroxyapatite in bones, teeth and more importantly in nucleotides [1]. Many naturally occurring minerals also feature phosphates and this fact is of great importance to inorganic chemists as much effort is being directed towards the production of designer phosphate frameworks. The term "phosphate" refers to oxyanions of pentavalent phosphorus, PO_4^{3-}. Phosphate esters find numerous applications, e.g. plasticizer [2], flame retardants [3], reagents in the preparation of organophosphorus polymers [4], in solvent extraction of heavy metal ions [5], and as insecticides [6]. However, all phosphate esters are highly susceptible to hydrolysis and this fact is of great importance in biological systems as phosphate is part of DNA and energy transfer cycles [7].

Due to the occurrence of many phosphate containing minerals in the environment and their utility in wide ranging applications, it remained a subject of much interest to inorganic chemists. Although phosphate containing minerals are abound in nature, they do not meet the complete need of the modern chemical industry in terms of their availability and properties such as larger pore size, high thermal stability and size–shape selectivity. The discovery of open framework aluminophosphates (ALPOs) by Flanigen and coworkers led to an outburst of activities towards the development of metal phosphates frameworks with tuneable porosity [8]. Using preformed molecular precursors, such extended solids can be built more rationally and with better control over the porosity. The chemistry of both molecular phosphates and extended phosphate frameworks has been recently reviewed by us [9].

Over the last decade, one of the major endeavours of our research group is to build main group and transition metal phosphate and phosphonate based cage complexes which can be regarded as soluble model of zeolite secondary building Units

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☆ Based on the lectures delivered by both R.M. and N.G. at IRIS-12, Goa, August 2009.
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(SBUs) [10–13]. Phosphoric acid, due to the presence of three acidic protons, tends to form extended polymeric complexes and many open frameworks metal phosphates have been reported earlier. However, the formation of extended superstructures can be prevented if mono or diesters of phosphoric acid are used, leading to isolation of discrete metal complexes. Contributions from Tilley and coworkers [14] and also from our laboratory [13] established that diesters of phosphoric acid, $(RO)_2P(O)(OH)$, are very similar to carboxylic acids in some ways (but different in many other ways), and form either mononuclear or dinuclear metal phosphates more readily than larger clusters. Phosphate monoesters, on the other hand, due to the presence of two acidic protons and one phosphoryl oxygen, tend to embrace more metal ions around them and form larger aggregates [11]. Our investigation of main group as well as transition metal coordination chemistry using

phosphate monoesters yielded plethora of novel complexes [10,11]. Many of these complexes display unprecedented and interesting structural geometry. In this contribution, the interdependence of various structural types isolated and also their possible inter-conversion routes are reviewed and highlighted. These rationalizations provide valuable insights and further investigations can help us to solve the zeolite jigsaw, which has been puzzling material chemists for decades.

2. Aluminum phosphates

It has been mentioned above that the discovery of microporous aluminophosphate materials fuelled research in this area for achieving novel microporous material with variable pore volume [8]. Another challenge pursued by many research groups in this
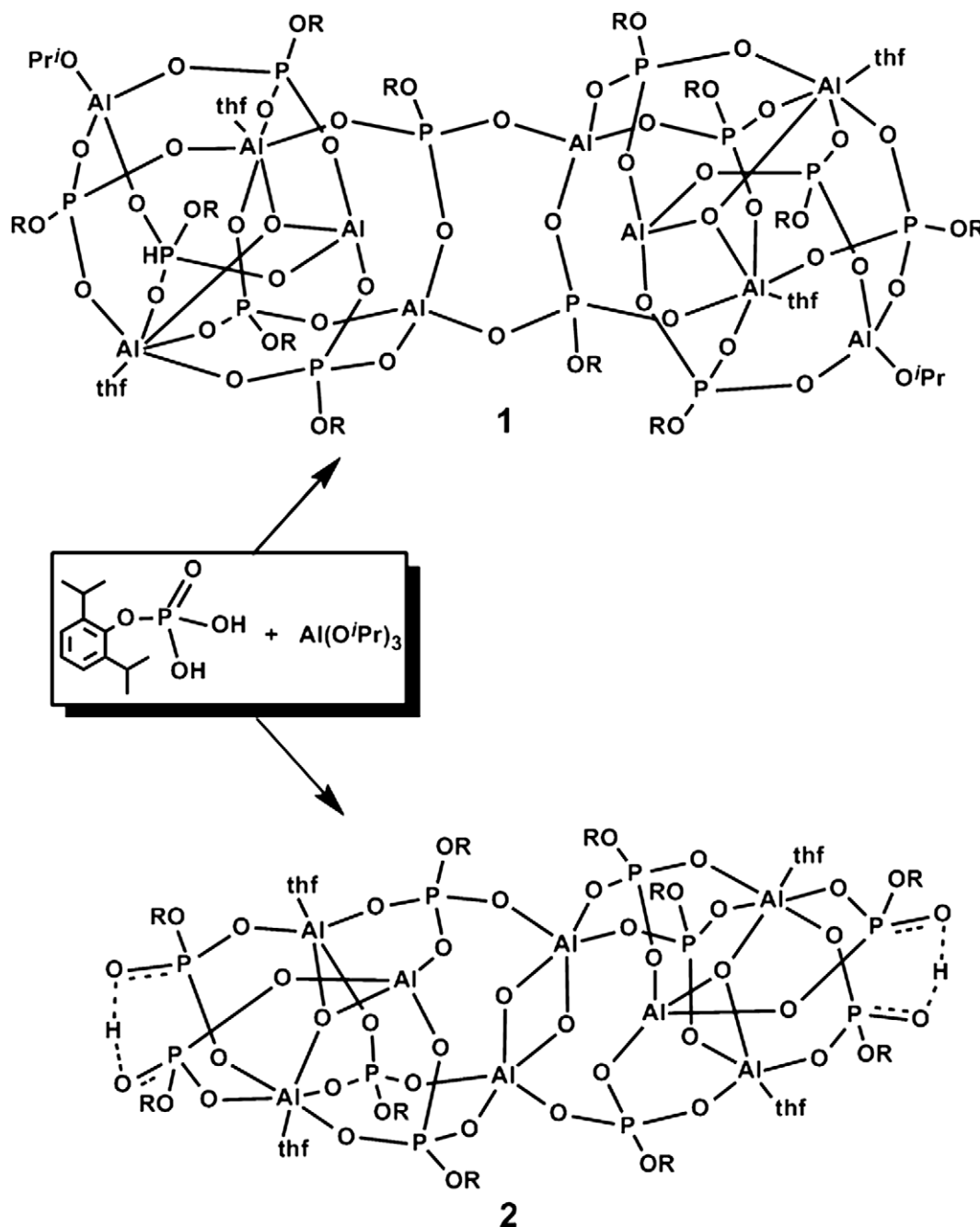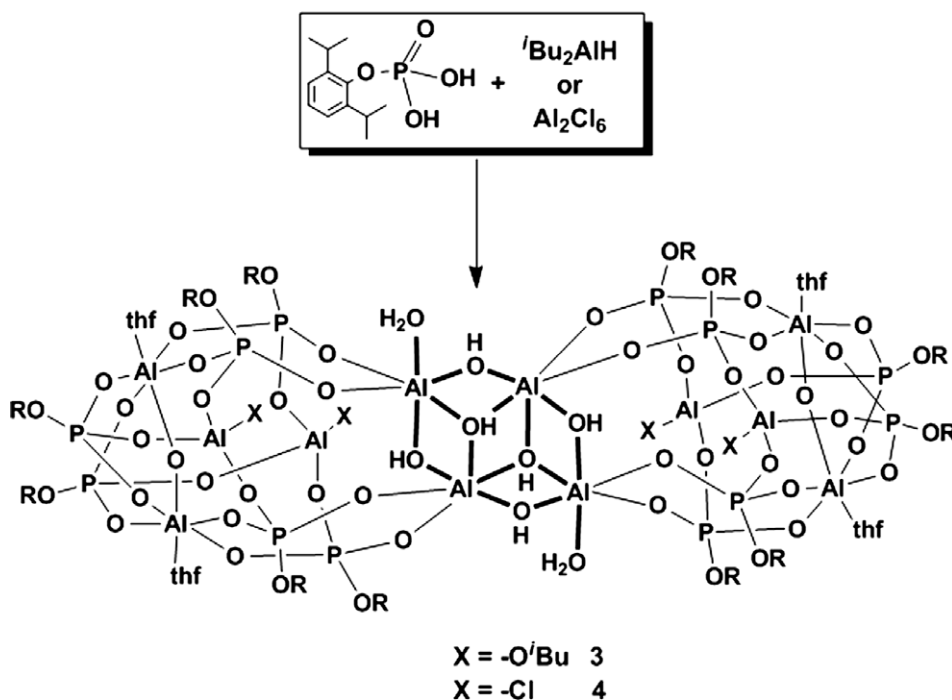

Scheme 1. Synthesis of decameric 1 and octameric 2.

area, is to build discrete and soluble aluminophosphate model compounds in order to gain an insight into the formation of zeolite. By using soft chemical routes Cassidy and coworkers have succeeded in assembling a tetranuclear aluminum phosphate by reacting aluminum chloride with phosphoric acid in an ethanol medium [15a]. Using phosphoric acid and an organic structure directing agent under solvothermal reaction conditions many aluminophosphate based materials have been reported earlier [15b–d]. Likewise gallophosphates, which are encountered in many microporous material structures such as cloverite, ULM-5, ULM-18, MU-15, etc. and has structures resembling the D4R cubane in zeolites with an occluded fluoride ion at the center are synthesized by using phosphoric acid under solvothermal conditions [15e–g]. However, the limited solubility of phosphoric acid in organic solvents and harsh reaction conditions employed leaves us with little or no control over the nature of the resulting porous materials. Tilley and coworkers have shown that, by using organic soluble di-*tert*-butylphosphate instead of phosphoric acid, discrete dinuclear aluminum phosphates can be synthesized. Elimination of *tert*-butyl groups at elevated temperatures provided an easy access to aluminophosphate xerogels or thin films with surface hydroxyl groups and remarkable porosity [14].

The dinuclear aluminum phosphates reported by Tilley can be regarded as the elementary unit during the formation of aluminophosphate frameworks [14]. We opted to use a monoester of phosphoric acid in order to realize high nuclearity aluminum phosphates, and have further unfolded the mechanism of formation of zeolites. This investigation yielded several aluminum phosphate complexes with varying nuclearity and enticing structural types [11a,b]. Reaction of a bulky aryl ester of phosphoric acid, di*iso*propylphenyl phosphate (dippH$_2$) with various aluminum precursors such as Al(O^{i}Pr)$_3$, ^{i}Bu$_2$AlH, AlCl$_3$ and (Me$_3$Si)$_3$CAlMe$_2$ was investigated under almost identical reaction conditions. A decameric aluminum phosphate, [Al$_{10}$(μ_3-O$_3$P(OR))$_{12}$(μ_3-O)$_2$(O^{i}Pr)$_2$(thf)$_4$]·(C$_7$H$_8$)$_6$ (**1**) is obtained when a thf solution of Al(O^{i}Pr)$_3$ was added to a thf solution of dippH$_2$ (Scheme 1). Surprisingly mere reversal of the order of addition of the reactants, changed the course of this

reaction to yield an octameric aluminum phosphate [Al$_8$(μ_3-O$_3$P(OR))$_8$(μ_2-HO$_3$P(OR))$_2$(μ_3-O)$_2$(μ_2-OH)$_2$(thf)$_4$]·(C$_7$H$_8$)$_2$ (**2**). More interestingly reaction of equimolar amounts of ^{i}Bu$_2$AlH and dippH$_2$ at room temperature in petroleum ether followed by a very slow crystallization of the concentrated reaction mixture with a few drops of thf resulted a dodecameric complex [Al$_{12}$(O^{i}Bu)$_4$(RO-PO$_3$)$_{12}$(μ_3-OH)$_2$(μ-OH)$_6$(OH$_2$)$_2$(thf)$_4$] (**3**) (Scheme 2). A similar reaction involving AlCl$_3$ and dippH$_2$ in thf followed by crystallization from toluene results in the isolation of another dodecameric aluminophosphate [Al$_{12}$Cl$_4$(ROPO$_3$)$_{12}$(μ_3-OH)$_2$(μ-OH)$_6$(OH$_2$)$_2$(thf)$_4$]·(toluene)$_4$ (**4**) (Scheme 2).

The mere reversal of order of addition of various reactants leading to the formation of octameric and decameric aluminophosphate complexes **1** and **2** from an 1:1 mixture of the reactants is puzzling. It is pertinent to note here that the equimolar reaction between RPO$_3$H$_2$ and AlR$_3$ normally leads to tetrameric cubanes [RAlO$_3$PR′]$_4$ [16], although hexameric and decameric cages also have been isolated in a few instances [17]. Formation of **1** and **2**, however, can be understood by careful examination of their core structures as both the complexes are structurally related and derived from the same set of reactants in identical stoichiometry. A plausible pathway leading to the formation of the octameric and decameric complexes is illustrated in Scheme 3. We presume that in both the cases the initial reaction between the two starting materials proceed via the formation of a S6R [(O^i-Pr)$_2$Al(O$_3$P(OR)]$_3$ unit. Although necessary precautions were undertaken to exclude air or moisture from the reaction mixture, water trapped in the hydrophilic phosphate ligand attack the S6R unit thus leading to the formation of the intermediate **B**. The formation of a S6R capped by a μ-oxo group has been observed earlier in gallophosphonates [18]. Subsequent addition of two more equivalents of aluminum isopropoxide and three equivalents of dippH$_2$ to **B** followed by dimerization reaction between P–OH and Al–O^{i}Pr terminals produces **1**. On the other hand, addition of only one equivalent of Al(O^{i}Pr)$_3$ and two equivalents of dippH$_2$ to **B** followed by dimerization and a slow Al–O^{i}Pr hydrolysis yields **2**.

X = -O^{i}Bu   **3**
X = -Cl   **4**

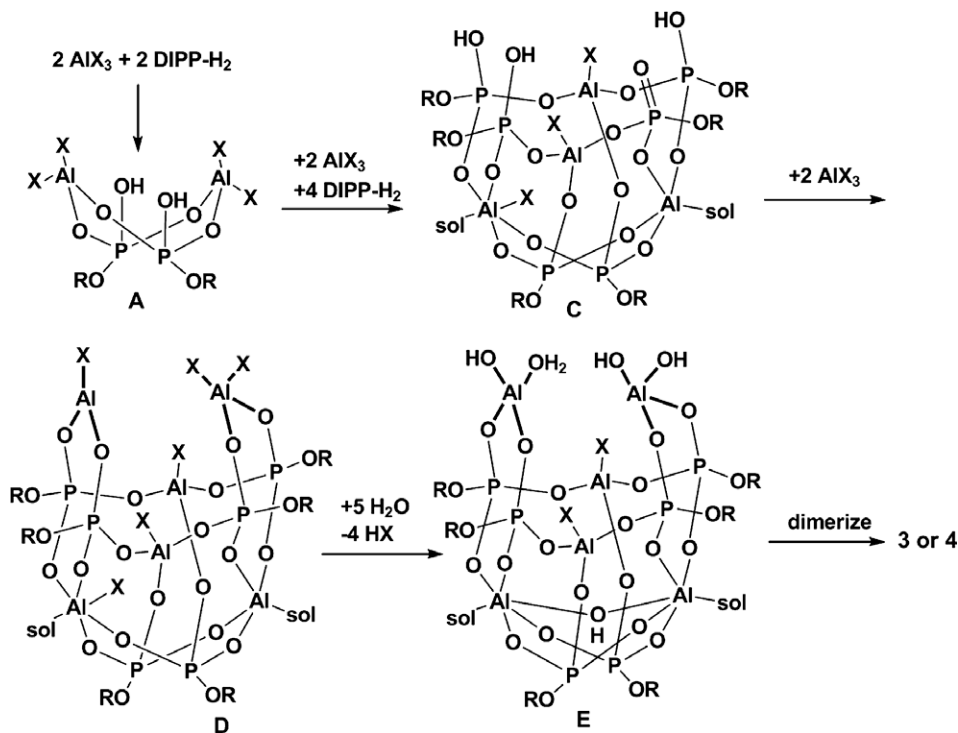**Scheme 2.** Synthesis of dodecameric **3** and **4**.
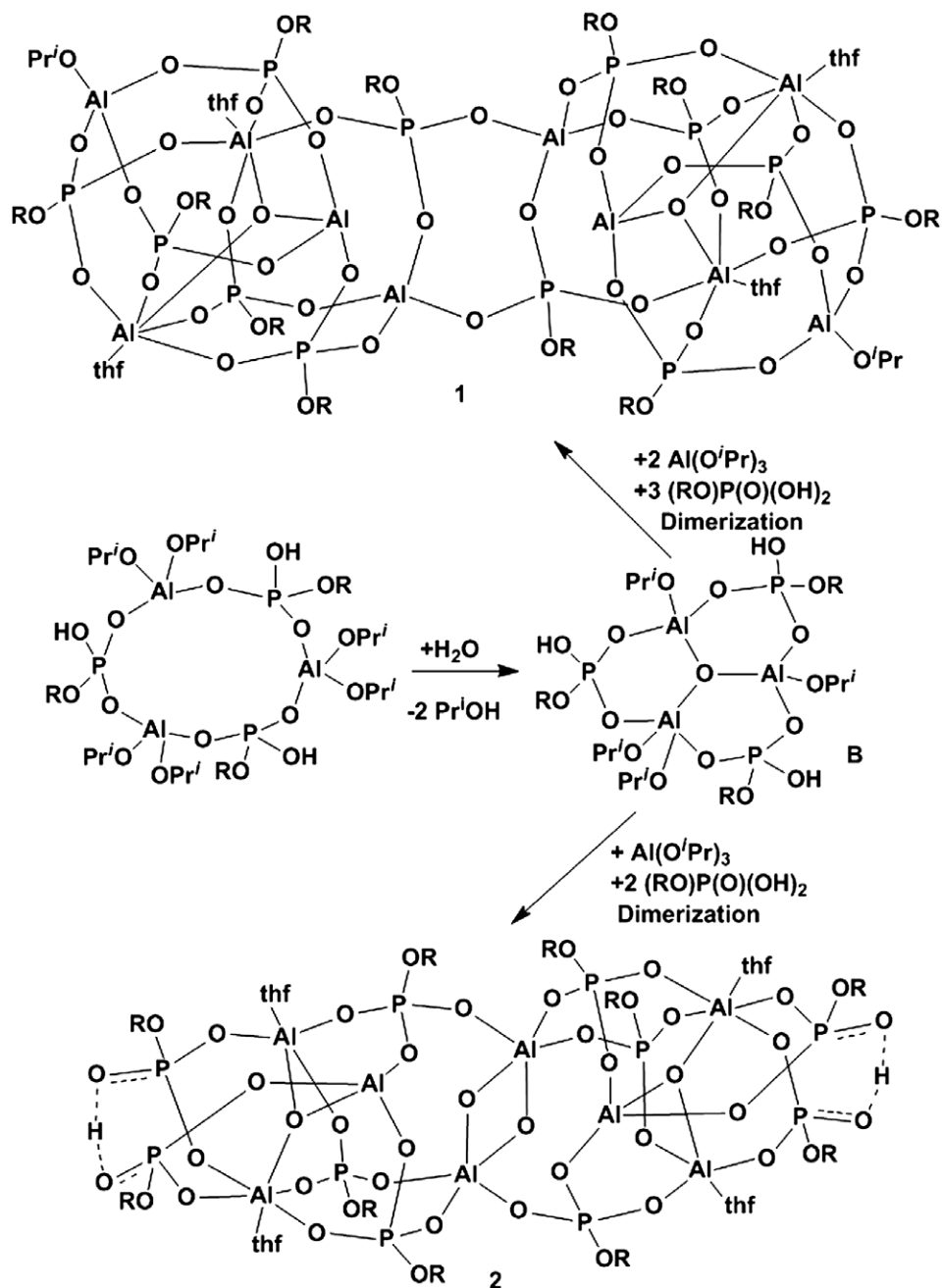
Scheme 3. Suggested pathway for the formation of decameric **1** and octameric **2**.

A careful examination of the core structures in the dodecameric complexes **3** and **4** reveal that both the complexes are derived via the dimerization of a hexameric unit rather than a 4+4+4 addition. A plausible pathway leading to the formation of the two dodecameric aluminophosphate complexes is illustrated in Scheme 4. At an initial stage of the reaction, we envisage the formation of a [Al$_2$(dipp)$_2$] eight-membered ring unit **A**, which resembles S4R building block of zeolites. It is pertinent to note here that several aluminum complexes modelling S4R SBU have been earlier reported [19]. Due to the presence of free PO–H and Al–X functionalities on the intermediate **A**, further reaction with either AlX$_3$ or dippH$_2$ is possible. Subsequently the two free PO–H groups on **A** can react with two additional AlX$_3$ groups, during which time the four Al–X bonds on **A** can also combine with four dipp-H$_2$ ligands to produce **B**, which contains four aluminum centers and six phosphate groups. The intermediate **B** features another three P–OH

groups and one phosphoryl P=O group. Because of the proximity of two P–OH groups and phosphoryl groups they react with another two AlX$_3$ unit only thus leading to the formation of the intermediate **C**. Slow hydrolysis of the Al–X bonds in **C** by the water that is introduced to the flask over a period of several days results in **D** which contains as many as three free PO–H groups pointing towards the same side. This trigger a facile condensation reaction of the hexanuclear intermediates leading to the formation of a dodecameric product. Although it has not been possible to study the intermediates in solution, mainly because the steps up to formation of **C** take place very rapidly, the proposed mechanism is the most plausible that could be conceived at this point of time.

The aluminophosphate complexes discussed herein are the largest examples among all the reported aluminophosphates and have polyhedral cage structure featuring AlO$_4$, AlO$_5$ and AlO$_6$ coordination geometries. Moreover, the core structures of these com-

Scheme 4. Suggested pathway for the formation of dodecameric **3** and **4**.

plexes represent new structural building units in zeolite chemistry. The above rationalization on the formation of different structural units using a retro-synthetic approach offer new dimensions to aluminophosphate chemistry.
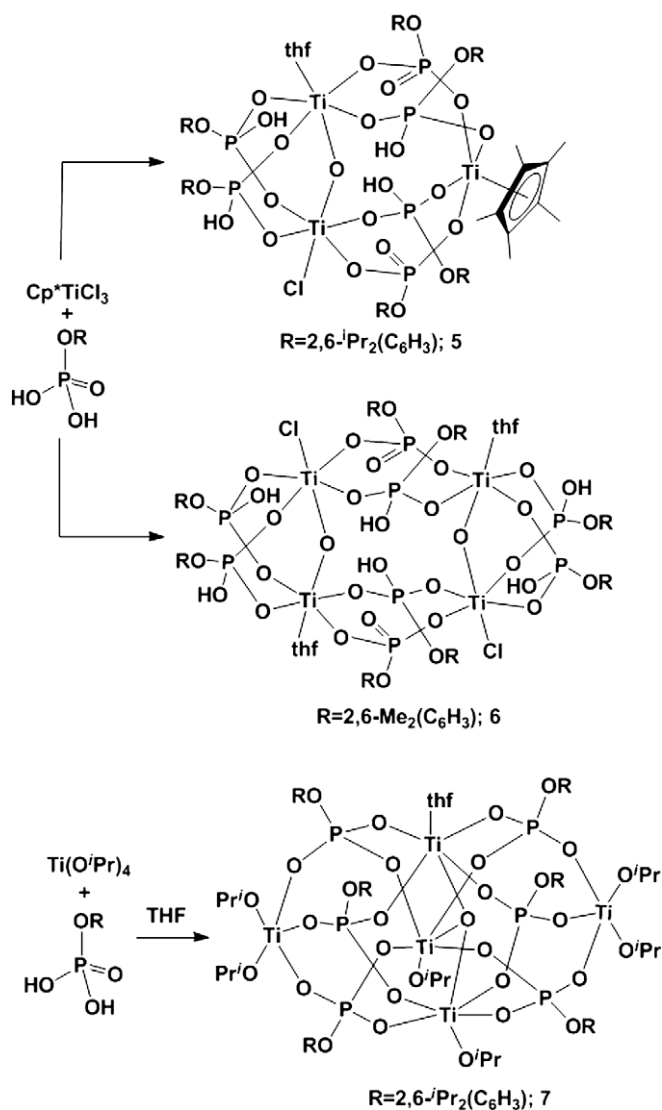
3. Titanium phosphates

Among the transition metal phosphates, titanium phosphates are particularly interesting due to their applications in a variety of applications such as ion-exchange materials, non-linear optical materials and fast ion conductors [20]. Thus several discrete titanium phosphates were reported earlier and the most notable example is a tetrameric oxo-titanium phosphate [TiO(OSiMe$_3$) (O$_2$P(O^{t}Bu)$_2$)]$_4$ [21]. We envisaged that by using a monoester of phosphoric acid high nuclearity complexes can be possibly isolated and investigated its reaction with various titanium precursors. This study resulted in the isolation of a trinuclear, a tetranuclear and a pentanuclear titanium phosphate complex [11f]. Herein, we have reviewed the common structural features among these complexes and thus derived the interdependency between various structural types. These rationalizations will allow us to devise a possible facile interconversion route between each structural types.

Reaction of Cp*TiCl$_3$ with two different bulky aryl esters of phosphoric acid, dimethylphenyl phosphate (dmppH$_2$) and di*iso*propylphenyl phosphate (dippH$_2$) under similar reaction conditions have been investigated and in both the cases products of different nuclearity were isolated. While dipp-H$_2$ reacts with Cp*TiCl$_3$ in thf at 25 °C to yield an air-stable trinuclear titanophosphate cage complex [(Ti$_3$Cp*Cl(μ_2-O)(dipp)$_2$(dippH)$_4$(thf)]·(toluene) (**5**), a similar reaction involving dmppH$_2$ yields the tetranuclear titanophosphate [Ti$_4$Cl$_2$(μ_2-O)$_2$(dmpp)$_2$(dmppH)$_6$-(thf)$_2$]·(toluene)$_2$ (**6**) (Scheme 5). More interestingly, Ti(O^{i}Pr)$_4$, react with dipp-H$_2$ to produce a pentanuclear titanophosphate, [Ti$_5$(μ_3-O)(O^{i}Pr)$_6$((dipp)$_6$(thf)] (**7**) (Scheme 5).

The structural elucidations reveal that in the reactions leading to **5** and **6**, extensive Cp*–Ti bond cleavage occurs, leaving only

one residual Cp*-ligand in cluster **5** and none in **6**. Closer analysis of the structures of **5**–**7** brought forward many common structural features present thus allowing us to relate the different structural types to each other. For example, all the compounds are built around a Ti–O–Ti dimeric building block which implies that the formation of all the three compounds have essentially followed a similar reaction pathway. However, in each case the cluster growth terminates at different stages, thus yielding products of different nuclearity. A plausible pathway to the formation of these clusters is illustrated in Scheme 6. The high reactivity of the intermediates prevented their characterization and thus no proof for existence of the intermediate species is available. It is likely that the initial reaction of Cp*TiCl$_3$ or Ti(O^{i}Pr)$_4$ with phosphate leads to the formation of a eight-membered titanophosphate via the elimination of either HCl or ^{i}PrOH (depending upon the titanium precursor). This dinuclear species undergoes hydrolysis to result an oxo-bridged intermediate **A**. Facile elimination of Cp*H from intermediate **A** takes place to produce **B**. The subsequent steps involve stepwise addition of two phosphate ligands and one titanium precursor to produce the trinuclear cluster **5** via **C**. The intermediate **C** can also react with another unit of **B** to produce the tetranuclear titanophosphate **6**. The formation of **5** versus **6** mainly depends on the steric bulkiness of the phosphate ligand. In the case of less bulkier dimethylphenyl phosphate, tetranuclear cluster formation seems to be the preferred reaction. Thus when the steric bulk is less two dimeric units can condense together to yield a tetranuclear product. However, in case of more bulky dipp-H$_2$ such a dimerization reaction is prevented and addition of another unit of Cp*TiCl$_3$ to eventually produce a trinuclear complex is facilitated. This hypothesis also supports the formation of pentanuclear **7** which has been isolated only when dipp-H$_2$ was used and which can be essentially derived by further addition of two units of titanium precursors to trinuclear **5**. Presumably the highly basic –O^{i}Pr terminal ligands in the reaction leading to **7** have induced complete deprotonation of all the acidic protons on the phosphate ligands. However, when Cp*TiCl$_3$ was used as the titanium precursor com-

Scheme 5. Synthesis of titanium phosphates **5–7**.

plete deprotonation of the phosphate ligand was not possible and the cluster growth eventually terminated at an early stage leading to the formation of trinuclear **5**. Although one may argue that such a mechanism is highly speculative, it is important to note that this sequence of events explain the formation of all the three products on the basis of both steric bulkiness of the ligand and the electronic modification of the metal precursor by other terminal ligands such as Cp^*, Cl, and O^iPr.
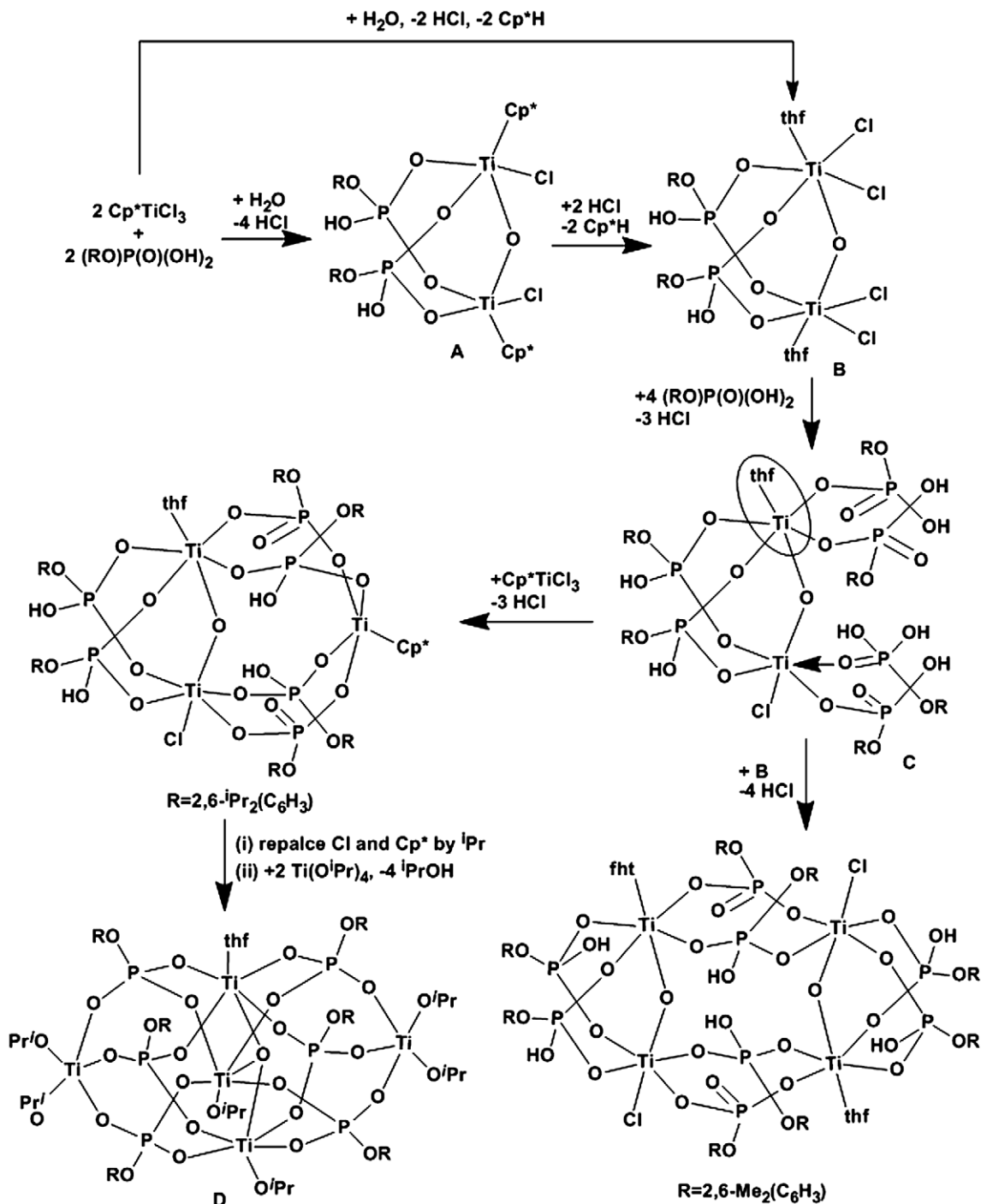
4. Iron phosphates

Oxo-bridged dinuclear iron units featuring phosphates are implicated in many proteins such as purple acid phosphatases from bovine spleen, ribonucleotide reductase from *Escherichia coli*, the invertebrate respiratory protein hemerythrin and the mammalian iron storage protein ferritin [22]. Consequently several diiron phosphate complexes modelling the active sites in the above proteins have been reported [23]. Quite surprisingly, excluding the dinuclear iron phosphates, all other structural types were elusive. However, by using a bulky monoester of phosphoric acid, we were successful in assembling low to medium nuclearity iron complexes with novel topological architectures [11h]. Reaction of 2,6-diiso-

propylphenyl dihydrogen phosphate (dipp-H_2) with ferrous acetate resulted in the formation of mononuclear, [Fe^{II}(dipp-H)$_2$(py)$_4$] (**8**) (py = pyridine), dinuclear [Fe_2^{III}O(dipp-H)$_4$(3,5-dmpz)$_3$(thf)]·(3,5-dmpz)·(thf)$_3$ (**9**) (3,5-dmpz = 3,5-dimethylpyrazole, thf = tetrahydrofuran) and trinuclear, [$Fe_2^{III}Fe^{II}$O(dipp-H)$_6$(thf)$_3$]·(collidine) (**10**) by changing the ancillary amine used in the reaction (Scheme 7). However, on using a preformed μ_3-oxo bridged trinuclear complex, [Fe_3^{III}O(O$_2$CR)$_6$(H$_2$O)$_3$]X (X = Cl and NO$_3$), tetranuclear iron phosphates, [Fe_4^{III}O(dipp)$_3$(py)$_4$-(PhCOO)$_4$]·(toluene)$_3$ (**11**), and [Fe_4^{III}O(dipp)$_3$(OAc)$_4$(py)$_4$]·(py)$_2$ (**12**) were obtained invariably. Moreover a pentanuclear iron complex, [Fe_5^{III}O(dipp)$_6$(py)$_4$Cl$_2$][pyH] (**13**), having a hitherto unknown metallic architecture is obtained by using a iron precursor as simple as FeCl$_3$·6H$_2$O. Surprisingly a seemingly identical pentanuclear iron complex, [Fe_5^{III}O(dipp)$_6$(PhCOOH)$_3$(CH$_3$CN)$_3$] (**14**) can be isolated when the trinuclear precursor complex, [Fe_3^{III}O(O$_2$CPh)$_6$-(H$_2$O)$_3$]Cl is treated with three equivalents of dipp-H_2 in the absence of any ancillary amine.

The interdependence of the structures of complexes **9–14** and how any one of these compounds can be theoretically derived from other complexes (at least in a few cases experimentally) is depicted schematically in Scheme 8. The mononuclear, dinuclear and trinuclear complexes **8–10** are isolated by reacting Fe(OAc)$_2$ and dipp-H_2 in presence of different amines and this advocates that all these complexes are formed following a similar reaction pathway. However, the aggregation terminated at different stages to eventually yield products of different nuclearity. As in case of titanium phosphates one would expect that in this case also basicity of the coligands will play a key role in deciding the nuclearity of the products formed. Our observations suggest that the solubility of the product formed also plays a crucial role in determining the nuclearity. When pyridine was used as the co-ligand, the product, a mononuclear iron phosphate immediately precipitates from the solvent as a green solid. Obtaining single crystalline product was possible only when the reaction is performed at a much smaller scale with minimal stirring. However, when 3,5-dimethylpyrazole was used as the co-ligand, we observed an immediate colour change indicating facile reaction but no solid could be isolated even after prolonged stirring of the reaction mixture. As the reaction mixture was left for crystallization for a longer duration, diffusion of atmospheric oxygen into the reaction mixture facilitates the oxidation of Fe(II) to Fe(III) and thus a dimerization reaction proceeds to eventually yield a dinuclear product. Even when collidine was used as the coligand, the reaction mixture immediately turns intense green indicating a facile reaction. Prolonged stirring did not yield any solid in this case also, thus confirming the high solubility of the product formed and the oxidation takes place when the reaction was left for crystallization yielding a Fe(II)/Fe(III) mixed valent oxo-bridged trinuclear product. However, in the final product obtained collidine could not be accommodated within the coordination sphere due to steric bulkiness and instead thf occupy the sixth coordination sites of iron.

The presence of un-deprotonated P–OH groups in several of these complexes **8–10**, offer possibilities for cluster growth either using more iron or other hetero-metal ions. Especially, this reaction can be efficiently carried out on trinuclear **10**, by utilizing the P–OH groups present on either side of the triangular [$Fe_2^{III}Fe^{II}(\mu_3$-O)]$^{6+}$ core, providing an opportunity to capture other trivalent metals ions. Presence of a μ_3-oxo bridged trinuclear iron unit in the trinuclear, tetranuclear and pentanuclear complexes advocate that all these compounds are formed following the same pathway. However, the aggregation terminated at different stages depending upon the ancillary amine used, to eventually result in products of different nuclearity. Moreover both the tetranuclear and pentanuclear complexes have been derived starting from a

Scheme 6. Suggested pathway for the formation of titanium phosphates 5–7.

μ_3-oxo bridged trinuclear iron carboxylate which has a structure similar to compound 10, thus further establishing our rationalization.

5. Conclusion

Our endeavour to build soluble model compounds of basic building blocks in zeolite structures have resulted in a plethora of main group and transition metal phosphate complexes. The structural variety of the metal phosphates presented herein also compliments the efforts to build similar super structures based on silanols [24] and phosphonic acids [25,26]. Many of these complexes show highly intriguing and novel structural features. Careful examination of the core structures allowed us to rationalize the interdependence between the different structural types and visualize their plausible pathway of formation. Due to the high reactivity and short life span of the intermediates it has not been possible to characterize many intermediates. However, the common structural features present in the isolated products drive us to arrive at a plausible mechanism. Further investigation and isolation of other structural types will definitely provide more credential to these hypotheses and help us to solve the zeolite jigsaw.
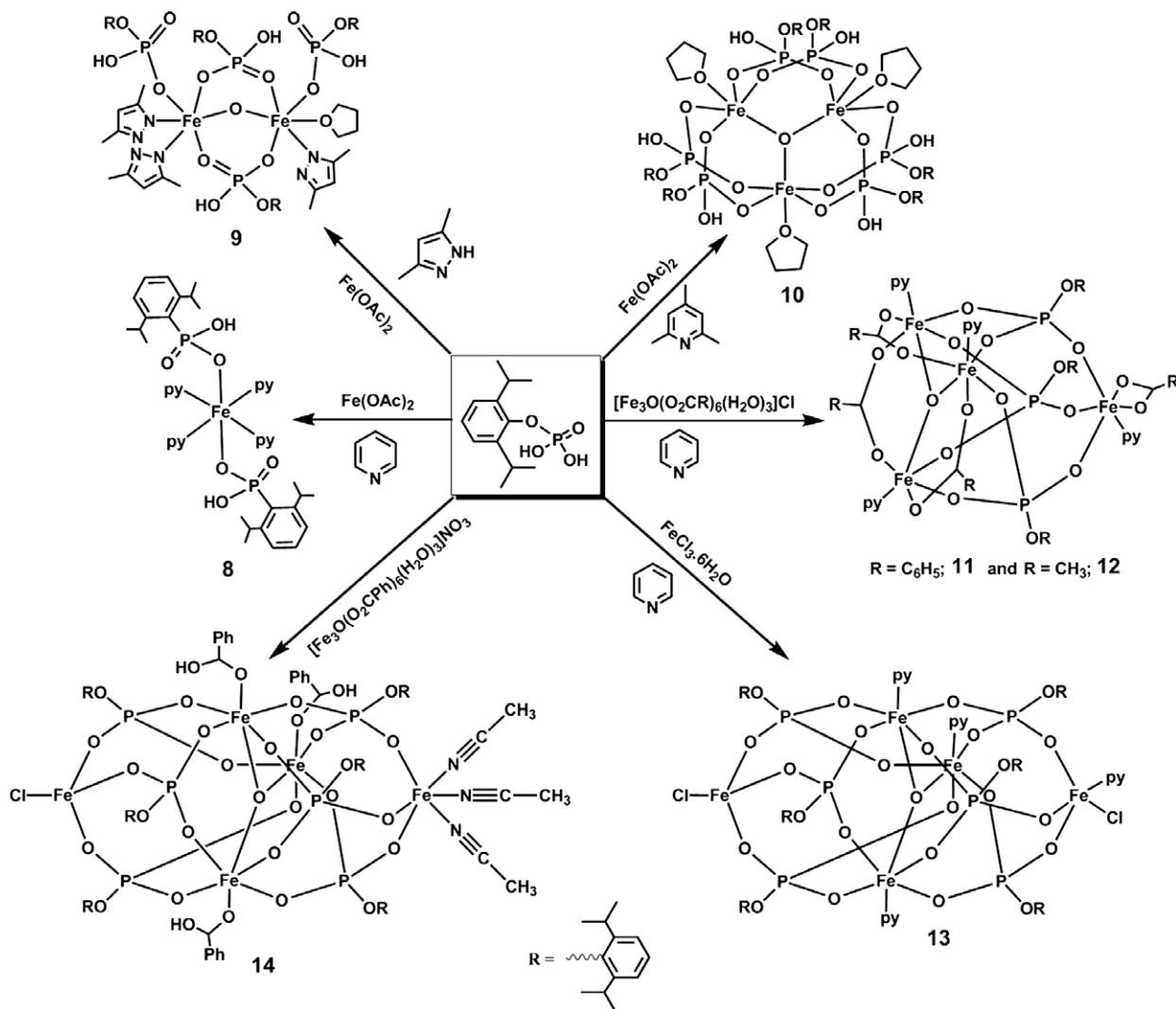
Scheme 7. Synthesis of iron phosphates **8–14**.
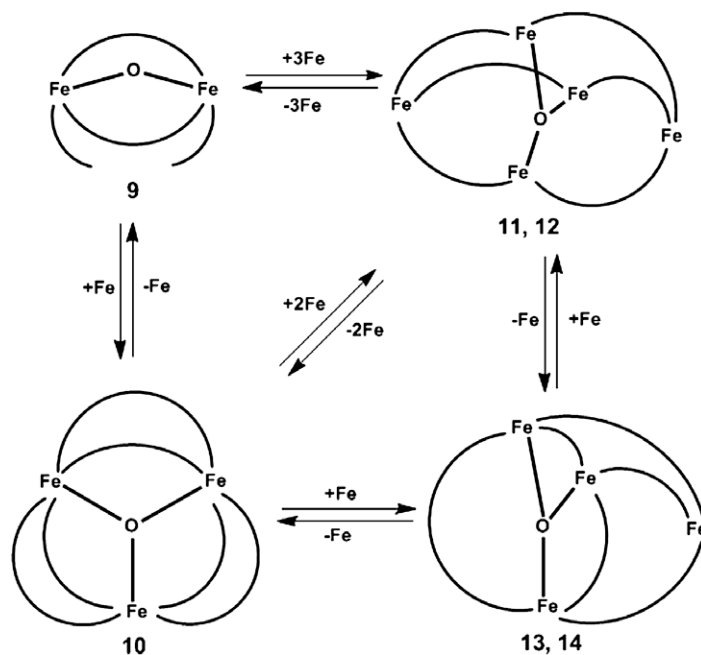
Scheme 8. Interdependence of various structural types among iron phosphates.

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