

A Novel Molecular Gallium Phosphonate Cage Containing Sandwiched Lithium Ions: Synthesis, Structure, and Reactivity

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Abstract: The reaction between *tert*-butylphosphonic acid and an equimolar quantity of LiGaMe₄ in THF and *n*-hexane (1:1) yields the first molecular lithium gallium phosphonate Li₄[(MeGa)₆(μ₃-O)₂(*t*-BuPO₃)₆](THF)₄ (**1**) in 70% yield. Compound **1** has been fully characterized by means of analytical and spectroscopic techniques as well as a single crystal X-ray diffraction study. Compound **1** represents the first molecular ionic gallophosphonate cage which contains coordinated lithium ions in the form of a one-dimensional wire and can be regarded as a potential precursor for the subsequent synthesis of molecular sieves and ion conductors. Compound **1** is unreactive toward air and moisture at room temperature. Treatment of **1** with D₂O even at 70 °C does not lead to the hydrolysis of the Ga–C bonds. Treatment of a benzene-*d*₆ solution of **1** with 12-crown-4 followed by D₂O leads to the facile conversion of the product into the neutral cubic gallium phosphonate cage [*t*-BuPO₃GaMe]₄ (**2**).

Introduction

Studies on small molecular clusters of metals and semiconductors, which have properties between isolated molecules and bulk phase, have received considerable attention as these materials seem to represent a logical extension of the trend toward ever smaller electronic devices.¹ One of the recent and intriguing developments in the area of materials science is the preparation of conductive polymeric materials² or metals³ trapped within the channels of zeolites. Zeolites⁴ provide novel hosts for the generation of both electronically isolated and connected conductive hyperlattices. The incorporation of metallic clusters in zeolite channels has been well studied, and there have been several ways of achieving this inclusion phenomenon.^{3–6} Most of these routes involve multistep procedure or the use of stringent and laborious conditions. Simple methods to incorporate metal ions in zeolite matrices, preferably under mild conditions, have always been sought.

Studies on metallaphosphates have gained importance due to their similarities in structure to many naturally occurring zeolites and mineral aluminosilicates.^{7,8} The common synthetic routes known till to date to prepare metallaphosphates or phosphonates employ hydrothermal conditions using phosphoric acid and/or phosphonic acid as starting materials and an organic

template as structure directing agent. Subsequent to the first successful preparation of aluminophosphates in 1982,⁹ group 13 metallophosphates received considerable attention¹⁰ owing to their potential catalytic and sorptive properties. Recently, there have been a few successful attempts to prepare smaller building units of boro-, alumino-, and gallophosphonates starting from easily available starting materials.^{11–17} Most of these phosphonates are made up of small neutral ring and cage structures, serving as secondary building units for phosphate superstructures. In this paper, we wish to report the synthesis, structure, and properties of a novel anionic gallophosphonate cage which contains sandwiched lithium ions in the form of a

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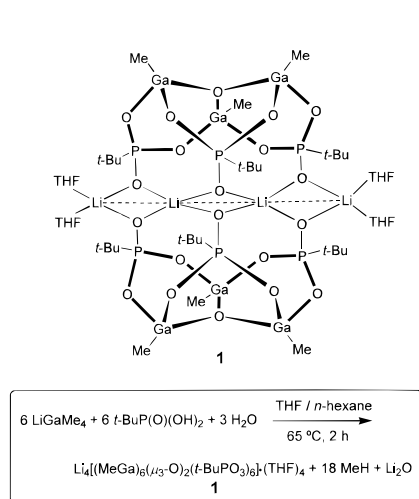
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Scheme 1



finite unidimensional wire. This compound can be regarded as a potential precursor for the preparation of molecular sieves and ion-conductors.

Results and Discussion

Synthesis and Spectra. Reaction of *tert*-butylphosphonic acid with an equimolar quantity of LiGaMe_4 in a mixture of THF and *n*-hexane (1:1) at 65 °C for 2 h yields $\text{Li}_4[(\text{MeGa})_6(\mu_3\text{-O})_2(\text{t-BuPO}_3)_6](\text{THF})_4$ (**1**) in 70% yield (Scheme 1). As it has been well documented in the case of metallasiloxane chemistry, the alkane elimination reaction between a metal alkyl and an acidic hydrogen containing phosphorus compound is the most facile route for synthesizing the title compound in good yields. The formation of **1** presumably proceeds via a reaction involving adventitious water present in the reaction medium. Chemical analysis of the starting materials and solvents used indicate that the phosphonic acid is the source of water.^{18–21}

Compound **1** has been fully characterized by means of analytical and spectroscopic techniques as well as a single crystal X-ray diffraction study. It is of interest to note that even under electron impact mass spectral conditions (70 eV), the Li/Ga/P framework in **1** is intact and shows the peak due to the molecular ion (M^+ , m/e 1674). The subsequent fragmentation is due to the loss of coordinated THF molecules and a butyl group (m/e 1327, base peak). The IR spectrum is devoid of any absorption in the region 3000–3500 cm^{-1} suggesting complete reaction of all P–OH groups of the starting material *tert*-butylphosphonic acid.

The integrated ^1H NMR intensities reveal that there is only one methyl group remaining on each gallium. While the protons

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(18) Commercially available *tert*-butylphosphonic acid contains traces of moisture. Even the sample dried *in vacuo* for 12 h in the ^1H NMR spectrum shows the presence of residual water.

(19) It is of interest to note that the presence of traces water in the phosphorus acids leads to very interesting products during their reactions with various metal alkyls. The O^{2-} anion formed by the reaction of water with metal alkyls in these reactions acts as multiply bridging ligand in these molecules leading to the formation of cage structures. For example, see refs 20 (reaction of ZnMe_2 with $(\text{t-BuO})_2\text{P(O)(OH)}$ in the presence of water) and 21 (reactions of Cp^*TiMe_3 with various alkyl and aryl phosphonic acids in the presence of traces of water).

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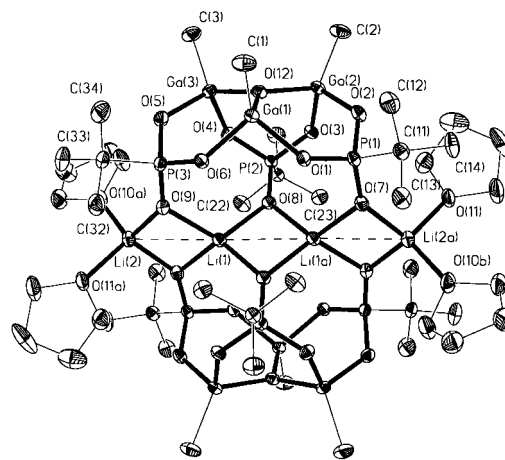


Figure 1. A perspective view of the molecular structure of **1** with the atom labeling scheme.

of the methyl group attached to the gallium atoms resonate as a singlet at δ 0.28 ppm, the protons of the *tert*-butyl group on the phosphorus atoms appear as a doublet at δ 1.14 ppm ($J_{\text{PH}} = 16.8$ Hz). The ^{31}P NMR spectrum displays a single resonance (δ 33.4 ppm) indicating that all the phosphorus centers in the molecule are in a similar environment. This resonance is considerably downfield shifted compared to the chemical shift of the phosphorus nuclei in neutral cubic gallium phosphonate $[\text{t-BuPO}_3\text{GaMe}]_4$ (δ 21.0 ppm in CDCl_3), which is also derived from *tert*-butylphosphonic acid and contains a very similar coordination environment around the phosphorus centers (*vide infra*).

Reactivity Studies of 1 by NMR Spectroscopy. In spite of the presence of easily hydrolyzable Ga–C bonds and Li^+ ions, compound **1** is remarkably stable toward moisture and air and can be left on the bench-top for several days without any detectable decomposition. In order to further evaluate the strength of the Ga–C bonds, we treated compound **1** with an excess of D_2O in C_6D_6 at 70 °C. The ^1H spectra of this solution does not show any change indicating that the Ga–Me bonds are not hydrolyzed even under these forcing conditions. Similarly compound **1** does not react with an additional equivalent of *tert*-butylphosphonic acid under the conditions employed for its preparation. These studies clearly indicate that any further reaction chemistry of cage **1** would require more forcing conditions.

Molecular Structure of 1. The final refined X-ray crystal structure of **1** (Figure 1) reveals that the molecule consists of two dinegatively charged gallophosphonate bowls of the formula $[(\text{t-BuPO}_3\text{GaMe})_3(\mu_3\text{-O})]$, made up of a nonplanar 12-membered macrocyclic ring. The three Ga centers in the macrocycle are bridged by a $\mu_3\text{-O}$ dianion (O(12)) resulting in three $\text{Ga}_2\text{O}_3\text{P}$ six-membered rings within the macrocyclic bowl. These two gallophosphonate bowls beautifully sandwich an unidimensional lithium wire consisting of four Li^+ ions through the P–O coordination. Each of the two peripheral lithium ions is further coordinated to two THF molecules. The net result is a remarkable cage system that consists of (a) *three* 4-membered Li_2O_2 rings, (b) *six* 6-membered $\text{Ga}_2\text{O}_3\text{P}$ rings, (c) *four* 8-membered GaPO_4Li_2 rings, (d) *two* 10-membered $\text{GaP}_2\text{O}_5\text{Li}_2$ rings, (e) *six* 12-membered $\text{Ga}_2\text{P}_2\text{O}_6\text{Li}_2$ rings, and (f) *two* 12-membered $\text{Ga}_3\text{O}_6\text{P}_3$ rings.

Selected bond lengths and angles in **1** are listed in Table 1. The Li_2O_2 rings are planar with the neighboring rings being perpendicular to each other. The six-membered rings are in a boat conformation. The larger rings in the molecule are in a distorted configuration. The molecule and its packing diagram,

Table 1. Selected Bond Lengths (Å) and Angles (deg) in **1**

Ga(1)–O(1)	1.850(2)	Ga(1)–O(6)	1.862(2)
Ga(1)–O(12)	1.885(2)	Ga(2)–O(2)	1.855(2)
Ga(2)–O(3)	1.867(2)	Ga(2)–O(12)	1.887(2)
Ga(2)–C(2)	1.940(4)	Ga(3)–O(5)	1.853(2)
Ga(3)–O(4)	1.861(2)	Ga(3)–O(12)	1.882(2)
Ga(3)–C(3)	1.940(4)	P(1)–O(7)	1.499(2)
P(1)–O(1)	1.540(2)	P(1)–O(2)	1.548(2)
O(7)–Li(2a)	1.914(6)	O(7)–Li(1a)	2.069(6)
O(8)–Li(1)	1.964(6)	O(8)–Li(1a)	1.970(6)
O(9)–Li(2)	1.909(6)	O(9)–Li(1)	2.040(6)
Li(1)–Li(2)	2.737(8)	Li(1)–Li(1a)	2.775(11)
O(1)–Ga(1)–O(6)	99.4(1)	O(1)–Ga(1)–O(12)	105.7(1)
O(6)–Ga(1)–O(12)	106.4(1)	O(1)–Ga(1)–C(1)	114.8(2)
O(6)–Ga(1)–C(1)	114.8(2)	O(12)–Ga(1)–C(1)	114.3(1)
O(7)–P(1)–O(1)	111.7(1)	O(7)–P(1)–O(2)	113.2(1)
O(1)–P(1)–O(2)	109.1(1)	O(7)–P(1)–C(11)	111.0(2)
O(1)–P(1)–C(11)	106.5(1)	O(2)–P(1)–C(11)	105.0(1)
Li(2a)–O(7)–Li(1a)	86.7(2)	Li(1)–O(8)–Li(1a)	89.7(2)
Li(2)–O(9)–Li(1)	87.7(2)	Ga(3)–O(12)–Ga(1)	120.0(1)
Ga(3)–O(12)–Ga(2)	116.2(1)	Ga(1)–O(12)–Ga(2)	121.1(1)
Li(2)–Li(1)–Li(1a)	177.6(4)		

^a Symmetry $a = 1 - x, 1 - y, 1 - z$.

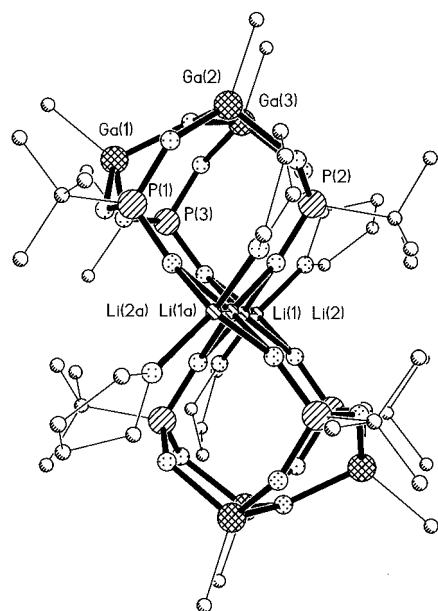


Figure 2. Plot showing the shape of the Ga/P/O bowl in **1**, made up of a 12-membered Ga–O–P ring and a μ_3 -O anion, and the large cavities present inside the molecule.

when viewed through the eight-membered rings, reveals the presence of channels (Figure 2). All the lithium cations in the molecule lie on a straight line with very short Li...Li separations (av 2.756 Å). We are unaware of such an arrangement for dissolved or dispersed Li ions in the channels of zeolites.^{3a}

The Ga– μ_2 -O distances (av 1.858 Å) are shorter than the Ga– μ_3 -O distances (av 1.885 Å). On the other hand, the P– μ_2 -O distances (1.545 Å) are substantially longer than those compared to the P– μ_3 -O distances which bridge the Li ions (1.500 Å). The Li–O distances within the molecule vary over a small range (1.900(6)–2.069(6) Å). The geometry around all the triply bridging oxygen atoms (O(7), O(8), O(9), and O(12)) is almost trigonal planar (av sum of the angles 358°).

A packing diagram of the Li₄ unit and the surrounded coordinated oxygen atoms in compound **1** is depicted in Figure 3. As it can be seen from this figure, there are no short-range intermolecular interactions between the lithium ions of the neighboring molecules owing to the bulky organic groups and the coordinated THF molecules present in the molecule.

Lithium Ion Abstraction and Attempted Ion-Exchange Studies. The presence of exposed univalent lithium ions in **1** (Figure 1) prompted us to explore the possibility of abstracting and/or exchanging them with other metal ions, using appropriate reaction conditions. In order to test the ease of abstracting lithium ions, we carried out two sets of NMR experiments, and the results are summarized in Scheme 2 (experiments 1 and 2). The observed spectral changes in these experiments are schematically represented in Figure 4.

A benzene-*d*₆ solution of **1** was treated with an excess of 12-crown-4 and D₂O at 70 °C, and the ¹H, ³¹P, and ⁷Li NMR spectra were recorded. In the ¹H NMR spectrum there were no significant changes in the resonances of various protons of **1**, indicating that the methyl groups and *tert*-butyl groups on gallium and phosphorus centers, respectively, remain intact. On the other hand, in the ³¹P NMR spectrum the single line observed at 33.4 ppm for pure **1** has completely disappeared with the appearance of a new resonance at δ 21.9 ppm (Figure 4, spectrum (b)). Similarly, in the ⁷Li NMR the original singlet observed at –0.03 ppm for **1** has completely shifted to 0.33 ppm revealing that the coordination environment around lithium ions has considerably changed. These multinuclear NMR observations indicate that the lithium ions could have moved out of the molecular framework of **1** (and now coordinated to 12-crown-4) leaving behind a pure Li-free gallium phosphonate species.

In order to further confirm this supposition, we subjected the resulting species from multinuclear NMR experiments (from Scheme 2, experiment 1) to EI mass spectral and IR studies in a THF solution. Thus, further characterization of this species by EI MS revealed the presence of a cluster ion at *m/e* 869 (base peak, Figure 5), with an isotope pattern that would correspond to a molecule containing a Ga₄P₄ unit, rather than a peak corresponding to a cluster ion containing a Ga₃P₃ unit (from one of the bowls of **1**). Although this observation was initially puzzling, an additional set of independent experiments (*vide infra*) clearly showed that the observed peak at *m/e* 869 arises from the loss of a methyl group from the neutral cubic gallium phosphonate [*t*-BuPO₃GaMe]₄ (**2**). To further support this assignment, we independently prepared compound **2** through an equimolar reaction between the neutral gallium alkyl compound GaMe₃ and *tert*-butylphosphonic acid. This procedure results in analytically pure **2** in more than 80% isolated yield. The IR and multinuclear NMR spectral data of **2** agree well with that of the species obtained in the NMR experiment described above, confirming our identification of the product.

To test the ease of formation of species **2** from **1** in the absence of 12-crown-4, a pure sample of **1** was treated with an excess D₂O at 70 °C (Scheme 2, experiment 2) and NMR spectra were recorded. As expected, the ³¹P NMR spectrum showed that the conversion of **1** to **2** was less than 10% (Figure 4, spectrum (c)), along with some unidentified decomposition products (12%). To this solution, 12-crown-4 was subsequently added and heated to 70 °C. The examination of this solution by ³¹P NMR spectroscopy showed almost no change in the conversion of **1** to **2** (Figure 4, spectrum (d)). The reduced rate of conversion of **1** could be ascribed to the fact that the sudden addition of a polar solvent such as water to a solution of **1** in nonpolar benzene solution would lead to aggregation of molecules of **1** in solution. Hence, owing to this aggregation of molecules of **1** (which contain large organic groups) in D₂O/benzene mixture, even the subsequent addition of 12-crown-4 does not promote the conversion of **1** to **2** (Scheme 2, Experiment 2).

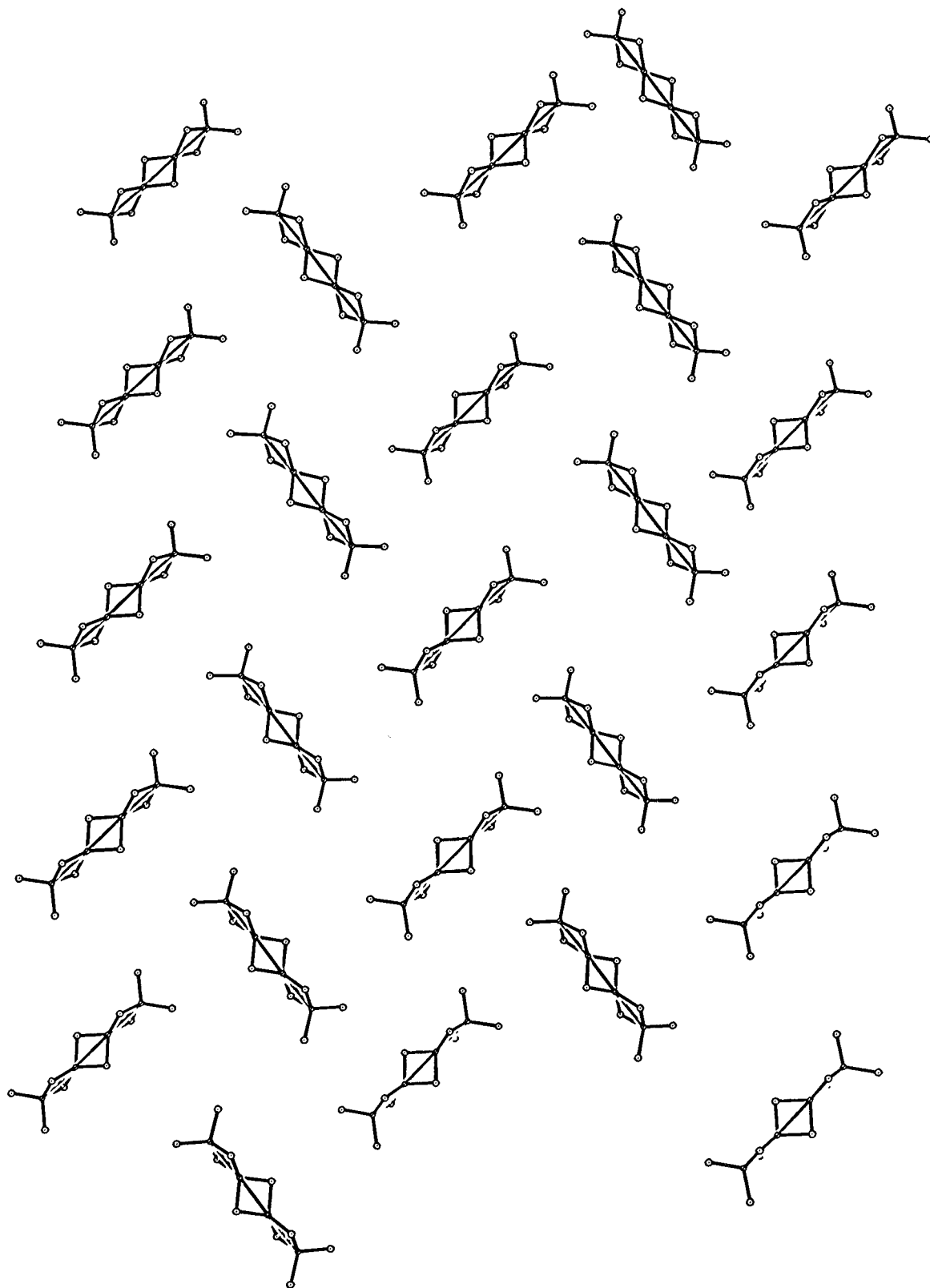


Figure 3. Solid-state packing of the central Li_4 unit and the surrounded oxygen atoms in **1**.

The neat conversion of the anionic cage **1** into the neutral cubic phosphonate **2** (Scheme 2, experiment 1), as shown in the balanced equation in Scheme 3, has somewhat limited our original plans of successfully exchanging lithium ions with other alkali or alkaline earth cations. However, there exists a possibility of synthesizing species of the type **1** with other alkali or alkaline earth metal ions by suitably starting from *t*-BuP(O)(OH)₂ and the corresponding anionic gallium precursors

such as NaGaR_4 , KGaR_4 , or CsGaR_4 . Our further studies in this area will focus toward this direction.

Conclusions

We have presented in this paper a simple and facile approach to synthesize a novel group 13 phosphonate which contains well dispersed alkali metal cations which are loosely bound to the gallium phosphonate anions. The solubility of the title com-

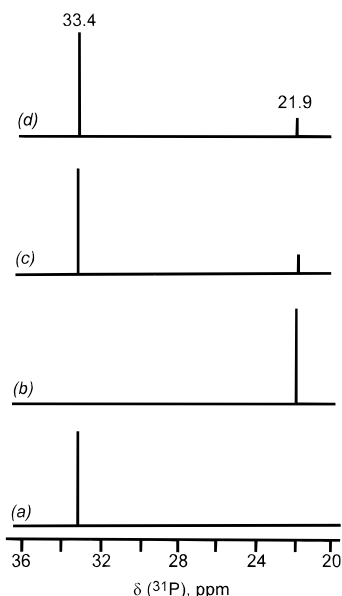


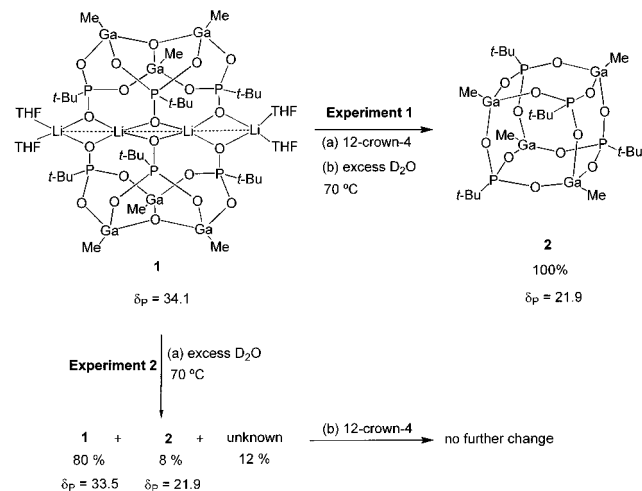
Figure 4. ^{31}P NMR spectra (162 MHz, C_6D_6) of (a) pure **1**, (b) **1** + (12-crown-4) + D_2O , (c) **1** + D_2O , and (d) **1** + D_2O + (12-crown-4).

found in common organic solvents offers several opportunities for its chemistry to be explored in detail. Especially, the multinuclear solution NMR studies on the abstraction of the lithium ions with the help of 12-crown-4 under mild conditions reveals the ease of conversion of **1** to the neutral cubic phosphonate **2**. Owing to the size of the lithium ions, we consider the title compound to be an ideal starting material for constructing ion conductors of molecular dimensions by employing high temperature cage fusion reactions in the presence of air or oxygen. Further, the structural similarities of **2** to that of the basic structural units found in cloverite, ULM-5,²² and gallophosphate-A²³ offer the possibility of using this class of compounds for the preparation of gallophosphate molecular sieves under mild conditions using sol-gel techniques.

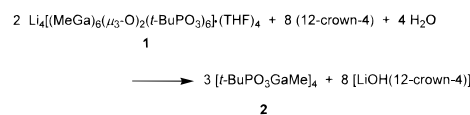
Experimental Section

General Data. All the experimental manipulations were carried out under a dry nitrogen atmosphere rigorously excluding air and moisture.²⁴ Samples for spectral measurements were prepared in a drybox. NMR

Scheme 2



Scheme 3



spectra were recorded on a Bruker AM 200 or a Bruker AS 400 instrument. The chemical shifts are reported in δ scale with reference to external SiMe_4 for ^1H , LiCl for ^7Li , and 85% H_3PO_4 for ^{31}P nuclei. The upfield shifts are negative. The NMR experiments were carried out in closed tubes under nitrogen. IR spectra were recorded on a Bio-Rad Digilab FTS7 spectrometer (only the strong absorption bands are given *vide infra*). Mass spectra were obtained on Finnigan MAT system 8230 and a Varian MAT CH5 mass spectrometer. Melting points were obtained on a HWS-SG 3000 apparatus and are reported uncorrected. CHN analyses were performed by the Analytical Laboratory of the Institute of Inorganic Chemistry at Göttingen.

Solvents and Starting Materials. Commercial grade solvents were purified employing conventional procedures and distilled twice prior to use.²⁵ Solvents for the reactions were *trap-to-trap* distilled prior to use. Trimethylgallium (Strem), methyllithium (1.6 M solution in diethyl ether, Acros), *tert*-butylphosphonic acid (Aldrich), and 12-crown-4 (Fluka) were used as received. LiGaMe_4 was synthesized from GaMe_3 and MeLi using a previously reported procedure.²⁶

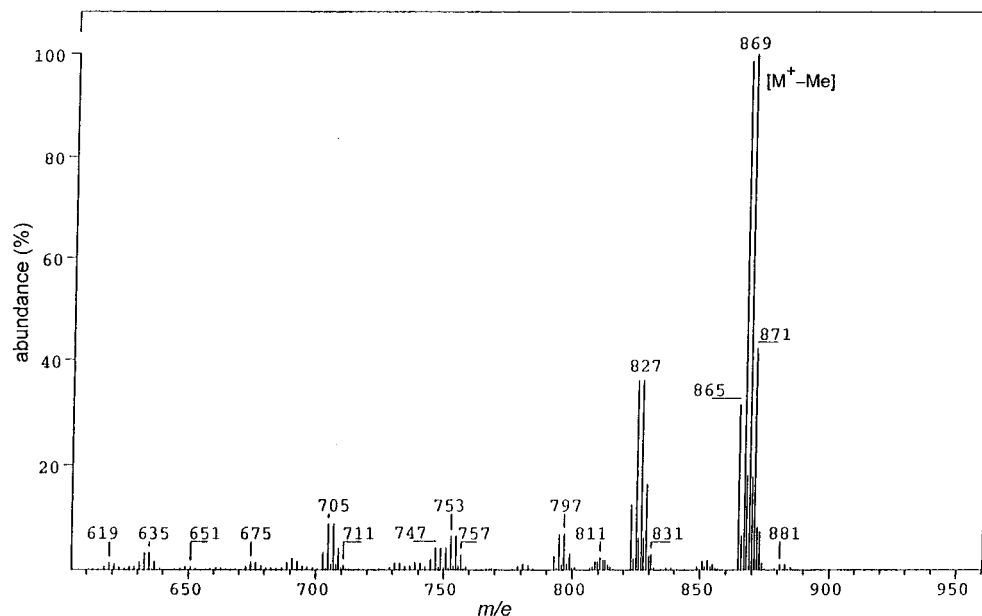


Figure 5. EI MS spectrum of the resulting solution from the treatment of **1** with 12-crown-4 and D_2O showing the peak due to $\text{M}^+ - \text{Me}$ ion (m/e 869) of **2**.

Synthesis of $\text{Li}_4[(\text{MeGa})_6(\mu_3\text{-O})_2(t\text{-BuPO}_3)_6]\cdot(\text{THF})_4$ (1**).** To a solution of LiGaMe_4 (136 mg, 1 mmol) in THF (20 mL) was added and stirred for 2 h solid *tert*-butylphosphonic acid (138 mg, 1 mmol). The reaction mixture was subsequently heated under reflux for 2 h during which the evolution of methane gas ceased. After cooling, the turbid reaction mixture (due to the formation of Li_2O) was passed through a short Celite column, and the solvent was removed under reduced pressure at room temperature. The residue was redissolved in THF (6 mL)/*n*-hexane (2 mL) mixture and cooled to -20°C to yield 195 mg (0.12 mmol, 70%) of analytically pure **1** as microcrystalline solid. $\text{Mp} > 350^\circ\text{C}$. Anal. Calcd for $\text{C}_{46}\text{H}_{104}\text{Ga}_6\text{Li}_4\text{O}_{24}\text{P}_6$ (1673.2): C, 33.02; H, 6.26. Found: C, 33.2; H, 6.4. MS (EI, 70 eV): *m/e* 1674 (1%, M^+), 1327 (100%, $\text{M}^+ - \text{Bu} - 4\text{THF}$). IR (Nujol): 1144, 1132, 1063, 1044, 988, 857, 835, 800, 725, 666, 531 cm^{-1} . ^1H NMR (C_6D_6 , 200 MHz, external standard SiMe_4): δ 0.06 (s, GaCH_3 , 18H), 1.14(d, $\text{C}(\text{CH}_3)_3$, 54H, $^3J_{\text{PH}} = 16.8$ Hz), 1.41 (t, CH_2 , 16H, $^3J_{\text{HH}} = 5.4$ Hz), 3.57 (t, OCH_2 , 16H, $^3J_{\text{HH}} = 5.4$ Hz). ^7Li NMR (C_6D_6 , 155.5 MHz, external standard LiCl) δ -0.03 (s). ^{31}P NMR (C_6D_6 , 101 MHz, external standard 85% H_3PO_4): δ 33.4 (s).

NMR Experiments. In experiment 1 (Scheme 2), **1** (10 mg) was dissolved in a NMR tube fitted with a septum in C_6D_6 (0.6 mL) inside a drybox, and the NMR spectra of the pure sample was recorded. To this tube was injected through a syringe 12-crown-4 (0.2 mL) and the resulting solution was warmed to 70°C , and again the multinuclear NMR spectra were recorded. Subsequently, D_2O (0.1 mL) was added to this tube and warmed to 70°C for 1 min, and the spectra were recorded.

Experiment 2 (Scheme 2) was carried out using same quantities of **1**, 12-crown-4, and D_2O , but reversing the order of addition of 12-crown-4 and D_2O to **1**.

Synthesis of $[t\text{-BuPO}_3\text{GaMe}]_4$ (2**).** To a solution of *t*-BuP(O)(OH) $_2$ (138 mg, 1 mmol) in THF (20 mL) was added a solution of GaMe_3 (115 mg, 1 mmol) in THF (1 mL) dropwise through a syringe at 25°C . The reaction mixture was stirred at that temperature for 24 h, and the solvent was removed *in vacuo* and washed with cold *n*-hexane (10 mL) to obtain analytically pure **2** (180 mg, 82%). $\text{Mp} > 200^\circ\text{C}$. Anal. Calcd for $\text{C}_{20}\text{H}_{48}\text{Ga}_4\text{O}_{12}\text{P}_4$ (883.38): C, 27.2; H, 5.5. Found: C, 27.1; H, 5.6. MS (EI, 70 eV): *m/e* 869 (100%, $\text{M}^+ - \text{Me}$). IR (Nujol): 1261, 1218, 1205, 1153, 1073, 1030, 835, 743, 666, 597, 508 cm^{-1} . ^1H NMR (CDCl_3 , 250 MHz, external standard SiMe_4): δ -0.26 (s, GaCH_3 , 12H), 1.10 (d, $\text{C}(\text{CH}_3)_3$, 36H, $^3J_{\text{PH}} = 16.7$ Hz). ^{31}P NMR (CDCl_3 , 101 MHz, external standard 85% H_3PO_4): δ 21.0 (s) (C_6D_6) 21.9 (s).

Crystal Structure Determination. Crystals of **1** suitable for X-ray diffraction studies were grown from a dilute 3:1 THF/*n*-hexane solution at 0°C over a period of 15 days. Crystal data: $\text{C}_{46}\text{H}_{104}\text{Ga}_6\text{Li}_4\text{O}_{24}\text{P}_6$, $\text{MW} = 1673.19$, monoclinic, space group $P2_1/n$, $a = 13.855(3)$, $b = 20.210(4)$, $c = 14.264(3)$ Å, $\beta = 104.68(3)^\circ$, $V = 3864(1)$ Å 3 , $Z = 2$, density(calcd) = 1.438 Mg/m 3 , $F(000) = 1720$, $\lambda = 0.71073$ Å, $T = 200$ K, $\mu(\text{Mo-K}\alpha) = 2.249$ mm $^{-1}$. Intensity data were collected on a Siemens-Stoe AED2 four-circle diffractometer using a $0.6 \times 0.4 \times 0.4$ mm 3 sized crystal. The data were collected using an ω - 2θ scan mode in the range $7 \leq 2\theta \leq 45^\circ$, $-14 \leq h \leq 14$, $-2 \leq k \leq 21$, $-15 \leq l \leq 15$. Of 6090 reflections collected, 5049 were independent.

The structure was solved by direct methods (SHELXS-90) 27 and refined by full matrix least squares method on F^2 using SHELXL-93 program. 28 All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were placed on calculated positions and refined isotropically. The residuals were $R1$ ($I > 2\sigma(I)$) = 0.030 and $wR2$ (all data) = 0.081. The maximum and minimum heights in final Fourier difference map were 0.463 and -0.340 e \cdot Å $^{-3}$.

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Supporting Information Available: Tables of positional and thermal parameters and estimated standard deviations for all atoms, bond distances, and angles and anisotropic thermal parameters for **1** (6 pages). See any current masthead page for ordering and Internet instructions.

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