^{71}Ga and ^{31}P solid state NMR: a powerful tool for the characterization of the first gallium phosphonates

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Two new gallium phosphonates $Ga(OH)(O_3PC_2H_4CO_2H)\cdot H_2O$ 1 and $Ga_3(OH)_3(O_3PC_2H_4CO_2)_2\cdot 2H_2O$ 2 are prepared and characterized, using ^{31}P MAS and ^{71}Ga static NMR spectroscopy, showing a good correspondence between the fitted NMR parameters and the crystallographic data.

In recent papers, we have demonstrated that catalytic complexes (*i.e.* manganese porphyrins)[1] could be efficiently heterogenised as divalent metal phosphonates, in which significant shape selectivity effects imposed by the inorganic framework were observed. The key feature of this approach is to functionalize the catalytic complex by phosphonic acid PO_3H_2 moieties, that are then 'polymerised' by reaction with a metal (M) salt in solution, to build up a $M(RPO_3)_x$ network.[2] Taking into account that the resulting immobilised catalysts are usually poorly crystalline, our interest was to find a good method for the characterisation of such materials (*i.e.* get information about both the metal and the PO_3 group environments). One attractive solution to achieve that goal should be to use solid state NMR, provided that the metal atom reacted with the PO_3 groups can be observed by this technique, with the potential advantage (in comparison with EXAFS) to be able to determine the number of metallic sites and their relative amounts, as well as their coordination. In this paper, we describe our attempts in this field, by studying gallium phosphonate systems, the preparation of which seemed possible by analogy with gallium phosphates.[3] As a matter of fact, the stabilities of these materials towards acidic and basic media are higher than the divalent metal analogues and this can be of interest, as far as catalytic applications are concerned. Thus, by reaction of (2-carboxymethyl)phosphonic acid with gallium(III) nitrate in water in an autoclave, two novel gallium hydroxyphosphonates were prepared: $Ga(OH)(O_3PC_2H_4CO_2H)\cdot H_2O$ **1** and $Ga_3(OH)_3(O_3PC_2H_4CO_2)_2\cdot 2H_2O$ **2**. It is worth noting that the presence of hydroxide groups in phosphonates is unusual, except for recent examples described by us in the copper(II) system.[4]

Solid state NMR study of gallium is rendered difficult as it undergoes strong quadrupolar couplings, which give rise to severe second order broadening of the powder spectrum of its central $<1/2>$ transition. Gallium has two NMR active isotopes, ^{69}Ga and ^{71}Ga, both having $I = 3/2$ spins with higher gyromagnetic ratio and lower quadrupolar momentum for ^{71}Ga, which is thus the easiest to observe. At the principal magnetic field of 9.4 T (122 MHz Larmor frequency for ^{71}Ga), the width of the ^{71}Ga spectra of these two new gallium phosphonates (400 **1**, 600 **2** kHz) exceeds the bandwidth accessible with a single experiment (typically 300 kHz). The spectra have thus been acquired in static conditions as a sum of nine full echo signals obtained by varying the offset of the carrier frequency (with a 100 kHz step), according to the VOCS protocol that we have recently described in a study of ^{69,71}Ga in β-Ga_2O_3.[5] The second order quadrupolar broadening is so high in these compounds that MAS experiments cannot give resolution (unlike aluminophosphonates, for which MQ ^{27}Al MAS has proved to be efficient),[6] while the possible DAS[7] or newly described QPASS[8] experiments remain ineffective.

Owing to these intrinsic experimental difficulties, there is little known on Ga solid state NMR, even though there is a well established and confirmed correlation that links gallium and aluminium chemical shifts for four- and six-fold coordination in silicate, phosphates, zeolites and organic complexes.[5,9,10] The results obtained from the simulation of the two observed ^{71}Ga spectra (Fig. 1) are summarized in Table 1, showing two different Ga sites for **1** in a 1 : 1 ratio and one single site for **2**. The chemical shifts of these signals can be unambiguously

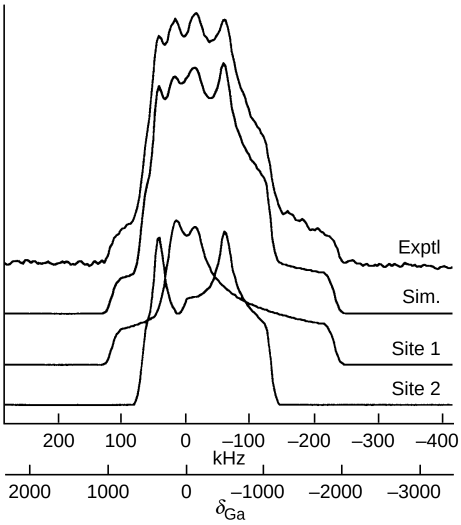

Fig. 1 Experimental ^{71}Ga static NMR spectrum of **1**, and simulated spectrum with second order quadrupolar broadened shape, according to parameters described in Table 1

Table 1 Experimental values for chemical shift and electric field gradient for compounds **1** and **2**

	$\delta_{iso}{}^{a}$	$C_Q{}^{b}$/MHz	ηQ^{c}
1	−6 (site 1: 50%)	13.5	0.85
	2 (site 2: 50%)	12.0	0.35
2	−3	17.0	0.9

[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.

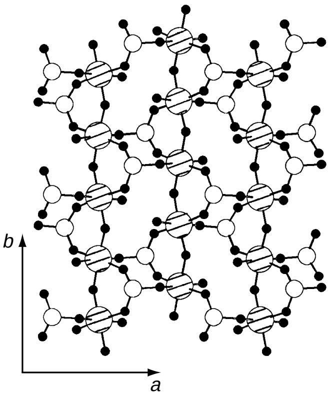

Fig. 2 Schematic representation of a $Ga(OH)(O_3P(CH_2)_2CO_2H)\cdot H_2O$ layer as seen perpendicular to the *c*-axis; Ga (hatched), P (white), O (black) and carbon atoms omitted for clarity. Selected interatomic distances (Å): Ga(1)–O 1.889(7), 1.906(6) (OH), 1.926(7) (OH), 1.978(8), 2.019(7), 2.061(7) (H_2O); Ga(2)–O 1.913(7) (OH), 1.922(6) (OH), 1.949(7), 1.965(7), 2.018(7), 2.060(7) (H_2O).

assigned to sixfold coordination, while their respective electric field gradient tensors characterize the asymmetry of their local environments. In the case of **1**, the presence of the two GaO_6 sites was confirmed by a structure determination from its powder X-ray diffraction pattern (Fig. 2).† On the other hand, even if six-coordinate gallium centres were clearly evidenced from the XANES–EXAFS spectra of this compound, it was however not possible to detect the two different independent metal atoms in this layered compound. Moreover, it is reasonable to think that in compound **1**, the most distorted gallium site Ga(1) [Ga–O bond lengths ranging from 1.889(7) to 2.061(7) Å; see Fig. 2] corresponds to the highest value measured for C_Q (13.5 MHz, site 1 in Table 1). For compound **2**, the observed value for C_Q (17 MHz) is significantly higher, thus giving evidence of a probably more distorted GaO_6 environment present in this latter phase. The structure of **1** consists of GaO_6 octahedra (composed of three phosphonate oxygens, two hydroxide groups and one water molecule) sharing two opposite vertices, thus forming chains parallel to the *b*-axis. These chains are connected by O–P–O bridges in the *a*-direction, to build a two-dimensional network. The organic chains are oriented roughly perpendicular to the layers, and the CO_2H groups are not coordinated, in contrast with **2** [ν(CO) 1590 cm^{-1}], for which a pillared layered structure is likely to be present, resulting from **1** by a probable coordination of the carboxylic acid moieties with gallium atoms. These two layered structures are in contrast to the only other reported gallium phosphonate, $Li_4[(MeGa)_6(\mu_3\text{-}O)_2(Bu^tPO_3)_6]\cdot 4thf$, an anionic molecular cage containing sandwiched lithium ions.[11]

Finally, from the simulation of the static and MAS ^{31}P spectra of gallium phosphonates **1** and **2**, the number of independent PO_3 groups was extracted together with their relative amounts and their respective chemical shift anisotropy parameters[12] [δ_{iso}, Ω (span), κ (skew)]. In a recent paper devoted to zinc phosphonates,[13] we have demonstrated that the κ parameter (chemical shift asymmetry) gave a good signature of the connectivity of the PO_3 groups (*i.e.* the number of zinc atoms connected to each of the three oxygen atoms bound to phosphorus). The value of κ is directly related to the range of variation of the bond strength at the phosphonate oxygens ($\Delta_P O^{2-}$),[14] that in this case, was different for the various types of connectivity, that were thus easily determined: (111) connectivity [$\kappa = -0.6$ to -0.5; $\Delta_P O^{2-} \approx 0.05$ to 0.1], (112) [$\kappa = -0.2$; $\Delta_P O^{2-} \approx 0.2$] and (122) [$\kappa = 0.05$–0.1; $\Delta_P O^{2-} \approx 0.3$]. Similarly in compound **1**, the highest value of the κ parameter is probably found for the highest $\Delta_P O^{2-}$ (0.29). As the two PO_3 sites exhibit the same (111) coordination mode, we can see, for a given connectivity, that the range of variation of $\Delta_P O^{2-}$ is far larger than it was in the case of zinc phosphonates. It would be very helpful to know if the differentiation of the various connectivities from the κ parameter is still possible in gallium phosphonates, but additional crystallographic references are necessary, and work is in progress for this purpose. Nevertheless, if we look at the κ values measured for compound **2** (Table 2), it is reasonable to think that the site at δ 25.3 ($\kappa = 0.0$) denotes a PO_3 group with a connectivity higher than (111).

Table 2 ^{31}P chemical shift tensor data for gallium phosphonates **1** and **2**

	δ_{iso}	Ω^b	κ^c	$\Delta_P O^{2-}$ (v.u.)^d
1	14.9 (site 1: 50%)	76.5	−0.3	0.29
	12.0 (site 2: 50%)	74.5	−0.5	0.15
2	25.3 (site 1: 50%)	53.1	0.0	—
	23.9 (site 2: 50%)	52.6	−0.2	—

^{a} Chemical shifts are referenced to ^{31}P resonance in 85% H_3PO_4. ^{b} Chemical shift span defined as $\delta_{11} - \delta_{33}$ with $\delta_{11} \geqslant \delta_{22} \geqslant \delta_{33}$, see ref. 12(*b*). ^{c} Chemical shift skew defined as $3(\delta_{22} - \delta_{iso})/\Omega$. ^{d} Bond strength range at oxygens, see ref. 14(*b*).

In summary, the work reported here illustrates that original gallium phosphonates can be obtained and efficiently characterized using ^{31}P MAS and ^{71}Ga static NMR spectroscopy.

Footnotes and References

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† *Structure* of **1**: $GaPO_7C_3H_8$, orthorhombic, space group $Pca2_1$, $a = 9.5111(2)$, $b = 7.2829(1)$, $c = 20.3977(5)$ Å. The structure was refined using the full X-ray powder pattern in GSAS, with final *R*-factors: $R_{wp} = 0.106$, $R_p = 0.083$, $R_F = 0.053$ for 1674 reflections (statistically expected $R_{wp} = 0.039$). CCDC 182/701.

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