Metal Phosphate Clusters

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Octameric and Decameric Aluminophosphates**

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Dedicated to Professor C. N. R. Rao

Since the discovery of a novel class of microporous aluminophosphate materials ($AlPO_4$-*n*) nearly 25 years ago, the chemistry of AlPOs has seen a tremendous growth.[1] In particular, use of structurally diverse organic templates has yielded a wide variety of lower dimensional (0D, 1D, and 2D)

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and framework (3D) metal phosphates.[2,3] Parallel to the developments in the area of aluminophosphate materials, there has also been considerable interest in synthesizing discrete and soluble model compounds (and/or structural building units (SBUs) of zeolites) for a better understanding of the mechanism of the formation of zeolites.[4–6] The use of H_3PO_4 for this purpose has limited scope owing to its poor solubility in solvents other than water. Tilley and co-workers[5a,b] and our group[7] have partially overcome this problem by using a diester of H_3PO_4 (di-*tert*-butylphosphate; dtbpH) for the preparation of a wide range of molecular phosphates which could be decomposed at low temperatures to yield metal phosphate materials with exceptional surface area. Significant among these results are a) the facile synthesis of cyclic aluminophosphates with a "single 4-ring" (S4R) core, which serve as precursors for the low-temperature preparation of aluminophosphate (AlPO)[5a] and silicoaluminophosphate (SAPO)[5b] materials, and b) the conversion of one of these molecular phases into 2D framework solids.[3a]

Although dtbpH has been a great success in terms of the preparation of thermally labile metal phosphates, the presence of only one P-OH group means that dtbpH produces only cyclic or 1D polymeric phosphates and not cage-like molecules.[7] We have now overcome this problem by using a phosphoric acid mono-aryl ester[8] to synthesize two novel nanometric aluminophosphate clusters **1** and **2**.

$[Al_{10}\{\mu_3\text{-}O_3P(OR)\}_{12}(\mu_3\text{-}O)_2(O\mathit{i}Pr)_2(thf)_4]\cdot 6\,C_7H_8$ **1**

$[Al_8\{\mu_3\text{-}O_3P(OR)\}_8\{\mu_2\text{-}HO_3P(OR)\}_2(\mu_3\text{-}O)_2(\mu_2\text{-}OH)_2(thf)_4]\cdot 2\,C_7H_8$ **2**

$R = 2,6\text{-}\mathit{i}Pr_2C_6H_3$

The title clusters have been obtained by stirring an equimolar solution of $Al(O\mathit{i}Pr)_3$ and diisopropylphenylphosphate ($dippH_2$) at room temperature in tetrahydrofuran (THF) under dry dinitrogen atmosphere.[9] Cluster **1** is obtained when a THF solution of $Al(O\mathit{i}Pr)_3$ was added to a THF solution of $dippH_2$, while a reverse addition was necessary to obtain **2**. Compound **1** is soluble in common organic solvents despite its very high molecular weight. A single-crystal X-ray diffraction study confirms the molecular formula for **1** with six cocrystallized toluene solvate molecules,[10] whereas the vacuum-dried sample has lost five toluene solvate molecules.[11] In the ^{31}P NMR spectrum, six separate resonances of similar intensity were observed in the upfield range $\delta = -16.1$ to -26.5 ppm, suggesting the presence of six magnetically non-equivalent $\{(OR)PO_3\}^{2-}$ ligands (Figure 1).

The elemental analysis of **2** reveals the complete loss of solvent toluene molecules during the vacuum drying of the sample. The IR spectrum of **2** is essentially identical to **1** but for the presence of an additional weak absorption at $\tilde{\nu} = 2280\ cm^{-1}$ arising from the P-OH group. Unlike **1**, compound **2** is insoluble in all common NMR spectroscopy solvents. Both clusters are thermally stable and do not melt up to 275 °C. Thermolysis of these clusters at higher temperatures results in their conversion into dense-phase $AlPO_4$ materials.

Compound **1** crystallizes in $P\bar{1}$ space group with a large cell volume (5663 $Å^3$), corresponding to the volume of a single molecule of **1** that contains as many as 286 non-hydrogen atoms and has a molecular weight of 4336. The molecule, which displays several interesting structural features, is made up of two units which are connected together across the crystallographic inversion center (Figure 2). The molecular dimensions of **1** are similar to the unit cell dimensions. In fact the length of the molecule (ca. 25.0 Å) is longer than the largest unit cell dimension (*c* axis: ca. 21.05 Å). The size of the inorganic core excluding the organic substituents on the cluster is about 2 nm. A view of the cluster shown in Figure 2 demonstrates the spherical nature of the two $[Al_5(O_3P(OR))_6]$ units (which are built around a μ_3-O center which bridges Al3, Al4, Al5) as well as the presence of

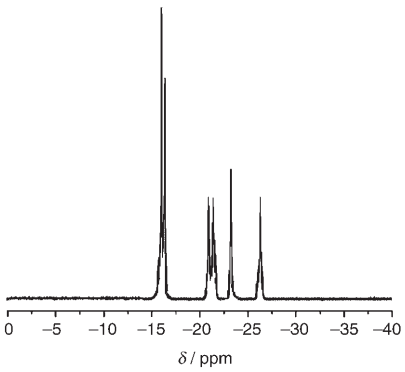


Figure 1. ^{31}P NMR spectrum of **1**.

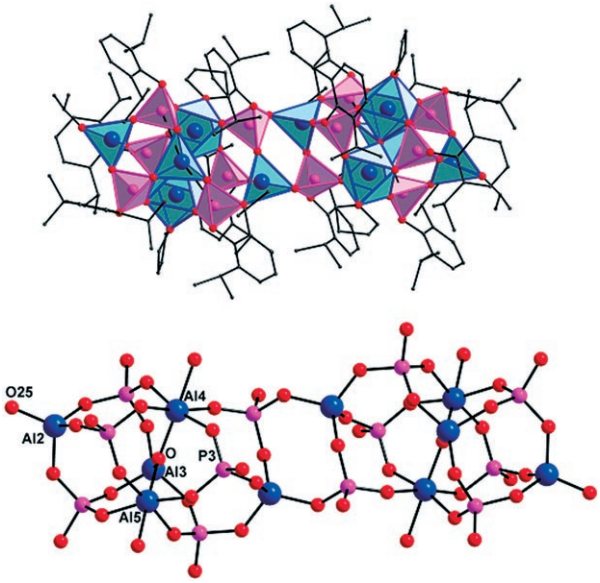


Figure 2. Molecular (top; Al and P coordination environments in polyhedral representation) and core (bottom) structure of **1** (C black, O red, Al blue, P pink). Selected bond lengths [Å] and angles [°]: Al–O(P) 1.723(2)–1.941(2) (av. 1.809), Al–O(*i*Pr) 1.656(2), Al–O(Al) 1.753(2), 1.917(2), 1.929(2), Al–O(thf) 1.966(2), 2.024(2), P–O(Al) 1.482(2)–1.538(2) (av. 1.514), P–O(Ar) 1.571(2)–1.587(2) (av. 1.577); O-Al1-O 107.9(1)–112.9(1), O-Al2-O 105.6(1)–113.2(1), O-Al3-O 102.2(1)–120.1(1), O-Al4-O (*cis*) 84.0(1)–95.5(1), (*trans*) 168.8(1), 172.6(1), 178.5(1), O-Al5-O (*cis*) 84.5(1)–96.5(1), (*trans*) 168.8(1), 175.6(1), 178.0(1), Al-O-P 118.4(1)–154.8(1), Al3-O-Al4 121.7(1), Al3-O-Al5 112.5(1), Al4-O-Al5 125.6(1); cluster dimensions [Å]: O25···O25′ 20.7, Al2···Al2′ 17.5.

a central 4-ring that connects the two units. A closer inspection reveals that each of these $[Al_5(O_3P(OR))_6]$ units is made up of three 3-rings, five 4-rings, and a 6-ring. The cluster as a whole encloses six 3-rings, eleven 4-rings, and two 6-rings and has an architecture which has not been, to our knowledge, observed in any of the known SBUs of aluminophosphate frameworks. Interestingly, the five aluminum ions in each half of the molecule have four different coordination environments. While two of the aluminum ions are six-coordinated with an octahedral geometry, the three tetrahedral aluminum ions have three different coordination environments (one aluminum atom surrounded by four phosphate oxygen atoms, one aluminum atom surrounded by three phosphate oxygen atoms and one O^{2-} ion, and one aluminum surrounded by three phosphate oxygen atoms and one isopropoxide). This varied coordination environments around the aluminum also introduces chemical inequivalence among the six phosphorus atoms on each part of the molecule and hence the six different ^{31}P NMR resonances observed (Figure 1).

The molecule of **2** which crystallizes in $P2_1/n$ space group is also made up of two units, each of which occupying an asymmetric part in the unit cell. The two units are joined together across the crystallographic inversion center (Figure 3). Unlike **1**, the molecular dimensions of **2** are somewhat smaller; the size of the inorganic core is about 1.6 nm in its longest direction. Each of the two $[Al_4(O_3P(OR))_5]$ units is built around a μ_3-O bridge (linking Al3, Al4, Al5), which resides in the center of an $Al_3P_3O_6$ ring. Compound **2** differs from **1** by the absence of one aluminum center and one phosphate ligand per unit. This deficiency in this unsaturated cluster **2** is however compensated by the presence of Al-(μ-OH)-Al and P-O-(μ-H)-O-P bridges. The four aluminum centers in each sub-unit display four different coordination environments. While Al5 is octahedrally coordinated by four phosphate oxygen atoms, one O^{2-} ion, and one thf, the trigonal bipyramidal Al4 is surrounded by three phosphate oxygen atoms, one O^{2-} ion, and one thf. Although both Al1 and Al3 are nearly tetrahedral, Al1 is surrounded by three phosphate oxygen atoms and a hydroxy group while in Al3 the position of hydroxy group is taken up by the oxo ligand. Thus the aluminum cations in **1** and **2** display AlO_4, AlO_5, and AlO_6 coordination geometries with many different environments.

The formation of cluster **1** and **2** from an 1:1 mixture of the reactants is puzzling because of the observations that the equimolar reaction between RPO_3H_2 and AlR_3 normally leads to tetrameric cubanes $[RAlO_3PR']_4$,[12] although hexameric and decameric cages also have been isolated in a few instances.[6b,12c,13] Formation of **1** and **2** however can be understood by invoking the pathway suggested in Scheme 1.[14] It appears that the initial reaction between the

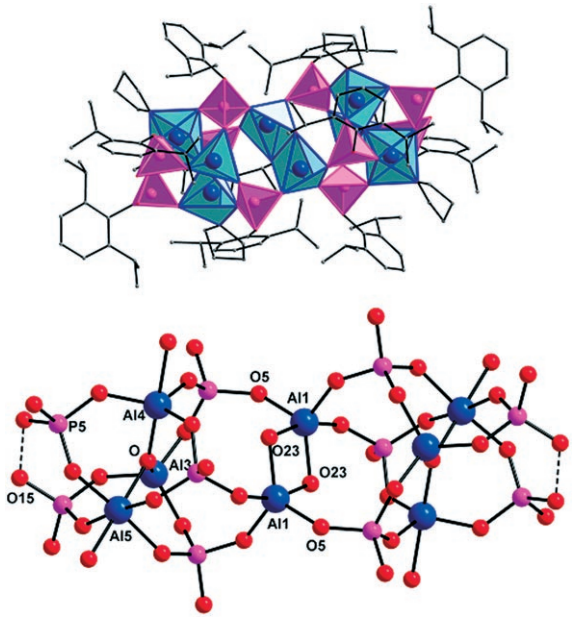
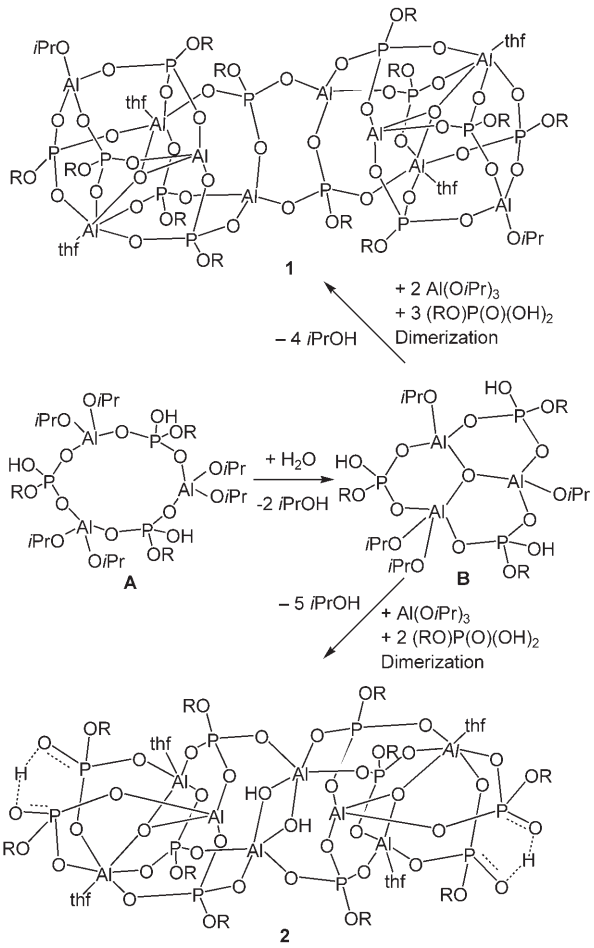


Figure 3. Molecular (top) and core (bottom) structure of **2** (color key as for Figure 2). Selected bond lengths [Å] and angles [°]: Al–O(P) 1.746(4)–1.888(4) (av. 1.807), Al–O(Al) 1.753(4), 1.858(4), 1.937(4), Al–O(thf) 1.959(2), 2.052(2), P–O(Al) 1.486(4)–1.536(4) (av. 1.509), P–O(Ar) 1.571(2)–1.598(2) (av. 1.586); O-Al1-O (tbp) 72.9(2)–97.8(2), 107.8(2)–127.2(2), 164.0(2), O-Al3-O (Td) 108.3(2)–111.0(2), O-Al4-O (tbp) 84.0(1)–96.9(2), 118.5(2)–123.1(2), 177.9(2), O-Al5-O (Oh) 87.1(2)–93.0(2), 174.9(2)–179.5(2), Al3-O-Al4 126.2(2), Al3-O-Al5 112.0(2), Al4-O-Al5 120.9(2), Al1-O23-Al′ 107.1(2); cluster dimensions [Å]: O15···O15′ 16.09, P5···P5′ 14.07. tbp = trigonal bipyramidal, Td = tetrahedral, Oh = octahedral.



Scheme 1. Suggested pathway for the formation of **1** and **2**; see text for details.[14]

two starting materials proceeds via the formation of a "single 6-ring" (S6R) $[(OiPr)_2Al(O_3P(OR)]_3$ unit (**A**) which is attacked by adventitious water to produce the intermediate **B**. The formation of an S6R, capped by a μ-oxo group, and which is similar to **B**, has been observed in gallophosphonates.[15] 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 $Al(OiPr)_3$ and two equivalents of $dippH_2$ to **B** followed by dimerization and a slow Al–O*i*Pr hydrolysis yields **2**.

In summary, by introducing minor modifications in the choice of aluminum and phosphorus sources (AlR_3 versus $Al(OR)_3$; $(RO)_2P(O)(OH)$ versus $(RO)P(O)(OH)_2$) as well as the reaction conditions, we have assembled the largest molecular aluminophosphate. The cores of **1** and **2** represent new SBUs in zeolite chemistry. Further, the presence of a number of interconnected 3-, 4- and 6-rings (3R, 4R, and 6R) and residual functional groups, such as terminal Al–O*i*Pr, Al–thf, Al–OH, P–OH, and hydrolysable P–OR linkages, makes the nanometer sized **1** and **2** ideal building blocks for realizing newer framework structures. We are presently exploring these possibilities.

Experimental Section

Synthesis of **1**: $Al(OiPr)_3$ (408 mg, 2 mmol) in THF (30 mL) was added drop wise to $dippH_2$ (620 mg, 2 mmol) in THF (20 mL), and stirred for 12 h at 25 °C. The solvent was removed in vacuo and the residue was dissolved in toluene (10 mL) and left for crystallization on the bench top. Colorless crystals of **1** were obtained after one week. Yield: 62 %. M.p. > 275 °C. Elemental analysis (%) calcd for $Al_{10}(O_3P(OR))_{12}(O)(OiPr)_2(thf)_4]\cdot C_7H_8$ (3875.4): C 53.62, H 6.71; found: C 53.76, H 6.82. IR (KBr): $\tilde{\nu}$ = 2965(s), 2929(s), 2871(m), 1633(br), 1467(m), 1440(m), 1384(w), 1364(w), 1338(w), 1259(m), 1182(s), 1105(m), 1070(vs), 942(m), 775(m) cm^{-1}. ^1H NMR ([D_6]benzene, 300 MHz): δ = 6.89–7.11 (m, Ar), 4.85 (s, thf), 3.58–3.87 (m, *i*Pr-CH), 2.11(s, CH_3), 1.14–1.42 ppm (m, *i*Pr-CH_3). ^{31}P NMR ($CDCl_3$, 121 MHz): δ = −16.1, −16.4, −21.1, −21.5, −23.4, −26.4 ppm (all singlets).

Synthesis of **2**: The synthesis was similar to **1**. In the present case, $dippH_2$ was added to $Al(OiPr)_3$ (reverse addition). Yield: 53 %. M.p. > 275 °C. Elemental analysis (%) calcd for $[Al_8\{O_3P(OR)\}_8\{HO_3P(OR)\}_2(O)_2(OH)_2(thf)_4]$ (3110.6): C 51.74, H 6.68; found: C 52.53, H 6.45. IR (KBr): $\tilde{\nu}$ = 2967(s), 2930(s), 2870(m), 2280(w), 1630(br), 1467(m), 1443(m), 1385(w), 1364(w), 1338(w), 1259(m), 1172(s), 1160(s), 1051(vs), 939(m), 773(m) cm^{-1}.

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[9] Synthesis of $AlPO_4$ materials is carried out from $Al(OiPr)_3$ and H_3PO_4 in water, see, S. T. Wilson in *Introduction to Zeolite Science to Practice, Studies in Surface Science and Catalysis 58* (Eds.: H. van Bekkum, E. M. Flanigen, J. C. Jansen), Elsevier, Amsterdam, **1991**, p. 137.

[10] Crystal data for $[Al_{10}\{\mu_3\text{-}O_3P(OR)\}_{12}(\mu_3\text{-}O_2)(OiPr)_2(thf)_4]\cdot 6C_7H_8$ (**1**): $C_{208}H_{298}Al_{10}O_{56}P_{12}$, M_r = 4335.9, triclinic, $P\bar{1}$, Z = 1, a = 15.683(5), b = 18.663(2), c = 21.105(2) Å, α = 83.814(8), β = 70.497(17), γ = 76.689(14)°, V = 5663(2) Å^3, T = 150(2) K, λ = 0.71073 Å, ρ_{calcd} = 1.271 g cm^{-3}, $\mu(Mo_{K\alpha})$ = 0.205 mm^{-1}, F-(000) = 2304, θ = 3–25°, reflections = 19801, parameters = 1288, crystal size = 0.37 × 0.22 × 0.2 mm^3, $R1$ ($I > 2\sigma(I)$) = 0.0498, wR_2 = 0.1049, GOF = 0.892. Crystal data for $[Al_8\{\mu_3\text{-}O_3P(OR)\}_8\{\mu_2\text{-}HO_3P(OR)\}_2(\mu_3\text{-}O)(\mu_3\text{-}OH)_2(thf)_4]\cdot 2C_7H_8$ (**2**): $C_{150}H_{222}Al_8O_{48}P_{10}$, M_r = 3318.82, monoclinic, $P2_1/n$, Z = 2, a = 16.528(4), b = 31.470(6), c = 16.6746(7) Å, β = 98.495(2)°, V = 8578(3) Å^3, T = 150(2) K, λ = 0.71073 Å, ρ_{calcd} = 1.285 g cm^{-3}, $\mu(Mo_{K\alpha})$ = 0.218 mm^{-1}, $F(000)$ = 3520, θ = 3–25°, reflections = 14485, parameters = 973, crystal size = 0.33 × 0.26 × 0.21 mm^3, $R1$ ($I > 2\sigma(I)$) = 0.0708, wR_2 = 0.1599, GOF = 0.832. The diffraction data were obtained on an Oxford Diffraction XCalibur-S CCD system. The structure was solved by direct methods (SHELXS-96[16a]) and refined using SHELXL-97.[16b] All non-hydrogen atoms were subjected to anisotropic refinement. The hydrogen atoms were placed on calculated positions, but were allowed to ride on their parent atoms during subsequent cycles of refinement. CCDC-606933 (**1**) and CCDC-611387 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[11] Both elemental analysis and thermogravimetric analysis (TGA) indicate the loss of five toluene molecules during the vacuum drying of the crystals.

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[13] Although **1** has some structural resemblance to the decameric aluminum phosphonate $[t\mathrm{BuAlO_3PMe}]_{10}$ reported in ref. [6b], there are essential differences in the constitution of these two clusters.

[14] In the absence of spectroscopic characterization or identification of the intermediates, the suggested pathway should be considered tentative.

[15] In spite of drying the phosphate ester over anhydrous $MgSO_4$ and storing the recrystallized sample in a glove-box, small amounts of moisture are always present owing to the hydrophilicity of the phosphate ester. For the formation of a structural unit similar to **B** in the presence of traces of water, see: M. G. Walawalkar, R. Murugavel, A. Voigt, H.-G. Schmidt, H. W. Roesky, *J. Am. Chem. Soc.* **1997**, *119*, 4656 – 4661.

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