

## Convenient Synthesis of Aluminum and Gallium Phosphonate Cages

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The reactions of  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$  and  $\text{GaCl}_3$  with 2-pyridylphosphonic acid (2PypoH<sub>2</sub>) and 4-pyridylphosphonic acid (4PypoH<sub>2</sub>) afford cyclic aluminum and gallium phosphonate structures of  $[(2\text{PypoH})_4\text{Al}_4(\text{OH})_{12}]\text{Cl}_8 \cdot 6\text{H}_2\text{O}$  (**1**),  $[(4\text{PypoH})_4\text{Al}_4(\text{OH})_{12}]\text{Cl}_8 \cdot 11\text{H}_2\text{O}$  (**2**),  $[(2\text{PypoH})_4\text{Al}_4(\text{OH})_{12}](\text{NO}_3)_8 \cdot 7\text{H}_2\text{O}$  (**3**),  $[(2\text{PypoH})_2(2\text{Pypo})_4\text{Ga}_8\text{Cl}_{12}(\text{OH})_4(\text{thf})_2](\text{GaCl}_4)_2 \cdot 8\text{thf}$  (**4**), and  $[(2\text{PypoH})_2(2\text{Pypo})_4\text{Ga}_8\text{Cl}_{12}(\text{OH})_4(\text{thf})_2](\text{NO}_3)_2 \cdot 9\text{thf}$  (**5**). Structures **1–3** feature four aluminum atoms bridged by oxygen atoms from the phosphonate moiety and show structural resemblance to the secondary building units found in zeolites and aluminum phosphates. The gallium complexes, **4** and **5**, have eight gallium atoms bridged by phosphonate moieties with two  $\text{GaCl}_4^-$  counterions present in **4** and nitrate ions in **5**. The cage structures **1–3** are interlinked by strong hydrogen bonds, forming polymeric chains that, for aluminum, are thermally robust. Exchange of the phosphonic acid for the more flexible 4PyCH<sub>2</sub>PO<sub>3</sub>H<sub>2</sub> afforded a coordination polymer with a 1:1 Ga:P ratio,  $\{[(4\text{PyCH}_2\text{PO}_3\text{H})\text{Ga}(\text{OH})_2]_x(\text{NO}_3)_2 \cdot 0.5\text{H}_2\text{O}\}_x$  (**6**). Complexes **1–6** were characterized by single-crystal X-ray diffraction, NMR, and mass spectrometry and studied by TGA.

## Introduction

The reactivity of phosphoric acid with aluminum and gallium species has been studied as early as 1975 by Cassidy et al.,<sup>1</sup> who prepared a tetrameric complex of aluminum phosphate from the reaction of  $\text{AlCl}_3$  with phosphoric acid in ethanol that on heating readily decomposes to aluminum phosphate. Later work in this area was pioneered by Roesky<sup>2</sup> and Barron<sup>3</sup> and led to the formation of molecular phosphonate cages. Investigations of phosphonic acid derivatives of the p-block elements have been more limited and for the most part have used methyl- or phenylphosphonic acids with

aluminum alkyls.<sup>2–4</sup> Experimental work on aluminum phosphonates was revived when their close relationship to the group of aluminum phosphates was realized. To date, most aluminum phosphonates have layered structures prepared from hydrothermal methods, under reflux, or by melting an alum salt together with a phosphonic acid.<sup>4</sup> Although hydrothermal methods give interesting products,<sup>4,5</sup> the isolated product is unpredictable and very sensitive to precise reaction conditions and reaction composition, and the exact method of crystallization is not well defined. Phosphonic acid derivatives make ideal candidates as spacers for metal phosphonates, as they can incorporate virtually any organic group, are prepared by facile syntheses,<sup>6</sup> and, when combined with a metal precursor, afford products that vary structurally from discrete molecules to multidimensional polymers.<sup>7</sup> Much of the recent work has been driven by the fact that

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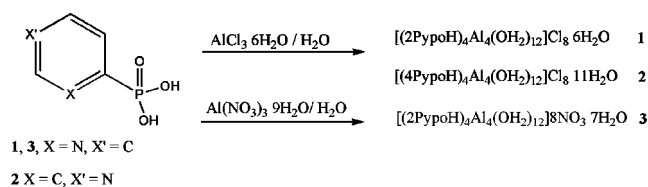
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these compounds have potential as ion exchangers, in catalysis, and as sensors.<sup>8</sup> The majority of work using pyridylphosphonates has focused on tetravalent transition-metal atoms.<sup>9</sup> We were interested in extending our recent work on pyridylphosphonic acids with late transition metals<sup>10</sup> to the main-group elements, to examine how the structural motif would vary with the nature of the metal ions, solvent, and temperature and how these factors would affect the extent of phosphonic acid deprotonation that, in turn, would govern dimensionality of the product. To this end, we investigated the reactivity of aluminum(III) chloride and nitrate and gallium(III) chloride with 2- or 4-pyridylphosphonic acids and of Ga(NO<sub>3</sub>)<sub>3</sub> with 4PyCH<sub>2</sub>PO<sub>3</sub>H<sub>2</sub>, employing room-temperature syntheses, and herein report our results.

## Results and Discussion

**Synthetic Methods.** In keeping with our recent work,<sup>10,11</sup> we wished to perform reactions in aqueous solutions using mild conditions. An array of water-soluble precursors was investigated, allowing reactions to be performed in open vials at ambient temperatures. Furthermore, hydrolysis of aluminum chloride and alkyls by hydrated salts is a mild, widely

**Scheme 1.** Synthesis of Complexes 1–3



used route for alumoxane synthesis;<sup>3,12</sup> therefore, it was anticipated that employing hydrated salts might combine these factors and would favor either discrete cages or polymeric materials. Gallium precursors proved more troublesome, as GaCl<sub>3</sub> readily forms Ga(OH)<sub>3</sub> under aqueous conditions.<sup>13,14</sup> To slow the hydrolysis process down and give gallium a chance to complex with the ligand, the reactions were performed and worked up under inert conditions, although solvents were used undried, directly from the bottle.

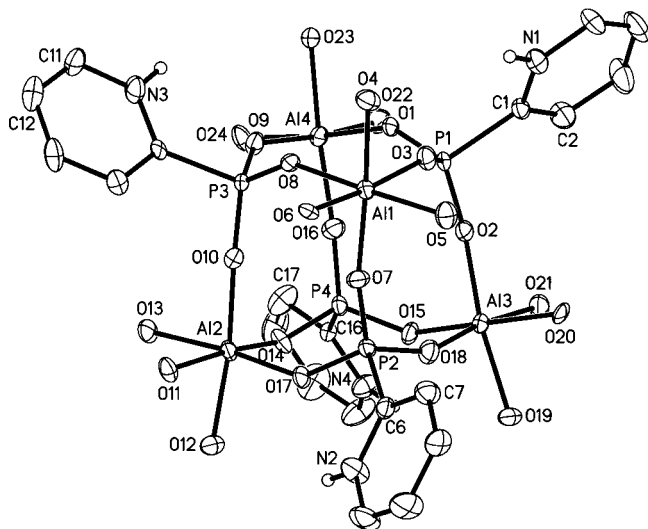
**Synthesis of Complexes 1–3.** Complexes **1** and **2** were isolated in moderate yield from the 1:1 reaction of AlCl<sub>3</sub>·6H<sub>2</sub>O and 2-pyridylphosphonic acid (2PyPoH<sub>2</sub>) or 4-pyridylphosphonic acid (4PyPoH<sub>2</sub>), as shown in Scheme 1. Using analogous conditions, the reaction of Al(NO<sub>3</sub>)<sub>3</sub> with 2PyPoH<sub>2</sub> afforded **3** in high yield.

A general rule established for the synthesis of aluminophosphates is that increased temperature favors three-dimensional structures over layered materials.<sup>15</sup> Therefore, the isolation of **1–3** from a room-temperature synthesis is not too surprising, because the high charge density of Al<sup>3+</sup> in solution drives the crystallization process. This high charge density leads to extensive hydrolytic processes and has often been used for the formation of oxy-hydroxy species containing from 13 to 30 aluminum centers.<sup>16</sup>

**Crystal Structures of Complexes 1–3.** Crystallographic analysis of complexes **1–3** revealed the formation of an interesting aluminum(III) phosphonate cluster, common to all three complexes, as shown for **1** in Figure 1 (crystal data for all compounds are given in Table 3).

Complex **1** features four aluminum centers and four pyridylphosphonate ligands in the asymmetric unit. All of the phosphonate groups are doubly deprotonated at oxygen but are protonated at the pyridyl nitrogen atom. Aluminum

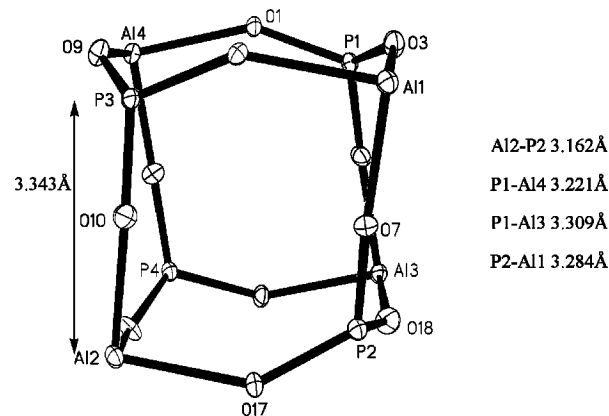
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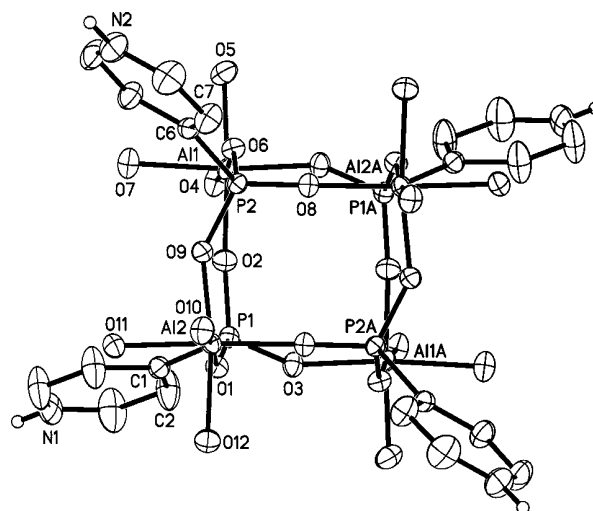
**Figure 1.** X-ray crystal structure of the cation of **1**, [(2PypOH)<sub>4</sub>-Al<sub>4</sub>(OH<sub>2</sub>)<sub>12</sub>]<sup>8+</sup>. Thermal ellipsoids are shown at the 50% probability level. Only the hydrogen atoms on the pyridyl nitrogen atoms are shown as circles of arbitrary size. Selected bond lengths (Å) and angles (deg) around Al2: Al2–O13 = 1.920(5), Al2–O10 = 8.863(5), P3–O10 = 1.491(5); O10–Al2–O12 = 173.2(2).

maximizes its coordination number, yielding coordinatively saturated metal centers with octahedral geometry made up by coordination to three  $\mu_2$ -phosphonate oxygen atoms, from three different ligands that interlink the Al centers through these oxide bridges. The remaining three coordination sites are made up of water molecules. Eight displaced Cl<sup>−</sup> ions are located around the cationic core. The net 8+ charge is created by four Al<sup>3+</sup> ions in addition to four protonated phosphonates, each having a 1− charge. A large quantity of water molecules and chloride ions in the structure leads to strong hydrogen bonding. The chloride ions are located in close proximity to both bound and free water molecules due to hydrogen bonding. This hydrogen bonding is seen throughout the structure and allows the molecule to propagate into a chain of cyclic rings held in place by hydrogen bonds. These structures are particularly interesting, as they have the potential to act as a template for the preparation of extended structures and because metal oxide/hydroxide structures are important in making controlled particles of a certain size and morphology.

Complexes **1–3** have a topology reminiscent of the alumoxane structures prepared by Roesky et al.<sup>2–4</sup> Like these alumoxanes, the structural motif of **1–3** can be considered as a distorted cubane type structure, with an Al<sub>4</sub>O<sub>12</sub>P<sub>4</sub> core made up of six M<sub>2</sub>O<sub>4</sub>P<sub>2</sub> rings. Alternate corners of the “cube” are made up of Al and P atoms that are linked by bridging oxygen atoms sitting between these corners and along the edge of the cube (Figure 2). This core atom arrangement resembles the secondary building units (D<sub>4</sub>R) found in zeolites<sup>2a</sup> and phosphonate molecular sieves, although in these the aluminum is most commonly three- or four-coordinate.<sup>17</sup>



**Figure 2.** Diagram showing the core geometry in **1**. Thermal ellipsoids are drawn at 30% probability level.



**Figure 3.** Drawing of the cation core of **2** as viewed down the 2-fold axis. Thermal ellipsoids are shown at the 50% probability level, and hydrogen atoms attached to the pyridine nitrogens are shown. Selected bond lengths (Å) and angles (deg) around Al2: Al2–O12 = 1.9475(16), Al2–O9 = 1.8295(14), P1–O1 = 1.5168(14); O12–Al2–O11 = 86.32(7).

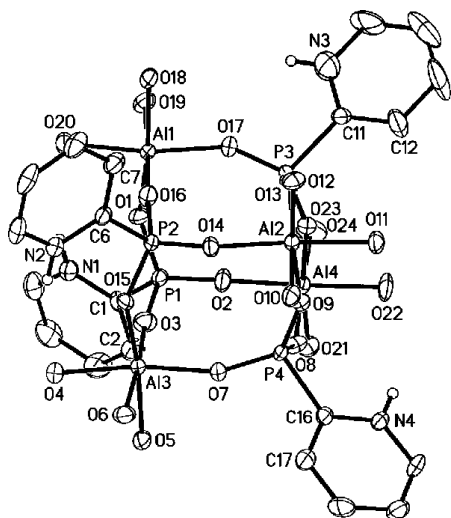
In an attempt to increase the cluster size, 2PypOH<sub>2</sub> was replaced with 4PypOH<sub>2</sub>, with the rationale being that the larger bite angle would increase dimensionality through Al–N (pyridyl) and Al–O (phosphonate) coordination. However, the reaction of 4PypOH<sub>2</sub> with AlCl<sub>3</sub>·6H<sub>2</sub>O yields essentially the same structure (Figure 3). The similarity of these two structures is attributed to protonation of the nitrogen under the employed reaction conditions. In contrast, the hydrothermal reactions of phenylphosphonic acid with AlCl<sub>3</sub>·6H<sub>2</sub>O affords polymeric chains of octahedrally coordinated aluminum, with five of the six positions taken by oxygen atoms of the phosphonate group and the sixth site being occupied by a water molecule.<sup>18</sup>

Complex **2** crystallized in the monoclinic space group P2/n with 2-fold crystallographic symmetry. Complexes **1** and **2** have comparable bond lengths and angles that correspond well to reported literature values.<sup>19</sup> As one would expect, the Al–O bond lengths for coordinated water are longer than

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**Figure 4.** View of the cation of the nitrate salt **3**, with thermal ellipsoids drawn at the 50% probability level. Selected bond lengths (Å) and angles (deg) around Al3: Al3–O7 = 1.840(3), Al3–O4 = 1.917(3), P1–O2 = 1.510(3); O5–Al3–O7 = 87.60(13).

**Table 1.** Comparison of Selected Bond Lengths (Å) and Angles (deg) for Complexes **1–3**<sup>a</sup>

bond length or angle	<b>1</b>	<b>2</b>	<b>3</b>
P–O	1.496(5)	1.5168(14)	1.503(3)
P–C	1.820(7)	1.8116(19)	1.823(4)
Al–O(oxo)	1.844(5)	1.8229(15)	1.858(3)
Al–O(water)	1.955(5)	1.9411(16)	1.945(3)
P–Al	3.184	3.316	3.207
O–P1–O	112.6(3)	113.41(8)	113.82(17)
O(oxo)–Al–O(oxo)	91.7(2)	92.70(6)	97.62(14)
O(H <sub>2</sub> O)–Al–O(H <sub>2</sub> O)	81.8(2)	87.71(7)	86.92(14)
O(H <sub>2</sub> O)–Al–O(oxo)	90.5(2)	92.12(7)	86.92(14)

<sup>a</sup> In each case the same bonds/angles are compared.

for the bridged oxygen atoms. As in **1**, the similar P–O bond lengths, along with charge balance, suggest a fully deprotonated phosphonate moiety. Attempts were made to perform the reactions under basic pH conditions to prevent protonation of the pyridyl nitrogen; however, these resulted in the isolation of amorphous, insoluble material that could not be used for further characterization.<sup>20</sup>

In order to check the generality of our synthesis, the aluminum chloride precursor was exchanged for aluminum(III) nitrate. The stoichiometric reaction of Al(III) nitrate with 2PypoH<sub>2</sub> resulted in the isolation of complex **3** in almost quantitative yield. Figure 4 shows the cationic component of cluster **3**, viewed perpendicular to a pseudo-2-fold axis. It can be seen that the symmetry is broken primarily by the position of the pyridyl group based on N3.

Complex **3** shows the same structural features as **1** and **2**, differing only in the presence of nitrate counterions. A comparison of the bond lengths and angles of **1–3** is given in Table 1.

Further work attempted reacting Al(OR)<sub>3</sub> (R = alkyl) with 2- and 4-pyridylphosphonic acids; however, no suitable material for analysis could be isolated.

**Spectroscopy and TGA Analysis of 1–3.** In D<sub>2</sub>O solution, <sup>31</sup>P NMR on complexes **1** and **2** exhibit single peaks at –6.2 and –0.17 ppm, respectively. Complex **3** exhibits two phosphorus signals in solution at –8.4 and –13.9 ppm. The single peaks displayed by **1** and **2** suggest that structural integrity is maintained in solution. Although complex **3** does not differ tremendously from these complexes, the two signals observed in the <sup>31</sup>P NMR suggest that in D<sub>2</sub>O the cage dissociates, affording a mixture of species, which could also explain the complicated aromatic signals in the <sup>1</sup>H NMR spectra from free and complexed ligand. No noteworthy features are observed in the <sup>1</sup>H NMR of **1** and **2**. Infrared spectroscopy of **1–3** shows clear stretches associated with free water molecules, P–O stretches, and distinctive N–H stretches.

Complexes **1–3** are air- and moisture-stable and show good thermal stability, not melting at a temperature of 250 °C; however, on heating, some mass loss is visible. TGA measurements on **1** revealed a mass loss of 48.5% on heating from 25 to 400 °C, which corresponds to the loss of approximately 24 water molecules and 8 chlorine atoms (theoretical loss 49.4%). TGA analysis of **3** exhibits a steady weight loss over the same temperature range (25–400 °C). The total weight loss of 13.7% corresponds to loss of 12 water molecules (calculated 14.1%). The mass spectrometry analysis of **1** showed the parent ion peak, and the fragmentation pattern reveals that the cluster core remains intact. The parent ion peak of **3** was not observed.

**Synthesis of the Gallium Complexes 4 and 5.** Hydrolysis products of gallium complexes have been less well studied than their aluminum counterparts, in part because hydrolysis of gallium(III) structures beyond an OH:Ga ratio of 2.5:1 produces a gel, followed at a ratio of 3:1 by the precipitation of polymeric GaO(OH) built from edge-linked GaO<sub>6</sub> units.<sup>21</sup> It has also been found that hydrolytic gallium species do not lend themselves well to crystallization: hence, the limited number isolated.<sup>22</sup> Nevertheless, gallium phosphate chemistry is expanding due to the ability of gallium to exist in more variable and expanded coordination modes, as opposed to the case for zeolites and aluminophosphates.<sup>2b,3c</sup>

The reaction of gallium(III) chloride with 2PypoH<sub>2</sub> in thf followed by workup in toluene afforded **4** in moderate yield and **5** in low yield (Scheme 2, Figure 5). Leaving the reaction mixture in thf and concentrating the thf solution can increase the yield of crystalline **4**.

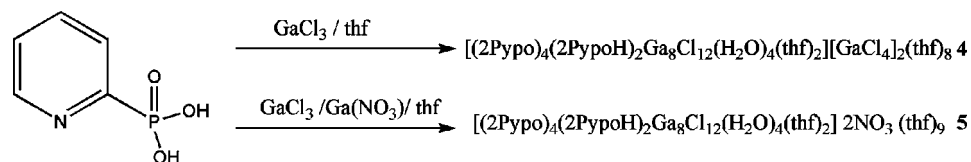
The main difference between the two structures **4** and **5** is the exchange of the counterion GaCl<sub>4</sub><sup>–</sup> in **4** for NO<sub>3</sub><sup>–</sup> in **5**. Complex **5** was isolated from the reaction of stoichiometric amounts of gallium(III) chloride, gallium(III) nitrate, and 2PypoH<sub>2</sub>. Gallium(III) nitrate was added to the reaction

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Scheme 2. Synthesis of Gallium Phosphonates **4** and **5**Table 2. Comparison of Bond Lengths (Å) and Angles (deg) within the Cationic Cores of **4** and **5**<sup>a</sup>

bond length or angle	<b>4</b>	<b>5</b>
Ga—O(oxo) (Ga octahedral)	1.943(5)	1.937(3)
Ga—O(thf)	2.113(6)	2.095(3)
Ga—O(H <sub>2</sub> O)	1.977(6)	1.991(3)
Ga—N	2.085(6)	2.084(3)
Ga—Cl	2.151(4)	2.1546(19)
Ga—O(tetrahedral)	1.830(6)	1.834(3)
P—O(oxo)	1.501(6)	1.510(3)
P—C	1.811(8)	1.831(4)
P—Ga	3.177	3.254
O(oxo)—Ga—O(oxo) (octahedral Ga)	95.1(2)	95.41(12)
O(oxo)—Ga—O(H <sub>2</sub> O) (octahedral Ga)	174.2(3)	172.06(13)
N—Ga—O(thf)	88.7(2)	84.73(14)
Cl—Ga—Cl (Ga tetrahedral)	109.77(13)	109.79(7)
O—P—O	115.0(4)	115.31(16)

<sup>a</sup> In each case the same bonds/angles are compared.

mixture in an attempt to prevent rapid hydrolysis of GaCl<sub>3</sub> to Ga(OH)<sub>3</sub>, which has been documented in gallium hydrolysis chemistry.<sup>22</sup> Unlike in complexes **1–3**, some of the Ga—halide bonds remain intact, in part because of the nonaqueous conditions employed but also because Ga<sup>3+</sup> is slightly less acidic than Al<sup>3+</sup>. The origin of hydrolysis is likely from the use of undried solvents. It is worth mentioning that reactions performed under completely anhydrous conditions afforded oils that could not be crystallized; therefore, we believe that the hydroxyl groups are a necessary requirement to help stabilize these cages through hydrogen bonding.

**Crystal Structures of **4** and **5**.** The structural similarities of complexes **4** and **5** are detailed in Table 2. In both complexes the cationic core can be broken down into an eight-membered “chairlike” arrangement in which the Ga atoms are bridged by O—P—O groups, (Figure 6).

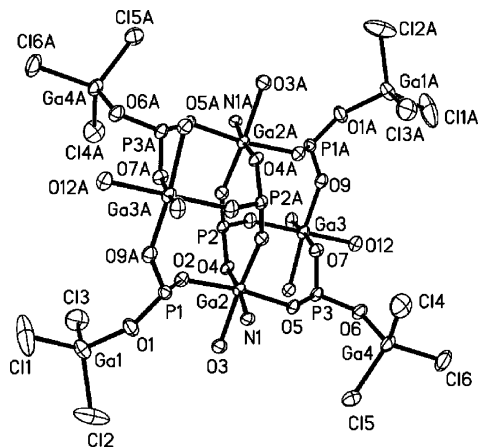


Figure 5. Drawing of the cationic portion of compound **4**. For clarity the pyridyl groups and hydrogen atoms are omitted. Thermal ellipsoids are drawn at the 30% probability level, and hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ga1—Cl3 = 2.157(4), Ga1—O1 = 1.830(6), P1—O1 = 1.501(6), Ga2—N1 = 2.085(6), Ga2—O2 = 1.943(5), Ga2—O3 = 2.113(6); Cl3—Ga1—O1 = 108.9(2), O3—Ga2—N1 = 88.7(2).

Within the Ga<sub>8</sub> cluster, gallium atoms can be observed in two different geometrical environments. The inner gallium atoms exhibit a slightly distorted octahedral geometry, while the outer gallium atoms (OGaCl<sub>3</sub>) have close to tetrahedral geometry. In complex **5** (Figure 7) the almost octahedral coordination sphere of Ga1 is comprised of four oxo bridges, a pyridyl nitrogen atom, and an oxygen atom of a thf molecule. Ga3 is coordinated to three oxo bridges, a nitrogen atom of a pyridyl group, and two water molecules. A third pyridyl nitrogen atom, N1, is not coordinated and bears a proton. Hydrogen bonding exists between the protonated pyridyl nitrogen and a GaCl<sub>4</sub><sup>−</sup> counterion in **4** and a NO<sub>3</sub><sup>−</sup> counterion in **5**. All phosphonate oxygens are deprotonated, giving a 12− charge that is balanced by the gallium’s positive charge of 24+ along with 2+ from the protonated pyridyl nitrogen atoms, 12 chloride atoms, and 2 counteranions. Likewise, in **4** and **5**, there is a difference in P—O bond lengths within the ring and toward the outer edges of the cluster. The external P—O bond lengths are on average longer than the internal P—O bond lengths, most likely because of the structural constraints within the cluster core.

Six phosphonate groups support the eight gallium atoms in complexes **4** and **5**. This gives rise to two different phosphorus environments that differ in their P—O coordination modes to the Ga centers. For example, in **4**, P2 is connected to an “inner” gallium atom that has a terminal water molecule, while P3 bonds via O6 to a GaCl<sub>3</sub> molecule (Figure 5), and in **5**, P2 is coordinated to OGaCl<sub>3</sub> while P1 is coordinated through its oxygen atoms to the octahedral Ga atom (Figure 7).

Unlike the plethora of work available for aluminum phosphonates, the gallium counterparts are less well developed for structural comparison. The asymmetric units of **4** and **5** show structural resemblance to the gallium cluster isolated from the reaction of <sup>1</sup>Bu<sub>3</sub>Ga with phosphonic acid;<sup>23</sup> however, the reaction of <sup>1</sup>Bu<sub>3</sub>Ga with phenylphosphonic acid affords a phosphonate-bridged dimer.<sup>24</sup> Complexes **4** and **5** differ from **1–3** in that the pyridyl nitrogen plays a role in cluster stabilization, as four of the six pyridyl N atoms coordinate to Ga atoms and only two pyridyl nitrogen atoms are protonated, while in **1–3**, the pyridyl nitrogen atoms are all protonated. Complexes **4** and **5** can be compared with the product from the reaction of phenylphosphonic acid with gallium chloride that afforded a layered lamellar structure.<sup>25</sup>

**Spectroscopic Data of **4** and **5**.** Attempts to observe the two different environments in **4** using <sup>31</sup>P NMR revealed peaks at −17.7 ppm and a broad peak at −3 to −5 ppm. Solution <sup>31</sup>P NMR on **5** exhibited no phosphorus or proton signals, indicating the presence of a possible radical or ligand scrambling leading to immeasurable signals. The hydrogen atoms on the protonated pyridyl nitrogen atoms were located

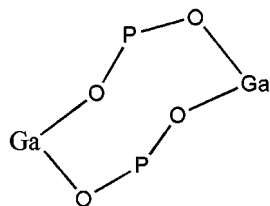


Figure 6. Diagram showing the bonding arrangement in the central "chair".

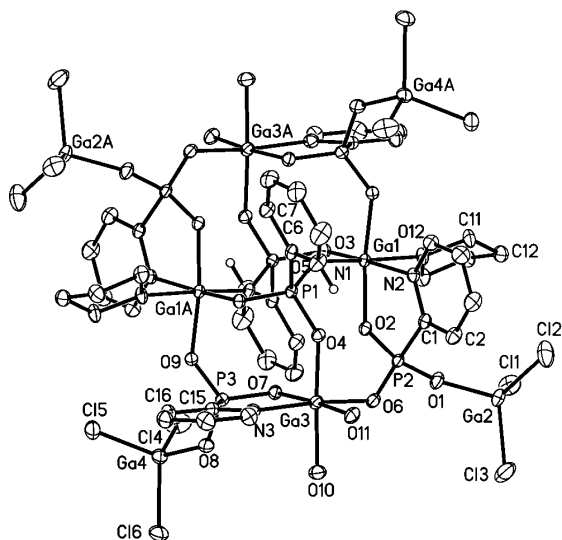


Figure 7. Solid-state structure of the cation of **5**. Only the hydrogens located on the nitrogen atoms of the pyridyl groups are shown for clarity. Thermal ellipsoids are drawn at the 30% probability level. Pertinent bond lengths (Å) and angles (deg): Ga2–C12 = 2.1549(16), Ga2–O1 = 1.834(3), O1–P2 = 1.525(3), Ga3–O10 = 1.991(3), Ga3–O6 = 1.937(3), Ga1–N2 = 2.084(3); C13–Ga2–O1 = 107.24(12), O10–Ga3–O11 = 85.42(14).

from the difference map and confirmed by infrared analysis with a distinct N–H stretch at  $3452\text{ cm}^{-1}$  for **4** and  $3254\text{ cm}^{-1}$  for **5**. Complexes **4** and **5** have low melting points, with **4** melting at  $42\text{--}43\text{ }^{\circ}\text{C}$  and **5** at  $80\text{--}81\text{ }^{\circ}\text{C}$ ; this is likely to be due to the presence of coordinated and lattice thf that, once lost, causes breakdown of the molecule. HRMS data of **4** exhibited no parent ion peak; however, peaks could be assigned that indicate the gallium phosphonate core remains intact, followed by sequential loss of  $\text{GaCl}_3$ .

**Isolation of the Coordination Polymer**  $\{[(4\text{PyCH}_2\text{PO}_3\text{H})\text{Ga}(\text{OH})_2(\text{NO}_3)_2 \cdot 0.5\text{H}_2\text{O}]_x\}$  (**6**). The reaction of 4PypOH<sub>2</sub> with gallium chloride was attempted but did not yield any crystals suitable for X-ray crystallography. To investigate whether the steric constraints of the ligand were preventing polymer growth, 4PyCH<sub>2</sub>PO<sub>3</sub>H<sub>2</sub> was prepared and its reactivity with gallium and aluminum(III) chlorides was investigated, but the products from both reactions were oils or amorphous solids. Exchange of the gallium halide salt for gallium(III) nitrate afforded a polymeric species, **6** (Figures 8 and 9).

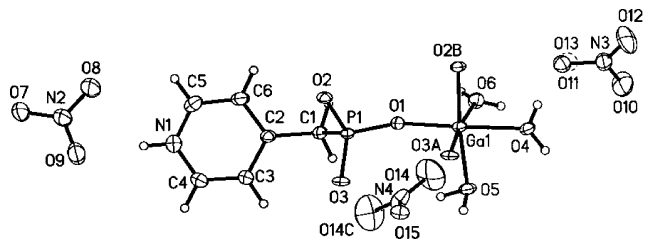


Figure 8. Asymmetric unit of **6**. Thermal ellipsoids are drawn at the 50% probability level. There is disorder in the nitrate group {N3,O10,O11,O12} which shares the same site with a molecule of water, represented by O13. Selected bond lengths (Å) and angles (deg): Ga1–O1 = 1.892(5), Ga1–O3 = 1.931(5), Ga1–O4 = 1.986(5), Ga1–O5 = 2.022(5), Ga1–O6 = 2.003(5), P1–O1 = 1.508(5), P1–O2 = 1.523(5), P1–O3 = 1.527(5); O4–Ga1–O5 = 86.0(2), O2B–Ga1–O5 = 174.7(2), O2–P1–O1 = 113.5(3).

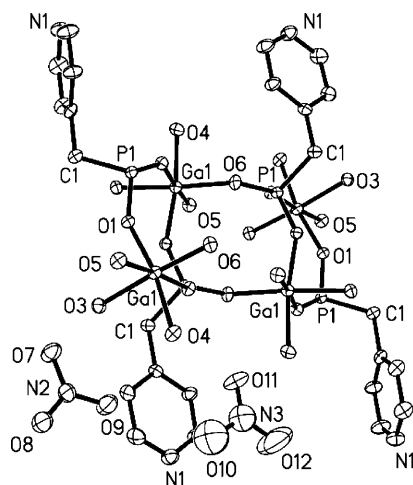


Figure 9. Drawing of the extended motif  $\{[(4\text{PyCH}_2\text{PO}_3\text{H})_4\text{Ga}_4(\text{H}_2\text{O})_{12}][\text{NO}_3]_8 \cdot 2\text{H}_2\text{O}\}$ . Thermal ellipsoids are drawn at the 30% probability level. Symmetry codes: (A)  $1 - x, 1 - y, 1 - z$ ; (B)  $\frac{1}{2} - x, y, 1 - z$ ; (C)  $\frac{1}{2} + x, 1 - y, z$ ; (D)  $x - \frac{1}{2}, 1 - y, z$ ; (E)  $\frac{3}{2} - x, y, 1 - z$ .

Polymer **6** crystallizes in the orthorhombic space group *Ibca*. In the asymmetric unit is one gallium atom, a phosphonate ligand, and two nitrate ions. The repeating unit can be thought of as  $\{[(4\text{PyCH}_2\text{PO}_3\text{H})_4\text{Ga}_4(\text{H}_2\text{O})_{12}][\text{NO}_3]_8 \cdot 2\text{H}_2\text{O}\}$ . The  $2\text{H}_2\text{O}$  arises because one of the nitrate groups is at half-occupancy and the site is shared by a water molecule. The repeating unit is generated by inversion and by the *a* glide. It therefore repeats at  $9.2230(11)\text{ \AA}$ , the length of the *a* axis.

Each gallium center adopts octahedral coordination geometry with three positions occupied by coordinated water molecules and the remaining three sites occupied by deprotonated oxygen atoms from the phosphonate moiety. The Ga–O bond lengths are as expected, with the Ga–OH<sub>2</sub> bonds longer than the Ga–O bonds that interlink the polymer. These distances compare well with those in related systems.<sup>26</sup> As with many gallium phosphonates, the Ga:P ratio is 1:1.<sup>27</sup> Polymer **6** is interesting, as a survey of the CCDC reveals a limited number of gallium polymers supported by organophosphonate derivatives.<sup>28</sup> Examination of the hydrogen bonding in **6** reveals the important role that the nitrate ions play; these anions maintain the electroneutrality of the polymer and have an important stabilization role. The anions are positioned between adjacent pyridyl groups and participate in H-bonding to the coordinated water molecules on

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**Table 3.** Crystal Data and Data Collection Summary for Complexes 1–6

	[2PyPoH) <sub>4</sub> Al <sub>4</sub> (OH) <sub>2</sub> ] <sub>12</sub> Cl <sub>8</sub> • 6H <sub>2</sub> O (1)	[4PyPoH) <sub>4</sub> Al <sub>4</sub> (OH) <sub>2</sub> ] <sub>12</sub> Cl <sub>8</sub> • 11H <sub>2</sub> O (2)	[2PyPoH) <sub>4</sub> Al <sub>4</sub> (OH) <sub>2</sub> ] <sub>12</sub> [NO <sub>3</sub> ] <sub>8</sub> • 7H <sub>2</sub> O (3)	[2PyPoH) <sub>2</sub> (2PyPo) <sub>4</sub> Ga <sub>8</sub> Cl <sub>12</sub> • (OH) <sub>2</sub> •4(thf) <sub>2</sub> ][GaCl <sub>4</sub> ] <sub>2</sub> •8thf (4)	[2PyPoH) <sub>2</sub> (2PyPo) <sub>4</sub> Ga <sub>8</sub> Cl <sub>12</sub> • (OH) <sub>2</sub> •4(thf) <sub>2</sub> ][NO <sub>3</sub> ] <sub>2</sub> •9thf (5)	C <sub>6</sub> H <sub>14</sub> Ga <sub>4</sub> N <sub>3</sub> O <sub>12.5</sub> P <sub>6</sub> orthorhombic
chem formula	C <sub>20</sub> H <sub>56</sub> Al <sub>4</sub> Cl <sub>8</sub> N <sub>4</sub> O <sub>30</sub> P <sub>4</sub>	C <sub>20</sub> H <sub>66</sub> Al <sub>4</sub> Cl <sub>8</sub> N <sub>4</sub> O <sub>33</sub> P <sub>4</sub>	C <sub>20</sub> H <sub>58</sub> Al <sub>4</sub> N <sub>12</sub> O <sub>55</sub> P <sub>4</sub>	C <sub>70</sub> H <sub>114</sub> Cl <sub>20</sub> Ga <sub>10</sub> N <sub>6</sub> O <sub>32</sub> P <sub>6</sub>	C <sub>74</sub> H <sub>122</sub> Cl <sub>12</sub> Ga <sub>8</sub> N <sub>8</sub> O <sub>39</sub> P <sub>6</sub>	C <sub>6</sub> H <sub>14</sub> Ga <sub>4</sub> N <sub>3</sub> O <sub>12.5</sub> P <sub>6</sub>
formula wt	1348.09	1438.17	1578.58	3143.69	2916.78	428.89
cryst syst	monoclinic	monoclinic	monoclinic	triclinic	triclinic	orthorhombic
space group	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>I</i> 2ca
<i>T</i> (K)	213(2)	213(2)	213(2)	213(2)	213(2)	213(2)
<i>a</i> (Å)	10.9580(12)	14.8394(7)	10.7007(19)	14.533(2)	13.2856(10)	9.2230(11)
<i>b</i> (Å)	11.8615(13)	11.2851(5)	24.348(4)	15.101(3)	15.3643(12)	20.733(3)
<i>c</i> (Å)	42.010(5)	18.3670(9)	25.701(3)	19.687(3)	16.9830(13)	29.734(4)
$\alpha$ (deg)	90	90	90	68.691(3)	69.1370(10)	90
$\beta$ (deg)	93.325(2)	97.887(3)	114.604(11)	88.293(3)	79.2890(10)	90
$\gamma$ (deg)	90	90	90	61.349(2)	65.0620(10)	90
<i>V</i> (Å <sup>3</sup> )	5451.2(10)	3046.7(2)	6088.2(16)	3476.8(10)	2934.7(4)	5685.9(10)
<i>Z</i>	4	2	4	1	1	8
no. of rflns collected	24 953	19 530	30 699	29 356	18 949	22 593
no. of indep rflns	9854	7233	11 001	12 481	12 818	3490
no. of data/restraints/params	9854/0/631	7233/0/397	11 001/11/852	13 493/213/588	12 818/60/655	3490/12/236
no. of unique data ( <i>R</i> <sub>int</sub> )	0.0566	0.0239	0.0893	0.0597	0.0276	0.0838
<i>D</i> <sub>calc</sub> (Mg/m <sup>3</sup> )	1.643	1.568	1.722	1.501	1.650	2.004
<i>F</i> (000)	2768	1484	3256	1572	1476	3472
<i>R</i> indices (all data)	<i>R</i> 1 = 0.1151, <i>wR</i> 2 = 0.1696	<i>R</i> 1 = 0.0481, <i>wR</i> 2 = 0.0997	<i>R</i> 1 = 0.1006, <i>wR</i> 2 = 0.1667	<i>R</i> 1 = 0.1578, <i>wR</i> 2 = 0.2675	<i>R</i> 1 = 0.0857, <i>wR</i> 2 = 0.1212	<i>R</i> 1 = 0.1381, <i>wR</i> 2 = 0.2071
final <i>R</i> indices ( <i>I</i> > 2 $\sigma$ ( <i>I</i> ))	<i>R</i> 1 = 0.0849, <i>wR</i> 2 = 0.1587	<i>R</i> 1 = 0.0361, <i>wR</i> 2 = 0.0904	<i>R</i> 1 = 0.0539, <i>wR</i> 2 = 0.1376	<i>R</i> 1 = 0.0793, <i>wR</i> 2 = 0.2385	<i>R</i> 1 = 0.0465, <i>wR</i> 2 = 0.1015	<i>R</i> 1 = 0.0590, <i>wR</i> 2 = 0.1451
largest diff peak, hole (e Å <sup>-3</sup> )	0.846, -0.637	0.837, -0.612	0.669, -0.739	1.650, -1.373	0.712, -0.561	1.202, -1.045



the gallium atom and to the deprotonated oxygen atoms of the phosphonate group. This leads to an extensively coordinated network that is relatively thermally robust, melting at 120–125 °C. Surprisingly, the analogous aluminum reaction afforded recrystallized ligand.

It is noteworthy to mention the lack of structurally characterized, single-crystal, molecular or polymeric indium phosphonates.<sup>25,29</sup> Our attempts to crystallize an indium pyridyl phosphonate species were all unsuccessful. From experimental work on thallium(III) halides and nitrates that afford one or two-dimensional polymeric species<sup>30</sup> it is possible that indium might be the crossover point in which a mixture of cyclic species and polymeric chains form, leading to insoluble and amorphous material.

## Conclusion

The reactions of 2PyPoH<sub>2</sub> and 4PyPoH<sub>2</sub> with Al(III) and Ga(III) chlorides afforded cyclic aluminum and gallium structures that show structural similarity with the secondary building units of zeolites. Exchange of the phosphonic acid for the more flexible 4PyCH<sub>2</sub>PO<sub>3</sub>H<sub>2</sub> afforded a polymeric structure with a Ga:P ratio of 1:1. We are currently investigating the reactions of functionalized phosphonic acids with aluminum and gallium alkyls and the synthesis of heteroelemental cages and clusters. Future work is focusing on reducing the steric bulk of the phosphonate to look at systems that may mimic the elusive MAO structure (methylalumoxane).<sup>31</sup>

## Experimental Section

2-/4-Pyridylphosphonic acids and 4PyCH<sub>2</sub>PO<sub>3</sub>H<sub>2</sub> were prepared according to literature procedures.<sup>6</sup> GaCl<sub>3</sub> was purchased from Strem Chemicals. All other chemicals were purchased from Aldrich and used as received. Crystal data were collected with a Bruker SMART 1000 diffractometer using molybdenum radiation ( $\lambda = 0.71073 \text{ \AA}$ ). The data were corrected for absorption. Structures

were solved by direct methods and refined<sup>32</sup> via full-matrix least-squares methods. Crystal data and data collection details are given in Table 3. The NMR data were recorded on a Varian XL-300; IR analyses were conducted on a MIDAC M4000 Fourier transform infrared (FT IR) spectrometer using KBr pellets. Thermogravimetric analyses (TGA) were carried out on a Seiko 220 instrument at a heating rate of 5 °C/min. LR mass spectrometry analysis (electrospray ionization) was carried out using a Bruker Esquire 6000 mass spectrometer. HRMS was carried out by the University of South Carolina Chemistry Department and microanalysis by Schwarzkopf Microanalytical Laboratory, Woodside, NY. Melting points were determined in capillaries, **1–3** and **6** under ambient conditions and **4** and **5** under a nitrogen atmosphere, and are uncorrected.

**Synthesis of [(2PyPoH)<sub>4</sub>Al<sub>4</sub>(OH)<sub>12</sub>]Cl<sub>8</sub>·6H<sub>2</sub>O (1).** AlCl<sub>3</sub>·6H<sub>2</sub>O (0.08 g, 0.31 mmol) and 2-PyPoH<sub>2</sub> (0.05 g, 0.31 mmol) were added together in an open vial containing 5 mL of water. The clear solution was stirred at ~90 °C for 2 h. After 2 h, the solution was gravity-filtered to remove any solid impurities and stored at room temperature for crystallization. From the solution, crystals suitable for X-ray diffraction were obtained. Yield: 0.23 g (56% based on AlCl<sub>3</sub>·6H<sub>2</sub>O). Mp: >250 °C. IR (KBr pellets;  $\nu$ , cm<sup>-1</sup>): 3295 (s), 2485 (w), 2350 (w), 1633 (s), 1609 (s), 1523 (m), 1445 (m), 1244 (s), 1177 (s), 1090 (s), 1009 (m), 766 (m), 729 (m). <sup>1</sup>H NMR (300 MHz, 25 °C, D<sub>2</sub>O;  $\delta$ , ppm): 8.79 (d,  $J = 6 \text{ Hz}$ , 1 H), 8.63 (tm,  $J = 8 \text{ Hz}$ , 1 H), 8.27 (t,  $J = 7.5 \text{ Hz}$ , 1 H), 8.11 (t,  $J = 7.5 \text{ Hz}$ , 1 H). <sup>31</sup>P{<sup>1</sup>H} NMR (121 MHz, 25 °C, D<sub>2</sub>O;  $\delta$ ): -6.2. MS (found (calcd);  $m/z$ ): M<sup>+</sup> not observed; 444.9 (445) (2PyPo)<sub>4</sub>Al<sub>4</sub>(OH)<sub>12</sub>·H<sub>2</sub>O; 262 (262), (2PyPo)<sub>2</sub>Al<sub>2</sub>(OH)<sub>7</sub>Cl. Anal. Found (calcd): C, 17.15 (17.82); H, 4.15 (4.2); N, 4.19 (4.2).

**Synthesis of [(4PyPoH)<sub>4</sub>Al<sub>4</sub>(OH)<sub>12</sub>]Cl<sub>8</sub>·11H<sub>2</sub>O (2).** AlCl<sub>3</sub>·6H<sub>2</sub>O (0.08 g, 0.31 mmol) and 4PyPoH<sub>2</sub> (0.05 g, 0.31 mmol) were added together in an open vial containing 5 mL of water. The clear solution was stirred at ~90 °C for 2 h. After 2 h, the solution was gravity-filtered to remove any solid impurities and stored at room temperature for crystallization. From the solution, crystals suitable for X-ray diffraction were obtained. Mp: >250 °C. Yield: 0.28 g (62%, based on AlCl<sub>3</sub>·6H<sub>2</sub>O). IR (KBr pellets;  $\nu$ , cm<sup>-1</sup>): 3394 (s), 1598 (s), 1505 (m), 1491 (s), 1233 (s), 1150 (s), 1092 (s), 1063 (m), 1007 (w), 730 (m). <sup>1</sup>H NMR (300 MHz, 25 °C, D<sub>2</sub>O;  $\delta$ , ppm): 8.59 (s, 2H), 7.95 (s, 2H). <sup>31</sup>P{<sup>1</sup>H} NMR (121 MHz, 25 °C, D<sub>2</sub>O;  $\delta$ ): -0.17.

**Synthesis of [(2PyPoH)<sub>4</sub>Al<sub>4</sub>(OH)<sub>12</sub>](NO<sub>3</sub>)<sub>8</sub>·7H<sub>2</sub>O (3).** In a small scintillation vial, solid Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O (0.23 g, 0.62 mmol) was added to 2PyPoH<sub>2</sub> (0.1 g, 0.62 mmol). Approximately 1–2 mL of DI water was added. The temperature was raised to ~70 °C for 30 min to allow complete dissolution of the reaction mixture, and a clear solution was observed. The reaction mixture was gravity-filtered to remove any insoluble impurities. Storage at room temperature for 2 days afforded crystalline **3** (0.88 g, 90%). Mp: >250 °C. IR (KBr pellets;  $\nu$ , cm<sup>-1</sup>): 3254 (s), 1610 (m), 1385 (s), 1242 (m), 1179 (m), 1163 (m), 1088 (s), 1002 (w), 825 (w), 769 (w), 728 (w). <sup>1</sup>H NMR (300 MHz, 25 °C, D<sub>2</sub>O;  $\delta$ , ppm): 8.10 (d,  $J = 6.0 \text{ Hz}$ , 1H), 8.35 (t,  $J = 7.5 \text{ Hz}$ , 1H), 8.65, 8.33 (overlapping doublets), 8.81 (d,  $J = 6.3 \text{ Hz}$ , 1H). <sup>31</sup>P{<sup>1</sup>H} NMR (121 MHz, 25 °C, D<sub>2</sub>O;  $\delta$ ): -8.4, -13.9 (br). MS ( $m/z$ ; found (calcd)): 1576.9 (1578.4) M<sup>+</sup>; 1380.5 (1381.5) M - 11H<sub>2</sub>O; 743.6 (740.5) M - 19H<sub>2</sub>O - 8NO<sub>3</sub><sup>-</sup>. Anal. Found (calcd): C, 14.3 (15.2); H, 3.82 (3.67); N, 10.51 (10.64).

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**Synthesis of [(2Pypo)<sub>4</sub>(2PypoH)<sub>2</sub>Ga<sub>8</sub>Cl<sub>12</sub>(H<sub>2</sub>O)<sub>4</sub>(thf)<sub>2</sub>][GaCl<sub>4</sub>]<sub>2</sub>·8thf (4).** GaCl<sub>3</sub> (0.25 g, 1.42 mmol) was weighed in the drybox. Under a nitrogen atmosphere, 2PypoH<sub>2</sub> (0.22 g, 1.42 mmol) was added along with 15 mL of thf. An immediate reaction was visible; both reactants dissolved, and a pale yellow solution resulted. The solution was stirred at ambient temperature for 16 h, after which time the solvent was removed in vacuo, affording a foamy solid. The solid was extracted into toluene and the extract filtered under nitrogen. Concentration of the solution to ~10 mL and storage at room temperature for 48 h afforded colorless crystals of **4**. Yield: 0.65 g (14%). Mp: 42–43 °C. IR (KBr pellets;  $\nu$ , cm<sup>-1</sup>): 3409 (s), 2957 (s), 2925 (s), 2850 (w), 1626 (s), 1462 (s), 1261 (s), 1095 (s), 1024 (s), 804 (s). <sup>1</sup>H NMR (300 MHz, 25 °C, CDCl<sub>3</sub>;  $\delta$ , ppm): 1.78 (m, 2H, thf CH<sub>2</sub>,  $J$  = 6.5 Hz), 3.68 (m, 2H, thf CH<sub>2</sub>O,  $J$  = 6.7 Hz), 8.02 (br s), 8.0 (d,  $J$  = 6.0 Hz), 7.98 (br s), 7.2 (br t). <sup>31</sup>P{<sup>1</sup>H} NMR (121 MHz, 25 °C, CDCl<sub>3</sub>;  $\delta$ ): -17.7 and a broad peak at -3 to -5, MS (found (calcd);  $m/z$ ): M<sup>+</sup> not observed; 1895.1 (1892.7) M - GaCl<sub>4</sub><sup>-</sup> - 4thf - 22Cl<sup>-</sup>. HRMS (found (calcd);  $m/z$ ): M<sup>+</sup> not observed; 1460 (1461) cluster core peak; 1532 (1531) Ga<sub>7</sub>P<sub>5</sub>O<sub>22</sub>N<sub>3</sub>Cl<sub>12</sub>.

The yield of **4** can be increased by addition of thf to GaCl<sub>3</sub> under a nitrogen atmosphere, followed by the solid addition of 2PypoH<sub>2</sub>. Stirring was maintained at room temperature for 5–6 h; following filtration of the reaction mixture under anaerobic conditions, crystals of **4** were obtained from the thf solution at room temperature overnight. Yield: 0.9 g, 20% (of crystalline material).

**Synthesis of [(2PypoH)<sub>2</sub>(2Pypo)<sub>4</sub>Ga<sub>8</sub>Cl<sub>12</sub>(OH)<sub>2</sub>(thf)<sub>2</sub>](NO<sub>3</sub>)<sub>2</sub>·9thf (5).** To solid GaCl<sub>3</sub> (0.25 g, 1.42 mmol) were added Ga(NO<sub>3</sub>)<sub>3</sub> (0.36 g, 1.42 mmol) and 2PypoH<sub>2</sub> (0.22 g, 1.42 mmol) under a flow of N<sub>2</sub>(g). Tetrahydrofuran was added and resulted in a yellow solution. Stirring was maintained for 4 h, after which time the

yellow solution was filtered from the white precipitate, concentrated, and stored at room temperature. After 24 h, colorless crystals of **5** were isolated. Yield: 0.49 g (12.2%) Mp: 81–82 °C. IR (KBr pellets;  $\nu$ , cm<sup>-1</sup>): 3452 (s), 2972 (s), 2926 (s), 1748 (m), 1612 (s), 1451 (m), 1385 (w), 1262 (s), 1029 (s), 868 (w), 803 (s), 625 (w). No protons or phosphorus nuclei could be detected by NMR experiments.

**Synthesis of {[(4PyCH<sub>2</sub>PO<sub>3</sub>H)Ga(OH)<sub>2</sub>]<sub>3</sub>(NO<sub>3</sub>)<sub>2</sub>·0.5H<sub>2</sub>O}<sub>x</sub> (6).** In an open scintillation vial, Ga(NO<sub>3</sub>)<sub>3</sub> (0.16 g, 0.63 mmol) and 4PyCH<sub>2</sub>PO<sub>3</sub>H<sub>2</sub> (0.11 g, 0.63 mmol) were dissolved in ~3 mL of H<sub>2</sub>O and stirred. The resultant clear reaction mixture was heated to ~85 °C for 2 h, after which time the solution was gravity-filtered to remove any impurities. Storage of the clear solution at room temperature for 4 days afforded colorless crystals of **6**. Yield: 0.06 g (22%). Mp: 120–125 °C. IR (KBr pellets;  $\nu$ , cm<sup>-1</sup>): 3192 (s), 2926 (s), 1637 (s), 1626 (m), 1508 (m), 1390 (s), 1391 (s), 1086 (m), 1028 (s), 952 (m), 822 (s), 705 (m). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 25 °C;  $\delta$ , ppm): complicated proton NMR, broad overlapping aromatic signals, 7.59–7.98. <sup>31</sup>P{<sup>1</sup>H} NMR (121 MHz, 25 °C, CDCl<sub>3</sub>;  $\delta$ ): 11.9 (br).

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**Supporting Information Available:** CIF files giving crystal data for **1–6**. This material is available free of charge via the Internet at <http://pubs.acs.org>. Crystallographic data have also been deposited with the CCDC and is available free of charge at <http://www.ccdc.cam.ac.uk>.

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