

because the pyrophosphate ethyl ester side chain is extremely flexible.

Significance

The present structure is only the third X-ray example showing the metal coordination to the thiamin base and the first of a thiamin monophosphate complexed with a metal atom. This is of particular importance because in five¹¹ of the seven^{11,12} X-ray-characterized thiamin-metal ion complexes there is no direct bond formed between a metal ion and thiamin, though there is some NMR evidence^{7,9,10} for metal ion binding to the thiamin base in solution. Metal coordination at the N(1') site is consistent with Schellenberger's suggestion⁷ from enzyme studies. Electronic rather than steric factors are responsible for the metal attachment to the N(1') but not to the N(3') sites.

Widespread occurrence of the stable F conformation of the thiamin molecule in a variety of the thiamin crystal structures, frequent observation of the participation of the thiazolium C(2)H in the formation of the hydrogen bonding with anions, and the participation of the thiazolium S(1) in the electrostatic interaction with anions suggest that pyruvate anion could be incorporated into the vicinity of the catalytic C(2) site in the enzyme system in a manner similar to the phosphate anion-thiamin moiety interactions observed in the present structure. We are aware that

this substrate fixation model is highly speculative. Particularly, this model has a disadvantage from a "least motion" concept which had been applied by Pletcher and Sax⁵⁰ to the addition mechanism of the thiazolium ylide to pyruvate, because in our model the carbonyl carbon atom of pyruvate, a site to be attacked, is rather far from the reaction center C(2) atom. Clearly, more crystallographic studies are necessary to understand the nature of the metal coordination, particularly the electronic effects on the thiamin base, in connection with a possible role of the metal ion in the enzymic processes on complexation with the pyrimidine base to induce an electron deficiency of the base, which is advantageous for the fixation of the substrate anion.

Supplementary Material Available: Listings of anisotropic temperature factors, hydrogen atom parameters, bond lengths and angles involving hydrogen atoms, observed and calculated structure amplitudes, selected structural parameters for the $\text{Rh}_2(\text{O}_2\text{CR})_4\text{L}_2$ framework, bond lengths and angles in the various thiamin structures, torsion angles in the various thiamin structures, and the molecular structure of $[\text{Rh}_2(\text{AcO})_4(\text{ADMP})_2]$ (19 pages). Ordering information is given on any current masthead page.

(50) Turano, A.; Furey, W.; Pletcher, J.; Sax, M.; Pike, D.; Kluger, R. *J. Am. Chem. Soc.* **1982**, *104*, 3089-3095.

A ³¹P Magic Angle Spinning NMR Study of the Cation Distribution in $\text{Zn}_{3-x}\text{Mg}_x(\text{PO}_4)_2$

R. J. B. Jakeman,^{1a} A. K. Cheetham,^{*1a} N. J. Clayden,^{1b} and C. M. Dobson^{1b}

Contribution from the Chemical Crystallography Laboratory, University of Oxford, Oxford OX1 3PD, England, and the Inorganic Chemistry Laboratory, University of Oxford, Oxford OX1 3QR, England. Received March 22, 1985

Abstract: Phosphates of the solid solution $\text{Zn}_{3-x}\text{Mg}_x(\text{PO}_4)_2$ with $x = 0, 0.5, 1.0, 1.2, 1.25, 1.5, 1.75, 1.9, 2.0, 2.1, 2.2, 2.5$, and 3.0 have been investigated by using ³¹P magic angle spinning NMR. All samples with $x > 0$ have the $\gamma\text{-Zn}_3(\text{PO}_4)_2$ structure which contains one phosphorus site and two cation sites, one octahedral and one five-coordinated. Single ³¹P resonances are observed at 3.9 ppm for $x = 0.5$ and at 0.1 ppm for $x = 3.0$ ($\text{Mg}_3(\text{PO}_4)_2$); for compositions in the range $1 < x < 3$, four resonances, with varying intensity ratios, are observed at 3.9, 3.1, 0.9, and 0.1 ppm, apparently resulting from the presence of four distinct phosphorus environments. These four environments can be rationalized in terms of the structure, and by equating the proportion of each type of environment to the intensity of the corresponding ³¹P resonance, the distribution of the cations over the two different sites can be calculated at each composition. The results suggest that magic angle spinning NMR will become a powerful tool for studying cation distributions in disordered systems.

Recent applications of magic angle spinning NMR (MASNMR) to the study of minerals and other inorganic solids have shown that chemical shift values are sensitive to a variety of structural factors.² In aluminosilicates, for example, ²⁷Al spectra can readily distinguish between Al in tetrahedral and octahedral sites³ and even between Al in crystallographically distinct tetrahedral sites, while ²⁹Si spectra clearly reveal differences between crystallographically equivalent silicon atoms that have slightly different, local environments.⁴ Studies of inorganic phosphates using ³¹P MASNMR have shown that the isotropic and anisotropic chemical shifts are influenced by the degree of condensation of the PO_4 tetrahedra.^{5,6} In a systematic study of

Table I.

	bond distances, Å		
	$\text{Mg}_3(\text{PO}_4)_2$ ¹³	$\gamma\text{-Zn}_3(\text{PO}_4)_2$ ¹²	$\text{Zn}_2\text{Mg}(\text{PO}_4)_2$ ¹⁴
	P-O		
P-O ₁	1.54	1.57	1.52
P-O ₂	1.51	1.58	1.59
P-O ₃	1.53	1.54	1.54
P-O ₄	1.53	1.58	1.50
	M ₁ -O		
M-O ₁	2.14	2.31	2.34
M-O ₂	1.97	2.02	1.89
M-O ₃	2.06	2.02	2.02
M-O ₄	2.01	2.16	2.00
M-O _{4'}	1.96	1.98	2.00
	M ₂ -O		
M-O ₁ (×2)	2.03	1.95	2.03
M-O ₂ (×2)	2.18	2.16	2.19
M-O ₃ (×2)	2.15	2.21	2.22

a large number of ortho- and pyrophosphates, we have found that the ³¹P chemical shift spans a wide range of values, making it, in some cases, extraordinarily sensitive to subtle differences in the structure. In this paper, we show that ³¹P MASNMR can

(1) (a) Chemical Crystallography Laboratory. (b) Inorganic Chemistry Laboratory.

(2) Magi, M.; Lippmaa, E.; Samoson, A.; Englehardt, G.; Grimmer, A.-R. *J. Phys. Chem.* **1984**, *88*, 1518.

(3) Klinowski, J.; Thomas, J. M.; Fyfe, C. A.; Gobbi, G. C. *Nature (London)* **1982**, *296*, 533.

(4) Lippmaa, E.; Magi, M.; Samoson, A.; Engelhardt, G.; Grimmer, A.-R. *J. Am. Chem. Soc.* **1980**, *102*, 4889.

(5) Grimmer, A.-R.; Haubenreisser, U. *Chem. Phys. Lett.* **1983**, *99*, 487.

(6) Duncan, T. M.; Douglass, D. C. *Chem. Phys.* **1984**, *87*, 339.

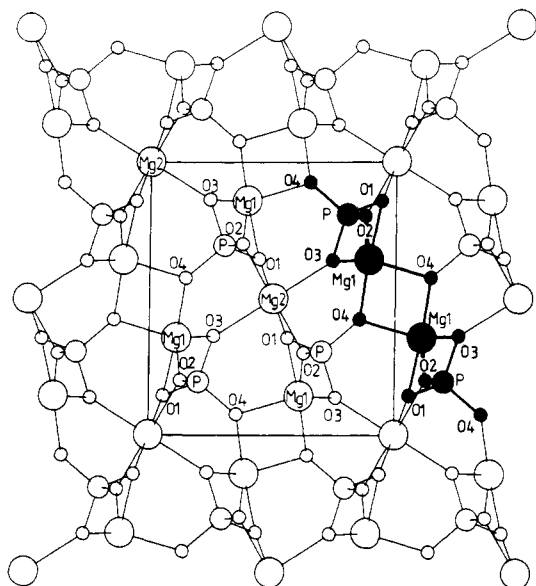


Figure 1. Projection of $\text{Mg}_3(\text{PO}_4)_2$ onto the 001 plane.¹³ The axes of one unit cell are shown (Mg1 = five-coordinated magnesium, Mg2 = octahedral magnesium).

be used to investigate the cation distribution in the solid solution $\text{Zn}_{3-x}\text{Mg}_x(\text{PO}_4)_2$.

Zinc orthophosphate, $\text{Zn}_3(\text{PO}_4)_2$, forms two modifications,⁷ the β phase, which is stable above 942 °C (by a reversible transformation), and the low-temperature α phase.⁸ The α phase, which contains only tetrahedral cation sites, can accommodate approximately 3 atom % added "impurity" cation, for example, Mn^{2+} or Mg^{2+} , but beyond this degree of substitution, a new phase, " γ - $\text{Zn}_3(\text{PO}_4)_2$ ", is formed. The γ -phase solid solutions have wide miscibility ranges, for example 4–27 atom % with $\text{Mn}_3(\text{PO}_4)_2$ ^{9,10} and 3–100 atom % with $\text{Mg}_3(\text{PO}_4)_2$,¹¹ the latter is isostructural with γ - $\text{Zn}_3(\text{PO}_4)_2$.

The structures of both γ - $\text{Zn}_3(\text{PO}_4)_2$ (lightly doped with Mn^{2+}) and $\text{Mg}_3(\text{PO}_4)_2$ have been determined.^{12,13} A particularly interesting feature of this structure type is the occurrence of two cation sites, one a regular octahedron and the other a distorted five-coordinated site (Figure 1); there are twice as many five-coordinated sites as there are octahedral positions. Bond lengths are given in Table I. Calvo has shown,¹² by powder X-ray diffraction measurements, that Mg^{2+} substitutes preferentially at the octahedral site when $\text{Mg}_3(\text{PO}_4)_2$ is doped into γ - $\text{Zn}_3(\text{PO}_4)_2$, and Nord has found that the ratio of octahedral to five-coordinated magnesium is approximately 3:1 in the stoichiometry $\text{MgZn}_2(\text{P-O}_4)_2$.¹⁴ In the present work, we show that the ^{31}P chemical shift is highly sensitive to the distribution of Mg^{2+} and Zn^{2+} over the two cation sites.

Experimental Section

Powder samples of the phase $\text{Zn}_{3-x}\text{Mg}_x(\text{PO}_4)_2$ with $x = 0, 0.5, 1.0, 1.20, 1.25, 1.5, 1.75, 1.9, 2.0, 2.1, 2.2, 2.5,$ and 3 were prepared by mixing stoichiometric quantities of the salts ZnO , $\text{Mg}(\text{NO}_3)_2 \cdot 9\text{H}_2\text{O}$, and $\text{NH}_4\text{H}_2\text{PO}_4$ in an acid solution. The solutions were dried and the resulting powders ground. The samples were fired at 1000 °C for at least 24 h and cooled rapidly to room temperature. The white polycrystalline products were examined by powder X-ray diffraction and found to contain only the γ -solid solution, with the exception of the sample $x = 0$ which is α - $\text{Zn}_3(\text{PO}_4)_2$; the compositions were confirmed by atomic absorption analysis for zinc.

The NMR spectra were acquired on a Bruker CXP200 spectrometer operating at 80.9 MHz for ^{31}P . Magic angle sample spinning was carried

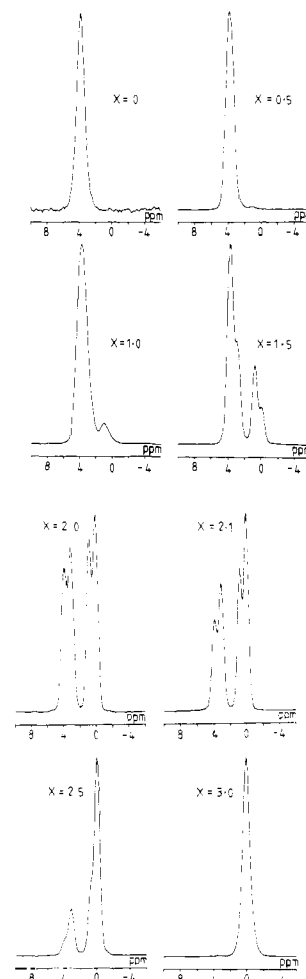


Figure 2. ^{31}P MASNMR spectra of $\text{Zn}_{3-x}\text{Mg}_x(\text{PO}_4)_2$ for $x = 0, 0.5, 1.0, 1.5, 2.0, 2.1, 2.5,$ and 3.

out with 0.2-g samples in Delrin Andrews-type rotors, using spinning speeds of ca. 4 kHz. At these speeds, the spinning sidebands in the NMR spectrum resulting from the formation of rotational echoes constitute less than 5% of the overall intensity. The sidebands were included in the estimated line intensities. Typically 100 transients were collected by using a 5- μs pulse and a recycle delay of 10 s. Increasing the recycle delay to 60 s caused no change in the relative intensities of the resonances in the NMR spectra, and in view of the partial saturation occurring with a 10-s recycle delay, this shows that all the resonances have similar relaxation times. This allows the direct use of the resonance intensities as a measure of the phosphate populations. Chemical shifts were measured with respect to an external reference of 85% H_3PO_4 and are reported taking upfield as negative.

Results and Discussion

The Qualitative View. The ^{31}P MASNMR spectra of the $\text{Zn}_{3-x}\text{Mg}_x(\text{PO}_4)_2$ solid solutions are shown in Figure 2. The sample with $x = 0$ (α - $\text{Zn}_3(\text{PO}_4)_2$) shows a single resonance with, coincidentally, the same ^{31}P chemical shift as that of the γ phase at low values of x (e.g., $x = 0.5$). All the other spectra correspond to the samples of the γ phase which, according to the published crystal structure, contains only one crystallographically distinct phosphorus atom. The spectra of the solid solutions, however, contain up to four resonances, arising, presumably, from phosphorus atoms with different local environments. The spectra can conveniently be discussed in two groups, one for preparations with $0 < x \leq 1$ and one for those having $1 < x < 3$. In the spectra of the first group, the dominant feature is a single peak at 3.9 ppm, which remains essentially unchanged between $x = 0$ and 1. A minor peak, which increases in intensity with increasing x , can be seen at approximately 0.9 ppm. As x increases above 1, the intensity of this second peak grows rapidly and additional structure becomes apparent at 3.1 and 0.1 ppm. At $x = 2$, the

(7) Katnack, F. L.; Hummel, F. A. *J. Electrochem. Soc.* **1958**, *105*, 125.

(8) Calvo, C. *Can. J. Chem.* **1965**, *43*, 436.

(9) Hummel, F. A.; Katnack, F. L. *J. Electrochem. Soc.* **1958**, *105*, 528.

(10) Nord, A. G.; Stefanidis, T. *Polyhedron* **1982**, *1* (4), 349.

(11) Sarver, J. F.; Katnack, F. L.; Hummel, F. A. *J. Electrochem. Soc.* **1959**, *106*, 960.

(12) Calvo, C. *J. Phys. Chem. Sol.* **1963**, *24*, 141.

(13) Nord, A. G.; Kieckegard, P. *Acta Chem. Scand.* **1968**, *22*, 1466.

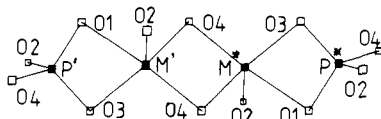
(14) Nord, A. G. *Mater. Res. Bull.* **1977**, *12*, 563.

line width is sufficiently narrow ($\Delta\nu_{1/2} < 1$ ppm) to reveal four peaks which have approximately equal intensities, but as x approaches 3, the lines at 3.9, 3.1, and 1.0 ppm diminish in intensity to leave a single peak at 0.1 ppm; this peak is characteristic of pure $Mg_3(PO_4)_2$.

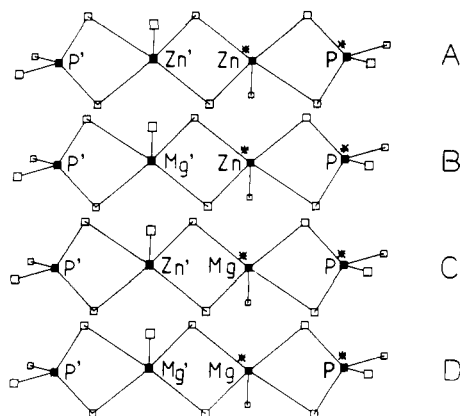
Our results show no appreciable change in the ^{31}P spectrum in the composition range $0 < x \leq 1$. Calvo and Nord^{12,14} have independently proposed that substitution of Mg^{2+} for Zn^{2+} in the γ -solid solution takes place primarily at the octahedral site in this composition range, enabling us to conclude that substitution of Mg^{2+} for Zn^{2+} at the octahedral site does not affect the ^{31}P isotropic chemical shift. If substitution occurs exclusively at the octahedral site in the first instance, this site will be filled at $x = 1$, and further substitution must take place at the five-coordinated site. It seems likely, therefore, that the more complex spectra in the composition range $1 < x < 3$ arise because of the effect of substitution at the five-coordinated site. To a first approximation, this gives rise to the peak at ~ 0.9 ppm, which is just discernible at $x = 0.5$ and grows rapidly for $x > 1$.

In order to understand the evolution of the spectra with increasing x , we must first examine the structure of γ - $Zn_3(PO_4)_2$ in more detail and, in particular, the environment around the phosphorus atom. The relevant phosphorus-to-metal distances are shown in Table II. We note that the shortest contact between the octahedral cation and phosphorus is 3.32 Å, whereas each five-coordinate site has a phosphorus neighbor at only 2.73 Å. We believe that, unlike substitution at the octahedral site, substitution at the five-coordinate site has a marked effect on the chemical shift of its nearest-neighbor phosphorus with which it shares two common oxygen atoms.

If the spectra were determined solely by the presence of magnesium or zinc at the nearest five-coordinate site, we would expect only the two peaks at ~ 3.9 and ~ 0.9 ppm, but these are clearly further split and other factors must therefore be considered. Is it possible to account for this finer detail by making a closer examination of the structure? It is our view that the splitting arises because each five-coordinated site shares not only an edge with a PO_4 unit but also a second edge with a symmetry equivalent cation site. The important structural element is highlighted in Figure 1 and shown schematically below. Bond lengths for this grouping are given in Table I.



We can now identify four possible environments around phosphorus atom P^* as shown.



The situation in scheme A is found in γ - $Zn_3(PO_4)_2$ and the situation in D obtained in $Mg_3(PO_4)_2$; these phosphorus resonances occur at 3.9 and 0.1 ppm, respectively. At intermediate compositions, two other cation distributions, B and C, should be observed. In B, the resonance of P^* , which does not have a Mg^{2+} ion at the nearest-neighbor five-coordinated site, is shifted slightly upfield from 3.9 ppm by the presence of Mg^{2+} at the M' site; this

Table II^a

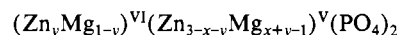
	phosphorus-to-metal dist, Å		
	$Mg_3(PO_4)_2$ ¹³	γ - $Zn_3(PO_4)_2$ ¹²	$Zn_2Mg(PO_4)_2$ ¹⁴
M_1'	2.67	2.73	2.71
M_1''	3.14	3.23	3.18
M_1'''	3.22	3.16	3.17
M_1''''	3.24	3.27	3.24
M_2'	3.31	3.32	3.30
M_2''	3.41	3.51	3.46
M_2'''	3.42	3.36	3.38

^a M_1 = five-coordinate metal site, M_2 = octahedral metal site.

gives a resonance at 3.1 ppm. In C, the resonance of P^* , which now does have an Mg^{2+} nearest neighbor on the M^* site, as in D, is shifted downfield from 0.1 to 1.0 ppm by the presence of Zn^{2+} , rather than Mg^{2+} , at the M' site. The presence of P^* in scheme B is, of course, always complemented by a P^* in scheme C. This model accounts qualitatively for the spectra in the composition range $1 < x < 3$.

The Quantitative View (for $x \geq 1$). The MASNMR spectra can be used to obtain quantitative information about the cation distribution in $Zn_{3-x}Mg_x(PO_4)_2$ by relating the intensities of the resonances to the relative probabilities of each of the four phosphorus environments (A–D).

First, we can write a general expression for the cation distribution



where the superscripts VI and V denote octahedral and five-coordinated sites, x is as in the general formula, and y gives the deviation from the completely ordered system (i.e., with only Mg in the octahedral site, $y = 0$).

Nord¹⁵ has expressed the cation distribution indicated by y in terms of a distribution coefficient K_D

$$K_D = \frac{X_{Zn}^V X_{Mg}^{VI}}{X_{Zn}^{VI} X_{Mg}^V}$$

where X^V and X^{VI} are the site occupancy factors for the respective cations at five- and six-coordinated sites.

Hence,

$$K_D = \frac{(3-x-y)(1-y)}{(y)(x+y-1)}$$

We can say, in general, that for a completely random distribution over all sites, $K_D = 1$ and $y = (3-x)/3$, and for a completely ordered situation with Mg in octahedral sites, $K_D = \infty$ and $y = 0$. Simulated spectra corresponding to these two limiting cases are shown in Figure 3 for $x = 1$ and 2. The fractions of zinc and magnesium on the octahedral and five-coordinated site are defined by the values of x and y . If we now assume that these fractions are randomly distributed on each of these two cation sites, then the probability of each P^* phosphorus environment, in schemes A–D, can be written

$$\begin{array}{l}
 P(A) = \frac{x}{(2)^2} \quad \quad \quad \frac{x=1}{(2-y)^2} \quad \quad \quad \frac{x=2}{(1-y)^2} \\
 P(B) = \frac{(3-x-y)(x+y-1)}{(2)(2)} \quad \quad \quad \frac{(2-y)(y)}{(2)(2)} \quad \quad \quad \frac{(1-y)(1+y)}{(2)(2)} \\
 P(C) = \frac{(x+y-1)(3-x-y)}{(2)(2)} \quad \quad \quad \frac{(y)(2-y)}{(2)(2)} \quad \quad \quad \frac{(1+y)(1-y)}{(2)(2)} \\
 P(D) = \frac{(x+y-1)^2}{(2)^2} \quad \quad \quad \frac{(y)^2}{(2)^2} \quad \quad \quad \frac{(1+y)^2}{(2)^2}
 \end{array}$$

where $P(A)$ is the probability of situation A occurring, etc. Hence

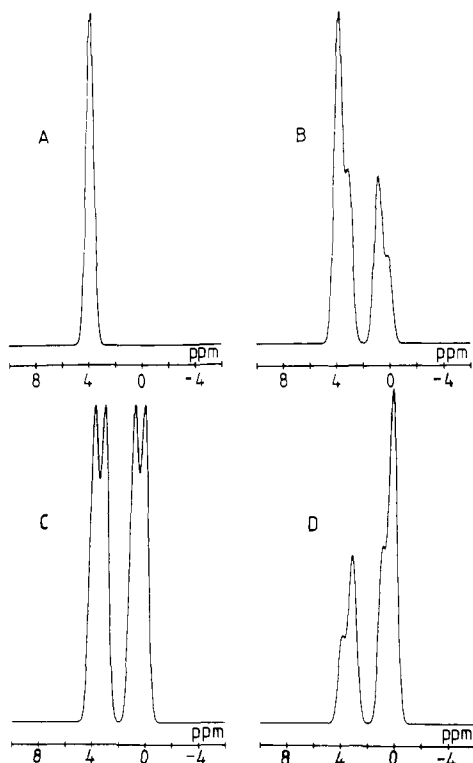


Figure 3. Simulated NMR resonances for four theoretical cases. The spectra were calculated by using a Gaussian peak shape (with the same half-width $\Delta\nu_{1/2} \sim 0.7$ ppm in each case). (A) $(\text{Mg})^{\text{VI}}(\text{Zn}_2)^{\text{V}}(\text{PO}_4)_2$ ($x = 1, y = 0$, completely ordered); (B) $(\text{Mg}_{1/3}\text{Zn}_{2/3})^{\text{VI}}(\text{Mg}_{2/3}\text{Zn}_{4/3})^{\text{V}}(\text{PO}_4)_2$ ($x = 1, y = 2/3$, completely random); (C) $(\text{Mg})^{\text{VI}}(\text{ZnMg})^{\text{V}}(\text{PO}_4)_2$ ($x = 2, y = 0$, completely ordered); (D) $(\text{Mg}_{2/3}\text{Zn}_{1/3})^{\text{VI}}(\text{Mg}_{4/3}\text{Zn}_{2/3})^{\text{V}}(\text{PO}_4)_2$ ($x = 2, y = 1/3$, completely random).

if we write $I(A) = KP(A)$, where $I(A)$ is the intensity of peak A at 3.9 ppm (including sidebands), and $I(B) = KP(B)$, etc., then the ratio, R , of the two major peaks is

$$\frac{I(A) + I(B)}{I(C) + I(D)} = \frac{3 - (x + y)}{(x + y) - 1}$$

Therefore,

$$(x + y) = \frac{3 + R}{1 + R}$$

Values of $(x + y)$, calculated from experimentally obtained values of R , together with the values of x, y , and K_D at each composition are given in Table III. The most notable feature is that the cation distribution coefficient is not constant as a function of composition but appears to vary systematically with a maximum value at approximately $x = 1.5$. The results indicate that the solid solution is far from ideal, in agreement with Nord's observation¹⁶ that the

Table III. Experimentally Determined Values of $(x + y)$ from the Intensities of the NMR Resonances, Including Spinning Sidebands. esd's, in Parentheses, Are an Estimation of the Error in the Stoichiometry (for x) and in the Peak Area Ratio (for $x + y$). A Mean Value for K_D Is Given for Each Set of Values

$(x + y)$	x	y	K_D
($\neq 0.01$)	($\neq 0.03$)	($\neq 0.03$)	
1.16	1.00	0.16	60
1.29	1.20	0.09	60
1.34	1.25	0.09	50
1.51	1.50	0.01	290 ^b
1.51 ^a	1.50	0.01	290 ^b
1.77	1.75	0.02	80 ^b
1.92	1.90	0.02	60 ^b
2.04	2.00	0.04	20
2.17	2.10	0.07	9
2.29	2.20	0.09	6
2.59	2.50	0.09	3

^aSecond preparation. ^bOrdered state ($y = 0$) within experimental error.

cell parameters in this system are not linear functions of the composition. On the other hand, Mössbauer measurements¹⁷ have shown that K_D has an almost constant value of 1.4 in the solid solution $\text{Mg}_{3-x}\text{Fe}_x(\text{PO}_4)_2$, in the range $0.15 \leq x \leq 1.8$. We find, however, that the preference of Mg cations for the octahedral site at the stoichiometry $\text{Zn}_2\text{Mg}(\text{PO}_4)_2$ is significantly greater than that found in an X-ray powder diffraction experiment carried out by Nord,¹⁴ in which the value of y was 0.24, giving $K_D = 20$. The discrepancy between our results, and those of Nord, may stem from the difference in thermal history of the samples.

Conclusion

The results of our MASNMR study of the $\text{Zn}_{3-x}\text{Mg}_x(\text{PO}_4)_2$ solid solution demonstrate that the ³¹P isotropic chemical shifts can be extremely sensitive to changes in the local environment. The chemical shift is certainly influenced by substitution at the nearest-neighbor cation site, but the nature of this influence is unclear, and further work is required in order to establish the factors that control chemical shifts in phosphates. We wish to emphasize, however, that an empirical approach has enabled us to establish cation distribution coefficients with a precision that is comparable with, if not better than, that obtained by diffraction methods. Data collection and analysis can be carried out in a matter of minutes, whereas the diffraction experiments, especially those using single crystals, are very time-consuming. In future work, we shall be exploring a wider range of applications of ³¹P MASNMR to problems of order and disorder in the solid state.

Acknowledgment. We thank the SERC for a grant toward the purchase of the NMR equipment and the provision of a research studentship for R.J.B.J. N.J.C. is grateful to Shell, Thornton Research Centre for financial assistance.

(16) Nord, A. G. *Mater. Res. Bull.* **1981**, *16*, 1121.

(17) Annersten, H.; Ericsson, T.; Nord, A. G. *J. Phys. Chem. Sol.* **1980**, *41*, 1235.