Solid-state Nuclear Magnetic Resonance Spectroscopic Study of γ-Zirconium Phosphate

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An idealised model for the structure of γ-$Zr(HPO_4)_2 \cdot 2H_2O$ is proposed on the basis of solid-state ^{31}P magic-angle spinning (m.a.s.) n.m.r. spectroscopy. Two types of phosphate environment are seen of which only one undergoes phosphate exchange with phosphate and phosphonate esters. ^{13}C Cross-polarisation m.a.s. n.m.r. confirms the phenyl phosphate exchange and indicates that the phenyl rings are rigid between the layers.

Two hydrates of zirconium monohydrogenphosphate, $Zr(HPO_4)_2$ are known: a monohydrate, α, and a dihydrate, γ.[1] The α phase has a layer structure consisting of layers of metal atoms in a plane bridged by phosphate groups above and below the plane of the metal atoms with the P–OH groups pointing between the layers.[2] A layer structure has been proposed for γ-$Zr(HPO_4)_2 \cdot 2H_2O$, based on the increased spacing of the d_{002} reflection in the *X*-ray diffraction pattern upon ion exchange;[3] however, the structure is at present unknown. A model structure, based on electron microscopy, has been proposed for the γ phase which is related to that of the α but with a more condensed packing arrangement in the layers.[4] This model does not readily explain the differences in the chemistry of the α and γ phases such as the ready partial exchange of the phosphate groups in the latter by phosphate[5,6] and phosphonate[7] esters nor its facile reaction with epoxides such as ethylene oxide.[8] In contrast the layer-type structures with phosphate and phosphonate esters based on the α phase can only be synthesised by direct reaction with a Zr^{IV} solution. The exchange reactions of the γ phase thus represent a novel approach to a mixed inorganic–organic structure and therefore an understanding of the phosphate exchange reaction is of interest. To a large degree the uncertainty regarding the exchange behaviour is because only microcrystalline γ-$Zr(HPO_4)_2 \cdot 2H_2O$ can be prepared which upon exchange tends to become even less crystalline, preventing *X*-ray diffraction studies.

An earlier report[9] illustrated the potential of ^{31}P magic-angle spinning (m.a.s.) n.m.r. for studying the phosphate environment in zirconium phosphates, although the conclusions drawn are uncertain in the light of the work presented here. The possibility of using ^{31}P m.a.s. n.m.r. to study zirconium phosphates was strengthened by our recent studies on phosphate solid solutions which have shown that the phosphate group chemical shift is remarkably sensitive to its local environment.[10–12] Phosphorus-31 m.a.s. n.m.r. is therefore a powerful technique for studying the environment of the γ phase upon exchange with phosphate esters. In this paper the reaction between γ-$Zr(HPO_4)_2 \cdot 2H_2O$ and phenylphosphonic acid, $PhPO_3H_2$, and phenyl dihydrogenphosphate, $PhOPO_3H_2$, as studied by ^{31}P m.a.s. n.m.r. is reported.

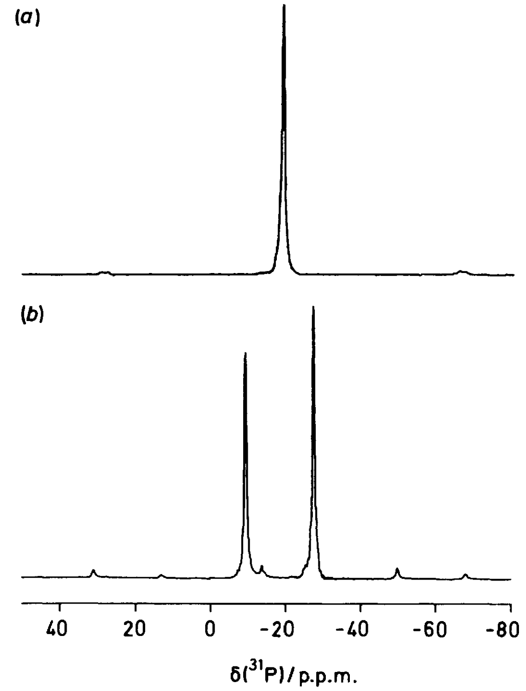

Figure 1. 81-MHz ^{31}P M.a.s. n.m.r. spectra of (*a*) α-$Zr(HPO_4)_2 \cdot H_2O$ and (*b*) γ-$Zr(HPO_4)_2 \cdot 2H_2O$. Four transients were acquired using a 5 μs $\frac{\pi}{2}$ pulse and a recycle delay of 300 s

Experimental

α-$Zr(HPO_4)_2 \cdot H_2O$ was prepared by the method of Clearfield and Stynes[13] using a 12 mol dm^{-3} phosphoric acid solution as the reflux medium and refluxing for 100 h. γ-$Zr(HPO_4)_2 \cdot 2H_2O$ was synthesised using the following procedure based on the method of Clearfield *et al.*[3] 1 Mol dm^{-3} $ZrOCl_2 \cdot 8H_2O$ (Aldrich) (50 cm^3) was added dropwise to $NaH_2PO_4 \cdot 2H_2O$ (AnalaR, BDH) (1 mol) in concentrated HCl (40 cm^3) and water (90 cm^3) whilst heating to dissolve fully all the sodium hydrogenphosphate. The resulting gelatinous zirconium phosphate and mother-liquor were transferred into a Teflon lined Parr bomb and subjected to hydrothermal treatment at 200 °C for 4 d. After filtration, the partially sodium ion exchanged γ phase was fully hydrogen ion exchanged on the filter paper by washing with 2 mol dm^{-3} HCl, followed by washing with 0.2 mol dm^{-3} phosphoric acid to remove Cl^- ions, and finally washed with distilled water and air-dried. *X*-Ray powder diffraction patterns of both the α and γ phases were in excellent agreement with reported *d* spacings.[4,14]

Exchange of the γ-$Zr(HPO_4)_2 \cdot 2H_2O$ phosphate groups with phenyl dihydrogenphosphate was carried out by dispersing the γ phase (1 g) in 1 mol dm^{-3} phenyl dihydrogenphosphate (100 cm^3) in a mixture of equal volumes of acetone and water and heating under reflux for 20 h.[7] After 20 h the exchanged γ phase was filtered off and then redispersed in a fresh phenyl dihydrogenphosphate solution and refluxed for a further 20 h.

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Table 1. Chemical shift anisotropies (p.p.m.)

	σ_{iso}	σ_{11}	σ_{22}	σ_{33}
α-Zr(HPO$_4$)$_2$·H$_2$O	−18.7	4.3	−23.7	−36.8
γ-Zr(HPO$_4$)$_2$·2H$_2$O	−9.4	18.5	−17.7	−30.0
	−27.4	−16.0	−24.7	−34.0

X-Ray powder diffraction of the exchanged product indicated an increase in the basal spacing to 15.1 Å, consistent with the incorporation of phenylphosphonate. Thermal gravimetric analysis (t.g.a.) of the exchanged phase gave the composition as $Zr(HPO_4)_{1.64}(PhPO_3)_{0.36}\cdot 1.1H_2O$ while microanalysis gave C = 12.21% and H = 1.74% and hence a composition of $Zr(HPO_4)_{1.4}(PhPO_3)_{0.6}\cdot 1.9H_2O$.

The reaction with phenyl dihydrogenphosphate was carried out by dispersing the γ phase (1 g) in 1 mol dm^{-3} phenyl dihydrogenphosphate (100 cm^3) in distilled water, obtained from Na_2PhOPO_3 (Aldrich) by ion exchange on an Amberlite IR-120 column, followed by reflux for 20 h.[5] After filtration the product was washed with distilled water and allowed to dry in the air. *X*-Ray powder diffraction of the exchanged product showed no evidence for unreacted γ-Zr(HPO$_4$)$_2$·2H$_2$O, with an increase in the basal spacing to 16.4 Å as expected for phenyl phosphate exchanged γ-Zr(HPO$_4$)$_2$·2H$_2$O. Microanalysis gave C = 16.6% and H = 1.84% consistent with the composition $Zr(HPO_4)_{1.18}(PhOPO_3)_{0.82}\cdot 0.8H_2O$.

The solid-state n.m.r. spectra were collected on a Bruker CXP200 n.m.r. spectrometer operating at 80.96 MHz for ^{31}P, 50.32 MHz for ^{13}C, and 200.13 MHz for ^{1}H. M.a.s.[15] was carried out at 3–4 kHz using Andrew–Beam type rotors made out of Delrin, ^{13}C spectra were acquired using deuteriated plexiglass rotors. Cross-polarisation (c.p.) experiments[16] using a single contact of variable duration were made using a 2.56 mT ^{31}P or 4.0 mT ^{13}C B_1 field and a 1.0 mT ^{1}H B_1 field to satisfy the Hartmann–Hahn condition. The magic angle was set using the ^{79}Br resonance in added KBr.[17]

Results and Discussion

The ^{31}P m.a.s. n.m.r. spectra of the α and γ phases are shown in Figure 1. Only one resonance is seen for the α phase despite the presence of two crystallographically inequivalent phosphorus atoms. In other phosphates crystallographically distinct phosphorus sites have in general been observed as different resolvable resonances.[10] This implies that the electronic environment of the phosphorus nuclei must be sufficiently similar to prevent the resolution of two resonances. Spinning sidebands are seen either side of the isotropic resonance;[18] however, their low intensity implies the chemical shift anisotropy (c.s.a.) is small and indeed this is confirmed by a static n.m.r. powder pattern from which the tensor components can be derived, see Table 1. In contrast the γ phase does show two ^{31}P resonances of equal integrated intensity. A rather large difference in chemical shift of 18 p.p.m. is observed for these two resonances which suggests two chemically distinct types of phosphate group rather than two similar but crystallographically inequivalent phosphorus atoms. Additional support for this interpretation is provided by the chemical shift anisotropies of these two resonances. Measurement of the c.s.a. is complicated by the overlap of the n.m.r. powder patterns but by making use of the different responses of the two resonances to cross polarisation the individual patterns can be seen. For the resonance at −9.4 p.p.m. this requires a short contact time of 100 μs and for the resonance at −27.4 p.p.m. a long contact time of 7 ms. The c.s.a. tensor components are shown in Table 1. Clearly the two resonances in the γ phase have different c.s.a. with the upfield resonance having quite a small anisotropy, implying a symmetric local environment. In fact the resonance at −27.4 p.p.m. is very similar to the ^{31}P resonances in the framework phosphate $HZr_2(PO_4)_3$ where the ^{31}P chemical shifts are −28.4 and −29.4 p.p.m. and $\Delta\sigma \leqslant 18$ p.p.m.[19] A tentative model for the local environment of the upfield resonance is therefore of a framework-type phosphate sharing all four phosphate oxygens with zirconium, *i.e.* P(OZr)$_4$.

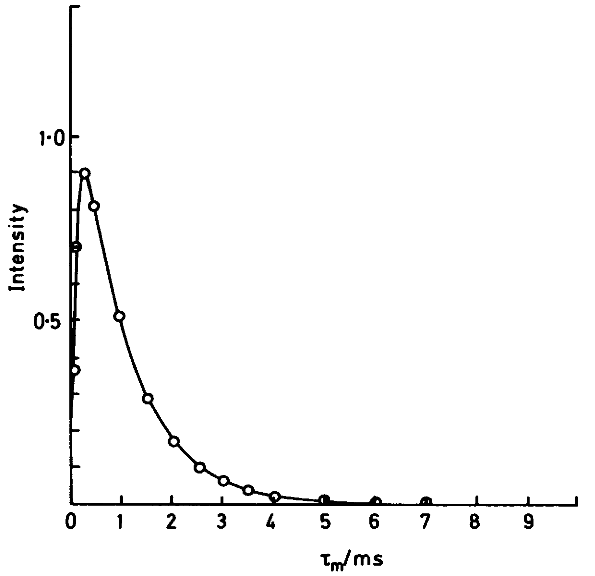

Figure 2. Variation in the cross-polarisation intensity with contact time, τ_m. The solid line is the computer best fit based on equation 4.167a of ref. 16. The derived time constants are T_{PH} = 0.15 ms and $T_{1\rho}{}^{H}$ = 0.72 ms

A possible local environment for the downfield resonance can also be proposed as follows. Substitution of zirconium by hydrogen in the local phosphate group co-ordination decreases the bond strength of the oxygens of the phosphate groups, causing a downfield shift in the ^{31}P chemical shift of *ca.* 10 p.p.m.; thus in $HZr_2(PO_4)_3$ with P(OZr)$_4$ $\sigma = -29$ p.p.m. while for α-Zr(HPO$_4$)$_2$·H$_2$O with P(OZr)$_3$(OH) $\sigma = -19$ p.p.m. In both cases the zirconium co-ordination remains constant as ZrO$_6$ octahedra. Now the downfield resonance in γ-Zr(HPO$_4$)$_2$·2H$_2$O has a chemical shift of −9.4 p.p.m., a further 10 p.p.m. downfield of α-Zr(HPO$_4$)$_2$·H$_2$O, so that if the previous trend continues the chemical shift is consistent with P(OZr)$_2$(OH)$_2$ groups. Changes in the c.s.a. are consistent with this model. Since a symmetric P(OZr)$_4$ will have a small c.s.a., replacing one zirconium by hydrogen will increase the c.s.a. by altering the bond strength on that oxygen; however, replacing another zirconium by hydrogen will not necessarily lead to any major changes in the range of bond strengths, the factor important in determining the chemical shift anisotropy.[12]

The asymmetry in the phosphorus local hydrogen environment implied by the above discussion is confirmed by the detailed analysis of the cross-polarisation intensity as a function of the contact time alluded to earlier. A typical computer fit of the intensity *versus* contact time is shown in Figure 2. Two time constants define the curve,[16] assuming a long nuclear spin–lattice relaxation time, $T_{1\rho}{}^{P}$, the rise time constant, T_{PH}, and the decay time constant, $T_{1\rho}{}^{H}$. T_{PH} depends on the magnitude of the phosphorus–hydrogen dipolar coupling through the second moment $M_2{}^{PH}$ and its effectiveness in allowing transfer of spin magnetisation. $T_{1\rho}{}^{H}$ is the relaxation time for the decay of the spin-locked proton magnetisation in the rotating frame. $T_{1\rho}{}^{H}$ and T_{PH} derived from the computer analysis are shown in Table 2. In general strong dipolar coupling between protons ensures a

Table 2. Cross-polarisation time constants

	σ_{iso}/p.p.m.	T_{PH}/ms	$T_{1\rho}^{H}$/ms
α-$Zr(HPO_4)_2 \cdot H_2O$	−18.7	0.85	4.0
γ-$Zr(HPO_4)_2 \cdot 2H_2O$	−9.4	0.15	0.72
	−27.4	1.5	1.5

common $T_{1\rho}^{H}$ for all protons regardless of their environment in a homogeneous solid owing to spin diffusion. However, in this case the two resonances clearly have different $T_{1\rho}^{H}$ indicating the absence of strong dipolar coupling between the protons cross-polarising these resonances. Furthermore, T_{PH} is significantly shorter for the resonance at −9.4 p.p.m. A somewhat simplistic interpretation of this is that M_2^{PH} is larger due to either shorter average phosphorus–hydrogen distances or simply a greater number of protons. Although interpretation of the time constants is complex the important feature is that the two resonances do behave differently and therefore do not have similar proton environments.

An idealised view of the structure of the γ phase is therefore of two chemically distinct types of phosphate group in equal proportions, one a framework-type phosphate and the second a dihydrogenphosphate group. This model can explain the ability of the γ but not the α phase to undergo phosphate group exchange in terms of the more open dihydrogenphosphate group. It is this group which is exchangeable and not a monohydrogenphosphate. Furthermore the maximum extent of the exchange of 50% follows simply from the relative proportions of the two types of phosphate environment since the framework phosphates are not able to exchange, so that once all the $P(OZr)_2(OH)_2$ groups have exchanged no further exchange is possible. Given this model, upon exchanging γ-$Zr(HPO_4)_2 \cdot 2H_2O$, only the downfield resonance at −9.4 p.p.m. should be affected.

Exchange with Phenylphosphonic Acid.—The ^{31}P m.a.s. n.m.r. spectrum of the phenylphosphonic acid exchanged γ phase is shown in Figure 3(*a*). Three resonances are observed, the most intense resonance with an integrated intensity equal to the sum of the other two is at −27.4 p.p.m. and corresponds to the framework-type resonance. At 5.6 p.p.m. is the resonance associated with the phenylphosphonate in the layer. This assignment is possible because phenylphosphonic acid in the solid state has a ^{31}P chemical shift of 21.3 p.p.m. and hence it will lie *ca.* 20 p.p.m. downfield of a phosphate group in a similar environment. The resonance at −14.8 p.p.m. is due to unexchanged $P(OZr)_2(OH)_2$ type groups although the change in chemical shift does suggest a modification to their local environment perhaps as the neighbouring group is exchanged. The difference in chemical shift between the 5.6 and −14.8 p.p.m. resonances of 20.4 p.p.m. is very close to the difference in chemical shift of the parent acids, 21.3 p.p.m., suggesting a similar environment in the exchanged γ phase. All three resonances show an increased linewidth over the pure γ phase caused by a reduction in the overall crystallinity. Using these assignments and an integration of the intensities of the resonances in the ^{31}P m.a.s. n.m.r. spectrum, acquired with a long recycle delay of 300 s to ensure a fully relaxed spectrum, allows the composition to be deduced. This composition is $Zr(HPO_4)_{1.49}(PhPO_3)_{0.51}$ in better agreement with the microanalysis than the t.g.a. results. The low intensity resonance at −5.4 p.p.m. can be assigned to an α-type phase $Zr(PhPO_3)_2$ showing that a small degree of hydrolysis of γ-$Zr(HPO_4)_2 \cdot 2H_2O$ takes place upon extended reflux. Thus the ^{31}P m.a.s. n.m.r. spectrum is consistent with exchange only of the phosphorus resonance at −9.4 p.p.m. in the original γ phase and the extent of the exchange of this resonance is roughly 50%.

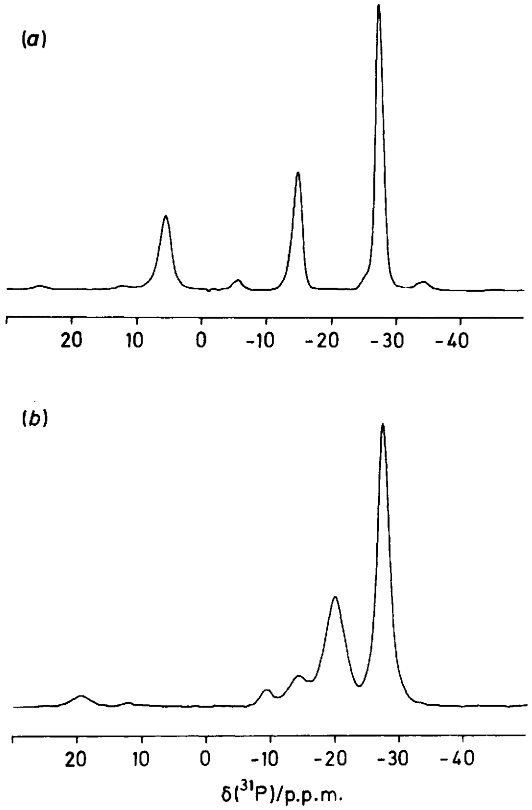

Figure 3. 81-MHz ^{31}P M.a.s. n.m.r. spectra of exchanged γ-Zr-$(HPO_4)_2 \cdot 2H_2O$: (*a*) with phenylphosphonate, (*b*) with phenyl phosphate

Exchange with Phenyl Dimethyl Phosphate.—The ^{31}P m.a.s. n.m.r. spectrum of the phenyl dimethyl phosphate exchanged γ phase is shown in Figure 3(*b*). As with the phenylphosphonate exchanged γ phase the most intense resonance is at −27.4 p.p.m. Three other resonances are present in addition to the spinning sidebands. At −19.8 p.p.m. is the layered phenyl phosphate ^{31}P resonance shifted upfield from the neutral phosphate (δ −5.85 p.p.m.) by *ca.* 14 p.p.m., exactly the same shift as observed for the remaining unexchanged $P(OZr)_2(OH)_2$ type groups at −14 p.p.m. Again this suggests similar environments within the layers. In contrast to the phenylphosphonic acid exchange a residual γ phase resonance at −9.4 p.p.m. is also observed. This resonance cannot be assigned to an α-type phase $Zr(PhOPO_3)_2$ since this has a chemical shift of ≈ −29 p.p.m. Although no unreacted γ phase could be seen in the *X*-ray powder diffraction pattern the greater sensitivity of the n.m.r. means that this cannot be ruled out. Alternatively the presence of this resonance can be seen as evidence that the exchange occurs in stages, so that rather than randomly exchanging phosphate for phenyl phosphate the exchange takes place in regions at a time leaving part of the layers essentially unchanged. Support for the latter interpretation is provided by the greater linewidth of the −9.4 p.p.m. resonance in the exchanged γ phase than in the unreacted γ phase. To explore this further it is necessary to examine the ^{31}P m.a.s. n.m.r. spectrum as a function of the degree of exchange.

Although the resonance at −27.4 p.p.m. is more striking than the downfield resonances, the integrated intensity of these resonances is 46% of the total integrated intensity, close to the

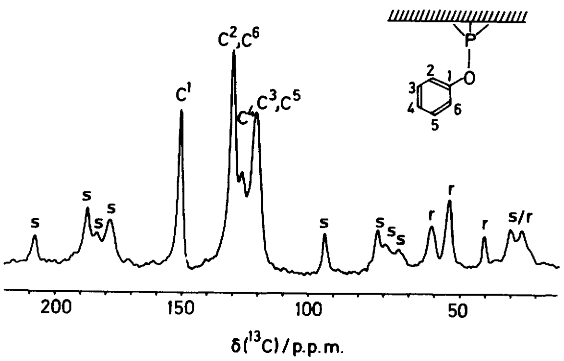

Figure 4. 50.3-MHz ^{13}C C.p. m.a.s. n.m.r. spectrum of phenyl phosphate exchanged γ-$Zr(HPO_4)_2\cdot 2H_2O$. A contact time of 2 ms was used and 16 750 transients were acquired. Spinning speed, 2 875 Hz. Spinning sidebands are labelled s and rotor resonances, r

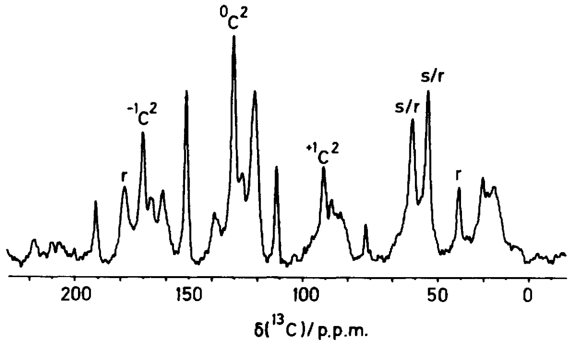

Figure 5. 50.3-MHz ^{13}C C.p. m.a.s. n.m.r. spectrum of phenyl phosphate exchanged γ-$Zr(HPO_4)_2\cdot 2H_2O$. A contact time of 2 ms was used and 25 890 transients were acquired. Spinning speed, 1 989 Hz. Spinning sidebands (order -1,0,+1 indicated) are labelled s and rotor resonances, r

required 50%. From the relative integrated intensity of both the resonances at −9.4 and −14.0 p.p.m. and the resonance at −19.8 p.p.m., the composition can be deduced to be $Zr(HPO_4)_{1.28}(PhOPO_3)_{0.72}$ in reasonable agreement with the microanalysis. Better agreement is found, however, if the resonance at −9.4 p.p.m. is assumed to be unreacted γ phase when the n.m.r. integration gives a composition $Zr(HPO_4)_{1.2}$-$(PhOPO_3)_{0.8}$.

Confirmation that the phenyl phosphate is indeed part of the layer structure is provided by a ^{13}C c.p. m.a.s. spectrum of phenyl phosphate exchanged γ-$Zr(HPO_4)_2\cdot 2H_2O$, see Figure 4. Resonances corresponding to all the phenyl ring carbons are clearly resolved. The broader and less intense nature of the C^3, C^5 resonance compared with the C^2, C^6 resonance suggests that C^3 and C^5 are in fact chemically inequivalent, implying that the aromatic ring is immobile. The intense spinning sidebands, especially at a slower spinning speed (Figure 5), which reflect the large c.s.a. of the aromatic carbons would tend to support this. A precise statement about the mobility of the phenyl ring is possible from a knowledge of the c.s.a. tensor components derived from these sideband intensities either by a graphical[20] or moment analysis.[18] More directly the sideband intensities can be compared with computer simulated sideband intensities. Three simple types of motion likely for a phenyl ring can be clearly distinguished using the C^2 carbon. These are (*a*) static, (*b*) 180° flips about the C_2 axis, and (*c*) continuous rotation about the C_2 axis. Simulated m.a.s. spectra, using the program SPIN,[21] for the three types of motion are shown in Figure 6. In the simulations it was assumed that the static c.s.a. is equal to that observed for the C^2 carbon in 1,4-dimethoxybenzene.[18] A comparison of the observed slower spinning sideband intensities and the simulated m.a.s. spectra, in particular for the ±1 sidebands, demonstrates that the phenyl ring must be static.

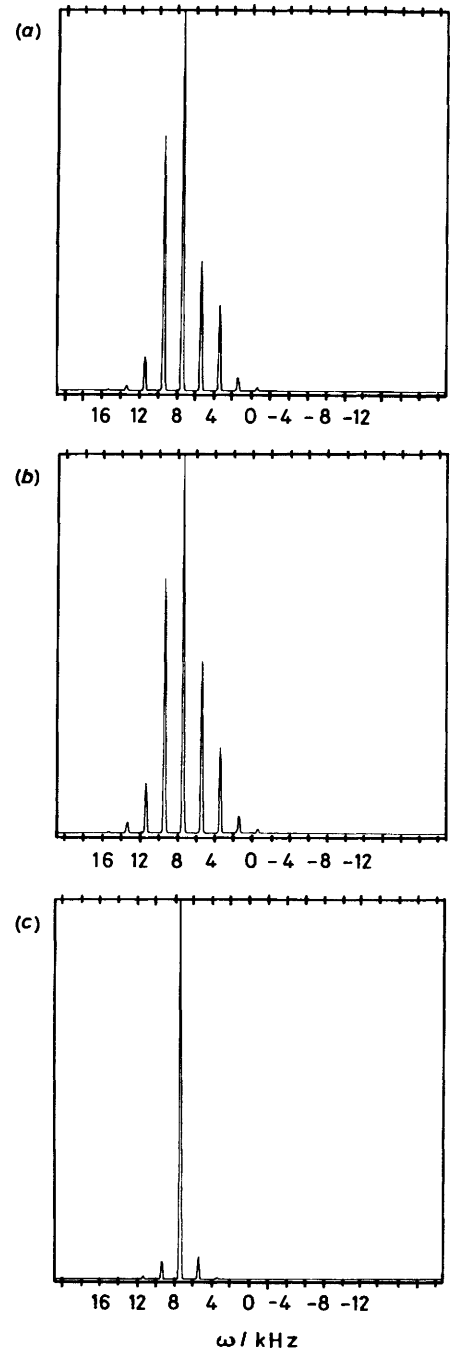

Figure 6. Simulated m.a.s. n.m.r. spectra for the C^2 carbon. Spinning speed, 1 989 Hz. C.s.a. tensor components: $\sigma_{11} = 208$, $\sigma_{22} = 146$, and $\sigma_{33} = 33$ p.p.m. (*a*) Static, (*b*) 180° flips, and (*c*) continuous rotation

Conclusions

The observation of two resonances in the solid-state ^{31}P m.a.s. n.m.r. spectrum of γ-$Zr(HPO_4)_2\cdot 2H_2O$ with quite different cross-polarisation behaviours and chemical shift anisotropies allows an idealised model for the structure of this phase to be constructed. Thus it can be considered to be composed of two types of phosphate group, one a framework type $P(OZr)_4$ which cannot undergo exchange, and a second a more open type called a dihydrogenphosphate $P(OZr)_2(OH)_2$ which can exchange. This model allows the difference between the α and γ phase phosphate group exchange to be explained since the α phase only has $P(OZr)_3(OH)$ groups which do not exchange. Moreover the maximum degree of exchange of 50% observed for the γ phase can be understood because the two phosphate environments are in equal proportions, so that once all the open phosphate has exchanged no further reaction is possible. However, the reasons for the different maximum degree of exchange actually observed for phosphate and phosphonate esters are unclear but steric factors may be important. The changes observed in the ^{31}P m.a.s. n.m.r. spectra of the exchanged phases are consistent with this model because a loss of intensity is only observed for the downfield resonance assigned to the open phosphate. In addition to confirming the structural model the ^{31}P m.a.s. n.m.r. results indicate a straightforward method for monitoring the reactions of the γ phase and the characterisation of products as noted earlier.[9] Direct evidence for the incorporation of the organic phosphate is provided by the ^{13}C c.p. m.a.s. n.m.r. spectrum of the phenyl phosphate exchanged γ phase. The absence of phenyl ring motion shown by the sideband intensities implies strong steric interactions are present between the aromatic rings in the interlayer space. Given the greater degree of exchange possible for phenyl phosphate than for phenyl phosphonate it is feasible that at a lower level of exchange the phenyl ring may be mobile. A combination of ^{13}C m.a.s. and ^{2}H wideline n.m.r. spectroscopy can thus be used to study the bilayer dynamics in n-alkyl phosphate exchanged γ-$Zr(HPO_4)_2 \cdot 2H_2O$.

Acknowledgements

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