# Gallophosphonates Containing Alkali Metal Ions. 2.[1] Synthesis and Structure of Gallophosphonates Incorporating $Na^+$ and $K^+$ Ions[†]

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The reactions between *t*-BuP(O)(OH)$_2$ and equimolar quantities of MGaMe$_4$ (M = Na, K) yield ionic and alkali metal containing molecular gallophosphonates $[Na_4(\mu_2\text{-}OH_2)_2(THF)_2][(Me_2GaO_3PBu\text{-}t)_2]_2\cdot 2THF$ (**2**) and $[K(THF)_6][K_5(THF)_2\{(Me_2GaO_3PBu\text{-}t)_2\}_3]$ (**3**), respectively. Compounds **2** and **3** are soluble in common organic solvents and have been characterized by means of analytical and spectroscopic techniques, as well as by single-crystal X-ray diffraction studies. These compounds represent the rare examples of molecular ionic phosphonate cages which contain coordinated $Na^+$ or $K^+$ ions. Compound **2** is constructed from two eight-membered $Ga_2O_4P_2$ gallium phosphonate rings which sandwich a central $Na_4(H_2O)_2$ unit. In the case of **3**, three eight-membered $Ga_2O_4P_2$ gallium phosphonate units envelope an aggregated $K_5$ core which exists in the form of a trigonal-bipyramidal polyhedron. The $Na^+$ and $K^+$ ions in **2** and **3** are also coordinated by the endocyclic oxygen atoms of the eight-membered gallophosphonate crowns, apart from the regular exocyclic P−O coordination. Unlike the lithium gallophosphonate $[Li_4(THF)_4][\{(MeGaO_3PBu\text{-}t)_3(\mu_3\text{-}O_2)\}_2]$ (**1**), compounds **2** and **3** do not undergo any clean cage conversion reaction in the presence of 15-crown-5 and 18-crown-6, respectively.

## Introduction

Naturally occurring zeolites and mineral aluminosilicates show structural similarities to metallophosphates.[2] Subsequent to the first successful preparation of aluminophosphate molecular sieves showing exceptional properties,[3] group 13 metallophosphates (Al, Ga, and In) have received considerable attention[4−6] owing to their potential catalytic, absorptive, and ion-exchange characteristics. The common synthetic routes known so far to prepare metallosilicates, metallophosphates, and phosphonates use hydrothermal conditions in the presence of an organic template molecule as the structure-directing agent.[4−6] In the last few years, there have been a few attempts to prepare smaller building units of boro-, alumino-, and gallophosphonates from easily available starting materials.[7−14] In particular, the work carried out on group 13 phosphonates by us[1,7−10] and others[11−14] has resulted in the synthesis of soluble molecular compounds which have (1) a double-four-ring (D4R or 4-4) type of core structure with a $M_4O_{12}P_4$ central unit (**A**),[7,8] (2) a double-six-ring (D6R or 6-6) type of core structure with a $M_6O_{18}P_6$ central unit (**B**),[10] or (3) a stable eight-membered $M_2O_4P_2$ ring structure (**C**)[12,13] which is conceived as the intermediate during the formation of D4R and D6R structures (Chart 1).

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[†] Dedicated to Professor Heinz Nöth on the occasion of his 70th birthday.

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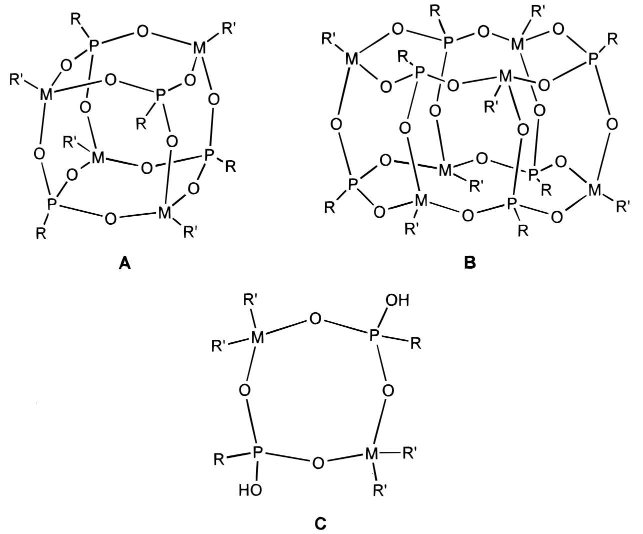
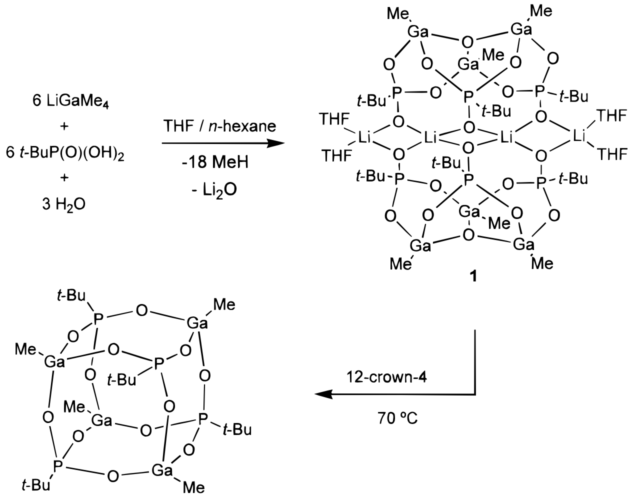
**Chart 1**



**Scheme 1**



The study of zeolites and conductive polymers which contain metal ions trapped inside their channels is one of the most intriguing developments in the area of materials science.[15,16] Electronically connected and as well as isolated conductive hyperlattices need appropriate host materials, and zeolites have been found to provide novel host lattices for a variety of metal ions and clusters.[17] The inclusion phenomenon of metallic clusters in zeolite matrices has been well studied,[18,19] and most synthetic methodologies known to date for this purpose involve multistep procedures or the use of stringent and laborious conditions. Simple methods to incorporate metal ions inside zeolite matrices under mild conditions have always been sought. Hence, we are currently concentrating our efforts in this area on the synthesis of alkali metal ion-containing group 13 silicate and phosphate molecules that would model the zeolite and zeolite-like systems.

In a recent paper,[1] we described a facile and simple organometallic route for the preparation of the $Li^+$ ion containing gallophosphate $[Li_4(THF)_4][\{(MeGaO_3PBu\text{-}t)_3(\mu_3\text{-}O_2)\}_2]$ (**1**) and demonstrated its high-yield conversion into a cubic neutral phosphonate which is made up of a core that resembles D4R building blocks of zeolites (Scheme 1). Continuing our efforts in this area, herein we wish to report the syntheses of heavier alkali metal ion ($Na^+$ and $K^+$) containing gallophosphonates which possess polyhedral framework structures. These compounds reveal several interesting structural features which have relevance to zeolite chemistry and as well as the crown-ether coordination chemistry of alkali metal ions.

## Syntheses and Spectra

As was well documented recently by us in the case of the preparation of neutral group 13 phosphonates[7,8] and as well as in the case of metallasiloxane chemistry,[20,21] the alkane elimination reaction between a metal alkyl and an acidic hydrogen containing phosphorus compound is the most facile synthetic route for the preparation of the title compounds in good yields. In the present case, in order to accommodate a second metal ion in the resulting structure, we have modified this procedure accordingly and started from alkali metal ion containing alkyls such as $NaGaMe_4$ and $KGaMe_4$. Moreover, in order to overcome the solubility problems of the resulting products, *tert*-butylphosphonic acid was chosen as the phosphorus source in these reactions.

**$[Na_4(\mu_2\text{-}OH_2)_2(THF)_2][(Me_2GaO_3PBu\text{-}t)_2]_2\cdot 2THF$ (2).** The reaction of *tert*-butylphosphonic acid with an equimolar quantity of $NaGaMe_4$ in THF at room temperature for 12 h followed by warming the reaction mixture at 65 °C for 2 h results in the formation of $[Na_4(\mu_2\text{-}OH_2)_2(THF)_2][(Me_2GaO_3PBu\text{-}t)_2]_2\cdot 2THF$ (**2**). The reaction mixture was concentrated to 5 mL, and to this solution was added 5 mL of *n*-hexane. This mixture, on cooling overnight at 0 °C, readily affords microcrystalline **2** in *ca*. 45% yield (Scheme 2). As in the case of the formation of **1**, formation of **2** also presumably proceeds via a reaction involving adventitious water present in the reaction medium. Chemical analysis of the starting materials and solvents used indicates that the commercial phosphonic acid is the source of water.[22,23]

Compound **2** has been characterized with the aid of its analytical and spectroscopic data, as well as a single-crystal X-ray diffraction study. Unfortunately, under EI-MS conditions, it was not possible to obtain any peaks due to molecular ion or

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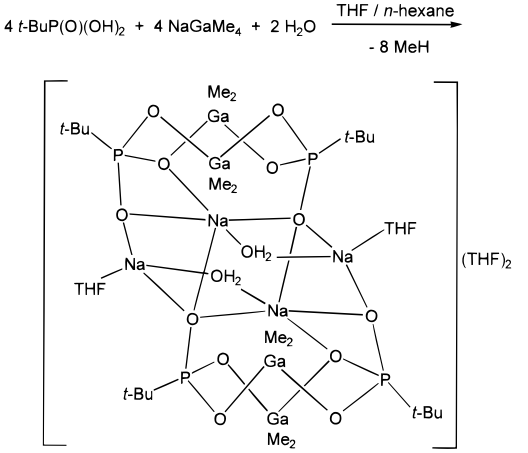
(22) Commercially available *tert*-butylphosphonic acid contains traces of moisture. Even the sample dried *in vacuo* for 12 h shows the presence of residual water in the $^1H$ NMR spectrum.

(23) It is of interest to note that the presence of traces of water in the phosphorus acids leads to very interesting products during their reactions with various metal alkyls. For example, see ref 9 for the reactions of $Cp^*TiMe_3$ with various alkyl- and arylphosphonic acids in the presence of traces of water and Lugmair et al. (Lugmair, C. G.; Tilley, T. D.; Rheingold, A. L. *Chem. Mater.* **1997**, *9*, 339) for the reaction of $ZnMe_2$ with $(t\text{-}BuO)_2P(O)(OH)$ in the presence of adventitious water.

**Scheme 2**



**2**

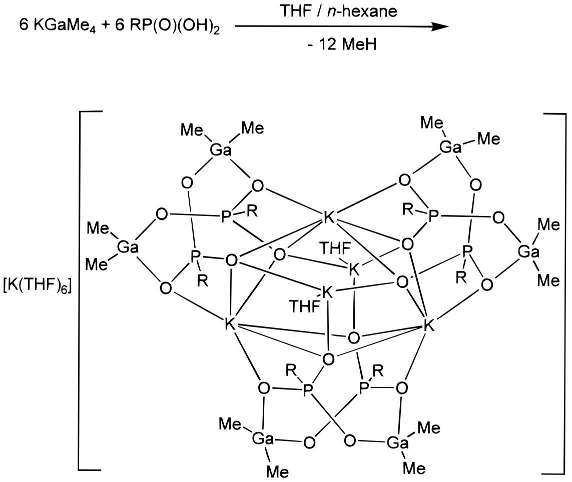
other high molecular weight fragments. This observation could be attributed to the ionic nature of the compound, which makes the ionization process under mass spectral conditions difficult. In case of FAB-MS experiments, the compound was found to be unstable in the wet matrix. The IR spectrum of **2** reveals the presence of strong absorptions due to coordinated water at 3161 and 1576 cm$^{-1}$.

The integrated $^1$H NMR intensities reveal that there are two methyl groups remaining on each gallium. While the protons of the methyl group attached to the gallium atoms resonate as three different singlets ($\delta$ −0.58, −0.55, and −0.49 ppm) probably due to their nonequivalence in solution, all the protons of the *tert*-butyl group on the phosphorus atoms appear as a single doublet ($\delta$ 1.14 ppm, $J_{PH} = 16.8$ Hz). The $^{31}$P NMR spectrum displays two closely spaced singlet resonances ($\delta$ 29.8 and 25.9 ppm) of almost equal intensity, possibly arising from the nonequivalence of the phosphorus centers due to the asymmetric coordination behavior of the oxygen atoms attached to them (*vide infra*).

**$[K(THF)_6][K_5(THF)_2\{(Me_2GaO_3PBu\text{-}t)_2\}_3]$ (3).** Reaction of *tert*-butylphosphonic acid with an equimolar quantity of $KGaMe_4$ in THF at room temperature for 12 h followed by warming at 65 °C for 10 min affords $[K(THF)_6][K_5(THF)_2\{(Me_2GaO_3PBu\text{-}t)_2\}_3]$ (**3**) in 38% yield (Scheme 3). In this case, heating of the reaction mixture for prolonged periods (*e.g.*, 2 h, as in the preparation of **2**) results in degradation of the product. As in the case of **2**, analytically pure microcrystals of **3** were obtained by cooling a concentrated THF/*n*-hexane solution (5 mL/5 mL) to 0 °C overnight. Single crystals for crystal structure determination were grown from a dilute solution at 0 °C over a period of 3−5 days. The crystals showed very high solubility in the mother liquor at room temperature.[24] As can be seen from Scheme 3, the formation of **3** does not involve the use of water present in the reaction medium.

The chemical constitution of compound **3** was established by means of analytical, spectroscopic, and X-ray diffraction techniques. As stated above in the case of Na$^+$ ion containing gallium phosphonate **2**, compound **3** also does not show peaks due to the M$^+$ ion under both EI-MS and FAB-MS conditions. In this case, the presence of several K$^+$ ions in the molecule possibly makes the compound even more ionic compared to **2**, thus causing the compound to be less volatile. The IR spectrum is devoid of any absorption in the region 3000−3500 cm$^{-1}$, indicating the absence of any coordinated water molecules and as well as the complete reaction of all P−OH groups in the starting material.

**Scheme 3**



R = *t*-Bu

**3**

The integrated $^1$H NMR intensities are suggestive of the fact that in **3** there are two methyl groups remaining on each gallium. While the protons of the methyl group attached to the gallium atoms resonate as two singlets ($\delta$ −0.61 and −0.51 ppm), the protons of the *tert*-butyl group on the phosphorus atoms appear as a doublet ($\delta$ 1.04 ppm, $J_{PH} = 14.0$ Hz). The $^{31}$P NMR spectrum displays a single resonance ($\delta$ 25.7 ppm), indicating that all the phosphorus centers in the molecule are in a similar environment. It is also instructive to note that the phosphorus resonances of compounds **1**−**3** are upfield shifted from the chemical shift of free *tert*-butylphosphonic acid ($\delta$ 42.4 ppm in $C_6D_6$).

It should however be noted that, in the case of both **2** and **3**, it has not been possible to obtain good NMR spectra in solvents other than THF-$d_8$. For example, when the spectra were recorded in a noncoordinating solvent such as $C_6D_6$, in the $^{31}$P NMR spectra several closely spaced signals were observed, indicating the possibility of several species existing in solution. The $^1$H NMR spectra were too complicated for any meaningful interpretation. We believe that the coordinated THF molecules, on dissolution in solvents other than THF-$d_8$, reorganize in various ways and form gallophosphonate molecules with different structures.

## Crystal Structures

**Molecular Structure of $[Na_4(\mu_2\text{-}OH_2)_2(THF)_2][(Me_2GaO_3PBu\text{-}t)_2]_2 \cdot 2THF$ (2).** Due to the nonobservance of molecular ion or any other high molecular weight peaks in the mass spectra of **2** and **3**, and as well as rather inconclusive NMR and other spectral data for arriving a definitive structure, single-crystal X-ray structure determinations were carried out to ascertain the structures in the solid state. The final refined structure of **2** with its atom-labeling scheme is shown in Figure 1. Selected structural parameters are listed in Table 1. The molecule essentially consists of two dinegatively charged gallophosphonate crowns (Ga−O−P−O−Ga−O−P−O) of the formula $[(Me_2GaO_3PBu\text{-}t)_2]^{2-}$ in the form of nonplanar eight-membered macrocyclic rings. These two gallophosphonate rings sandwich

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(24) Owing to the low isolated yields of **3**, the mother liquor was examined by $^{31}$P NMR spectroscopy after removing the crops of crystals. The observed spectrum showed the presence of several phosphorus-containing species in solution. However, to date, we are not able to identify or crystallize of any of these products.

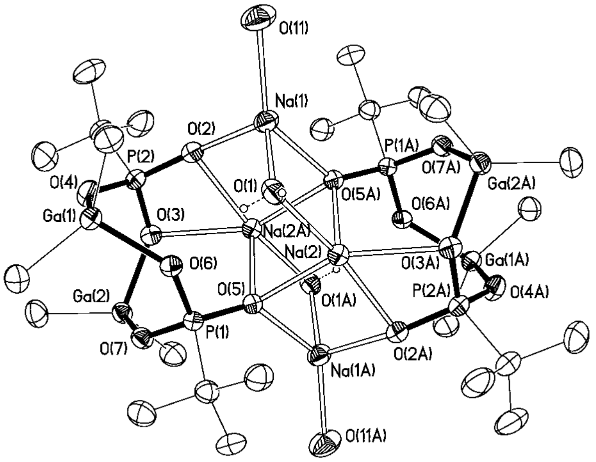

**Figure 1.** Perspective view of the molecular structure of **2**. The lattice THF solvent molecules and the carbon atoms of the coordinated THF molecules are omitted for clarity.

**Table 1.** Selected Bond Lengths (Å) and Bond Angles (deg) for **2**

| | | | |
|---|---|---|---|
| Ga(1)−O(4) | 1.908(2) | Ga(1)−O(6) | 1.946(2) |
| Ga(2)−O(3) | 1.928(2) | Ga(2)−O(7) | 1.917(2) |
| P(1)−O(5) | 1.520(2) | P(2)−O(2) | 1.504(2) |
| P(1)−O(6) | 1.553(2) | P(2)−O(3) | 1.537(2) |
| P(1)−O(7) | 1.526(2) | P(2)−O(4) | 1.555(2) |
| Na(1)−O(1) | 2.322(3) | Na(2)−O(1) | 2.334(3) |
| Na(1)−O(2) | 2.210(3) | Na(2)−O(2A) | 2.350(3) |
| Na(1)−O(5A) | 2.334(3) | Na(2)−O(3A) | 2.390(2) |
| Na(1)−O(11) | 2.276(3) | Na(2)−O(5) | 2.350(2) |
| Na(2)−O(5A) | 2.339(2) | Na(1)···Na(2) | 3.304(2) |
| Na(2)···Na(2A) | 3.252(3) | Na(1)···Na(2A) | 3.229(2) |
| Na(1)−O(1)−Na(2) | 90.40(9) | O(1)−Na(1)−O(5A) | 89.86(9) |
| Na(1)−O(5A)−Na(2) | 89.99(8) | O(1)−Na(2)−O(5A) | 89.48(9) |
| Na(2A)−O(2)−Na(1) | 90.09(8) | O(2)−Na(1)−O(5A) | 91.11(8) |
| Na(2)−O(5)−Na(1A) | 87.82(8) | O(5)−Na(2)−O(2A) | 87.36(8) |
| O(1)−Na(2)−O(2A) | 165.39(10) | O(1)−Na(1)−O(11) | 112.41(11) |

four $Na^+$ ions through the P−O coordination bonds. Further, there are two coordinated $H_2O$ molecules, each of which bridges two of the four $Na^+$ ions. Unlike in the lithium gallophosphonate **1**, where the lithium ions are in the form of a one-dimensional wire, the sodium ions in **2** are arranged in the form of two $Na_2O_2$ rings which are further connected to each other through Na−O bonds (Figure 1). As a result, there are five $Na_2O_2$ rings in the molecule which are sandwiched by the two gallophosphonate rings. There are two types of $Na^+$ ions present in the molecule. The two tetracoordinated peripheral sodium ions have one coordinated THF molecule each. The other two sodium ions, which are located well inside the cage, are coordinated also to the endocyclic oxygen atoms, thus making these two $Na^+$ ions pentacoordinated with an approximate trigonal-bipyramidal geometry. The two lattice THF molecules present as the solvent of crystallization show no interaction with the gallophosphonate cage of **2**.

All the $Na_2O_2$ rings in the molecule are largely planar, with the adjacent $Na_2O_2$ rings being approximately perpendicular to each other. The Ga−O distances vary over a range (1.908(2)−1.946(2) Å), and the average value (1.913 Å) is comparable to the Ga−O distances found in **1**. The exocyclic P−O distances (average 1.512 Å) are considerably shorter than the ring Ga−O bonds (average 1.543 Å), possibly indicating a partial double-bond character of the exocyclic P−O bonds. The Na−O distances within the molecule vary over a range (2.210(3)−2.390(3) Å). Further, the $Na^+$ ions show short Na···Na contacts (3.252(3)−3.304(2) Å). The angles around Na centers vary over a large range (89.48(9)−165.39(10)°), indicating considerable distortion from ideal tetrahedral and trigonal-bipyramidal geometries of the two types of $Na^+$ ions, respectively.

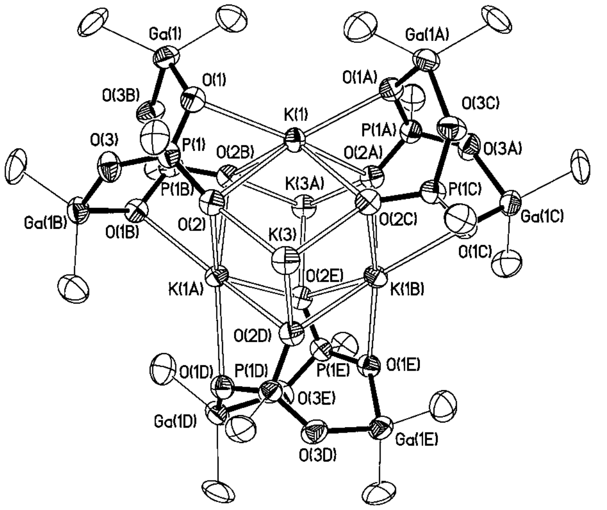

**Figure 2.** Core structure of the $[K_5(THF)_2\{(Me_2GaO_3PBu\text{-}t)_2\}_3]$ part of **3**. The THF molecules on K(3) and K(3A) and the peripheral carbon atoms are omitted for clarity.

**Table 2.** Selected Bond Lengths (Å) and Bond Angles (deg) for **3**

| | | | |
|---|---|---|---|
| Ga(1)−O(1) | 1.919(3) | Ga(1)−O(3B) | 1.889(3) |
| P(1)−O(1) | 1.540(4) | P(1)−O(2) | 1.505(4) |
| P(1)−O(3) | 1.526(4) | K(1)−O(1) | 2.744(3) |
| K(1)−O(2) | 2.816(3) | K(1)−O(2A) | 2.816(3) |
| K(1)−O(2B) | 2.804(3) | K(1)−O(2C) | 2.805(3) |
| K(3)−O(2) | 2.584(3) | K(3)−O(40) | 2.670(8) |
| K(1)···K(1A) | 3.913(3) | K(1)···K(3) | 3.970(2) |
| O(1)−K(1)−O(2) | 53.34(1) | O(1)−K(1)−O(2B) | 81.4(1) |
| O(1)−K(1)−O(1A) | 132.5(1) | O(1)−K(1)−O(2A) | 160.8(1) |
| O(1)−K(1)−O(2C) | 119.6(1) | O(2)−K(1)−O(1A) | 128.9(1) |
| O(2)−K(1)−(O2B) | 77.9(1) | O(2)−K(1)−O(2C) | 80.9(1) |
| O(2)−K(3)−O(2A) | 89.7(1) | O(2)−K(3)−O(40) | 128.0(5) |

**Molecular Structure of $[K(THF)_6][K_5(THF)_2\{(Me_2GaO_3PBu\text{-}t)_2\}_3]$ (3).** Compound **3** crystallizes in the chiral hexagonal space group $P6_322$ with one-sixth part of both the enantiomers coexisting in the asymmetric unit of the unit cell. The final refined molecular structure of the anionic part of one of the enantiomers of **3** is shown in Figure 2. Selected bond lengths and angles are listed in Table 2.

Compound **3** consists of a cationic $[K(THF)_6]^+$ and an anionic $[K_5(THF)_2\{(Me_2GaO_3PBu\text{-}t)_2\}_3]^-$ part. In turn, the more interesting anionic part of the molecule is basically constructed from three dinegatively charged nonplanar eight-membered gallophosphonate rings (Ga−O−P−O−Ga−O−P−O) of the formula $[(Me_2GaO_3PBu\text{-}t)_2]^{2-}$ which coordinate to the five $K^+$ ions through the exo- and endocyclic P−O bonds. The five $K^+$ ions form the central core of the anionic part and are arranged in a trigonal-bipyramidal geometry. The three basal $K^+$ ions are related to each other by a 3-fold axis on which the two other axial $K^+$ ions are located above and below the basal plane. The three gallophosphonate rings are located around this K-polyhedron and are displaced from each other by 120° from the center of the polyhedron.

It is of interest to note that the axial $K^+$ ions are considerably different from the basal $K^+$ ions in terms of their coordination geometry. The two axial $K^+$ ions are coordinated by an exocyclic P−O bond from each of the three $Ga_2O_4P_2$ gallophosphonate rings. Further, the two axial $K^+$ ions are additionally coordinated by a THF molecule, resulting in tetrahedral geometry. The three basal $K^+$ ions are hexacoordinated and

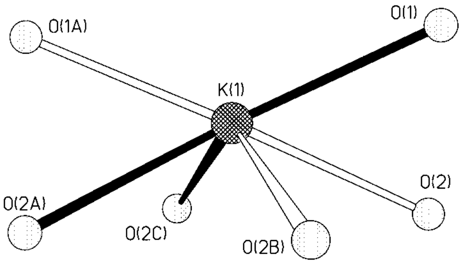

**Figure 3.** Plot showing the local coordination geometry around K(1) in **3**.

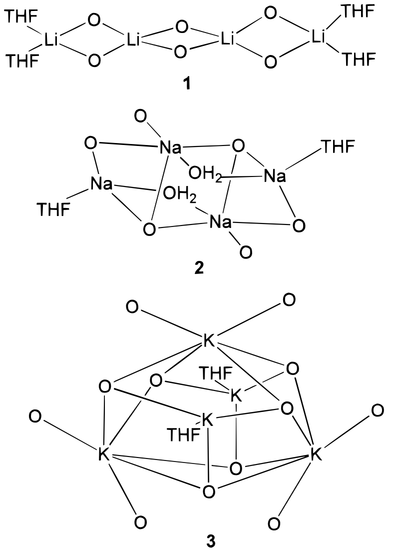

**Figure 4.** Arrangement of the alkali metal ions in the gallophosphonate clusters **1**−**3**.

display a rather peculiar coordination geometry (Figure 3). The coordination geometry arising from the coordination of four exocyclic and two ring oxygen atoms can be described as "two intersecting trigonal planes".

The Ga−$\mu_2$-O distances (1.889(3) Å) are slightly shorter than the Ga−$\mu_3$-O distances (1.919(3) Å). Similarly, the exocyclic P−O distances (average 1.505 Å) within the Ga−O−P rings are substantially shorter than the endocyclic P−O distances (average 1.533 Å). The K-O distances within the molecule vary over a large range (2.584(3)−2.816(3) Å). The shortest K···K distances in the $K_5$ polyhedron are in the order of 3.9 Å.

**Comparison of Gallophosphonates 1−3.** It is of interest to compare some of the structural features and properties of the alkali metal containing gallophosphonates **1**−**3**. All three compounds were synthesized from the same type of gallium source ($MGaMe_4$; M = Li, Na, K) and the same phosphonic acid ($t$-$BuP(O)(OH)_2$) by employing almost similar reaction conditions. Hence, the large variations in the structures of the resultant products can only be attributed to the size of the different alkali metal ions at present. The smaller four-coordinated lithium ions in **1** have an open and linear arrangement (Figure 4). On the other hand, the larger four-, five-, or six-coordinated sodium and potassium cations in **2** and **3** tend to aggregate and form a closed core (Figure 4).

The core structures and the arrangement of alkali metal ions in compounds **2** and **3** (Figure 4) also have implications in their attempted alkali metal ion abstraction reactions with organic crown ethers. While the lithium gallophosphonate **1** undergoes clean and facile cage-to-cage conversion in the presence of 12-crown-4,[1] the sodium gallophosphonate **2**, when reacted with 15-crown-5 under similar reaction conditions in THF-$d_8$, shows no new signals. However, the relative intensity of the two original signals of **2** is slightly altered in the presence of the crown ether. Similarly, the potassium gallophosphonate **3**, on treatment with 18-crown-6 in THF-$d_8$ under similar conditions, shows no change in the $^{31}P$ NMR spectrum, suggesting that the anionic part of the molecule remains unchanged.[25] The observance of almost no change in the spectra in these compounds could be due to the location of the $Na^+/K^+$ ions well inside the cage structures. Alternatively, this observation could also be attributed to the rather strong and extensive coordination of the endocyclic gallophosphonate ring oxygen atoms in **2** and **3**, as in the case of conventional crown-ether complexes.[26]

## Conclusions

In this paper, we have shown the use of simple organometallic group 13 compounds in the preparation of cage phosphonates that contain both gallium and alkali metal ions. It appears from our studies that the sizes of the alkali metal ions determine the sizes and shapes of the resultant phosphonate cages. Aggregation of the alkali metal ions and the coordination of endocyclic oxygen atoms in **2** and **3** do not allow us to carry out any clean cage transformation reactions in the presence of organic crown ethers, in contrast to the observed ease of lithium ion abstraction in the related compound **1**. The results presented herein indicate that this synthetic methodology could be extended to the rational synthesis of bimetallic phosphonates with divalent metals such as Zn or Mg, starting from precursors of the type $M[GaMe_4]_2$. We are currently investigating these and the related aspects.

## Experimental Section

**General Data.** All experimental manipulations were carried out under a dry nitrogen atmosphere, rigorously excluding air and moisture.[27] Samples for spectral measurements were prepared in a drybox. NMR spectra were recorded on a Bruker AM 200 or a Bruker AS 400 instrument. The chemical shifts are reported on the $\delta$ scale with reference to external $SiMe_4$ for $^1H$ nuclei and 85% $H_3PO_4$ for $^{31}P$ nuclei. The upfield shifts are negative. 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 a Finnigan MAT 8230 system and a Varian MAT CH5 mass spectrometer. Melting points were obtained on an 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 by employing conventional procedures and were distilled twice prior to their use.[28] Solvents for the reactions were trap-to-trap distilled prior to use. Trimethylgallium (Strem), *tert*-butylphosphonic acid (Aldrich), 15-crown-5 (Fluka), and 18-crown-6 (Fluka) were used as received. $NaGaMe_4$ and $KGaMe_4$ were synthesized from $GaMe_3$ and the respective alkali metals using a previously reported procedure.[29]

**$[Na_4(\mu_2\text{-}OH_2)_2(THF)_2][(Me_2GaO_3PBu\text{-}t)_2]_2\cdot 2THF$ (2).** To a solution of $NaGaMe_4$ (153 mg, 1 mmol) dissolved in THF (25 mL) was directly added solid *tert*-butylphosphonic acid (138 mg, 1 mmol), and the mixture was stirred for 12 h. The reaction mixture was subsequently heated at 60 °C for 2 h, during which the evolution of methane gas ceased. The solution was concentrated *in vacuo* to 5 mL, and $n$-hexane (5 mL) was added. The resulting concentrated solution was cooled at

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(25) This observation however does not rule out the possible 18-crown-6 coordination to the free $K^+$ ion which is present in **3** as $[K(THF)_6]^+$.

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0 °C overnight to yield 140 mg (45%) of analytically pure **2** as microcrystals. Mp: >300 °C. Anal. Calcd for $C_{40}H_{96}Ga_4Na_4O_{18}P_4$ (MW 1360): C, 35.3; H, 7.0. Found: C, 37.0; H, 7.6. IR (Nujol): 3161, 1576, 1261, 1202, 1142, 1110, 1075, 1020, 982, 918, 800, 723, 661 cm$^{-1}$. $^{1}$H NMR (THF-$d_8$, 200 MHz, external standard $SiMe_4$): $\delta$ $-0.58$, $-0.55$, $-0.49$ (all s, $GaCH_3$, 24H), 1.06, 1.04 (d, $C(CH_3)_3$, 36H, $^{3}J_{PH} = 14.3$ Hz), 3.18 (s, $H_2O$, 4H). $^{31}$P NMR (THF-$d_8$, 101 MHz, external standard 85% $H_3PO_4$): $\delta$ 29.8 (s), 25.9 (s).

**$[K(THF)_6][K_5(THF)_2\{(Me_2GaO_3PBu\text{-}t)_2\}_3]$ (3).** To a solution of $KGaMe_4$ (169 mg, 1 mmol) in THF (20 mL) was added solid *tert*-butylphosphonic acid (138 mg, 1 mmol), and the mixture was stirred for 12 h. The reaction mixture was subsequently warmed to 60 °C for 10 min, during which the evolution of methane gas completely ceased. After cooling, the turbid reaction mixture was filtered, and the solvent was concentrated under reduced pressure at room temperature to 5 mL. To this solution was added 5 mL of *n*-hexane, and the resulting solution was cooled to 0 °C to yield 210 mg (38%) of analytically pure **3** as a microcrystalline solid. Mp: >300 °C. Anal. Calcd for $C_{68}H_{154}Ga_6K_6O_{26}P_6$ (MW 2226.7): C, 36.7; H, 7.0. Found: C, 35.7; H, 6.7. IR (Nujol): 1261, 1198, 1089, 1019, 866, 800, 723, 659 cm$^{-1}$. $^{1}$H NMR (THF-$d_8$, 200 MHz, external standard $SiMe_4$): $\delta$ $-0.61$, $-0.51$ (s, $GaCH_3$, 36H), 1.04 (d, $C(CH_3)_3$, 54H, $^{3}J_{PH} = 14.0$ Hz). $^{31}$P NMR (THF-$d_8$, 101 MHz, external standard 85% $H_3PO_4$): $\delta$ 25.7 (s).

**Crystal Structure Determinations.** Crystals of **2** and **3** suitable for X-ray diffraction studies were grown from dilute THF/*n*-hexane (1/1) solutions at 0 °C over a period of 5 d. Intensity data for both **2** and **3** were collected from chosen crystals on a STOE-Siemens-Huber four-circle-diffractometer that is coupled to a Siemens CCD area detector using graphite-monochromated Mo Kα radiation ($\lambda = 0.710\,73$ Å).

Crystal data for **2**: $C_{40}H_{96}Ga_4Na_4O_{18}P_4$, MW = 1359.89, monoclinic, space group $P2_1/n$, $a = 12.367(5)$ Å, $b = 13.788(7)$ Å, $c = 19.498(8)$ Å, $\beta = 102.34(1)°$, $V = 3248(2)$ Å$^3$, $Z = 2$, $d$(calcd) = 1.391 Mg/m$^3$, $F(000) = 1416$, $T = 133$ K, $\mu$(Mo Kα) = 1.823 mm$^{-1}$, crystal size = 0.2 × 0.2 × 0.1 mm$^3$, data collection range = $4.5 \le 2\theta \le 52.8°$, $-15 \le h \le 15$, $0 \le k \le 17$, $0 \le l \le 24$, unique reflections = 6639, R1($I > 2\sigma(I)$) = 0.0413 and wR2(all data) = 0.0765 (R1 = $\sum||F_o| - |F_c||/\sum|F_o|$ and wR2 = $(\sum w(F_o^2 - F_c^2)^2/\sum w(F_o)^2)^{0.5}$), maximum and minimum heights of the residual peaks = 0.506 and $-0.434$ e·Å$^{-3}$.

Crystal data for **3**: $C_{68}H_{154}Ga_6K_6O_{26}P_6$, MW = 2226.65, hexagonal, space group $P6_322$, $a = 17.812(3)$ Å, $c = 39.241(5)$ Å, $V = 10782(3)$ Å$^3$, $Z = 4$, $d$(calcd) = 1.372 Mg/m$^3$, $F(000) = 4640$, $T = 133$ K, $\mu$(Mo Kα) = 1.858 mm$^{-1}$, crystal size = 0.5 × 0.4 × 0.3 mm$^3$, data collection range = $4.1 \le 2\theta \le 53.0°$, $-18 \le h \le 0$, $0 \le k \le 22$, $0 \le l \le 49$, unique reflections = 7504, R1($I > 2\sigma(I)$) = 0.0564 and wR2(all data) = 0.1023 (R1 = $\sum||F_o| - |F_c||/\sum|F_o|$ and wR2 = $(\sum w(F_o^2 - F_c^2)^2/\sum w(F_o)^2)^{0.5}$), maximum and minimum heights of the residual peaks = 0.405 and $-0.344$ e·Å$^{-3}$.

The structures of both the compounds were solved by direct methods (SHELXS-96)[30] and refined by full-matrix least-squares methods against $F^2$ using the SHELXL-97 program.[31] All non-hydrogen atoms were refined anisotropically. The hydrogen atoms bonded to O(1) in **2** were found in the difference electron density map and were refined using distance and isotropic thermal parameter restraints. All other hydrogen atoms in **2** and **3** were placed on calculated positions using a riding model and refined isotropically. For both compounds, the disordered THF molecules (coordinated and lattice) were refined with the help of partial occupancy factors and similarity restraints on bond distances, angles, and anisotropic displacement parameters along with rigid-body restraints for the latter. In the case of **3**, the molecule crystallizes in the chiral space group $P6_322$. A search for any other higher symmetry with the program INVERS,[32] which uses the Le Page algorithm,[33] confirmed the acentric chiral space group.

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**Supporting Information Available:** Tables of crystal data and structure refinement details, positional and thermal parameters, and bond distances and angles for **2** and **3** (22 pages). See any current masthead page for ordering information.

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