Relationship between Solid-State ^{31}P NMR Parameters and X-ray Structural Data in Some Zinc Phosphonates

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Metal phosphonate chemistry is attracting increasing interest because of the variety of properties than can be introduced via the phosphonate ligand.[1] These hybrid materials contain a PO_3/metal inorganic core, separated by the organic moiety bound to phosphorus.

In our group, we conceived the idea of preparing covalently immobilized catalysts (manganese porphyrins, bipyridine rhodium complexes, etc.) simply by a functionalization of the desired catalytic complexes with phosphonic acid units, followed by the polymerization of the phosphonate network around these complexes, according to an encapsulation concept.[2] However, to have a better understanding of the catalytic activity of the resulting supported catalysts, structural information is required regarding the environment of the catalytic site as well as the porosity of the material that is related to the nature of the inorganic framework. The main problem generally lies in the amorphous nature of this type of compound and even X-ray powder structure determinations, which have proved to be helpful in the case of polycrystalline phosphonates,[3] cannot be used in this case.

As the main part of our catalytic complexes were immobilized as diamagnetic zinc phosphonates, we wanted to know if solid-state ^{31}P NMR spectroscopy could be used as an investigation tool to provide structural information about the environment of the phosphorus atoms. We can note that solid-state NMR spectroscopy has already been used to characterize phosphonic acids[4] (^{31}P CP-MAS) and zirconium carboxyalkylphosphonates[5] $Zr(O_3PCH_2CO_2H)_2$ (^{31}P and ^{13}C CP-MAS, to get structural details of the organic pendant groups present in the interlayer space).

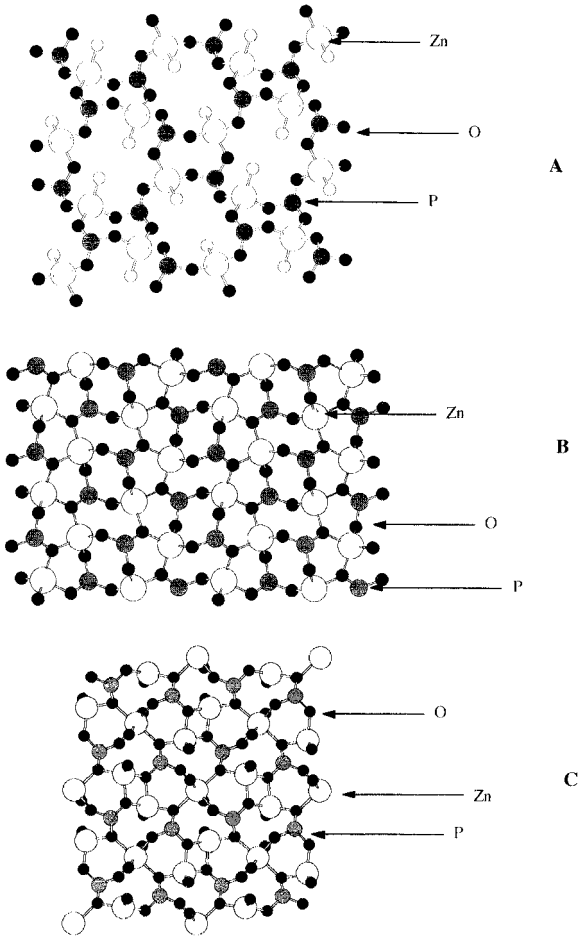

Figure 1. Examples of in-plane structure of layered zinc phosphonates showing (A) a (111) connectivity for the PO_3 groups $[Zn(O_3PC_2H_4NH_2)]$, (B) a (112) connectivity $[Zn_3(O_3PC_2H_4CO_2)_2{\cdot}3H_2O]$, (C) a (122) connectivity $[Zn_3(O_3PC_2H_4CO_2)_2]$.

In previous studies, we have prepared many crystallized zinc phosphonates, the structure of which have been determined, thus allowing us to use these compounds as references. From these structural data, we have noticed that the PO_3 groups, when no proton was retained on the oxygen atoms, could be coordinated in three different ways: (i) either each of the three oxygen atoms of the phosphonate unit is coordinated to only one zinc atom (Figure 1A) and the connectivity is noted (111); (ii) in the second case, one of these oxygens is bridging two zinc atoms, while the two others are bonded only to one metal atom and the connectivity is (112) (Figure 1B); (iii) in the last case, two bridging oxygens are now present with a (122) connectivity (Figure 1C). We have recorded the solid-state ^{31}P NMR spectra of our series of reference samples at different spinning rates, in order to know if these different connectivities could be differentiated using this technique. ^{1}H-to-^{31}P cross polarization and ^{1}H decoupling (50 kHz field strength, 5 s recycle delay, 16−64 transients, DSX 300 Bruker spectrometer) were used in all cases, with both magic angle spinning (MAS, 2−6 kHz) and static conditions. The isotropic chemical shifts were extracted from the high-speed MAS spectra, which

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Table 1. ^{31}P Chemical Shift Tensor Data for a Series of Zinc Phosphonates

compound	ref	connectivity	δ_{iso}[a] (ppm)	η[b]	Δ[c]	δ_{11} (ppm)	δ_{22} (ppm)	δ_{33} (ppm)	η_e[d]
$Zn(O_3PC_2H_4NH_2)$	7	(111)	27.0	0.4	50.5	−7.1	10.6	77.5	0.4
$Zn(O_3PC_2H_4CO_2H)\cdot{}^1/_2C_6H_5NH_2$ (site 1 (50%))	8	(111)	28.9	0.4	43.1	−1.3	16.0	72.0	0.4
$Zn(O_3PC_2H_4CO_2H)\cdot{}^3/_2H_2O$	9	(111)	29.8	0.4	46.8	−3.0	15.8	76.6	0.4
$Zn_3(O_3PC_2H_4CO_2)_2\cdot 3H_2O$	9,10	(112)	32.4	0.8	46.9	−9.8	27.7	79.3	0.8
$Zn(O_3PC_2H_4CO_2H)\cdot{}^1/_2C_6H_5NH_2$ (site 2 (50%))	8	(112)	34.4	0.8	43.1	−4.4	30.1	77.5	0.8
$Zn_3(O_3PC_2H_4CO_2)_2$	9	(122)	35.9	0.9	−33.8	68.0	37.6	2.1	1.1
$Zn(O_3PC_2H_4CO_2H)\cdot H_2O$[e]	9	(122)	38.1	0.9	−38.2	73.5	41.0	−0.1	1.1
$Zn(O_3PC_2H_5)\cdot H_2O$[e]	9	(122)	37.7	0.9	−35.8	71.7	39.5	1.9	1.1

[a] All values are given with respect to the isotropic chemical shift constant for 85% H_3PO_4. [b] Chemical shift asymmetry defined as $|\delta_{22} - \delta_{11}|/|\delta_{33} - \delta_{iso}|$ with the Haeberlen convention.[11] [c] Chemical shift anisotropy defined as $\delta_{33} - \delta_{iso}$. [d] Extended value of η defined as $\eta_e = \eta$ ($\Delta > 0$); $\eta_e = 2 - \eta$ ($\Delta < 0$). [e] Same in-plane structure, simply differing by the nature of the organic chain bound to phosphorus.

consisted of a center band which was a single narrow line (half-height line width 70 Hz), except for $Zn(O_3PC_2H_4CO_2H)\cdot{}^1/_2C_6H_5NH_2$, where two sites [(111) 50%, (112) 50%] are present. The principal components of the chemical shift tensors were measured using the spinning sidebands fitting routine,[6] and a recapitulative list of the values that led to the best fits for the different observation conditions (static and MAS at different spinning rate) is given in Table 1.

We can first notice that the isotropic chemical shifts δ_{iso} move downfield as the connectivity increases, corresponding to an increase in the paramagnetic contribution to the nuclear shielding, as the number of zinc atoms connected to the PO_3 groups varies from 3 to 5. A similar behavior was recently reported by Aime et al. in tricadmium phosphates.[12] If we look now at the variation of the chemical shift asymmetry, a δ_{22} value close to that of δ_{11} is observed in the case of a (111) connectivity, where a pseudoaxial symmetry is present. Then, as the connectivity gets higher to (112) and (122) δ_{22} moves from the right side to the left side of the static band, respectively (Figure 2), with a change in the sign of the chemical shift anisotropy (in the case of a (122) site). This discontinuity in the sign of the tensor axiality Δ arises from the sorting protocol of the δ_{xx} values established by Haeberlen[11] (where δ_{33} has the maximum absolute distance to δ_{iso}) and might be misleading. A better representation of the evolution of the ^{31}P NMR spectra with the connectivity is given by the η parameter, made continuous defining η_e (extended chemical shift asymmetry), ranging from 0 to 2 and calculated as indicated in Table 1.

These preliminary results clearly show that on the basis of the η_e value, it is possible to differentiate (111) [η_e = 0.4], (112) [η_e = 0.8], and (122) [η_e = 1.1] connectivities of the PO_3 groups in our series of zinc phosphonates. Thus, this simple method gives a satisfactory correlation between the ^{31}P chemical shift and

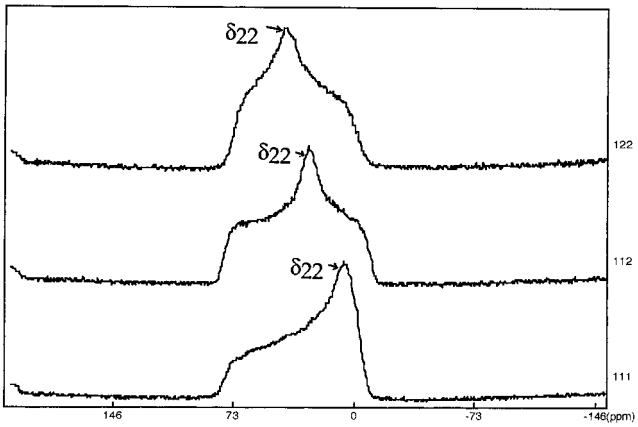

Figure 2. Characteristic ^{31}P static spectra of the three types of connectivity present in zinc phosphonates.

the crystallographic sites of RPO_3 groups in various zinc phosphonates structures. To apply this method for the determination of PO_3 environments in zinc phosphonates of unknown structure, additional data, using structurally characterized zinc phosphonates present in the literature, are actually collected to complete our series of reference compounds. To strengthen the validity of this method, measurements were carried out on two zinc phosphonates for which X-ray data were not available: $Zn(O_3PCH_3)$ and $Zn(O_3PCH_3)\cdot n\text{-}C_4H_9NH_2$. From a XANES-EXAFS study,[8] we had previously assumed that a (112) connectivity was present for the former compound, while the latter compound corresponded to a (111) environment for the PO_3 groups. The ^{31}P MAS NMR results are in very good agreement with this hypothesis: a η_e value of 0.8 for $Zn(O_3PCH_3)$ [δ_{iso} = 32.6; $\delta_{11} = -5.1$; $\delta_{22} = 28.4$; $\delta_{33} = 74.4$; $\Delta = 41.8$ ppm] and a η_e value of 0.4 for $Zn(O_3PCH_3)\cdot n\text{-}C_4H_9NH_2$ [δ_{iso} = 27.7; $\delta_{11} = -8.0$; $\delta_{22} = 11.7$; $\delta_{33} = 79.4$; $\Delta = 51.7$ ppm]. The influence of the metal associated to the PO_3 groups (i.e., Zr(IV), Al(III), Ga(III), Bi(III), Cd(II), etc.) are also under investigation, in order to estimate the possible extension of the method to other metal phosphonates. For example, in the case of $Zr(O_3PC_2H_5)_2$, a structural analogue of α-ZrP in which a (111) connectivity is present,[13] a η_e value of 0.4 was found [$\delta_{iso} = 7.8$; $\delta_{11} = -8.4$; $\delta_{22} = 1.6$; $\delta_{33} = 30.3$; $\Delta = 22.5$ ppm], consistent with the observations made in the zinc phosphonates series. In conclusion, this method would be the ideal complement of Zn K-edge EXAFS spectroscopy, to get structural informations about both metal and phosphorus environments.

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