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Synthesis and Structural Features of the Gallium Phosphonate Cluster ^{t}Bu$_7$Ga$_3$P$_3$O$_8$(OH)

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*Summary: Characterization of the cluster ^{t}Bu$_7$Ga$_3$P$_3$O$_8$(OH) (**1**) by X-ray crystallography reveals a structure that differs significantly from previously synthesized gallium phosphonates due to the boat configuration of its central Ga$_2$P$_2$O$_4$ ring. This configuration is confirmed by ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy.*

Introduction

"Building block" approaches to the synthesis of porous materials have been receiving study in recent years.[1] For example, the cubic double-four-ring silicate structure (RSiO$_{3/2}$)$_8$, a type of polyhedral silsesquioxane, is frequently found in zeolitic materials and can be synthesized as an isolated organometallic unit with reactive organic functionalities on the corners of the cube.[2] It has been speculated that reaction of these functionalities could produce a microporous material.[3] Such reactions would eliminate the need for a separate organic templating species to control pore structures, since the sizes and shapes of the void spaces in these materials would be dependent only upon the geometries of the starting clusters.

Although a variety of main group organometallic clusters other than organosilicates exist, their use as possible building units for covalently bonded extended structures has been largely unexplored. Group 13 organometallic clusters are suitable for these reactions, particularly in light of recent work where alumoxane and galloxane clusters were isolated by using sterically hindered organic functionalities such as *tert*-butyl or mesityl.[4,5] One advantage to the use of the later group 13 elements such as gallium and indium is that organometallic complexes of these elements are substantially less reactive than their aluminum-containing counterparts; each successive removal of an organic group increases the stability of the remaining M−C bonds, with the result that organometallic clusters containing these elements can be quite stable. For example, the clusters [^{t}Bu$_{12}$Ga$_{12}$O$_{10}$(OH)$_4$][4c] and (^{t}BuGaS)$_4$[6] are stable in air, and the latter can be suspended in water without reaction.

The use of phosphonates as bridging units in these clusters provides a new avenue into cluster linkage reactions, since the organic group on the phosphorus atom provides another point at which such reactions may be performed. The ability to change the type of phosphonate used allows the formation of mixed clusters containing one type of organic group on the group 13 metal and a different type of organic group on the phosphorus. This provides another means of controlling the directionality of the linkage reactions and therefore the three-dimensional structures of the products. As part of our investigations into the synthesis of clusters with a potential for directional reactions, we have synthesized a gallium phosphonate cluster with bonding characteristics unique from those that have previously been reported.

Results and Discussion

Refluxing ^{t}Bu$_3$Ga with ^{t}BuPO(OH)$_2$ in a toluene/THF mixture followed by crystallization yields the gallium phosphonate cluster ^{t}Bu$_7$Ga$_3$P$_3$O$_8$(OH) (**1**). The molecular structure of **1**·THF is shown in Figure 1. The molecule is best viewed as a Ga$_2$P$_2$O$_4$ ring with a dialkyl gallium above and a phosphonate moiety below it. This eight-membered ring is a common motif for AlPO and GaPO materials, appearing in expanded aluminum and gallium phosphate and oxyfluoride structures[7] and in the related organometallic compounds [^{t}Bu$_2$Ga{μ-O$_2$P(Ph)O−Ga^{t}Bu$_2$}]$_2$ (**2**),[8] [Me$_2$Ga(μ_2-O$_2$PPh$_2$)]$_2$ (**3**),[9] [Et$_2$Ga(μ_2-O$_2$PPh$_2$)]$_2$ (**4**),[10] [^{t}Bu$_2$Ga(μ_2-O$_2$PPh$_2$)]$_2$ (**5**),[11] [^{t}BuGa-

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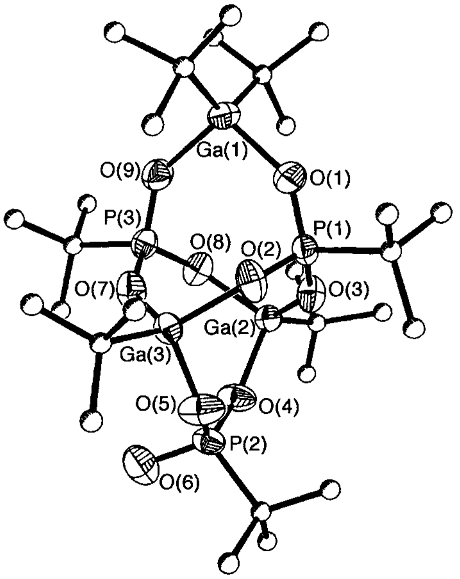

Figure 1. Molecular structure of **1**·THF. ^{t}Bu groups have been plotted as spheres; Ga, P, and O atoms are shown as thermal ellipsoids at the 40% confidence level. Hydrogen atoms and the molecule of THF have been removed for clarity. Selected bond lengths are given in Table 1. Selected bond angles (deg): O(9)−Ga(1)−O(1) 100.2(2), Ga(1)−O(1)−P(1) 146.9(3), O(1)−P(1)−O(3) 112.5(2), P(1)−O(3)−Ga(2) 143.0(2), O(3)−Ga(2)−O(8) 105.1(2), Ga(2)−O(8)−P(3) 137.2(2), O(3)−Ga(2)−O(4) 103.3(2), Ga(2)−O(4)−P(2) 142.0(2), O(4)−P(2)−O(6) 110.0(2), O(4)−P(2)−O(5) 114.9(2).

Table 1. Gallium−Oxygen Bond Distances for 1·THF

location	bond	distance (Å)
intraring	Ga(2)−O(3)	1.855(3)
	Ga(2)−O(8)	1.854(3)
	Ga(3)−O(2)	1.853(3)
	Ga(3)−O(7)	1.858(3)
ring to capping phosphonate	Ga(2)−O(4)	1.889(3)
	Ga(3)−O(5)	1.884(4)
extraring	Ga(1)−O(1)	1.922(3)
	Ga(1)−O(9)	1.925(4)

Table 2. Phosphorus−Oxygen Bond Distances for 1·THF

location	bond	distance (Å)
intraring	P(1)−O(2)	1.533(3)
	P(1)−O(3)	1.530(4)
	P(3)−O(7)	1.532(3)
	P(3)−O(8)	1.540(3)
ring to capping dialkylgallium	P(1)−O(1)	1.509(4)
	P(3)−O(9)	1.510(4)
extraring	P(2)−O(4)	1.515(3)
	P(2)−O(5)	1.510(4)
	P(2)−O(6)[a]	1.544(5)

[a] O(6) bears a hydrogen atom.

Table 3. Crystallographic Data for 1·THF

formula	$C_{32}H_{72}Ga_3O_{10}P_3$
fw	918.97
temp, K	233(2)
wavelength, Å	0.71073
cryst syst	orthorhombic
space group	*Pbca*
a,Å	18.8043(3)
b,Å	194492(2)
c,Å	26.7860(3)
V,Å^3	9796.4(2)
Z	8
density (calcd, g cm^{-3})	1.246
abs coeff, mm^{-1}	1.778
F(000)	3856
θ range, deg	1.52−28.22
no. of reflns collected	36 164
no. of indep reflns	11 235 (R_{int} = 0.0433)
refinement method	full-matrix least-squares on F^2
no. of data/restraints/parameters	11234/0/464
goodness of fit on F^2	1.022
final *R* indices [$I > 2\sigma I$)]	R1 = 0.0594, wR2 = 0.1500
R indices (all data)	R1 = 0.1015, wR2 = 0.1796
largest diff peak and hole, e Å^{-3}	0.963 and −0.756

(μ_2-$O_2P(OH)Ph]_2$ (**6**),[12] and [^{t}BuGa(μ_2-O_3PPh)]$_4$ (**7**).[12] In these compounds the ring exists in a chair conformation or is approximately planar (an ab initio study on the model compound [$(HO)_2Ga(\mu_2$-$OP(OH)_2)]_2$ predicts approximate planarity of the ring).[13] In our compound, however, the ring exists in a boat conformation, placing the oxygen ligands of the ring in an appropriate geometry to bond to the capping dialkylgallium and phosphonate (Figure 2). The result is that although the Ga and P atoms in the ring are approximately tetrahedral [Ga, 100.4(2)−118.1(2)°; P, 106.7(2)−112.5(2)°], there is a clear difference in bond angles within and outside of the ring (Table 1). The gallium−oxygen bond distances within the ring are shorter than those observed for the related dimers [av 1.856 Å vs 1.896 (**2**), 1.934 (**3**), 1.940 (**4**), 1.942 (**5**), and 1.931 Å **6**)] and are in fact most similar to those found in the tetrameric cluster (**7**) [1.843 Å]. The ring-to-external phosphonate Ga−O bonds in **1** are slightly longer [av 1.887 Å], and finally the completely extraring Ga(1)−O bonds are in the range expected [av 1.924 Å]. On the other hand, the phosphorus−oxygen bond distances [av 1.525 Å] are *longer* than any of those previously reported for **2**−**7** [av 1.503, 1.515, 1.519, 1.491, 1.489, and 1.495 Å, respectively], and although the P−O bond lengths are not crystallographically different, they may be placed into extra- and intraring groups. These differences in Ga−O and P−O bond lengths are most likely due to the unique structural features of **1** with respect to the other compounds.

The only oxygen not bonded into the $Ga_2P_2O_4$ ring, O(6), bears a hydrogen atom and is hydrogen bonded to a THF molecule present as solvent of recrystallization. The distance between O(6) and the oxygen of the THF ring is within an acceptable hydrogen-bonding range [O(6)−O(THF) = 2.552 Å, O(6)−H(6a)−O(THF) angle = 139.4°]; similar distances have been reported for solvent molecules in gallium oxide/hydroxide clusters.[4c] The THF molecule may be successfully removed by evacuation and repeated recrystallization in toluene.

The ^{t}Bu$_7$Ga$_3$P$_3$O$_8$(OH) cluster thus exhibits an interesting anisotropy. The differences in bonding within the eight-membered ring and outside it, in addition to the presence of an extra alkyl group on Ga(1) and the hydroxyl group on P(2), may lend reactivity to the axis of the molecule rather than the equator. Further condensation, induced by heating or by exposure to

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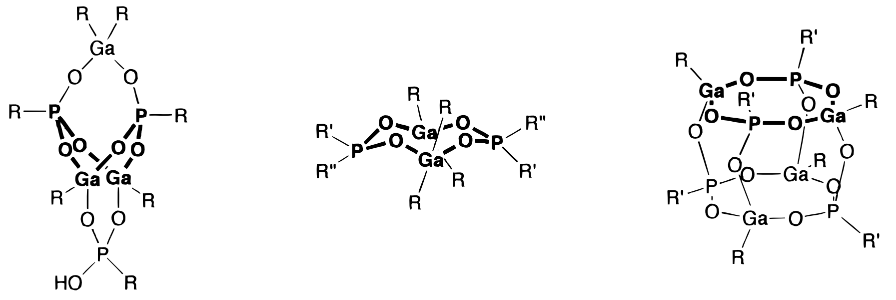

1 **2 - 6** **7**

Figure 2. Comparison of the $Ga_2P_2O_4$ rings found in **1**−**6**. **1**, R = ^{t}Bu; **2**, R = ^{t}Bu, R′ = Ph, R″ = OGa^{t}Bu$_2$; **3**, R = Me, R′ = R″ = Ph; **4**, R = Et, R′ = R″ = Ph; **5**, R = ^{t}Bu, R′ = R″ = Ph; **6**, R = ^{t}Bu, R′ = Ph, R″ = OH; **7**, R = ^{t}Bu, R′ = Ph.

moisture, should result in a unique chainlike hexamer, similar to the one-dimensional chains and two-dimensional sheets formed by gallium oxyfluorides.[14] These reactions are currently under investigation.

Compounds **2** and **6** show an interesting cis−trans isomerism around the eight-membered ring in solution as observed by ^{1}H NMR, while only the trans form crystallizes. **1** may be considered locked in the cis conformation by the capping groups and thus even in solution does not display this type of isomerism. ^{1}H NMR of **1** shows two distinct peaks at $\delta = 1.41$ and $\delta = 1.26$ ppm for the two *tert*-butyl groups bound to gallium atoms on the ring and the *tert*-butyl groups on the capping gallium atom, respectively. Another interesting feature of the ^{1}H NMR spectrum is the inequivalency of the *tert*-butyl substituents on the ring phosphonates. This is due to the asymmetry of the capping phosphonate; one of the ring *tert*-butyl groups bound to the ring phosphorus atoms is trans with respect to the *tert*-butyl of the capping phosphonate, while the other is cis, creating two separate doublets ($\delta = 1.24$ and 1.20 ppm). Inequivalent resonances for the ring phosphonates are also observed in the ^{13}C and ^{31}P NMR spectra of **1**. This inequivalency confirms that the conformation around the $Ga_2P_2O_4$ ring is retained in solution.

Experimental Section

General Procedures. All reactions were performed under nitrogen by using standard Schlenk techniques. Solvents were purified by distillation from Na or Na/benzophenone. Microanalyses were performed by Galbraith Laboratories, Knoxville, TN.

Synthesis of ^{t}Bu$_7$Ga$_3$P$_3$O$_8$(OH) (1). ^{t}BuP(O)(OH)$_2$ (0.60 g, 4.35 mmol) was dissolved in THF (15 mL) and added dropwise to a solution of ^{t}Bu$_3$Ga (1.04 g, 4.31 mmol) in a mixture of toluene (25 mL) and THF (5 mL). The mixture was refluxed overnight and then concentrated; crystallization at −15 °C yielded clear colorless crystals suitable for X-ray diffraction. Removal and further concentration of the supernatant yielded a second crop of crystals. Repeated precipitation in toluene produced the compound free of THF. Total yield of **1**: 0.55 g (0.65 mmol, 45.2%). ^{1}H NMR (500 MHz, C_6D_6): $\delta = 4.03$ [br s, 1H, P−O*H*], 1.41 [s, 18H, GaC(C*H*$_3$) (ring)], 1.26 [s, 18H, GaC(C*H*$_3$) (cap)], 1.24 [d, *J*(P−H) = 16.63 Hz, 9H, PC(C*H*$_3$) (ring)], 1.20 [d, *J*(P−H) = 16.60 Hz, 9H, PC(C*H*$_3$) (ring)], 1.00 [d, *J*(P−H) = 17.27 Hz, 9H, PC(C*H*$_3$) (cap)]. ^{13}C NMR (125.7 MHz, C_6D_6): 31.62 [d, *J*(P−C) = 156.66 Hz, P*C*(CH$_3$)$_3$ (ring)], 31.58 [d, *J*(P−C) = 155.67 Hz, P*C*(CH$_3$)$_3$ (ring)], 31.46 [d, *J*(P−C) = 148.28 Hz, P*C*(CH$_3$)$_3$ (cap)], 30.78 [s, GaC(*C*H$_3$)$_3$ (ring)], 29.42 [s, GaC(*C*H$_3$)$_3$ (cap)], 25.63 [s, PC(*C*H$_3$)$_3$ (ring)], 24.41 [s, PC(*C*H$_3$)$_3$ (ring)], 22.90 [s, PC(*C*H$_3$)$_3$ (cap)], Ga*C*(CH$_3$)$_3$ not observed. ^{31}P NMR (202.5 MHz, C_6D_6, ref 85% H_3PO_4): $\delta = 35.0$ (cap), 26.0 (ring), 25.6 (ring). Upon standing, **1** polymerizes in the manner described in the text (through loss of 2-methylpropane) to yield $[^t\mathrm{Bu}_6\mathrm{Ga}_3\mathrm{P}_3\mathrm{O}_9]_n$. Completely solvent-free samples suitable for analysis proved very difficult to obtain. Anal. Calcd for $[C_{24}H_{54}Ga_3P_3O_9]$: C, 36.54; H, 6.85. Found: C, 37.11; H, 7.13.

X-ray Crystallography. Suitable crystals for X-ray diffraction were obtained by crystallization from a toluene/THF mixture. The systematic absences in the diffraction data for **1** are uniquely consistent for space group *Pbca*. The structure was solved using direct methods, completed by subsequent difference Fourier syntheses and refined by full-matrix least-squares procedures. Atoms C(2), C(3), C(4), C(10), C(11), and C(12) are equally disordered over two positions each. The asymmetric unit also contains a solvent molecule of THF which was refined isotropically. All non-hydrogen atoms in the molecule of the complex were refined with anisotropic displacement coefficients. Hydrogen atoms were treated as idealized contributions. All software and sources of the scattering factors are contained in either the SHELXTL(5.1) or the SHELXTL PLUS(4.2) program libraries (G. Sheldrick, Siemens XRD, Madison, WI).

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Note Added in Proof: Similar compounds have been recently reported in another paper. See: *Inorg. Chem.* **1998**, *37*, 3734.

Supporting Information Available: Crystallographic details, tables of all bond lengths and angles, anisotropic displacement coefficients, H atom coordinates, and a crystal packing diagram for **1**·THF (11 pages). See any current masthead page for ordering information and Internet access instructions.

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