

Relationship between Solid State NMR Parameters and X-ray Structural Data in Tricadmium Phosphates

S. Aime,* G. Digilio, and R. Gobetto

Dipartimento di Chimica Inorganica, Chimica Fisica e Chimica dei Materiali, Università di Torino, Via P. Giuria 7, 10125, Torino, Italy

A. Bigi, A. Ripamonti,* and N. Roveri

Dipartimento di Chimica "G. Ciamician", Università di Bologna, Via Selmi 2, 40126, Bologna, Italy

M. Gazzano

Centro di studio per la Fisica delle Macromolecole (CNR), c/o Dipartimento di Chimica "G. Ciamician", Università di Bologna, Via Selmi 2, 40126, Bologna, Italy

Received April 20, 1995[⊗]

³¹P and ¹¹³Cd MAS NMR spectra of solid β'-tricadmium phosphate (β'-TCdP) show a number of highly resolved resonances that agree well with the number of independent crystallographic sites indicated by the results of X-ray diffraction studies. A correlation of the ³¹P chemical shifts with the crystallographic sites for the six different PO₄³⁻ groups in the unit cell of β'-TCdP has been obtained by a method based on the computation of bond strength at oxygen atoms in phosphate moieties. The assignment of the ¹¹³Cd resonances has been carried out on the basis of the relationship between the asymmetry of the chemical shift tensor (evaluated by analysis of the spinning side bands intensities in the MAS spectrum) and a geometric parameter related to the distortion from the bipyramidal trigonal coordination at each cadmium center. Samples of tricadmium phosphate with different degrees of magnesium substitution for cadmium were investigated by ³¹P MAS NMR, ¹¹³Cd MAS NMR, and X-ray diffraction. The results of these investigations showed that the magnesiums distribute randomly in the cadmium sites, inducing a marked decrease in the order of the structure.

Introduction

Since the introduction of the MAS (magic angle spinning) NMR technique, much attention has been devoted to the study of calcium phosphate in synthetic and biological materials for their outstanding importance in medicine and biology.^{1a-g} Unfortunately NMR spectroscopy did not provide a response consistent with the original expectations as the high resolution ³¹P MAS NMR of a number of calcium phosphate minerals invariably afforded poorly resolved signals within a very limited chemical shift range. Nevertheless, Griffin and co-workers^{1b} were able to extract useful information about these systems on the basis of the small differences in chemical shifts, in chemical shift anisotropy tensors, and in the proximity of the protons to the ³¹P nuclei. Furthermore they were able to obtain some useful insight into the composition of bones.^{1c}

The broad featureless absorption often obtained in calcium phosphate samples arises from the dispersion of ³¹P chemical shifts, which makes it difficult to obtain any correlation with the crystallographic information.

An intrinsic limitation to the application of NMR spectroscopy to the study of calcium phosphates is that observation of metal atom spectra is prevented since the magnetically active ⁴³Ca isotope (spin 7/2, natural abundance 0.13%) is one of the most insensitive NMR nuclei in the periodic table. Among the divalent ions which can be substituted for calcium in phosphates of biological interest, ¹¹³Cd has spin 1/2 (natural abundance 12.34%) and is then expected to provide well-resolved NMR spectra. It is well established that cadmium can enter in the crystal structure of hydroxyapatite (the phase which is indicated as a model system for biological apatites), where it can replace calcium in the whole range of composition.² Heat treatment of hydroxyapatite at high cadmium content induces its thermal conversion into β'-tricadmium phosphate (β'-TCdP). The structure of β'-TCdP, which crystallizes in the monoclinic system, is isomorphous with that of β'-Mn₃(PO₄)₂,^{3,4} differing in the triplication of the *c*-axis of the unit cell. The structure contains nine crystallographically independent cadmium atoms and six crystallographically independent phosphate groups.⁵ Magnesium substitution into β'-TCdP structure gives a phase isomorphous with β'-Zn₃(PO₄)₂ and contains three M²⁺ and two PO₄³⁻ crystallographically independent ions.⁶ Magnesium can

[⊗] Abstract published in *Advance ACS Abstracts*, November 15, 1995.

(1) (a) Williams, R. J. P.; Giles, R. F. G.; Posner, A. M. *J. Chem. Soc., Chem. Commun.* **1981**, 20, 1051. (b) Aue, W. P.; Roufosse, A. H.; Glimcher, M. J.; Griffin, R. J. *Biochemistry* **1984**, 23, 6110. (c) Roufosse, A. H.; Aue, W. P.; Roberts, J. E.; Glimcher, M. J.; Griffin, R. J. *Biochemistry* **1984**, 23, 6115. (d) Brown, C. E.; Allaway, J. R.; Brown, K. L.; Battocletti, J. H. *Clin. Chem.* **1987**, 33, 227. (e) Brown, C. E.; Battocletti, J. H.; Shinivassan, R.; Allaway, J. R.; Moore, J.; Sigmann, P. *Clin. Chem.* **1988**, 34, 1431. (f) Miquel, J. L.; Facchini, L.; Legrand, A. P.; Rey, C.; Lemaitre, J. *Colloids Surf.* **1990**, 45, 427. (g) Roberts, J. E.; Bonar, L. C.; Griffin, R. G.; Glimcher, M. J. *Calcif. Tissue Int.* **1992**, 50, 42.

(2) Bigi, A.; Gazzano, M.; Ripamonti, A.; Foresti, E.; Roveri, N. *J. Chem. Soc. Dalton Trans.* **1986**, 241.

(3) Stephen, J. S.; Calvo, C. *Can. J. Chem.* **1969**, 47, 2215.

(4) Stephen, J. S.; Calvo, C. *Can. J. Chem.* **1967**, 45, 2303.

(5) Bigi, A.; Foresti, E.; Gazzano, M.; Ripamonti, A.; Roveri, N. *J. Chem. Res., Miniprint* **1986**, 1471.

(6) Ripamonti, A.; Bigi, A.; Foresti, E.; Gazzano, M.; Roveri, N. *Gazz. Chim. Ital.* **1986**, 116, 543.

replace up to 19% of the cadmium atoms, inducing a linear shrinkage of the lattice parameters and a significant disordering of the PO_4^{3-} groups.⁶ In this paper we report our observation on the β' -TCdP system which yields highly resolved ^{31}P and ^{113}Cd MAS NMR spectra that fit well with the results obtained from the X-ray diffraction data.⁵ Furthermore, the comparison of the high resolution solid state NMR and X-ray data in samples with different degrees of magnesium substitution for cadmium in tricadmium phosphate allows greater insight into the structural effects induced by the presence of magnesium in tricadmium phosphate.

Experimental Section

β' -TCdP was prepared by solid state reaction of $\text{Cd}(\text{OH})_2$ and $(\text{NH}_4)_2\text{HPO}_4$ in the stoichiometric ratio at 700 °C.

$\text{Mg}_3(\text{PO}_4)_2$ (TMgP) was prepared by solid state reaction of $\text{Mg}(\text{CO}_3)\cdot\text{Mg}(\text{OH})_2\cdot 5\text{H}_2\text{O}$ and $\text{MgHPO}_4\cdot 3\text{H}_2\text{O}$ in the stoichiometric ratio at 1000 °C.

Mg-substituted β' -TCdP was prepared by solid state reaction of β' -TCdP and TMgP at 1000 °C for 15 h. The synthesis was carried out for different amounts of magnesium substitution for cadmium up to 19 atom %. All the solid state reactions were carried out at air under atmospheric pressure. Aliquots of all the samples were characterized by X-ray diffraction prior to undergoing NMR investigations.

X-ray Diffraction. The X-ray diffraction analysis was carried out on β' -TCdP and Mg-substituted β' -TCdP samples by means of a Philips PW 1050/81 diffractometer controlled by a PW1710 unit using Ni-filtered Cu K radiation. The diffractometer was equipped with Soller slits and proportional detector PW 1711/10. The 2θ range was from 10 to 65° at a rotation rate of 0.5°/min. The lattice constants were determined by least square refinements.

Solid State NMR. The high resolution ^{31}P and ^{113}Cd magic angle spinning (MAS) NMR spectra were performed on a JEOL GSE 270 (6.34 T) spectrometer operating at 109.4 and 59.9 MHz respectively. H_3PO_4 , 85%, and solid $\text{Cd}(\text{NO}_3)_2\cdot 4\text{H}_2\text{O}$ were used as a reference $\delta = 0$ for ^{31}P and ^{113}Cd respectively. Cylindrical 6 mm o.d. zirconia rotors with sample volume of 120 μL were employed with spinning speed in the range from 1.8 to 5.5 kHz. For all samples the magic angle was carefully adjusted from the ^{79}Br MAS spectrum of KBr by minimising the line width of the spinning side bands satellite transitions.

Results and Discussion

In Figures 1 and 2 we report the isotropic region of the ^{31}P and ^{113}Cd MAS NMR spectra of β' -TCdP as observed at room temperature and at magnetic field strength of 6.4 T. The line width of less than 1 ppm of the ^{31}P resonances indicates high regularity in the polycrystalline sample, as confirmed by the powder X-ray diffraction pattern which shows that β' -TCdP synthesized by a solid state reaction is highly crystalline and exhibits cell parameter very close to that reported for β' -TCdP single crystal.⁵ β' -TCdP crystallizes in the monoclinic system with space group $P2_1/c$. The six almost equally intense resonances in the ^{31}P MAS NMR spectrum are due to the six independent PO_4^{3-} groups contained in the monoclinic unit cell. The ^{31}P chemical shifts span a range of more than 13 ppm whereas in the various form of calcium phosphates they distribute in a smaller range (maximum 10 ppm). On the basis of their positions in the ^{31}P MAS NMR spectrum they may be grouped in two sets formed by the three resonances at 7.2, 9.9, and 11.2 ppm and the three resonances at 18.7, 20.7, and 21.1 ppm respectively.

The spinning side bands manifold was analyzed using an adaptation^{7,8} of the Herzfeld and Berger method⁹ to give values

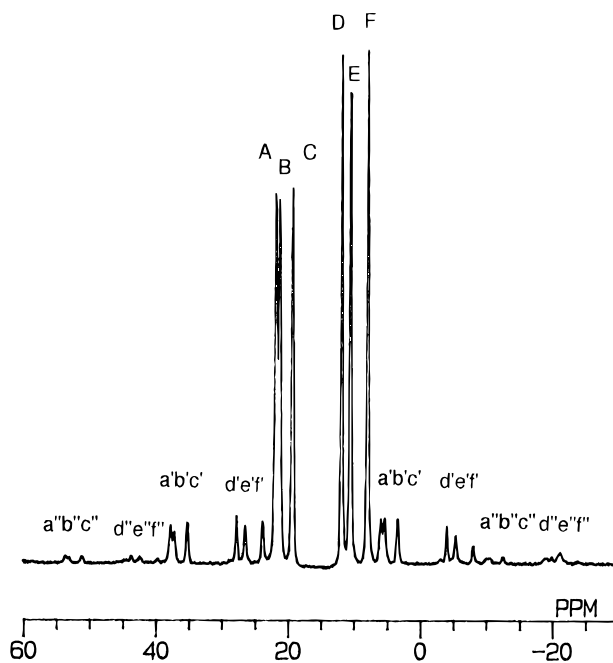


Figure 1. ^{31}P MAS NMR spectrum of β' -TCdP: 4 scans, pulse delay 200 s, and sample spinning rate 1.8 kHz. Chemical shift values are referenced to a solution of H_3PO_4 85%. Isotropic peaks are labeled with capital letters, while spinning side bands are marked with small letters.

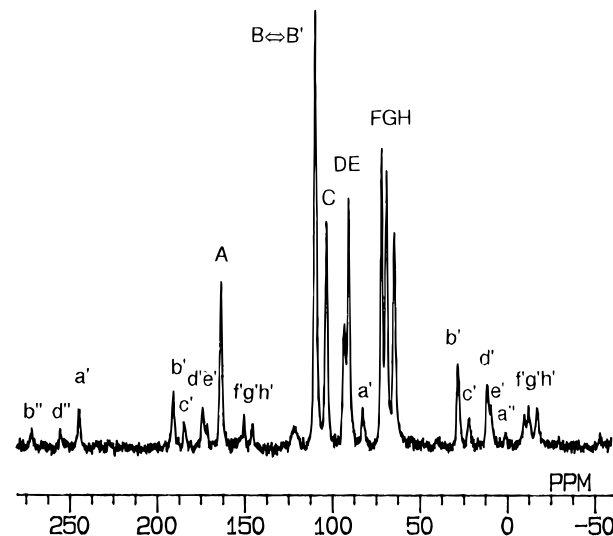


Figure 2. ^{113}Cd MAS NMR spectrum of β' -TCdP: 660 scans, pulse delay 30 s, and sample spinning rate 4.86 kHz. Chemical shifts are referenced to solid $\text{Cd}(\text{NO}_3)_2\cdot 4\text{H}_2\text{O}$. Isotropic peaks are labeled with capital letters, while spinning side bands are marked with small letters.

for the principal elements of the nuclear shielding tensor and the chemical shift anisotropy, $\Delta\sigma$, that is defined as $\Delta\sigma = \sigma_{33} - (\sigma_{11} + \sigma_{22})/2$. The results given in Table 1 show low values of the chemical shift anisotropies in agreement with the nearly symmetric environment at the phosphorus atoms in the phosphate groups. Furthermore the $\Delta\sigma$ values do not change significantly for the six different resonances hampering any correlation between this NMR parameter and X-ray diffraction data.

In order to correlate ^{31}P chemical shifts and crystallographic sites, we have applied the method proposed by Brown et al.^{10,11}

(7) Hawkes, G. E.; Sales, K. D.; Lian, L. Y.; Gobetto, R. *Proc. R. Soc. London A* **1989**, *93*, 424.

(8) Hawkes, G. E.; Sales, K. D.; Aime, S.; Gobetto, R.; Lian, L. Y. *Inorg. Chem.* **1991**, *30*, 1489.

(9) Herzfeld, J.; Berger, A. E. *J. Chem. Phys.* **1980**, *73*, 6021.

(10) Brown, I. D.; Shannon, R. D. *Acta Crystallogr., Sect. A* **1973**, *29*, 295.

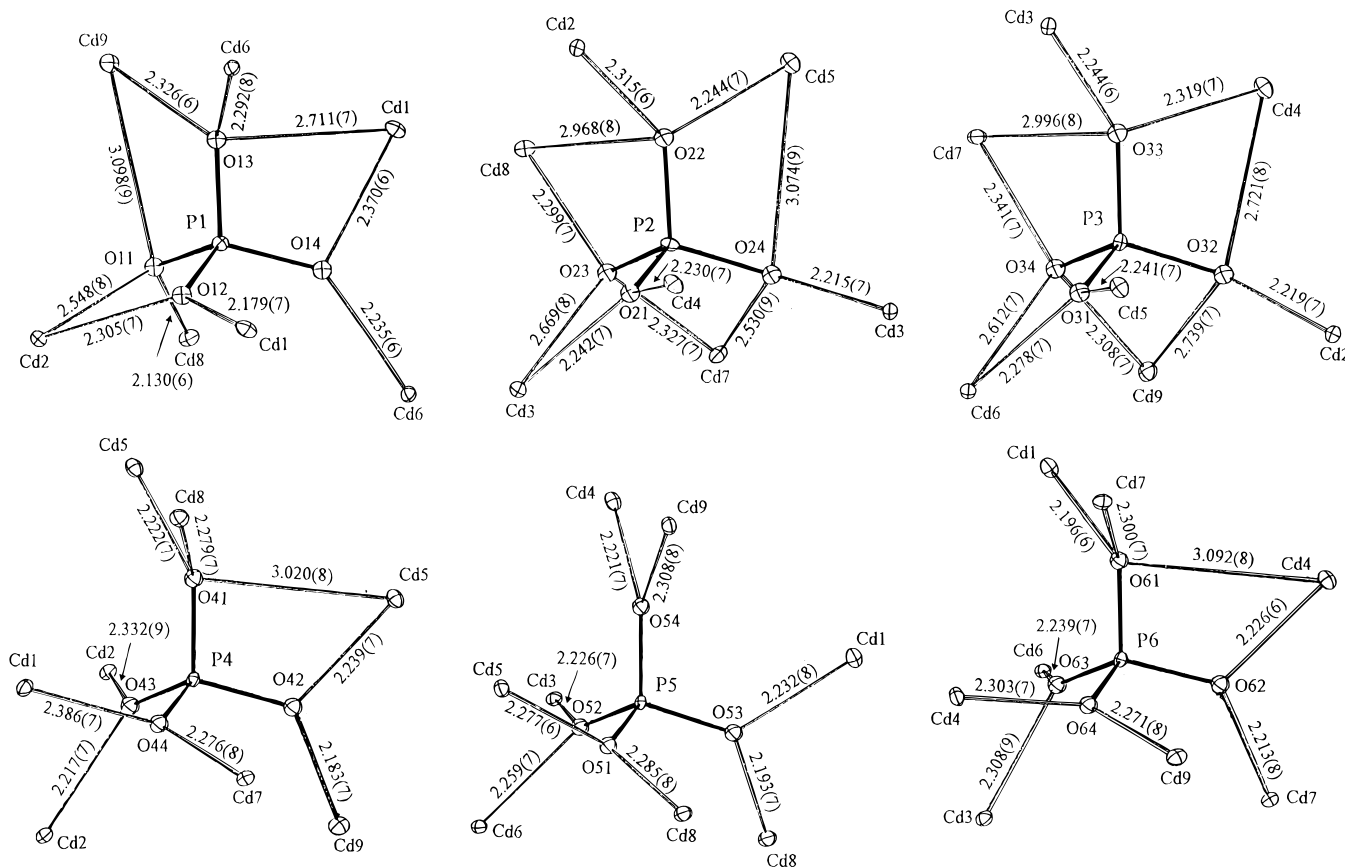


Figure 3. Cationic environments of the six independent phosphate groups in β' -TCdP.

Table 1. NMR Anisotropies and Principal Components of the Chemical Shift Tensor for the Resonances in the Slow Spinning ^{31}P NMR MAS Spectrum of β' -TCdP^a

peak label ^b	σ_{iso}	σ_{11}	σ_{22}	σ_{33}	$\Delta\sigma$
A	-21.1	-40.6	-18.8	-6.3	23.4
B	-20.7	-40.7	-14.1	-9.0	18.4
C	-18.7	-37.6	-17.8	-2.9	24.8
D	-11.2	-24.8	-15.7	4.7	24.9
E	-9.9	-18.7	-18.7	5.6	24.3
F	-7.2	-16.9	-14.1	7.1	22.6

^a Values are obtained by the Herzfeld–Berger method (see text for references). Chemical shifts are expressed in ppm and are referenced to 85% H_3PO_4 , which resonance has been set to 0 ppm. ^b See Figure 1.

which is based on the computation of bond strengths at oxygen atoms. The summed bond strengths (Σp) at oxygen atoms, which are related to the coordination number and therefore to the covalence of the bond, have been successfully used as a means of assigning the ^{31}P resonances in other inorganic phosphates.¹² In fact, the isotropic chemical shifts move upfield as the bond strength at oxygen increases, corresponding to a decrease in the paramagnetic contribution to the nuclear shielding.

The structure of β' -TCdP indicates⁵ that three of the phosphate groups, P(1), P(2), and P(3), display 11 O–Cd contacts at variance with the other groups where the number of cation–oxygen contacts is eight or nine as reported in Figure 3. Although the higher number of interactions arises from contacts longer than 2.5 Å, it is likely that this situation is responsible for the differentiation of the two sets of ^{31}P resonances. Table

Table 2. Phosphorus–Oxygen Bond Lengths and Bond Strengths (p) at Oxygen Atoms in β' -TCdP (ν = Valence Units)

	bond length (Å)	$p(\text{O}^{2-})$ (vu)		bond length (Å)	$p(\text{O}^{2-})$ (vu)
P(1)–O(11)	1.528(8)	2.096	P(4)–O(41)	1.519(9)	2.180
P(1)–O(12)	1.536(6)	2.111	P(4)–O(42)	1.551(6)	2.134
P(1)–O(13)	1.544(8)	1.969	P(4)–O(43)	1.540(6)	2.008
P(1)–O(14)	1.530(7)	1.983	P(4)–O(44)	1.536(7)	1.894
P(2)–O(21)	1.533(6)	2.119	P(5)–O(51)	1.529(7)	2.017
P(2)–O(22)	1.549(8)	2.007	P(5)–O(52)	1.551(6)	2.039
P(2)–O(23)	1.537(7)	2.032	P(5)–O(53)	1.537(6)	2.175
P(2)–O(24)	1.528(9)	1.954	P(5)–O(54)	1.522(9)	2.092
P(3)–O(31)	1.525(6)	2.086	P(6)–O(61)	1.518(9)	2.192
P(3)–O(32)	1.531(9)	1.921	P(6)–O(62)	1.543(6)	2.131
P(3)–O(33)	1.535(8)	2.048	P(6)–O(63)	1.553(6)	1.957
P(3)–O(34)	1.530(7)	2.054	P(6)–O(64)	1.542(7)	1.957

2 reports phosphorus–oxygen bond lengths and bond strengths at oxygen atoms. Σp values at oxygen atoms have been obtained by adding the cation oxygen bond strengths for all the cations bonded to the four oxygen atoms of the tetrahedron, that is the phosphate ion itself and all the cadmium ions which are coordinated to these oxygen atoms. The values calculated for the six independent PO_4^{3-} groups provide a route to the assignment of the six different ^{31}P resonances as reported in Table 3. Thus this simple method allows a satisfactory correlation between the ^{31}P chemical shift and the crystallographic sites of the six different PO_4^{3-} groups in the unit cell of β' -TCdP.

As shown in Figure 2, the ^{113}Cd NMR MAS spectrum shows eight resonances. Apart the casual overlap of two resonances at 109.9 ppm, the spectrum is in good agreement with the X-ray structure that contains nine crystallographically independent cadmium atoms. The observation of such a well-resolved ^{113}Cd

(11) Brown, I. D.; Wu, K. K. *Acta Crystallogr., Sect. B* **1976**, 32, 295.

(12) Cheetham, A. K.; Clayden, N. J.; Dobson, C. M.; Jakeman, R. J. B. *J. Chem. Soc., Chem. Commun.* **1986**, 195.

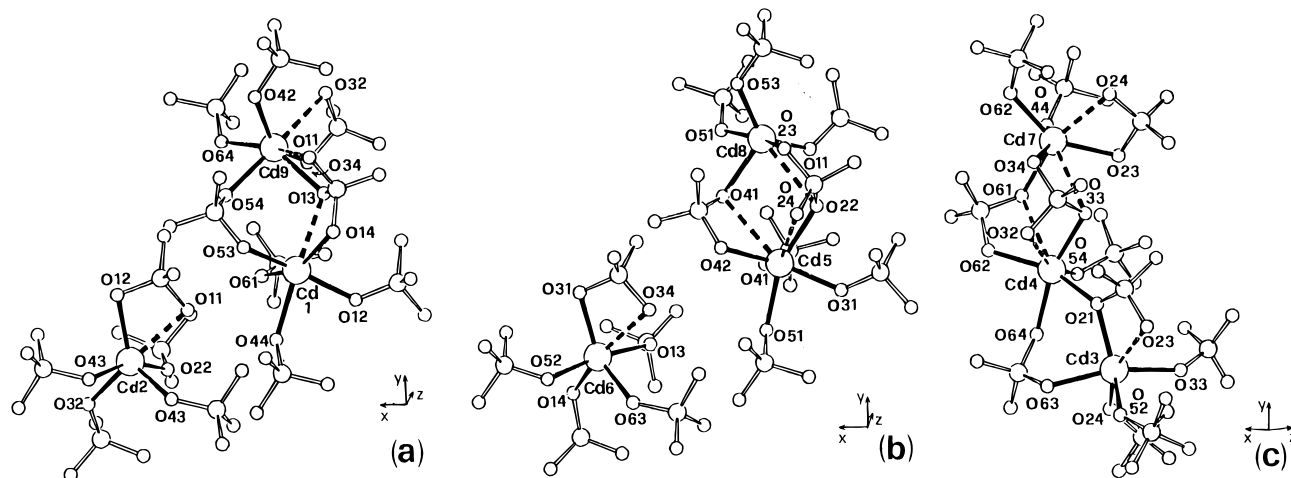


Figure 4. Views of the nine crystallographically independent cadmium coordination polyhedra: (a) Cd(1), Cd(2), Cd(9); (b) Cd(5), Cd(6), Cd(8); (c) Cd(3), Cd(4), Cd(7). Dashed lines indicate Cd–O bonds in the range 2.5–3.1 Å.

Table 3. Summed Bond Strengths at Oxygen Atoms (Σp) Calculated for the Six Independent Phosphate Groups of β' -TCdP and Relative ^{31}P MAS NMR Isotropic Chemical Shifts (δ)

phosphate group	Σp (vu)	peak label ^a	δ (ppm)
P(3)	8.109	A	21.1
P(2)	8.112	B	20.7
P(1)	8.159	C	18.7
P(4)	8.216	D	11.2
P(6)	8.237	E	9.9
P(5)	8.323	F	7.2

^a See Figure 1.

Table 4. NMR Anisotropies, Principal Components of the Chemical Shift Tensor and Asymmetry Parameter for the Resonances in the Slow Spinning ^{113}Cd NMR MAS Spectrum of β' -TCdP^a

peak label ^b	σ_{iso}	σ_{11}	σ_{22}	σ_{33}	$\eta =$		$\Delta\sigma$
					$ \sigma_{11} - \sigma_{22} $	$ \sigma_{33} - \sigma_{\text{iso}} $	
A	-163.6	-167	-282	-41	0.94	183	
B	-109.9	-66	-38	-225	0.24	108	
B'	-109.9	-66	-38	-225	0.24	108	
C	-103.5	-96	-21	-194	0.83	124	
D	-93.1	-54	39	-263	0.55	198	
E	-90.6	-58	-17	-196	0.39	110	
F	-71.9	-47	-9	-159	0.44	94	
G	-69.1	-43	7	-171	0.49	114	
H	-64.6	-20	-4	-170	0.15	91	

^a σ_{11} , σ_{22} , σ_{33} , and η values are obtained by the Herzfeld–Berger method but are ordered here according to the convention proposed by Haeberlen so that $0 \leq \eta \leq 1$. $\Delta\sigma$ is expressed as $\Delta\sigma = \sigma_{33} - 1/2(\sigma_{11} + \sigma_{22})$ with σ values ordered so that $\sigma_{33} \geq \sigma_{22} \geq \sigma_{11}$ (see text for references). Chemical shifts are expressed in ppm and are referenced to solid $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, which resonance has been set to 0 ppm. ^b See Figure 2.

spectrum prompted us to tackle the problem of the correlation between NMR parameters and structure in order to allow the assignment of each cadmium resonance to the different metal environments. The isotropic shifts span a range of about 100 ppm, and this is rather large if one considers that the same chemical species is involved. However it is not immediately obvious how to relate this parameter to the degree of symmetry around the Cd(II) centers, as generally stated in the literature.^{13–15} Moreover it is not reliable to follow the same procedure used

for the assignment of the ^{31}P resonances, because the coordination polyhedra around the metal ion are much more irregular than the ones around the phosphate ions. The difference in the type of bonding between the Cd–O and P–O interactions further hampers such an approach. In order to circumvent these difficulties we decided to resort to the use of other NMR parameters, such as the principal components of the chemical shift tensor (σ_{11} , σ_{22} , σ_{33}), the chemical shift anisotropy ($\Delta\sigma$) and the asymmetry parameter (η). These parameters appear more promising for the investigation of a possible correlation with the degree of symmetry of the cadmium ions environments. Only a few papers concerning this approach have been published. Du Bois Murphy et al.^{15,16} and Lacelle et al.¹⁷ related chemical shift anisotropies with the local environments of Cd(II) ions in $3\text{Cd}(\text{SO}_4) \cdot 8\text{H}_2\text{O}$, $\text{Cd}(\text{SO}_4) \cdot \text{H}_2\text{O}$, and $\text{Cd}_{10}(\text{SCH}_2\text{CH}_2\text{OH})_{16}^{4+}$. They were able to obtain accurate estimates of chemical shift anisotropies by computer fitting of static ^{113}Cd NMR solid state powder spectra. The higher number of crystallographic sites for cadmium atoms in β' -TCdP hampered such a measurement, so we evaluated the principal components of the chemical shift tensor from the analysis of the spinning side band intensities. The results of these calculations are summarized in Table 4, where each signal is labeled with a letter. The NMR parameters related to the signal at 109.9 ppm is reported twice because this peak clearly arises from the overlap of two resonances, and we will refer to them as to B and B'.

From X-ray data we know that each cadmium in the various crystalline sites is tightly bound to five oxygen atoms, resulting in a distorted bipyramidal trigonal coordination pattern,⁵ while a variable number of weaker interactions is observed for each site (Figure 4). In terms of simple considerations based on the crystalline ligand field theory, we may safely assume that only the five oxygen atoms surrounding each cadmium center are effective in modifying the factors determining the chemical shielding parameters of the metallic nucleus. We therefore assume that the information of the effect of the whole crystal lattice on the NMR parameters for each cadmium ion is brought to the metal center *via* the positions of the closest ligand atoms. In order to get a quantitative estimate of the structural differences

(13) Ellis, P. D. In *The Multinuclear Approach to NMR Spectroscopy*; Lambert, J. B., Riddell, F. G., Eds.; 1983; Chapter 22.

(14) Mennitt, P. G.; Shatlock, M. P.; Bartuska, V. J.; Maciel, G. E. *J. Phys. Chem.* **1981**, *85*, 2087–2091.

(15) Du Bois Murphy, P.; Gerstein, B. C. *J. Am. Chem. Soc.* **1981**, *103*, 3282–3286.

(16) Du Bois Murphy, P.; Stevens, W. C.; Cheung, T. T. P.; Lacelle, S.; Gerstein, B. C.; Kurtz, D. M., Jr. *J. Am. Chem. Soc.* **1981**, *103*, 4400–4405.

(17) Lacelle, S.; Stevens, W. C.; Kurtz, D. M., Jr.; Richardson, J. W., Jr.; Jacobson, R. A. *Inorg. Chem.* **1984**, *23*, 930–935.

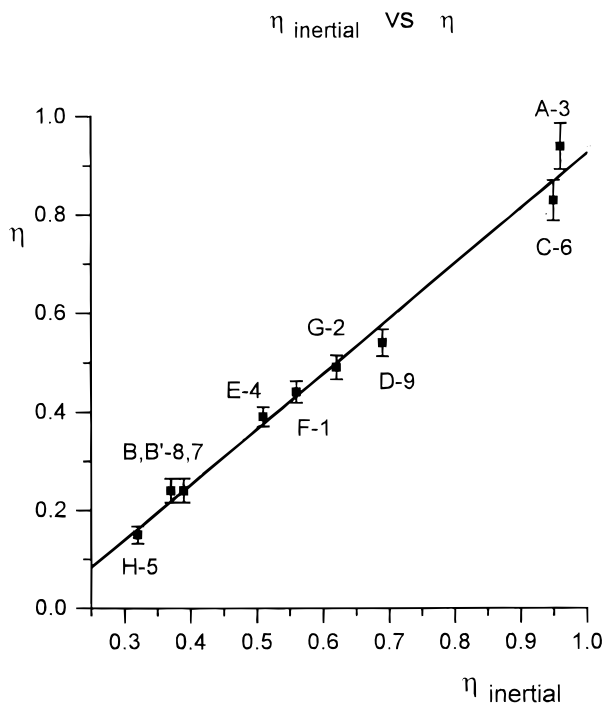


Figure 5. Plot of the asymmetry geometric parameter vs the asymmetry of the chemical shift tensor with error bars. The coupling number—letter provides the assignment of the ^{113}Cd resonance (letter) to a particular crystalline site (number). See text for details.

between the nine cadmium coordination cages, we consider the moments of inertia of the polyhedra made by cadmium ions and the most tightly bound oxygen atoms. The values of the principal components of the ellipsoid of inertia, I_{11} , I_{22} , and I_{33} , can be used to calculate the required structural asymmetry parameter using the same relationship used to evaluate the asymmetry of the chemical shift tensor:

$$\eta = |\sigma_{11} - \sigma_{22}| / |\sigma_{33} - \sigma_{\text{iso}}|$$

$$\eta_{\text{inertial}} = |I_{11} - I_{22}| / |I_{33} - I_{\text{iso}}|$$

where $I_{\text{iso}} = 1/3(I_{11} + I_{22} + I_{33})$. For the compound studied here the shielding components evaluated by the Herzfeld-Berger method do not agree with the Haerberlen convention:¹⁸

$$|\sigma_{33} - \sigma_{\text{iso}}| \geq |\sigma_{22} - \sigma_{\text{iso}}| \geq |\sigma_{11} - \sigma_{\text{iso}}|$$

and we decided to use the latter convention for σ_{11} , σ_{22} , and σ_{33} in order to obtain $0 \leq \eta \leq 1$. We used the convention:

$$|I_{33} - I_{\text{iso}}| \geq |I_{22} - I_{\text{iso}}| \geq |I_{11} - I_{\text{iso}}|$$

for the choice of I_{11} , I_{22} , and I_{33} according to $0 \leq \eta_{\text{inertial}} \leq 1$.

The plot of the geometric asymmetry parameter vs the asymmetry of the chemical shift tensor is a well defined straight line (Figure 5). We reiterate that the resonance at 109.9 ppm is due to two cadmium resonances and that we had to take into account that two crystallographically nonequivalent metal sites have the same magnetic properties. A linear least-squares calculation of the parameters of this straight line gives a correlation coefficient of 0.98. On the basis of this empirical relationship we propose the following assignment for the resonances in the ^{113}Cd NMR solid state spectrum, where the

same numbering system as that reported in the crystallographic study (Figure 4) is used here:

peak	H	B ↔ B'	E	F	G	D	C	A
Cd atom	5	8	7	4	1	2	9	6
								3

However, despite the high value of the correlation coefficient, one must be aware that there may be a significant error in the evaluation of η . A source of inaccuracy arises from the application of the Herzfeld-Berger procedure. In fact it is known that this method provides accurate values for the principal tensor components where a large set of positive and negative spinning side bands are available to the computation. In our system both the small chemical shift anisotropy and the relative crowding (eight signals in less than 100 ppm) allowed us to deal with two or three pairs of spinning side bands only. Next, another contribution to the error in η arises from the degree of reproducibility of the ^{113}Cd MAS NMR experiment. We have recorded the ^{113}Cd MAS spectrum at six different rotation speeds and we found that the obtained η values resulted within a range of $\pm 5\%$. It follows that, to account for both source of errors, the inaccuracy in η has to be somewhat bigger than $\pm 5\%$, even though we can not provide an estimation of the error associated to the use of the Herzfeld-Berger procedure. It turns out that alternative assignments may then be possible for the peaks showing small differences in their η values.

Magnesium Substitution for Cadmium in β' -TCdP. The ^{31}P MAS NMR spectra of tricadmium phosphate at magnesium substitutions for cadmium of 8 and 16 atom % are reported in Figure 6 and show two broad ^{31}P absorptions centered at the

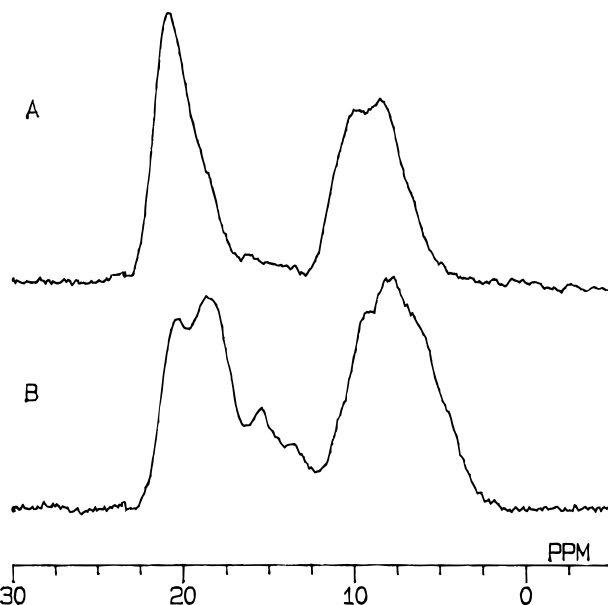


Figure 6. ^{31}P MAS NMR spectrum of β' -TCdP substituted with magnesium: (a) 8 atom%; (b) 16 atom %. Sample spinning rate 5.0 kHz; number of scans 4.

averaged chemical shifts of the two groups of resonances of β' -TCdP, respectively. Thus the partial substitution of cadmium by magnesium ions causes the collapse of the ^{31}P chemical shifts from the original six sharp resonances in two broad absorptions, as a result of an overall disordering of the crystal structure with respect to that of β' -TCdP. ^{31}P MAS NMR spectra recorded at -30 and -60 °C of magnesium substituted tricadmium phosphate samples do not show substantial differences with respect to the room temperature pattern reported in Figure 6, thus confirming that the nature of the disorder is static and not dynamic.

(18) Haerberlen, U. High Resolution NMR in Solids—Selective Averaging. In *Advances in Magnetic Resonance*; Academic Press: New York, London, 1976; Suppl. 1, p. 9.

The NMR results are in agreement with the X-ray data showing that magnesium substitution for cadmium disrupts the supercell of β' -TCdP, causing a reduction of the c -axis to $1/3$ and, as a consequence, of the number of crystallographically independent phosphate groups and metal ions from six to two (namely P'(1) and P'(2)) and from nine to three, respectively. The occupancy factors of cadmium indicates that magnesium substitutes randomly over the three cationic sites. Among the two crystallographically independent phosphate groups in the magnesium substituted samples, one group (that we will call P'(2)) exhibit C_{3v} symmetry with a longer P–O distance and three shorter ones. The apparent bond deformation is due to the exceptional anisotropy of the electron density of the three oxygen atoms at shorter distances, which is a consequence of the random distribution of magnesium in the cation sites.

The comparison of the cationic environments of the crystallographically independent phosphate groups in magnesium substituted tricadmium phosphate⁶ with the phosphate groups in β' -TCdP allows the assignment of the resonance at about 8 ppm to P'(2) and the one centered at 19.5 ppm to P'(1). In fact, the cationic environment of P'(2) is similar to those of P(4), P(5), and P(6) of β' -TCdP, which display eight or nine Cd–O contacts and where the polyhedron of at most one cadmium atom shares one edge with the phosphate tetrahedron. On the other hand the environment of P'(1) is more similar to those of P(1), P(2) and P(3), since the tetrahedron shares four edges with four cadmium polyhedra and displays 11 Cd–O contacts. We did not rely upon the summed bond strengths methods to make an assignment because the anomalous short distances of three of the oxygen atoms surrounding P'(2) lead to an overestimation of the bond strengths at oxygen atoms.

The ^{113}Cd MAS NMR spectra of tricadmium phosphate containing 8 and 16 magnesium atom % exhibit a very broad signal centered at 100 ppm ($\Delta\nu_{1/2} = 2850$ Hz) and do not allow the distinction of the three crystallographically independent metal atoms (Figure 7). The collapse of cadmium resonances

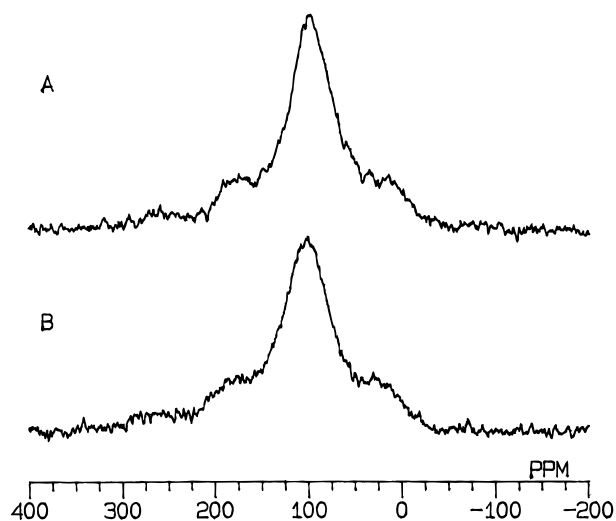


Figure 7. ^{113}Cd MAS NMR spectrum of β' -TCdP substituted with magnesium: (a) 8 atom %; (b) 16 atom %. Sample spinning rate 4.80 kHz; 900 scans; pulse delay 60 s.

in just one broad signal must be related to the disorder induced by the presence of magnesium into the structure, whereby all the independent metal atoms are surrounded by at least two exceptionally anisotropic oxygen atoms.

In summary we think that the results herein reported strongly support the involvement of solid state NMR techniques in the structural elucidation of phosphate salts. Furthermore we have shown that a relationship between structural data and spectral pattern may be drawn not only in terms of the correspondence between the number of resonances and crystallographically independent sites, but also through the assignment of a chemical shift value to a specific atom in a crystal.

IC950462R