Investigation of the Structure of New Gallium Phosphonate Based Hybrid Materials by ^{31}P, ^{71}Ga, and ^{1}H Solid-State NMR

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Modern high-resolution solid-state NMR is a powerful tool for probing the structure of phosphonate-based hybrid materials, in the organic as well as in the inorganic region. This is illustrated in the case of a series of new gallium phosphonates $[Ga(OH)(O_3PCH_3) \cdot x\,H_2O$ [x = 1 (**1**); x = 0 (**1′**)] and $Ga(OH)(O_3PCH_2C_6H_5)$ (**2**)], that were characterized by X-ray diffraction and FTIR, and then studied using ^{71}Ga, ^{31}P, and ^{1}H NMR.

Introduction

Metal phosphonates are organic-inorganic hybrid materials in which the structure can be tuned by the choice of the organic moiety covalently bonded to the inorganic portion.[1] These materials are attracting increasing interest because of the large variety of applications they can offer, among which supported catalysis has particularly attracted our attention.[2] For a better understanding of the structure/property relationships in these solids, modern high-resolution solid-state NMR offers a wide variety of methods that can selectively examine the inorganic part, the organic part, and their connection, provided NMR-observable nuclei are present. In this paper we describe a new series of gallium phosphonates and their study by recently developed experimental NMR techniques which demonstrate the potential of these methods to give access to detailed structural information. Layered phosphonates are now well documented,[1] but to date, only one example of the gallium series has been reported;[3] in this study, two new layered gallium phosphonates $[Ga(OH)(O_3PCH_3) \cdot H_2O$ (**1**) and $Ga(OH)(O_3PCH_2C_6H_5)$ (**2**)] were prepared under hydrothermal conditions. The metal/PO_3 arrangement within the slabs of compound **1** can be described as edge-sharing octahedra (made of four phosphonate oxygen atoms and two μ-2 hydroxide groups) forming infinite chains parallel to the *b* axis.

These chains are connected via the PO_3 groups, thus leading to a 2D network (Figure 1), with the methyl substituents oriented perpendicular to the layers, and the non-coordinated water molecules located between the sheets, weakly hydrogen-bonded to some phosphonate and hydroxide oxygen atoms (Figure 2).

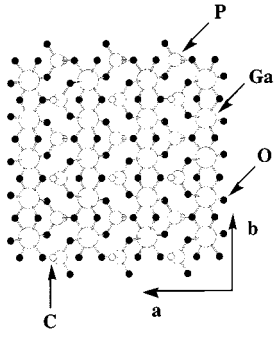

Figure 1. Schematic representation of a $Ga(OH)(O_3PCH_3) \cdot H_2O$ (**1**) layer viewed down the *c* axis; selected interatomic distances [Å]: Ga−O: 1.967(3) [X 2], 2.006(3) [X 2], 1.941(3) [X 2−OH]

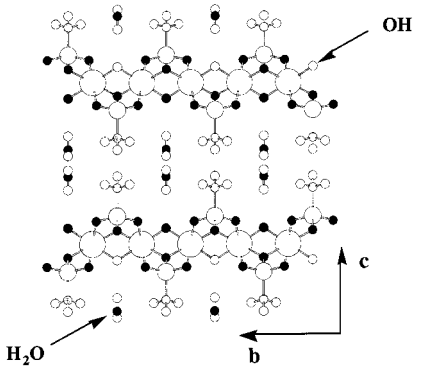

Figure 2. Schematic representation of the layered arrangement of **1** shown perpendicular to the *a* axis

No modification of the inorganic network occurs after the loss of the water molecule [performed by heating **1** at 100 °C for 1 h to yield **1′**] since the infrared spectrum is not modified, except in the ν(OH) region. As FTIR is very sensitive to the metal−O_3P arrangement in metal phosphonates, the strong similarities observed in the IR data

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collected for **2** and **1′** (for the OH and PO_3 absorptions − see Experimental Section) give clear evidence that the structural features in these three products are quite similar.

As far as the inorganic component in these materials is concerned, the six-coordinate nature of the gallium atoms is clearly evident from the isotropic chemical shift measured from the ^{71}Ga VOCS NMR[3,4] spectra [$\delta_{iso} = -13 \pm 10$ for **1** and **1′**, and 10 ± 10 for **2**] shown in Figure 3.

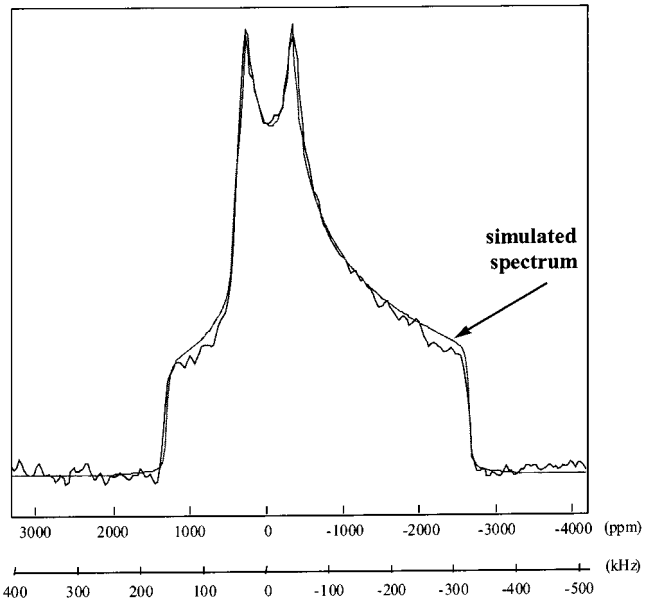

Figure 3. Experimental ^{71}Ga static NMR spectrum of **1**, and simulated spectrum with second-order quadrupolar broadened shape, according to parameters described in Table 1

On the other hand, as previously demonstrated in the case of zinc phosphonates,[5] it appears that 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) can be deduced from the ^{31}P MAS NMR spectra, by the chemical shift asymmetry parameter κ (skew) of the individual phosphorus sites (reported in Table 1). Interestingly, in the previously described gallium phosphonate $Ga(OH)(O_3PC_2H_4CO_2H) \cdot H_2O$[3] (and more generally in the case of aluminum phosphonates with well-established structures[6]) the highest connectivity observed for the PO_3 groups was (111) and the range of variation of the κ value for the P sites was then [−0.3, −0.5]. As evidenced by the X-ray structure of **1**, a (112) connectivity is found for the first time in such compounds, with a markedly different κ value observed for the P sites: $\kappa = 0$ for **1** and +0.2 for **1′** and for **2**.

Resolved ^1H NMR solid-state spectra cannot be obtained using simple acquisition sequences, due to dominant homonuclear couplings between the protons. We acquired 2D $\{^1H\}$-^1H correlation spectra using the Phase Modulated Lee−Goldburg (PMLG) experiment recently proposed by Vinogradov and co-workers.[7] In this experiment a better resolved proton (homonuclear decoupled under Lee−Goldburg excitation) spectrum is obtained in the indirect dimension of a 2D experiment and is correlated with the usual low-resolution MAS spectrum.

The resulting 2D spectrum of **1** is presented in Figure 4. We observe two resolved signals at $\delta = 4.6$ and 1.5 in **1** in a ca. 1:1 ratio. The most deshielded signal ($\delta = 4.6$) is ascribed to water molecules and hydroxide groups (H_2O + OH) and the signal at $\delta = 1.5$ to CH_3 units. In the case of the water-free compound **1′**, these signals at $\delta = 4.5$ and 1.7 are in a ca. 1:3 ratio and correspond to hydroxide and methyl groups respectively, in agreement with the stoichiometry. Under similar acquisition conditions, the broad MAS spectrum of **2** splits in two resolved contributions ascribed to (OH + CH_2) at $\delta = 4.5$ and C_6H_5 at $\delta = 7$.

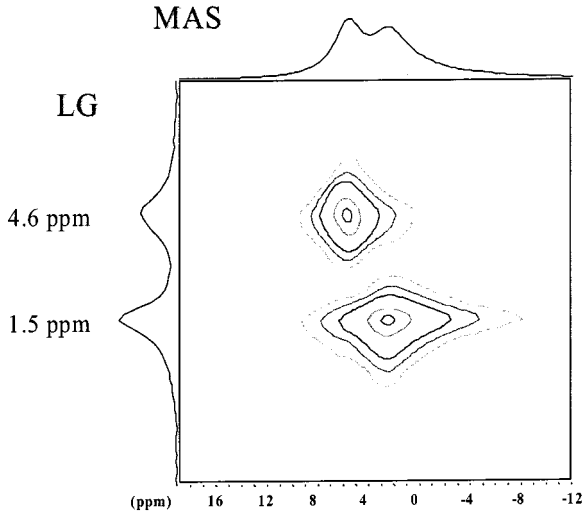

Figure 4. 2D PMLG/MAS $\{^1H\}/^1H$ spectrum of **1**

Table 1. Experimental values for ^{71}Ga chemical shift and electric field gradient, and for ^{31}P chemical shift tensor, for compounds **1**, **1′**, and **2**

$Ga(OH)(O_3PCH_3) \cdot H_2O$ (**1**)	^{71}Ga ^{31}P	δ_{iso}[a] = −13 δ_{iso}[d] = 32.2	C_Q[b] = 16.2 MHz Ω[e] = 60.4	η_Q[c] = 0.8 κ[f] = 0
$Ga(OH)(O_3PCH_3)$ (**1′** from dehydration of **1**)	^{71}Ga ^{31}P	Same values as for **1** δ_{iso}[d] = 30.5	Ω[e] = 69.7	κ[f] = 0.2
$Ga(OH)(O_3PCH_2C_6H_5)$ (**2**)	^{71}Ga ^{31}P	δ_{iso}[a] = 10 δ_{iso}[d] = 25.6	C_Q[b] = 17.5 MHz Ω[e] = 89.4	η_Q[c] = 0.8 κ[f] = 0.2

[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 $3(\delta_{22} - \delta_{iso})/\Omega$.

In conclusion, solid-state NMR appears to be an efficient tool to provide accurate insights into the local environments of P, Ga, and H present in these hybrid (organic/inorganic) compounds. Work is in progress to investigate a wider range of model gallium phosphonate compounds which should allow us to establish a stronger correlation between NMR parameters and local structure: δ_{iso} and skew of chemical shift anisotropy of ^{31}P, δ_{iso} and quadrupolar tensor of ^{71}Ga and δ_{iso} for resolved ^{1}H. This approach should easily be transferred to the case of aluminum phosphonates using the recently established correlation between ^{27}Al and ^{71}Ga NMR parameters.[4] The improved resolution obtained in the Lee−Goldburg decoupled ^{1}H spectra opens the possibility of exploring the whole material on different scales using spin diffusion between protons with possible encoding through the other NMR active nuclei. These experiments are expected to be very fruitful in the case of polycrystalline or amorphous materials involving phase-separated domains as well as organic/inorganic interfaces.

Experimental Section

Syntheses of 1 and 2: A mixture of gallium nitrate (1 mmol) and methylphosphonic (**1**) or benzylphosphonic (**2**) acid (10 mmol) in water (20 mL) was placed in the PTFE cell of an autoclave, which was sealed and kept at 160 °C (**1**) or 170 °C (**2**) in a drying oven for 8 (**1**) or 5 d (**2**). Compound **1** was obtained in 32% yield (64 mg) as white crystals, used for the X-ray structure determination, while **2** was isolated as a white powder in 45% yield (115 mg). − **1:** CH_6GaPO_5 (198.7): calcd. C 6.04, H 3.04, P 15.58; found C 6.12, H 2.94, P 15.29. − FTIR (KBr): $\tilde{\nu}$ = 3589 m, 3512 s, 3453 m, 3382 m, 1324 m, 1099 vs, 1058 vs, 995 vs, 912 s cm^{-1}. − TGA (25−300 °C): 8.90% (calcd. 9.05%; $-H_2O$, 35 °C). − After dehydration of **1** (performed by heating at 100 °C for 1 h to yield **1′**), the infrared spectrum was unchanged, except in the ν(OH) region where only a strong (3515 cm^{-1}) and a broad band (3400 cm^{-1}) remained. − **2:** $C_7H_8GaPO_4$ (256.8): calcd. C 32.73, H 3.14, P 12.06; found C 32.89, H 3.10, P 12.18. − FTIR (KBr): $\tilde{\nu}$ = 3519 s, 3400 b, 1151 m, 1100 vs, 1060 vs, 990 vs, 910 s cm^{-1}. − TGA (25−300 °C): 0%.

Solid-State NMR Experiments: NMR solid-state spectra of ^{71}Ga, ^{31}P, and ^{1}H have been acquired with a Bruker DSX400 spectrometer operating at 9.4 T. The wide ^{71}Ga spectra extend over several hundreds of kHz and have been acquired in static following the VOCS protocol[8] (Magic Angle Spinning would not provide any gain in resolution). The ^{31}P spectra have been acquired using CP-MAS $\{^{1}H\}$-^{31}P excitation, as previously described[3] with a typical contact time of 1.5 ms and 1 s of recycle time. The Lee−Goldburg/MAS $\{^{1}H\}/^{1}H$ correlation spectra have been acquired using the Phase Modulated Lee−Goldburg decoupling scheme[7] with a ^{1}H radio-frequency field of 50 kHz. The two-dimensional spectra were typically obtained within 10 mins with two transients per slice and up to 256 slices, depending on resolution. Spectra were simulated using a modified version of the Bruker Winfit program.[9]

Structure Determination of 1: Data collection was carried out with a single crystal approximately 0.3×0.2×0.04 mm in size with a STOE Imaging Plate Diffraction System,[10] using graphite-monochromatized Mo-K-$L_{2,3}$ radiation (λ = 0.71073 Å). Data intensities were corrected for Lorentz polarization and absorption (Gaussian analytical correction) and subsequently merged according to the *mmm* point group (R_{int} = 0.051), giving rise to a set of 409 independent reflections at a 2σ level. Although the systematic extinctions suggested *Pnmn* as the most probable space group, *Pnma* was found to be the correct space group, both at the residue factor and the structure coherence level. A starting model was found with the Shelxtl V5.0 direct method program[11] and refined (F^2, all reflections included) with the Jana2000 program.[12] All subsequent calculations were carried out with the Jana2000 program package. Missing atoms, including hydrogen atoms, were found in difference Fourier synthesis maps. Non-hydrogen atoms were refined with anisotropic displacement parameters and hydrogen atoms were kept at fixed positions with a common fixed isotropic displacement parameter. At the last stage of the refinement, a secondary extinction coefficient[13] was introduced and the residue factor smoothly converged with R/R_w = 0.0303/0.0681 for 409 reflections with $I/\sigma(I) > 2$ and 47 parameters. − Crystal Data: $Ga(OH)(O_3PCH_3) \cdot H_2O$; orthorhombic *Pnma*; a = 4.5193(7), b = 5.9965(7), c = 19.556(2) Å, V = 530.0(2) $Å^3$ from 3096 reflections collected with the STOE IPDS; monochromatized Mo-K-$L_{2,3}$ radiation; Z = 4; M = 198.75; $\rho_{calcd.}$ = 2.490 $g \cdot cm^3$; μ = 54.25 cm^{-1}; residual electron density [−0.84/+0.62] $e \cdot Å^3$. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no.CCDC-142094. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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