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Water in Organoaluminum Chemistry! *Three-in-One* Aluminophosphate Clusters That Incorporate Boehmite Repeating Units

Ramaswamy Murugavel*[a, b] **and Subramaniam Kuppuswamy**[a]

Dedicated to Dr. Thirumalachari Ramasami on the occasion of his 60th birthday

The reaction of water with compounds containing M–C bonds has been a fascinating theme in chemistry since the discovery of Cadet's fuming liquid in a Paris pharmacy in 1747[1] and Frankland's organozinc compounds in Bunsen's laboratory in the 1850s.[2] A recent research account entitled '*Is Water a Friend or Foe in Organometallic Chemistry? The case of Group 13 Organometallic Compounds*,' addressed the role of both adventitious and deliberately added water in the reactions of Group 13 alkyls with various substrates.[3] The skillful experiments carried out in the 1990s on the hydrolysis of organoaluminum and -gallium compounds resulted in unraveling some of the mechanistic details associated with the methylaluminoxane(MAO)-catalyzed polymerization of olefins.[4,5] More recent work by Roesky et al. on the synthesis of $RAl(OH)_2$ demonstrated the power of careful hydrolysis of Al–Me bonds.[6] One of our endeavors in rationally building hierarchical metal phosphate structures,[7–10] which resemble and function as zeolites, centers around the search for new alumniophosphate (AlPO) clusters. There has been a great deal of interest in microporous AlPO materials since their discovery in the 1980s,[11] and subsequently a range of aluminophosphate frameworks has been synthesized.[12] While varied strategies have been adopted by others to build molecular AlPOs,[13] we used phosphoric monoesters for the buildup of larger clusters (octameric and decameric cages) starting from aluminum isopropoxide.[7] The latter studies revealed significantly that the cluster growth takes place in a stepwise manner and that the growth terminates by the hydrolysis of peripheral functions on aluminum. Herein, we now report how slow introduction of adequate amounts water in the reaction between an Al^{III} source and a aryl phosphate leads to the isolation of compartmentalized dodecanuclear clusters, comprising two tetranuclear aluminophosphate units and a tetrameric aluminum hydroxide unit.

Stirring an equimolar solution of $i\mathrm{Bu}_2\mathrm{AlH}$ and diisopropylphenylphosphate (dipp-H_2) at room temperature in petroleum ether followed by a very slow crystallization of the concentrated reaction mixture with a few drops of THF led to the isolation of **1**; $R = 2,6\text{-}i\mathrm{Pr}_2\mathrm{C}_6\mathrm{H}_3$) as single crystals in 90 % yield. A similar reaction involving $AlCl_3$ and dippH_2 in THF followed by crystallization from toluene over several days results in the isolation of **2** in 60 % yield (Scheme 1).

$$[\mathrm{Al}_{12}(\mathrm{O}i\mathrm{Bu})_4(\mathrm{ROPO}_3)_{12}(\mu_3\text{-OH})_2(\mu\text{-OH})_6(\mathrm{OH}_2)_2(\mathrm{thf}_4)]\cdot(\mathrm{THF})_4 \quad \mathbf{1}$$

$$[\mathrm{Al}_{12}\mathrm{Cl}_4(\mathrm{ROPO}_3)_{12}(\mu_3\text{-OH})_2(\mu\text{-OH})_6(\mathrm{OH}_2)_2(\mathrm{thf}_4)]\cdot(\mathrm{toluene})_4 \quad \mathbf{2}$$

The lattice THF molecules in **1** and the toluene in **2** were partially lost during the drying of the samples in vacuum, as shown by the elemental analysis of various batches of crystals. The IR spectral characteristics of both the compounds are very similar. The absence of any absorption at 2350 cm^{-1} indicates the complete deprotonation of all dipp ligands in the clusters. Compounds **1** and **2** display four resonances each in the ^{31}P NMR spectra at room temperature, which indicates four different chemical environments for the dipp ligands in the clusters (vide infra). Both clusters are thermally stable and do not melt up to 275 °C. Thermolysis of these clusters at higher temperatures results in their conversion to dense-phase $AlPO_4$ materials. The ^{27}Al NMR spectra of both samples show a broad spectral pattern with two peaks corresponding to the octahedral and tetrahedral Al centers

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[a] Prof. R. Murugavel, S. Kuppuswamy
Department of Chemistry, IIT-Bombay
Powai, Mumbai-400076 (India)
Fax: (+91) 22-2572-3480
URL: www.chem.iitb.ac.in/people/Faculty/prof/rmv.html
E-mail: rmv@chem.iitb.ac.in

[b] Prof. R. Murugavel
Center for Research in Nanotechnology and Science (CRNTS)
IIT-Bombay, Powai, Mumbai-400076 (India)

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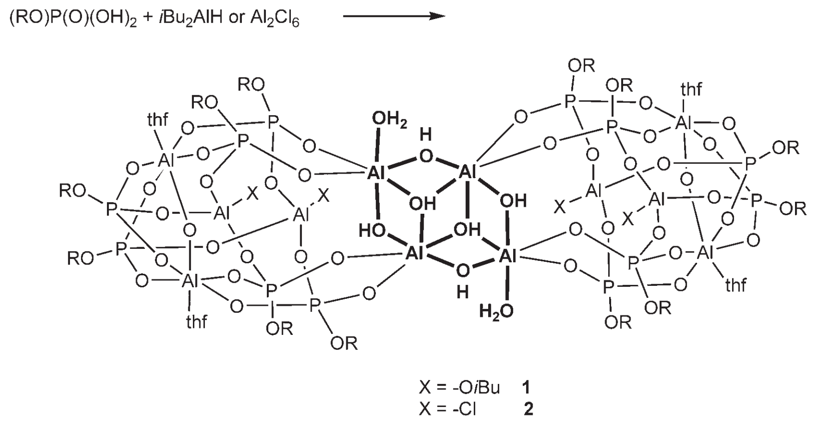


Scheme 1. Synthesis of dodecamers **1** and **2**

at $\delta = -2.4$ and 54.7 ppm for **1** and $\delta = -6.0$ and 58.8 ppm for **2**, respectively.

A single-crystal X-ray diffraction study on both the compounds revealed them to be structurally similar dodecameric clusters. Since the molecular structures of **1** and **2** are quite similar, only the structure of **2** is described here in detail.[14] Compound **2** crystallizes in the $P\bar{1}$ space group with a cell volume of 5493 Å^3, corresponding to the volume of a single molecule of **2** that contains 278 non-hydrogen atoms and 280 hydrogen atoms (molecular weight 4369). Compound **1** also has a similar molecular weight (4440).

Compound **2** displays several interesting structural features, the most significant of which is the architecture of the cluster core itself. The molecular structure of **2** (Figure 1) is rugby-ball shaped, made up of twelve aluminum centers and twelve oganophosphate ligands together with hydroxide and chloride ligands. The molecule is about 25 Å long, and the inorganic core, excluding the organic substituents, is about 2 nm. Although the cluster is very large, its architecture can be easily understood by viewing it as a *three-in-one* cluster, in which two aluminophosphate bowls are stitched together through a central aluminum hydroxide unit. Each of the two aluminophosphate bowls contains four aluminum centers and six phosphate ligands (Figure 1, bottom left). All four phosphate groups situated closer to the rim of the bowl have one free P=O group each, which points outwards (O11, O15, O17, O21). These oxygen atoms of the bowls act as a glue to bind to the central $Al_4(OH)_6$ unit (Figure 1, bottom right), resulting in the final rugby-ball-shaped cluster (Figure 1, top).

The central $Al_4(OH)_6$ unit in **2** contains four six-coordinate aluminum atoms (Al5, Al5′, A16, and Al6′) held together by two μ_3-OH and four μ-OH groups, which can be best described as two face-shared cubes, in which two of the diagonally opposing aluminum vertices are absent (Figure 1; bottom right), Quite interestingly, the mineral boehmite and its polymorph diaspore also

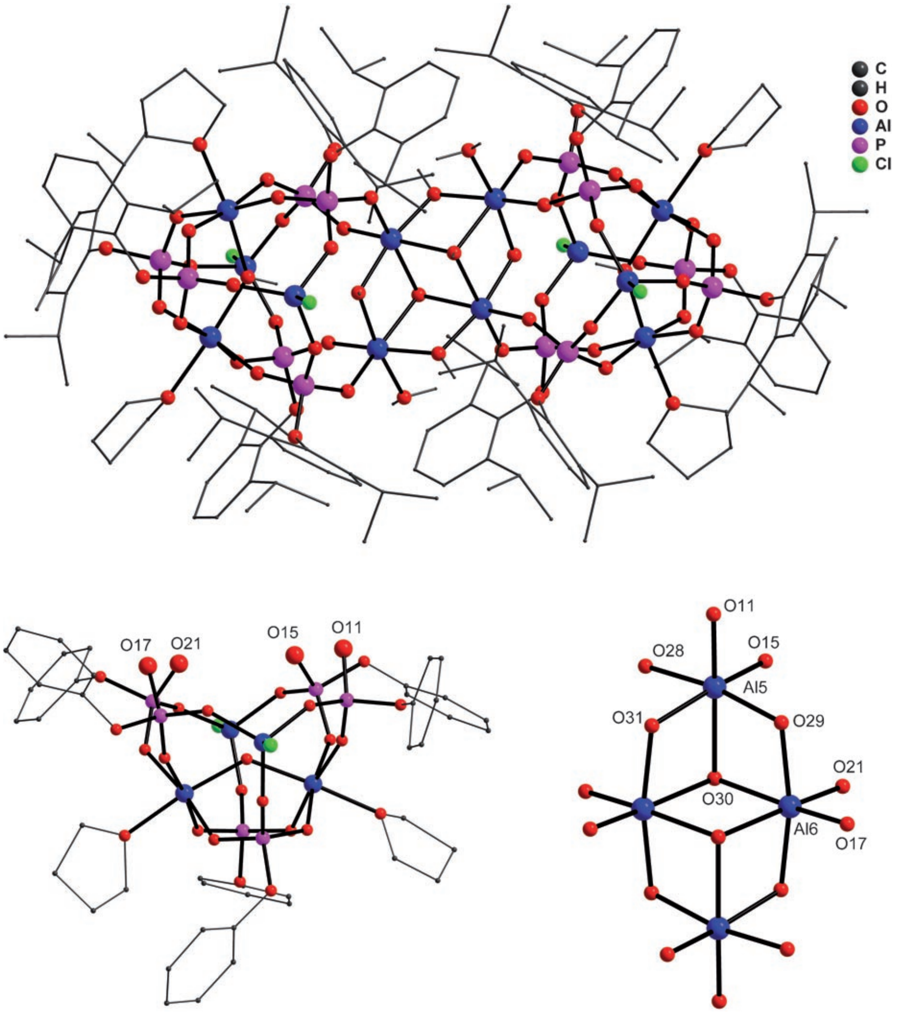


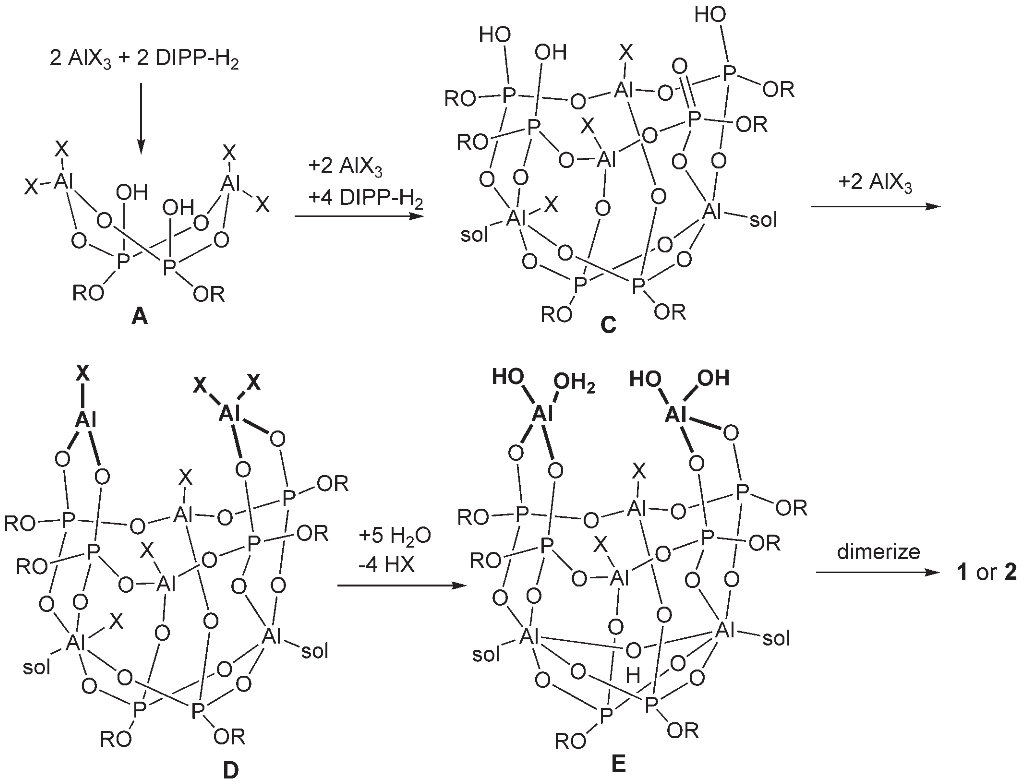
Figure 1. Molecular structure of **2** (top); aluminophosphate (bottom left) and aluminum hydroxide (bottom right) fragments of **2**.

contain Al_4O_6 repeating units (as well Al_3O_4 units),[15–17] and hence clusters **1** and **2** can be considered as AlPO clusters that incorporate small repeating units of boehmite.

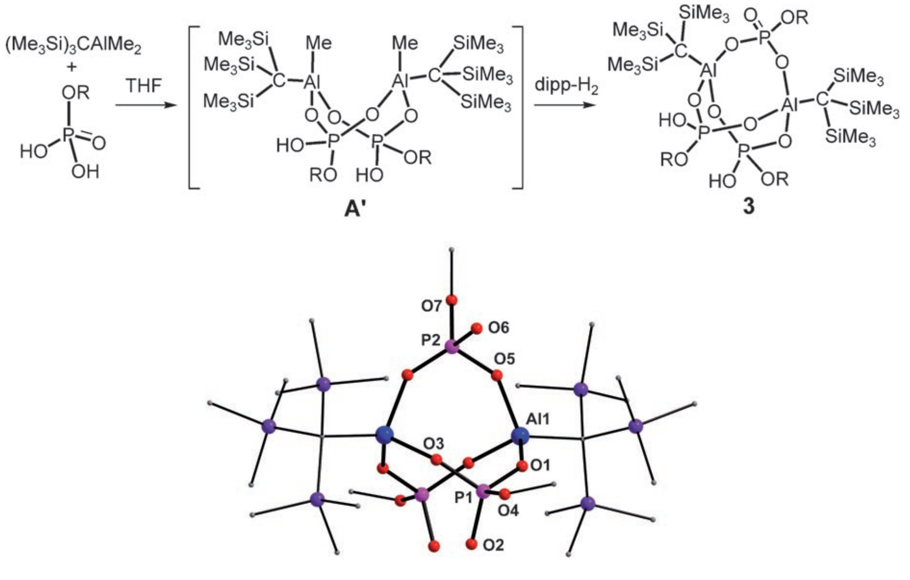
The six aluminum centers in the centrosymmetric half of the molecule show four different coordination environments. The basal aluminum centers Al1 and Al2 at the bottom of the bowl are hexacoordinate with a regular octahedral geometry, in which the metal ions are surrounded by four phosphate oxygen atoms, a μ-OH group that bridges Al1 and Al2, and a solvent THF molecule. Al3 and Al4, which are located in the middle of the bowl, are the only tetracoordinate tetrahedral Al centers. Each of these metal ions is surrounded by three oxygen atoms belonging to three different phosphate ligands and an X ligand. Whereas in **2**, X is an unreacted chloride ligand, in **1** the isobutyl group has undergone oxidation to yield an O*i*Bu substituent on aluminum. The Al ions in the central core, Al5 and Al6, which appear to be similar in terms of the octahedral coordination geometry, differ with respect to the ligating atoms around them. Whereas Al5 is surrounded by two phosphate oxygen atoms, three bridging hydroxide lidands, and a terminal aqua ligand, the central Al6 is ligated by two phosphate oxygen atoms and four bridging hydroxide ligands.

Although it is convenient to view and understand molecules **1** and **2** as three-compartmental systems, it is highly unlikely that in reality the AlPO bowls and the Al hydroxide central unit were formed simultaneously in solution (in a 2:1 ratio!) and then joined together later to form the final cluster. A closer look at the clusters **1** and **2** indicates that they should have essentially formed by a dimerization reaction of the hexameric cluster units, rather than a [4+4+4] addition. A plausible pathway for the formation of clusters **1** and **2** is outlined in Scheme 2. The cluster growth clearly begins with the formation of a $[Al_2(dipp)_2]$ eight-membered-ring unit (**A**), which resembles several model compounds synthesized for the S4R building block of zeolites (vide infra).[13] Due to the presence of free PO−H and Al−X functionalities on **A**, additional molecules of AlX_3 and $dippH_2$ can add on to this unit. For example, the two free PO−H groups on **A** can react with two more AlX_3 groups to produce **B**, during which time the four Al−X bonds on **A** can also combine with four more dipp-H_2 ligands to produce **C**, which contains four aluminum centers and six phosphate groups. The cluster fragment **C** presumably undergoes a slow hydrolysis by the water that is introduced to the flask over a period of several days and results in **E**.[18] Since **E** contains as many as three free PO−H groups pointing towards the same side, a facile dimerization reaction is triggered to form the final cluster. Although it has not been possible to study the intermediates in solution, mainly because the steps up to the formation of **D** take place very rapidly, the proposed mechanism is the most plausible that can be conceived at this point of time.

Apart from the fact that eight-membered-ring aluminophosphates of type **A** have already been isolated, additional evidence for the above mechanism has been obtained by the successful synthesis and structural characterization of **3** (Scheme 3) starting from a more kinetically stable aluminum



Scheme 2. Plausible mechanism for the formation of **1** and **2**.



Scheme 3. Synthesis and core structure of **3**.

alkyl that is more stable to attack by water. The reaction of $(Me_3Si)_3CAlMe_2$ with dipp-H_2 under identical conditions leads to the formation of the dinuclear compound **3** and not a polynuclear aluminophosphate. Compound **3**, which has been characterized by analytical, spectroscopic, and single-crystal X-ray diffraction studies,[14] is made up of two aluminum atoms that are bridged by two dipp-H and one dipp ligand. Each aluminum atom is tetracoordinate, attached to a bulky $C(SiMe_3)_3$ group in addition to three phosphate oxygen atoms. The ^{31}P NMR spectrum of **3** displays three different signals for the three phosphate ligands in the molecule. The ESI mass spectrum of **3** shows the molecular ion peak (minus water) at *m*/*z* 1289 (100 %).

$$[\{(Me_3Si)_3CAl\}_2(dippH)_2(dipp)] \cdot (toluene)_3 \cdot (H_2O) \quad \mathbf{3}$$

The formation of **3** also clearly proceeds initially in the same way as that of **1** and **2**, with the formation of the eight-membered ring intermediate **A′** with free P–OH groups. However, due to the presence of the sterically bulky and chemically inert $C(SiMe_3)_3$ group on aluminum, neither the cluster expansion reaction nor the Al–C hydrolysis takes place during the synthesis of **3**. It appears that the Al–Me groups on **A′** consume another molecule of dipp-H_2 to form **3**. Thus, the isolation of **3** provides mechanistic insights into the formation of clusters **1** and **2**, at least at the early stages of the reaction.

In summary, we have shown that controlled hydrolysis of functional aluminophosphate clusters under ambient conditions can lead to the assembly of large clusters in a highly reproducible manner. The clusters retain the aluminophosphate and aluminum hydroxide identities in the respective regions of the clusters. Insights into the mechanism for the formation of such large clusters have been gleaned by an independent synthesis of a dimeric aluminophosphate bearing a bulky, chemically inert R group. With the successful synthesis of octa-, deca-, and dodecameric aluminophosphate clusters, it appears that the nuclearity can be further increased by suitable changes in the aluminum and phosphate starting materials. We are currently investigating these aspects.

Experimental Section

Synthesis of 1: Solid dipp-H_2 (516 mg, 2 mmol) was added to *i*Bu_2AlH (2 mL; 1.0 M solution in heptane, 2 mmol) in petroleum ether (20 mL). The reaction mixture was stirred overnight at room temperature and concentrated to 10 mL under vacuum. A few drops of tetrahydrofuran was added to the above solution, which was then left to crystallize. Colorless crystals of this compound were obtained after one week. Yield: 90 %; m.p. > 275 °C; ^{1}H NMR (300 MHz, [D$_6$]benzene, 25 °C, TMS): δ = 7.05 (br), 3.56–3.93 (br), 3.06–3.15 (br), 1.73–1.80 (br), 1.24–1.29 (br), 1.06 (d), 0.87–0.91 (m), 0.73–0.79 (br), 0.28 (s), −0.01 (s), −0.02 ppm (s); ^{31}P NMR (121 MHz, [D$_6$]benzene, 25 °C, H_3PO_4): δ = −0.03, −9.5, −15.4, −23.3 ppm; ^{27}Al NMR (78 MHz, [D$_6$]benzene, 25 °C, $Al(NO_3)_3$): δ = 54.7, −2.4 ppm; IR (KBr): $\tilde{\nu}$ = 3410 (br), 3067 (w), 2965 (s), 2931 (w), 2871 (w), 1627 (br), 1467 (m), 1442 (m), 1383 (w), 1363 (w), 1337 (w), 1258 (m), 1178 (s), 1159 (w), 1105 (w), 1051 (vs), 1031 (w), 937 (m), 773 cm^{-1} (m); elemental analysis calcd (%) for $Al_{12}C_{176}H_{284}O_{66}P_{12}$: C 50.92, H 6.90; found: C 51.66, H 7.04.

Synthesis of 2: Solid Al_2Cl_6 (267 mg, 1 mmol) was dissolved in THF (30 mL), and dipp-H_2 (516 mg, 2 mmol) in THF (20 mL) was added dropwise through a syringe at room temperature over 10 min. The reaction mixture was stirred 24 h at room temperature. The solvent was removed in vacuo and the residue was dissolved in toluene (10 mL) and left for crystallization. Colorless crystals **2**·(toluene)$_4$ were obtained after one week. Yield: 60 %; m.p. > 275 °C; ^{31}P NMR (121 MHz, [D$_6$]benzene, 25 °C, H_3PO_4): δ = −17.2 (s), −18.1 (s), −25.2 (s), −26.3 ppm (s); ^{27}Al NMR (78 MHz, [D$_6$]benzene, 25 °C, $Al(NO_3)_3$): δ = 58.8, −6.0 ppm; IR (KBr): $\tilde{\nu}$ = 3421 (br), 3067 (w), 2964 (s), 2930 (w), 2870 (w), 1627 (br), 1466 (m), 1441 (m), 1384 (w), 1364 (w), 1336 (w), 1257 (m), 1182 (s), 1104 (w), 1070 (vs), 939 (m), 775 cm^{-1} (m); elemental analysis calcd (%) for $Al_{12}C_{167}H_{256}O_{62}P_{12}Cl_4$: C 49.01, H 6.30; found: C 49.17, H 6.65.

Synthesis of 3: Solid $(Me_3Si)_3CAlMe_2$ (289 mg, 1 mmol) was dissolved in THF (30 mL), and dipp-H_2 (387 mg, 1.5 mmol) in THF (20 mL) was added dropwise through a syringe at room temperature. The reaction mixture was stirred 24 h and the solvent was removed in vacuo. The residue was dissolved in toluene (10 mL), filtered, and the clear solution was left for crystallization at −30 °C. Colorless crystals of this compound were obtained after one week. Yield: 65 %; m.p. > 275 °C; ^{1}H NMR (400 MHz, [D$_6$]benzene, 25 °C, TMS): δ = 7.02–7.11 (m, 9H; Ar-H), 3.88 (septet, ^3J(H,H) = 6.8 Hz, 4H; *i*Pr-CH), 3.58 (septet, ^3J(H,H) = 6.8 Hz, 2H; *i*Pr-CH), 1.30 (d, ^3J(H,H) = 6.8 Hz, 36H; *i*Pr-CH$_3$), 0.29 (s, 27H; Si-CH$_3$), 0.28 ppm (s, 27H; Si-CH$_3$); ^{31}P NMR (121 MHz, [D$_6$]benzene, 25 °C, H_3PO_4): δ = −12.66 (s), −12.73 (s), −16.2 ppm (s); ^{27}Al NMR (78 MHz, [D$_6$]benzene, 25 °C, $Al(NO_3)_3$): δ = 51.3 ppm; IR (KBr): $\tilde{\nu}$ = 3068 (w), 2971 (m), 2930 (w), 2872 (w), 2280 (br), 1631 (br), 1464 (w), 1438 (w), 1384 (w), 1331 (w), 1252 (m), 1175 (s), 1109 (m), 1051 (s), 1029 (s), 855 cm^{-1} (m); ESI-MS (70 eV): *m*/*z* (%): 1289 (100) [$M^+ - H_2O$]; elemental analysis calcd (%) for $Al_2C_{56}H_{109}O_{13}P_3Si_6$: C 51.51, H 8.41; found: C 51.34, H 8.38.

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Keywords: aluminum · cluster compounds · hydrolysis · phosphates · X-ray diffraction · zeolite analogues

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[14] Crystal data for **1**: $C_{192}H_{316}Al_{12}O_{70}P_{12}$, $M_r = 4439.85$, monoclinic, $P2_1/a$, $Z = 2$, $a = 16.853(2)$, $b = 40.711(5)$, $c = 19.057(1)$ Å, $\beta = 109.080(7)°$, $V = 12\,356(2)$ Å^3, $T = 150(2)$ K, $\lambda = 0.71073$, $\rho_{calcd} = 1.193$ g cm^{-3}, $\mu(Mo_{K\alpha}) = 0.200$ mm^{-1}, $F(000) = 4728$, θ range = 2.98 to 25.00°, reflections = 120318, parameters 1273, crystal size = 0.40 × 0.36 × 0.30 mm^3, $R1$ $(I > 2\sigma(I)) = 0.1255$, $wR_2 = 0.3097$, GOF = 1.188. Crystal data for **2**: $C_{188}H_{280}Al_{12}Cl_4O_{62}P_{12}$, $M_r = 4369.3$, triclinic, $P\bar{1}$, $Z = 1$, $a = 16.694(1)$, $b = 18.729(2)$, $c = 18.976(2)$ Å, $\alpha = 88.142(8)°$, $\beta = 78.899(8)°$, $\gamma = 70.743(7)°$, $V = 5493.3(9)$ Å^3, $T = 150(2)$ K, $\lambda = 0.71073$, $\rho_{calcd} = 1.321$ g cm^{-3}, $\mu(Mo_{K\alpha}) = 0.268$ mm^{-1}, $F(000) = 2308$, θ range = 3.01 to 25.00°, reflections = 53200, parameters 1242, crystal size = 0.40 × 0.36 × 0.31 mm^3, $R1$ $(I > 2\sigma(I)) = 0.0679$, $wR_2 = 0.1885$, GOF = 0.985. Crystal data for **3**: $C_{77}H_{133}Al_2O_{13}P_3Si_6$, $M_r = 1582.24$, monoclinic, $C2/c$, $Z = 4$, $a = 26.047(5)$, $b = 13.567(5)$, $c = 26.736(5)$ Å, $\beta = 106.258(5)°$, $V = 9070(4)$ Å^3, $T = 150(2)$ K, $\lambda = 0.71073$, $\rho_{calcd} = 1.159$ g cm^{-3}, $\mu(Mo_{K\alpha}) = 0.218$ mm^{-1}, $F(000) = 3146$, θ range = 1.59 to 25.97°, reflections = 8845, parameters 497, crystal size = 0.35 × 0.32 × 0.29 mm^3, $R1$ $(I > 2\sigma(I)) = 0.0942$, $wR_2 = 0.2469$, GOF = 1.063. The diffraction data were obtained on an Oxford Diffraction XCalibur-S CCD system. The structure was solved by direct methods (SHELXS-96[19a]) and refined using SHELXL-96.[19b] 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. The crystal structure of **3** is severely disordered. Intensity data collection carried out on three different crystals yielded the same results although it has been possible to fully solve the structure. This precludes any detailed description of structure of **3**. CCDC-671754, CCDC-671755, and CCDC-671756 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.

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[16] Apart from boehmite, the Al_4O_6 units have also been found in other Al clusters $Al_{10}(OH)_{16}(OSiEt_3)_{14}$,[17a] $[Al_{13}(OH)_{18}(heidi)_6(H_2O)_6]^{3+}$,[17b] $[Al_{13}(OH)_{24}(H_2O)_{24}]^{15+}$,[17c] $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$,[17d] and $[Al_{15}(O)_4(OH)_{20}(hpdta)_4]^{3-}$.[17e]

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[18] Additionally, it was also found that trace amounts of water always remain in dippH_2, in spite of the procedure employed to dry dippH_2.

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