New Pillared Layered Gallium Phosphonates in the Gallium/1,2-Ethylenediphosphonic Acid System

Martine Bujoli-Doeuff,[†] **Michel Evain,**[†] **Pascal Janvier,**[‡] **Dominique Massiot,**[§]
Abraham Clearfield,[||] **Zhehong Gan,**[⊥] **and Bruno Bujoli***[,‡]

Institut des Matériaux Jean Rouxel, UMR CNRS 6502, 2 Rue de la Houssinière, BP92208,
44322 Nantes Cedex 03, France, Laboratoire de Synthèse Organique, UMR CNRS 6513,
2 Rue de la Houssinière, BP92208, 44322 Nantes Cedex 03, France, CRMHT, UPR CNRS 4212,
1D Avenue de la Recherche Scientifique, 45071 Orléans Cedex 02, France, Department of Chemistry,
Texas A&M University, College Station, Texas 77843, and NHMFL, 1800 East Paul Dirac Drive,
Tallahassee, Florida 32310

Received June 4, 2001

1,2-Ethylenediphosphonic acid reacts with gallium nitrate in water to give new pillared layered gallium phosphonates, the structure of which depends on the experimental conditions used for their preparation. Thus, $Ga_4(O_3PC_2H_4PO_3)_3$ (**1**) and $Ga_2(OH)_2(O_3PC_2H_4PO_3)$ (**2**) were isolated and the structure of **1** was solved by single-crystal X-ray diffraction, while **2** was shown to have the same metal/PO_3 arrangement as the previously described $Ga(OH)(O_3PCH_3)$. $Ga_4(O_3PC_2H_4PO_3)_3$ (**1**) is triclinic, with space group $P\bar{1}$ with $Z = 2$, $a = 5.1480(4)$, $b = 8.0354(7)$, and $c = 12.383(1)$ Å; $\alpha = 91.34(1)$, $\beta = 101.40(1)$, and $\gamma = 90.86(1)°$; $V = 501.9(1)$ Å^3. The structure of **1** is unusual with (i) mixed GaO_4 and GaO_5 sites while a 6-fold coordination is observed for gallium in (**2**) and (ii) the presence of the organic moiety within both the layers and the interlayer space. The two compounds were fully characterized using ^{31}P and ^{71}Ga solid-state NMR.

Introduction

Metal phosphonate chemistry, initially centered around zirconium compounds, has been rapidly extended to elements with oxidation states from +2 to +6, and a wide array of novel structure types has been prepared.[1] The phosphonic acid precursors can be synthesized with a variety of organic groups (exhibiting any conceivable property) attached to the phosphorus atom, thus allowing the design of materials with specific properties, among which supported catalysis has particularly retained our attention.[2] In the simplest case of monoalkylphosphonates, layered compounds are usually obtained. The possibility to create three-dimensional porous structures has been explored using bisphosphonates, and the significant role played by the organic chain separating the two PO_3H_2 moieties in the structure and dimensionality of the corresponding hybrid architectures is well documented.[3] Only a few series of layered gallium phosphonates have been reported in the literature,[4] but no example of pillared layered structure was known, if we except the case of a recently reported gallium fluorobisphosphonate described as structurally related to $Al_2(O_3PC_2H_4PO_3)(H_2O)_2F_2\cdot H_2O$.[5] Moreover, our interest in such systems was also justified by the presence of NMR-observable nuclei that offer the possibility to selectively examine the inorganic part, the organic part, and their connection. The ability to get detailed structural information on poorly crystalline hybrids is very challenging, and we have shown that the combined use of modern high-

---

* Corresponding author. Fax: 33-2/ 5112 5402. E-mail: bujoli@chimie.univ-nantes.fr.

[†] UMR CNRS 6502.

[‡] UMR CNRS 6513.

[§] UPR CNRS 4212.

[||] Texas A&M University.

[⊥] NHMFL.

(1) See, for example: Clearfield, A. In *Progress in Inorganic Chemistry*; Karlin, K. D., Ed.; John Wiley &Sons: New York, 1998; Vol. 47, pp 371−510.

(2) (a) Deniaud, D.; Schöllhorn, B.; Mansuy, D.; Rouxel, J.; Battioni, P.; Bujoli, B. *Chem. Mater.* **1995**, *7*, 995−1000. (b) Deniaud, D.; Spyroulias, G. A.; Bartoli, J. F.; Battioni, P.; Mansuy, D.; Pinel, C.; Odobel, F.; Bujoli, B. *New J. Chem.* **1998**, *22*, 901−905. (c) Pénicaud, V.; Maillet, C.; Janvier, P.; Pipelier, M.; Bujoli, B. *Eur. J. Org. Chem.* **1999**, 1745−1748. (d) Maillet, C.; Janvier, P.; Pipelier, M.; Praveen, T.; Andres, Y.; Bujoli, B. *Chem. Mater.* **2001**, *13*, 2879−2884.

(3) See, for example: (a) Bonavia, G.; Haushalter, R. C.; O'Connor, C. J.; Zubieta, J. *Inorg. Chem.* **1996**, *35*, 5603−5612. (b) Brousseau, L. C., III; Mallouk, T. E. *Anal. Chem.* **1997**, *69*, 679−687. (c) Brousseau, L. C., III; Aurentz, D. J.; Benesi, A. J.; Mallouk, T. E. *Anal. Chem.* **1997**, *69*, 688−694. (d) Alberti, G.; Vivani, R.; Marmottini, F.; Zappelli, P. *J. Porous Mater.* **1998**, *5*, 205−220. (e) Petruska, M. A.; Talham, D. R. *Chem. Mater.* **1998**, *10*, 3672−3682. (f) Clearfield, A. *Chem. Mater.* **1998**, *10*, 2801−2810. (g) Distler, A.; Lohse, D. L.; Sevov, S. C. *J. Chem. Soc., Dalton Trans.* **1999**, 1805−1812. (h) Alberti, G.; Brunet, E.; Dionigi, C.; Juanes, O.; de la Mata, M. J.; Rodriguez-Ubis, J. C.; Vivani, R. *Angew. Chem., Int. Ed.* **1999**, *38*, 3351−3353. (i) Zheng, L.; Song, H.; Lin, C.; Wang, S.; Hu, Z.; Yu, Z., Xin, X. *Inorg. Chem.* **1999**, *38*, 4618−4619. (j) Zheng, L.; Song, H.; Duan, C.; Xin, X. *Inorg. Chem.* **1999**, *38*, 5061−5066. (k) Serre, C.; Ferey, G. *Inorg. Chem.* **1999**, *38*, 5370−5373. (l) Cao, G.; Guillou, N.; Nogues, M.; Cheetham, A. K.; Ferey, G. *Chem. Mater.* **1999**, *11*, 2937−2947. (m) Neff, G. A.; Helfrich, M. R.; Clifton, M. C.; Page, C. J. *Chem. Mater.* **2000**, *12*, 2363−2371. (o) Riou, D.; Belier, F.; Serre, C.; Nogues, M.; Vichard, D.; Ferey, G. *Int. J. Inorg. Mater.* **2000**, *2*, 29−33. (p) Altomare, A.; Bellitto, C.; Ibrahim, S. A.; Mahmoud, M. R.; Rizzi, R. *J. Chem. Soc., Dalton Trans.* **2000**, 3913−3919, and references therein.

(4) (a) Fredoueil, F.; Massiot, D.; Poojary, D.; Bujoli-Doeuff, M.; Clearfield, A.; Bujoli, B. *Chem Commun.* **1998**, 175−176. (b) Bujoli-Doeuff, M.; Evain, M.; Fayon, F.; Alonso, B.; Massiot, D.; Bujoli, B. *Eur. J. Inorg. Chem.* **2000**, 2497−2499. (c) Morizzi, J.; Hobday, M.; Rix, C. *J. Mater. Chem.* **2000**, *10*, 1693−1697.

(5) Harvey, H. G.; Teat, S. J.; Attfield, M. P. *J. Mater. Chem.* **2000**, *10*, 2632−2633.

10.1021/ic010588q CCC: $20.00

resolution solid-state NMR and FTIR spectroscopies can provide structural data that are very attractive to the materials chemist.[6] In this study, two new three-dimensional (3-D) gallium phosphonates [$Ga_4(O_3PC_2H_4PO_3)_3$ (**1**) and $Ga_2(OH)_2(O_3PC_2H_4PO_3)$ (**2**)] were prepared under hydrothermal conditions, and the relationship between structure and ($^{31}P + ^{71}Ga$) solid-state NMR parameters is discussed.

Experimental Section

Synthesis of $Ga_4(O_3PC_2H_4PO_3)_3$. A mixture of gallium nitrate (1.34 mmol) and 1,2-ethylenediphosphonic acid (1 mmol) in 20 mL of water was placed in the PTFE cell of an autoclave, which was sealed and kept at 170 °C in a drying oven for 7 days. $Ga_4(O_3PC_2H_4PO_3)_3$ was obtained in 47% yield (132 mg) as white crystals, used for the X-ray structure determination. Elemental analysis: found: P, 22.13; C, 8.65; H 1.39; calcd for $Ga_4P_6O_{18}C_6H_{12}$: P, 22.20; C, 8.61; H, 1.44. FTIR ν (KBr): 1245 s, 1202 s, 1116 vs, 1077 vs, 1059 vs, 1030 vs, 1016 vs, 784 s cm^{-1}. TGA (25 °C to 300 °C): 0%.

Synthesis of $Ga_2(OH)_2(O_3PC_2H_4PO_3)$. A mixture of gallium nitrate (0.67 mmol), 1,2-ethylenediphosphonic acid (0.5 mmol), and 1 M sodium hydroxide (2 mL) in 20 mL of water was placed in the PTFE cell of an autoclave, which was sealed and kept at 160 °C in a drying oven for 25 days. $Ga_2(OH)_2(O_3PC_2H_4PO_3)$ was obtained in 25% yield (60 mg) as a white powder. Elemental analysis: found: Ga, 38.59; P, 17.28; C, 7.01; H, 1.75; calcd for $Ga_2P_2O_8C_2H_6$: Ga, 38.79; P, 17.23; C, 6.68; H, 1.68. FTIR ν (KBr): 3518 vs, 1211 m, 1122 vs, 1102 vs, 1060 vs, 988 vs, 914 vs cm^{-1}. TGA (25−300 °C): 0%; the first weight loss was observed above 430 °C, corresponding to the removal of the hydroxo group and the carbon chain at the same time. XRD d (intensity): 7.3 (100), 4.15 (7), 3.52 (13), 3.11 (9) Å.

Solid-State NMR Experiments. Nuclear magnetic resonance solid-state spectra of ^{71}Ga and ^{31}P have been acquired on a Bruker DSX400 spectrometer operating at 9.4 T. The ^{31}P spectra have been acquired using CP-MAS $\{^1H\}-^{31}P$ excitation, as previously described[4a] with typical contact time of 1.5 ms and recycle time of 1 s. Spectra were simulated using a modified version of the Bruker Winfit program[7] to obtain a complete characterization of the chemical shift anisotropy tensor of the different sites. At 9.4 T the ^{71}Ga spectra, extending over several hundreds of kilohertz, have been acquired in static following the VOCS protocol.[8] For compound **1** “high-speed” MAS (35.7 kHz) at very high field (19.5 T; NHMFL)] was necessary to obtain a resolved spectrum.

Structure Determination of $Ga_4(O_3PC_2H_4PO_3)_3$. Data collection was carried out at room temperature with a single crystal approximately 0.2 × 0.2 × 0.1 mm in size on a STOE Imaging Plate Diffraction System,[9] using graphite-monochromatized Mo K-$L_{2,3}$ radiation (λ = 0.710 73 Å). Data intensities were corrected for Lorentz polarization and absorption (Gaussian analytical correction). $P\bar{1}$ was found to be the correct space group, at both the residue factor and the structure coherence level. A starting model was found with the SHELXTL V5.0 direct method program[10] and refined (F^2, all reflections included) with the JANA2000 program.[11] All subsequent calculations were carried out with the JANA2000 program package. Non-hydrogen atoms were refined with anisotropic displacement parameters, and hydrogen atoms were kept at fixed positions with a common refined isotropic displacement parameter. At the last stage of the refinement, a secondary extinction coefficient[12] was introduced and the residue factor smoothly converged with $R/R_w = 0.0240/0.0513$ for 1770 reflections with $I/\sigma(I) > 2$ [from 8253 collected reflections; $R(int)_{all} = 0.041$] and 155 parameters. Crystallographic details for the structure of **1** are summarized in Table 1. Selected bond lengths and angles for **1** are given in Table 2.

Table 1. Summary of Crystallographic Data for the Structure of $Ga_4(O_3PC_2H_4PO_3)_3$ (**1**)

chemical formula	$Ga_2P_3O_9C_3H_6$
fw	418.43
space group	$P\bar{1}$ (no. 2)
a, Å	5.1480(4)
b, Å	8.0354(7)
c, Å	12.3827(1)
α, (deg)	91.341(1)
β, (deg)	101.400(1)
γ, (deg)	90.857(1)
V, Å^3	501.9(1)
Z	2
D_{calc}, g cm^{-3}	2.768
temp, K	298
λ, Å	0.71073
μ, cm^{-1}	58.8
R(obs)	0.0240
wR_F^2(obs)	0.0513
residual electron density, e/Å^3	−0.52/0.66

[a] $R(F_o) = \sum||F_o| - |F_c||/\sum|F_o|$; $wR_F^2 = [\sum w_F^2(|F_o|^2 - |F_c|^2)^2/\sum w_F^2|F_o|^4]^{1/2}$; $w_F^2 = 1/(\sigma^2(I_0) + (2 \times 0.016 \times I_0)^2)$.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for the Non-Hydrogen Atoms in $Ga_4(O_3PC_2H_4PO_3)_3$[a]

$Ga1^a-O1^a$	1.855(2)	$Ga2^a-O6^a$	1.836(2)
$Ga1^a-O2^a$	2.032(2)	$Ga2^a-O7^a$	1.810(2)
$Ga1^a-O3^a$	1.860(2)	$Ga2^a-O8^a$	1.823(2)
$Ga1^a-O4^a$	1.915(2)	$Ga2^a-O9^a$	1.799(2)
$Ga1^a-O5^a$	1.840(2)		
$P1^a-O1^a$	1.517(2)	$P2^a-O2^d$	1.509(2)
$P1^a-O3^b$	1.517(2)	$P2^a-O6^a$	1.547(2)
$P1^a-O8^c$	1.539(2)	$P2^a-O7^e$	1.528(2)
$P1^aC1^a$	1.795(3)	$P2^{a-}C2^a$	1.793(3)
$P3^a-O4^f$	1.502(2)	$C1^a-C2^a$	1.534(4)
$P3^a-O5^d$	1.517(2)	$C3^a-C3^g$	1.539(4)
$P3^a-O9^a$	1.548(2)		
$P3^a-C3^a$	1.786(3)		
$O1^a-Ga1^a-O2^a$	89.9(1)	$O3^a-Ga1^a-O5^a$	132.6(1)
$O1^a-Ga1^a-O3^a$	111.9(1)	$O4^a-Ga1^a-O5^a$	91.4(1)
$O1^a-Ga1^a-O4^a$	92.3(1)	$O6^a-Ga2^a-O7^a$	106.1(1)
$O1^a-Ga1^a-O5^a$	115.2(1)	$O6^a-Ga2^a-O8^a$	108.4(1)
$O2^a-Ga1^a-O3^a$	87.54(9)	$O6^a-Ga2^a-O9^a$	113.1(1)
$O2^a-Ga1^a-O4^a$	177.7(1)	$O7^a-Ga2^a-O8^a$	107.4(1)
$O2^a-Ga1^a-O5^a$	88.07(9)	$O7^a-Ga2^a-O9^a$	114.1(1)
$O3^a-Ga1^a-O4^a$	91.2(1)	$O8^a-Ga2^a-O9^a$	107.5(1)

[a] Atoms related by $^a x, y, z$; $^b 1 + x, y, z$; $^c 1 - x, 2 - y, 1 - z$; $^d -x, 1 - y, 1 - z$; $^e -1 + x, y, z$; $^f x, y, -1 + z$; $^g -x, 2 - y, -z$.

Results and Discussion

The reactivity of ethylenediphosphonic acid with gallium nitrate was first tested under the conditions previously described by us for the synthesis of highly crystalline gallium phosphonates: i.e., with a large excess of phosphonic acid over gallium (P/Ga > 5, pH ≈ 1). By this method, a mixture of two phases was isolated, the main part of which was identified as $Ga_4(O_3PC_2H_4PO_3)_3$ (**1**), present as very small platelets among which diamondlike crystals as a minor phase were also observed. Some

---

(6) (a) Massiot, D.; Drumel, S.; Janvier, P.; Bujoli-Doeuff, M.; Bujoli, B. *Chem. Mater.* **1997**, *9*, 6−7. (b) Penicaud, V.; Massiot, D.; Gelbard, G.; Odobel, F.; Bujoli, B. *J. Mol. Struct.* **1998**, *470*, 31−38. (c) Fredoueil, F.; Massiot, D.; Janvier, P.; Gingl, F.; Bujoli-Doeuff, M.; Evain, M.; Clearfield, A.; Bujoli, B. *Inorg. Chem.* **1999**, *38*, 1831−1833.

(7) Massiot, D.; Thiele, H.; Germanus, A. *Bruker Rep.* **1994**, *140*, 43−46.

(8) Massiot, D.; Farnan, I.; Gautier, N.; Trumeau, D.; Trokiner, A.; Coutures, J. P. *Solid State NMR* **1995**, *4*, 241−248.

(9) IPDS software; STOE & Cie GmbH: Darmstadt, Germany, 1996.

(10) Sheldrick, G. M. SHELXTL V5.0; Analytical X-ray Instruments Inc.: Madison, WI, 1995.

(11) Petricek, V.; Dusek, M. JANA2000 programs for modulated and composite crystals; Institute of Physics: Praha, Czech Republic, 2000.

(12) Becker, P. J.; Coppens, P. *Acta Crystallogr.* **1974**, *A30*, 129−147.

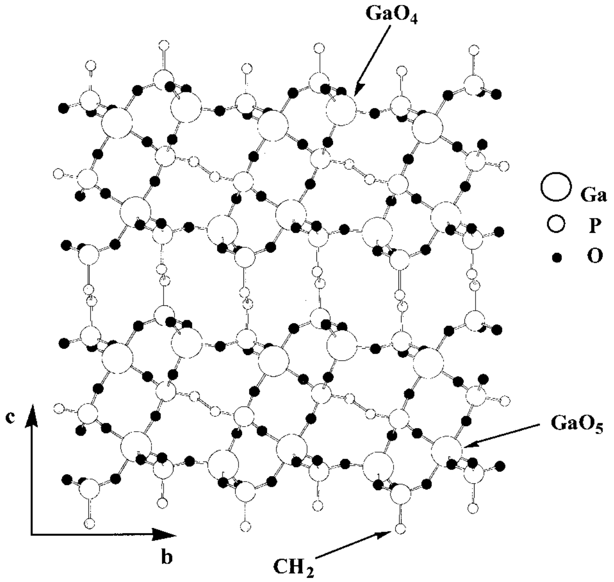

Figure 1. Schematic representation of the pillared layered arrangement in $Ga_4(O_3PC_2H_4PO_3)_3$ (**1**) viewed down the *a*-axis.

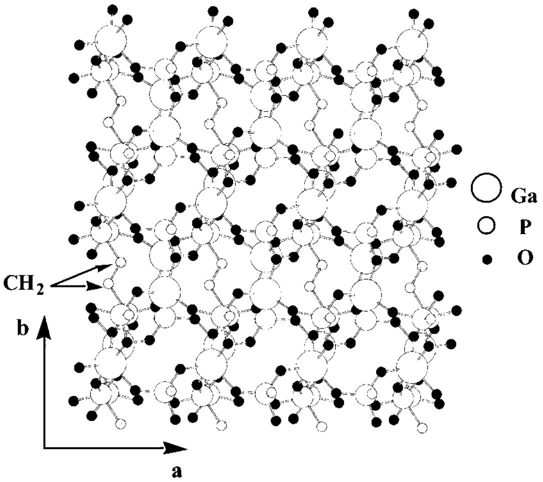

Figure 2. Schematic representation of a layer of $Ga_4(O_3PC_2H_4PO_3)_3$ as seen perpendicular to the *c*-axis.

of these crystals were removed from the sample, and the formulation of this minor product was thus found to be $Ga(HO_3PC_2H_4PO_3)\cdot H_2O$ [orthorhombic, $a = 9.6790(5)$ Å, $b = 9.3600(7)$ Å, $c = 15.8583(8)$ Å].[13] The quality of these crystals was not good enough to give satisfying X-ray structure refinements. All attempts to synthesize a pure sample of this compound failed since this phase is relatively unstable under hydrothermal conditions; this is probably due to the presence of a noncoordinated P−OH function that tends to react to form compound **1**. The synthesis was then optimized to prepare **1** selectively as crystals of suitable size to allow its structure determination by X-ray diffraction. The adjustment of the starting Ga/P ratio to 2/3 (the stoichiometry of the desired compound) was found to be the best choice, and the structure determination revealed a densely packed 3-D pillared layered network, as shown in Figures 1 and 2. One of the remarkable features in this compound is the presence of a mixed GaO_5 (trigonal bipyramid) and GaO_4 (50/50) environment for the gallium atoms; that is unprecedented even in the closely related aluminum phosphonates.[14] As usual, the bisphosphonic acid blocks act as pillars between the slabs (*c*-axis), but surprisingly one-third of these units are also part of the sheets, being sandwiched between two gallium/PO_3 layers (*ab* plane). Consequently, the organic and inorganic components are intimately mixed, unlike usual pillared layered phosphonates in which the organic moiety is segregated in the interlayer region. The PO_3 groups are coordinated to gallium according to a (111) connectivity with two-thirds of the crystallographic sites bonded to two GaO_5 and one GaO_4, while the others are linked to two GaO_4 and one GaO_5; this is consistent with the ^{31}P MAS NMR spectrum of **1** in which two resonances are observed at 20.4 and 11.7 ppm respectively in a 2:1 ratio.

It is important to note that the behavior of ethylenediphosphonic acid is markedly different from that of monoalkylphosphonic acids; in fact, when a 5- to 10-fold excess of methyl- or benzylphosphonic acid was reacted with gallium nitrate, layered $Ga(OH)(O_3PR)$ compounds were isolated [$R = CH_3$ and $CH_2C_6H_5$], in which similar gallium/PO_3 arrangements were observed. Under the same experimental conditions, however, the expected analogue $Ga_2(OH)_2(O_3PC_2H_4PO_3)$ (**2**) did not form. The synthesis of **2** was only possible when the pH value was raised to ca. 5, leading to a poorly crystalline powder (with only one strong XRD line close to 7.3 Å), making necessary the use of spectroscopic methods to demonstrate its parent structure with the above-mentioned methyl and benzyl derivatives. In this context, FTIR and ^{31}P MAS NMR spectroscopies have proved to be efficient tools to probe the metal/PO_3 arrangement in phosphonates.[5] The IR spectrum of **2** in the OH and PO_3 vibration domains [3518 (vs); 1122 (vs), 1102 (vs), 1060 (vs), 988 (vs), 914 (vs)] compares well with that of $Ga(OH)(O_3PCH_2C_6H_5)$ [3519 (vs); 1097 (vs), 1061 (vs), 989 (vs), 910 (vs)] and $Ga(OH)(O_3PCH_3)$ [3515 (vs); 1101 (vs), 1058 (vs), 1000 (vs), 913 (vs)]. The presence of two bands of equivalent intensities [1102 and 1122 cm^{-1}] in the 1100 cm^{-1} region, instead of one for $Ga(OH)(O_3PR)$ [$R = CH_3$ or $CH_2C_6H_5$], is probably due to a splitting of this band as a result of a higher distortion of the PO_3R tetrahedra in compound **2**, as previously observed in the case of other metal phosphonates. In addition, the ^{31}P chemical shift tensors measured for compound **2** (i.e., isotropic chemical shift δ_{iso}, chemical shift asymmetry κ, and anisotropy Ω; see Table 3) and $Ga(OH)(O_3PCH_3)$ are very similar as are the ^{71}Ga NMR data, with particularly close values for the quadrupolar coupling constant C_Q. These observations give clear evidence that the metal/PO_3 structural features within the layers have the same nature for both compounds (see Figure 3).

Recently, some of our efforts were focused on the use of solid-state NMR to provide accurate insights into the local

---

(13) The unit-cell parameters were obtained from single-crystal studies on some of these diamondlike crystals. The formulation was determined from the structure solution thus obtained. However, as all the crystals examined were invariably twinned, the quality of the refinement was not good enough for reporting the structure of this minor phase in this paper. This minor product could not be isolated in sufficient amount to perform elemental analysis or FTIR and TGA measurements. Nevertheless, the Ga/P ratio was confirmed by EDX (energy dispersive X-ray) analysis.

(14) (a) Maeda, K.; Akimoto, J.; Kiyozumi, Y.; Mizukami, F. *J. Chem. Soc., Chem Commun.* **1995**, 1033−1034. (b) Maeda, K.; Akimoto, J.; Kiyozumi, Y.; Mizukami, F. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1199−1201. (c) Sawers, L. J.; Carter, V. J.; Armstrong, A. R.; Bruce, P. G.; Wright, P. A.; Gore, B. E. *J. Chem. Soc., Dalton Trans.* **1996**, 3159−3161. (d) Cabeza, A.; Aranda, M. A. G.; Bruque, S.; Poojary, D. M.; Clearfield, A.; Sanz, J. *Inorg. Chem.* **1998**, *37*, 4168−4178. (e) Hix, G. B.; Carter, V. J.; Wragg, D. S.; Morris, R. E.; Wright, P. A. *J. Mater. Chem* **1999**, *9*, 179−185. (f) Zakowsky, N.; Hix, G. B.; Morris, R. E. *J. Mater. Chem* **2000**, *10*, 2375−2380. (g) Chaplais, G.; Le Bideau, J.; Leclercq, D.; Mutin, H.; Vioux, A. *J. Mater. Chem* **2000**, *10*, 1593−1601.

Table 3. Experimental Values for ^{71}Ga Chemical Shift and Electric Field Gradient, and for ^{31}P Chemical Shift Tensor, for Compounds **1** and **2** Compared to Other Gallium Phosphonates from the Literature

compound	nucleus site	δ_{iso} (ppm)	C_Q (MHz) Ω (ppm)	η_Q κ
$Ga_4(O_3PC_2H_4PO_3)_3$ (**1**)				
CN = 4: $Ga(OP)_4$	^{71}Ga (CN = 4) (50%)	$\delta_{iso}{}^{a} = 117$	$C_Q{}^{b} = 9.7$	$\eta_Q{}^{c} = 0.3$
CN = 5: $Ga(OP)_5$	^{71}Ga (CN = 5) (50%)	$\delta_{iso}{}^{a} = 10$	$C_Q{}^{b} = 8.3$	$\eta_Q{}^{c} = 0.3$
	^{31}P (111)			
	site 1 (33%)	$\delta_{iso}{}^{d} = 11.7$	$\Omega^{e} = 61.1$	$\kappa^{f} = 0.0$
	site 2 (67%)	$\delta_{iso}{}^{d} = 20.4$	$\Omega^{e} = 69.5$	$\kappa^{f} = -0.15$
$Ga_2(OH)_2(O_3PC_2H_4PO_3)$ (**2**)				
CN = 6: $Ga(OP)_4(OH)_2$	^{71}Ga (CN = 6)	$\delta_{iso}{}^{a} = 1$	$C_Q{}^{b} = 16.7$	$\eta_Q{}^{c} = 1.0$
	^{31}P (112)	$\delta_{iso}{}^{d} = 29.9$	$\Omega^{e} = 78.3$	$\kappa^{f} = 0.15$
$Ga(OH)(O_3PCH_3)$				
CN = 6: $Ga(OP)_4(OH)_2$ [from ref 4b]	^{71}Ga (CN = 6)	$\delta_{iso}{}^{a} = -13$	$C_Q{}^{b} = 16.2$	$\eta_Q{}^{c} = 0.8$
	^{31}P (112)	$\delta_{iso}{}^{d} = 30.5$	$\Omega^{e} = 69.7$	$\kappa^{f} = 0.2$
$Ga(OH)(O_3PCH_3)\cdot H_2O$				
CN = 6: $Ga(OP)_4(OH)_2$ [from ref 4b]	^{71}Ga (CN = 6)	$\delta_{iso}{}^{a} = -13$	$C_Q{}^{b} = 16.2$	$\eta_Q{}^{c} = 0.8$
	^{31}P (112)	$\delta_{iso}{}^{d} = 32.2$	$\Omega^{e} = 60.4$	$\kappa^{f} = 0.0$
$Ga(OH)(O_3PCH_2C_6H_5)$				
CN = 6: $Ga(OP)_4(OH)_2$ [from ref 4b]	^{71}Ga (CN = 6)	$\delta_{iso}{}^{a} = 10$	$C_Q{}^{b} = 17.5$	$\eta_Q{}^{c} = 0.8$
	^{31}P (112)	$\delta_{iso}{}^{d} = 25.6$	$\Omega^{e} = 89.4$	$\kappa^{f} = 0.2$
$Ga(OH)(O_3PC_2H_4CO_2H)\cdot H_2O$				
CN = 6: $Ga(OP)_3(OH)_2(H_2O)$ [from ref 4a]	^{71}Ga (CN = 6)			
	site 1 (50%)	$\delta_{iso}{}^{a} = -6$	$C_Q{}^{b} = 13.5$	$\eta_Q{}^{c} = 0.85$
	site 2 (50%)	$\delta_{iso}{}^{a} = 2$	$C_Q{}^{b} = 12.0$	$\eta_Q{}^{c} = 0.35$
	^{31}P (111)			
	site 1 (50%)	$\delta_{iso}{}^{d} = 14.9$	$\Omega^{e} = 76.5$	$\kappa^{f} = -0.3$
	site 2 (50%)	$\delta_{iso}{}^{d} = 12.0$	$\Omega^{e} = 74.5$	$\kappa^{f} = -0.5$

[a] Chemical shifts are referenced to ^{71}Ga resonance in a 1 M gallium nitrate solution; error in the measured value ±10 ppm. [b] Quadrupolar coupling constant ($C_Q = e^2qQ/h$); error in the measured value ±0.25 MHz. [c] Asymmetry factor. [d] Chemical shifts are referenced to ^{31}P resonance in 85% H_3PO_4. [e] Chemical shift span defined as $\delta_{11} - \delta_{33}$ with $\delta_{11} \geq \delta_{22} \geq \delta_{33}$. [f] Chemical shift skew defined as $3(\delta_{22} - \delta_{iso})/\Omega$.

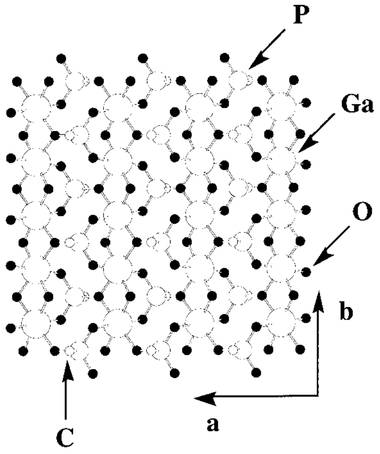

Figure 3. Schematic representation of the metal/PO_3 arrangement in $Ga(OH)(O_3PCH_3)$ [according to ref 4b], similar to that observed in $Ga_2(OH)_2(O_3PC_2H_4PO_3)$ (**2**).

environments of P and Ga in gallium phosphonates.[4a,b] For this purpose the NMR parameters of compounds **1** and **2** were determined (Table 3) and compared to those of other reported members of the Ga/P system, for which the structures were well established. Although the number of model gallium phosphonates available is still relatively limited, a correlation between NMR parameters and local structure seems to be present: (i) for the P sites, according to the connectivity of the PO_3 groups (i.e., the number of metal atoms connected to each of the three oxygen atoms bound to the phosphorus atom), different ranges of variation are observed for the δ_{iso} ([11.7, 20.4] (111 connectivity), [25.6, 32.2] (112 connectivity)) and κ ([−0.5, 0] (111 connectivity), [0, 0.2] (112 connectivity)) values, respectively; (ii) for the Ga sites, we examined if a relationship between ^{71}Ga chemical shifts and the coordination number could be established. As previously described,[4a,b,8] a VOCS protocol was used for the acquisition of the ^{71}Ga spectra, but no resolution was observed for compound **1** and magic angle spinning did not provide any gain in resolution. The second-order line broadening from the quadrupolar coupling can be reduced by high magnetic fields. In addition, fast MAS pushes spinning sidebands further away the main peaks, making the resolution of two ^{71}Ga sites possible. Under these extreme conditions ["high-speed" MAS (35.7 kHz) at very high field (19.5 T; NHMFL)], we finally obtained a resolved spectrum (Figure 4) from which we can measure the quadrupolar tensor parameters and estimate the CSA tensor and its orientation in the principal axis of the quadrupolar interaction. From Table 3, 6-coordinate Ga give shifts in the range −13 to 10 ppm whereas the first and only example of 4-coordinate phosphonate Ga site was observed at 117 ± 10 ppm, consistent with the values previously reported[15] for Ga^{IV} sites in gallium phosphates [100 ppm for $GaPO_4$ quartz and 118 ppm for $GaPO_4$ cristoballite]. Concerning Ga^{V} coordination, there exists only one mention in gallium phosphates with centers of gravity in the range of 29 to −4 ppm[16] and thus higher isotropic chemical shift, but no example of phosphonate. In compound **1** the isotropic chemical shift of the Ga^{V} site [10 ± 10 ppm] corresponds to a $Ga(OP)_5$ environment with a downshift of ~100 ppm compared to the $Ga(OP)_4$ site. However, this also means that the $Ga(OP)_5$ chemical shift signature is close to that of Ga^{VI} environments [$Ga(OP)_4(OH)_2$ or $Ga(OP)_3(OH)_2(H_2O)$; Table 3], these two types of sites being mostly differentiated by their quadrupolar couplings, twice as large in the case of Ga^{VI}−OH coordinated sites as in the case of the $Ga(OP)_5$ site of compound **1**.

---

(15) Massiot, D.; Vosegaard, T.; Magneron, N.; Trumeau, D.; Montouillout, V.; Berthet, P.; Loiseau, T.; Bujoli, B. *Solid State NMR* **1999**, *15*, 159−169.

(16) Taulelle, F.; Samoson, A.; Loiseau, T.; Ferey, G. *J. Phys. Chem. B* **1998**, *102*, 8588−8598.

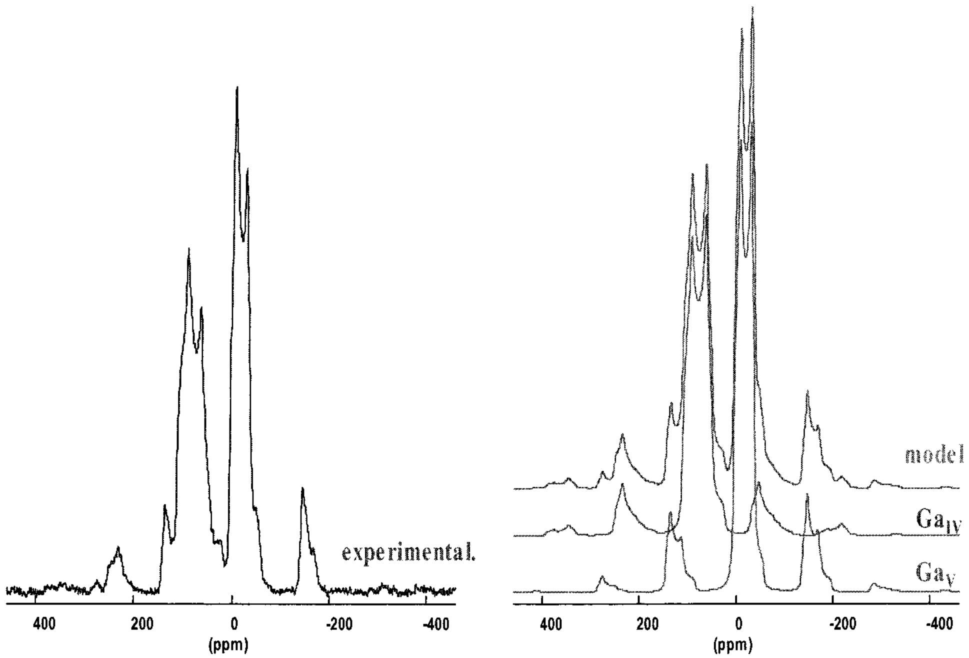

Figure 4. Experimental and simulated ^{71}Ga NMR spectrum (19.5 T, 35.7 kHz) of $Ga_4(O_3PC_2H_4PO_3)_3$ (**1**) showing the Ga^{IV} and Ga^V resolved contributions.

Additional model compounds would of course be helpful to confirm this trend, but these first results confirm all the interest of ^{31}P and ^{71}Ga solid-state NMR for the structural investigation of gallium phosphonates.

Acknowledgment. D.M. acknowledges financial support from EEC Contract No. HPRI-CT-1999-00042.

Supporting Information Available: X-ray crystallographic file for $Ga_4(O_3PC_2H_4PO_3)_3$ (**1**), in CIF format, is available. FTIR spectra for compound (**2**) and Ga(OH)(O_3PR) [with R = CH_3 and $CH_2C_6H_5$] (3 pages). This material is available free of charge via the Internet at http://pubs.acs.org.

IC010588Q