A 2D ^{31}P MAS NMR Study of Polycrystalline Cd$_3$(PO$_4$)$_2$

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Abstract: It is demonstrated on a polycrystalline powder sample of Cd$_3$(PO$_4$)$_2$, given a known single-crystal X-ray structure, that two-dimensional ^{31}P double-quantum single-quantum MAS correlation experiments allow unique assignment of multiple ^{31}P resonances to specific P sites in the structure of such inorganic orthophosphates. The eigenvalues of the ^{31}P and ^{113}Cd shielding tensors of Cd$_3$(PO$_4$)$_2$ are reported, the determination of which requires usage of a 2D MAS spinning sideband separation experiment.

Introduction

In terms of solid-state ^{31}P NMR, most crystalline orthophosphates M$_x$(PO$_4$)$_y$ have in common a relatively small spread of ^{31}P shielding anisotropies, resulting from minor distortions of the PO$_4$$^{3-}$ moiety from perfect tetrahedral T_d symmetry in the crystal structure. Usually these deviations from tetrahedral symmetry are such that no *unique* assignment of individual ^{31}P resonances in ^{31}P MAS spectra of polycrystalline powders to specific crystallographic P sites is possible: neither based on isotropic chemical shifts δ_{iso} ^{31}P nor from consideration of the anisotropy of ^{31}P shielding. Owing to relatively small ^{31}P shielding tensors for crystalline orthophosphates, in conjunction with typical (multiple) next-nearest neighbor P−P distances of ca. 370−500 pm in the three-dimensional M$_x$(PO$_4$)$_y$ structure and the high gyromagnetic ratio and the 100% natural abundance of ^{31}P, determination of meaningful ^{31}P shielding tensor principal components for such crystalline solids M$_x$(PO$_4$)$_y$ requires the careful choice of suitable experimental ^{31}P NMR conditions. Here we report on a new ^{31}P double-quantum (2Q) MAS NMR experiment for the unique assignment of ^{31}P resonances to specific crystallographic P-sites and on the application of a two-dimensional (2D) experiment, suitable to obtain ^{31}P shielding tensor components for cases with multiple ^{31}P resonances. Because of its known structure, the compound chosen for this study is Cd$_3$(PO$_4$)$_2$ (**1**): it is important to obtain chemical shielding information for unambiguously assigned crystallographic sites in *known* structures. There is no simple, reliable, or generally applicable relationship between structural properties and chemical shielding, and studies on compounds such as **1** can provide well-defined experimental data for further use in, for instance, *ab initio* calculations of chemical shielding parameters. In particular, for many inorganic compounds it is of practical importance to be able to obtain such data from polycrystalline powder samples since only very rarely will single crystals suitable for NMR work be available.

Experimental Section

Sample Preparation. Cd$_3$(PO$_4$)$_2$, **1**, was made from a finely ground mixture of reagent grade CdCl$_2$ and (NH$_4$)$_2$HPO$_4$ in a molar ratio of 3:2. This mixture was pelleted and heated in a platinum crucible at 800 °C in air for 16 h. The reaction produces **1** and liberates NH$_4$Cl and HCl. The reaction product was examined by powder X-ray diffraction in order to estimate the amount of non 3:2 cadmium−phosphates present. After adding the required small amounts of the appropriate reactant to adjust the composition to pure Cd$_3$(PO$_4$)$_2$, the reaction was repeated until the the reaction product was found to be pure **1**, both by means of powder X-ray diffraction and ^{31}P MAS NMR.

Solid-State NMR Measurements. The single pulse ^{31}P MAS spectrum was recorded on a Bruker MSL 300 spectrometer operating at 121.5 MHz. The $\pi/2$ pulse duration was 3.0 μs, and 16 transients with a relaxation delay of 30 s were accumulated. The 44.4-MHz single-pulse ^{113}Cd MAS spectrum was obtained on a Bruker MSL 200 spectrometer. A pulse duration of 2 μs (36°) was used, and the relaxation delay was 30 s.

The ^{31}P 2Q spectrum was obtained on a Bruker ASX 500 spectrometer at a Larmor frequency of 202.5 MHz with a 4 mm MAS probe. The spinning frequency was 14 652 Hz, stabilized to within ±3 Hz. 2Q coherences were excited by using the C7 sequence by Lee *et al.*[1] The 2π-pulse durations were set to 9 μs and the phases were adjusted by a combined digital/analogue phase shifter with the digital part shifting the $2\pi/7$ phase increments within 1.5 μs and the analogue part shifting the $n \cdot \pi/2$ increments within <0.2 μs. The duration of the exciting pulse sequence was set to 8 rotor periods ($t_{exc} = 8T_R = 546$ μs). After evolution during t_1, 2Q coherences were reconverted by using the exciting pulse sequence with an overall constant phase shift of $\pi/2$ to achieve time reversal. Before the read pulse, a dephasing delay (t_d) of 50 ms was introduced to remove residual transverse magnetization. The selected phase cycle allowed the detection of a pure 2Q signal after $4n$ transients. One hundred and ninety-six t_1 increments with eight transients were applied.

The 66.6-MHz ^{113}Cd 2D PASS spectrum was recorded on a Bruker ASX 300 spectrometer with a $\pi/2$ pulse duration of 5.0 μs; 243 transients spaced by relaxation delays of 60 s were accumulated. In order to obtain a sufficient number of sidebands, a spinning frequency of 2500 Hz was chosen. The delays between the π pulses were calculated according to Antzutkin *et al.*[2] The 202.5-MHz ^{31}P 2D PASS spectrum was obtained on a Bruker DSX 500 spectrometer with use of a $\pi/2$ pulse duration of 2.2 μs, a relaxation delay of 45 s, and a spinning frequency of 1500 Hz.

Isotropic chemical shifts are given with respect to external H$_3$PO$_4$ (0 ppm) (^{31}P) and to solid Cd(NO$_3$)$_2$·4H$_2$O (−100.0 ppm) (^{113}Cd), respectively.

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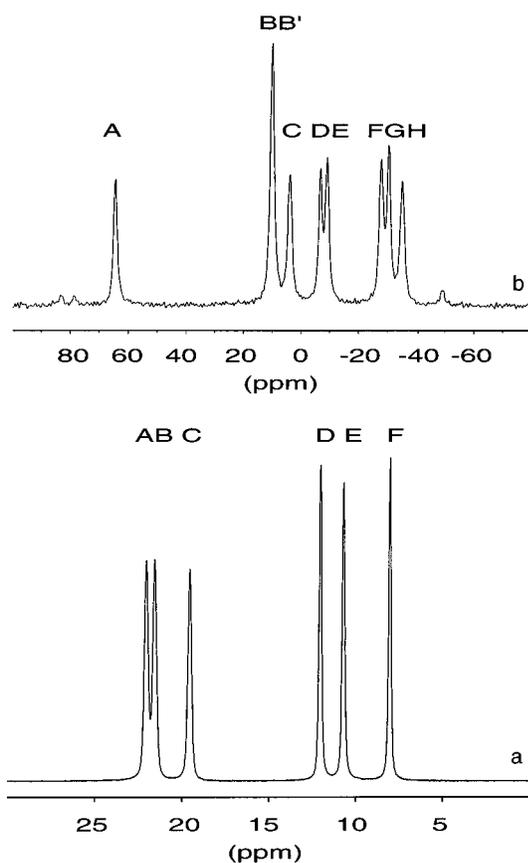[⊗] Abstract published in *Advance ACS Abstracts,* April 1, 1997.

(1) Lee, Y. K.; Kurur, N. D.; Helmle, M.; Johannessen, O. G.; Nielsen, N. C.; Levitt, M. H. *Chem. Phys. Lett.* **1995,** *242,* 304.
(2) Antzutkin, O. N.; Shekar, S. C.; Levitt, M. H. *J. Magn. Reson. A* **1995,** *115,* 7.

Figure 1. The 121.5-MHz ^{31}P (a) and 44.4 MHz ^{113}Cd (b) MAS NMR spectra of $Cd_3(PO_4)_2$. The MAS frequencies were 9 and 5 kHz, respectively.

Results and Discussion

The single-crystal X-ray structure of $Cd_3(PO_4)_2$, **1**, has been reported;[3] the structure is monoclinic with space group $P2_1/c$. There are six crystallographically independent P sites and nine independent Cd sites in the asymmetric unit. How this is reflected in the ^{31}P and ^{113}Cd MAS spectra of **1** is shown in Figure 1.

The six P sites give rise to six completely resolved ^{31}P resonances, while only eight resolved ^{113}Cd resonances result from the nine independent Cd sites in the structure of **1**. It is impossible to uniquely assign these resonances to the respective crystal sites from consideration of empirical parameters such as δ_{iso} ^{31}P, ^{113}Cd. Inspection of the single-crystal X-ray data of **1** reveals that the three-dimensional PO_4^{3-} distribution in **1** is characterized by the specific interatomic P—P distances reported in Table 1.

For instance, the shortest P—P distances (<400 pm) are between P2 and P3 and between P1 and P1, respectively. A set of distance connectivities with P—P distances in the range 400—410 pm connects P1—P5, P2—P4, P3—P6, and P6—P6. All P sites have several further neighbored P sites within a radius of 500 pm. If we wish to assign the six ^{31}P resonances A—F in the ^{31}P MAS spectra of **1** to the six crystallographic P sites P1—P6, we have to employ a ^{31}P MAS NMR experiment, which faithfully reproduces this distance-connectivity network. The magnitude of dipolar coupling constants D strongly depends on internuclear distances r ($D \propto r^{-3}$), hence the NMR interaction to be exploited for this purpose is homonuclear ^{31}P—^{31}P dipolar coupling.

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

(4) Gottwald, J.; Demco, D. E.; Graf, R.; Spiess, H. W. *Chem. Phys. Lett.* **1995**, *243*, 314.

Table 1. Distance Connectivities in the PO_4^{3-} Structure of $Cd_3(PO_4)_2$, **1**, within a Radius of 500 pm from Each Individual P Site[a]

P sites	P1	P2	P3	P4	P5	P6
P1	383	475	482	470 494	476 408	
P2	475		370 455	408	488	485
P3	482	370 455		480	484	489 407
P4	470 494	408	480	500		491
P5	476 408	488	484		480	489
P6		485	489 407	491	489	

[a] Numbering scheme P1—P6 follows the numbering scheme given for the X-ray crystal stucture;[3] mutual distances are given in pm.

Scheme 1. 2Q—1Q Correlation Experiment with the C7 Pulse Sequence[1] for 2Q Excitation and Reconversion[a]
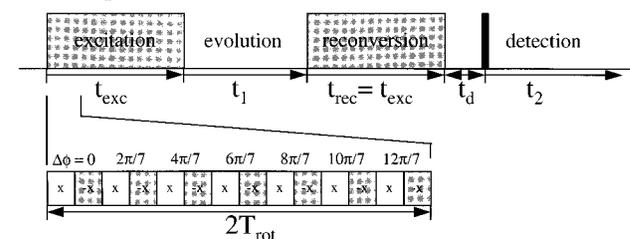
[a] The 2Q-evolution period t_1 is incremented in steps of T_{rot}.

2Q MAS NMR methods are a suitable approach to obtain such distance connectivities,[4-6] with the efficiency of the 2Q excitation being dependent on the magnitude of the respective dipolar coupling constant. The pulse sequence used to excite (and to reconvert) 2Q coherences should effect homonuclear recoupling under MAS conditions with high efficiency; the efficiency of the 2Q excitation should be insensitive to differences in isotropic and anisotropic chemical shifts. Several methods for achieving homonuclear recoupling under MAS conditions have been described in the literature.[7-18] Recently, a pulse sequence C7, fulfilling these criteria of efficient and broadbanded 2Q excitation properties for powder samples under MAS conditions, has been introduced.[1] These properties render C7 a well-suited basic building block for a two-dimensional (2D) ^{31}P 2Q—1Q correlation MAS experiment as is shown in Scheme 1.

(5) Feike, M.; Demco, D. E.; Graf, R.; Gottwald, J.; Hafner, S.; Spiess, H. W. *J. Magn. Reson A* **1996**, *122*, 214.

(6) Feike, M.; Graf, R.; Schnell, I.; Jäger, C.; Spiess, H. W. *J. Am. Chem. Soc.* **1996**, *118*, 9631.

(7) Gullion, T.; Vega, S. *Chem. Phys. Lett.* **1992**, *194*, 423.

(8) Bennett, A. E.; Ok, J. H.; Griffin, R. G.; Vega, S. *J. Chem. Phys.* **1992**, *96*, 8624.

(9) Nielsen, N. C.; Creuzet, F.; Griffin, R. G.; Levitt, M. H. *J. Chem. Phys.* **1992**, *96*, 5668.

(10) Sodickson, D. K.; Levitt, M. H.; Vega, S.; Griffin, R. G. *J. Chem. Phys.* **1993**, *98*, 6742.

(11) Tycko, R.; Smith, S. O. *J. Chem. Phys.* **1993**, *98*, 932.

(12) Tycko, R. *J. Am. Chem. Soc.* **1994**, *116*, 2217.

(13) Nielsen, N. C.; Bildsoe, H.; Jakobsen, H. J.; Levitt, M. H. *J. Chem. Phys.* **1994**, *101*, 1805.

(14) Zhu, W.; Klug, C. A.; Schaefer, J. *J. Magn. Reson. A* **1994**, *108*, 121.

(15) Weintraub, O.; Vega, S.; Hoelger, Ch.; Limbach, H. H. *J. Magn. Reson. A* **1994**, *109*, 14.

(16) Sun, B.-Q.; Costa, P. R.; Kocisko, D.; Lansbury, P. T.; Griffin, R. G. *J. Chem. Phys.* **1995**, *102*, 702.

(17) Geen, H.; Titman, J. J.; Gottwald, J.; Spiess, H. W. *J. Magn. Reson. A* **1995**, *114*, 264.

(18) Gregory, D. M.; Mitchell, D. J.; Stringer, J. A.; Kiihne, S.; Shiels, J. C.; Callahan, J.; Mehta, M. A.; Drobny, G. P. *Chem. Phys. Lett.* **1995**, *246*, 654.
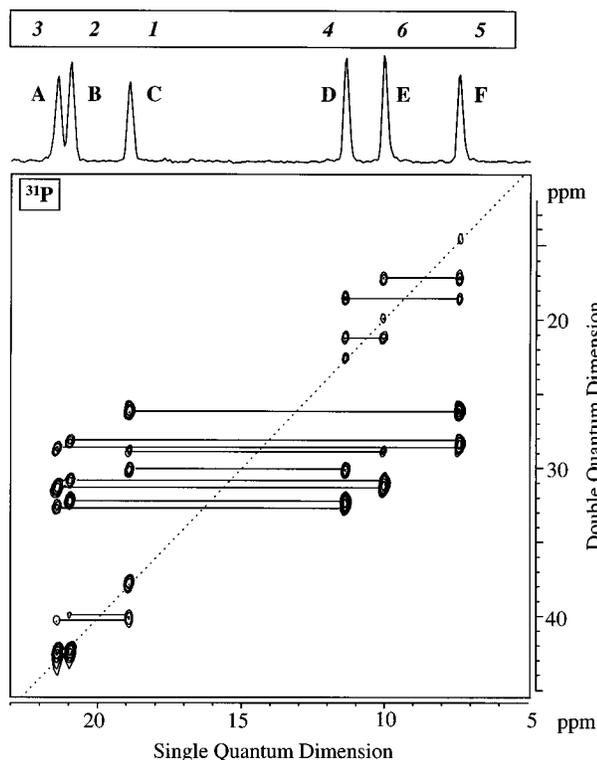
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Figure 2. High-resolution ^{31}P 2Q spectrum of Cd$_3$(PO$_4$)$_2$ correlated to the 1Q dimension. The 2Q coherences between the six different resonances A−F are indicated. The numbers assigned to the ^{31}P resonances refer to the crystallographic P sites as given in the single-crystal X-ray structure investigation by Bigi *et al.*[3]

A rotorsynchronized C7 2Q excitation period is followed by a rotorsynchronized evolution period t_1, before a second rotorsynchronized C7 block is used for reconversion of 2Q coherences. After a dephasing delay (t_d) of suitable duration, a $\pi/2$ read pulse is followed by data acquisition in t_2. Timing and phase cycling requirements for the C7 sequence are also given in the original report on this pulse sequence.[1] The result of this 2D 2Q−1Q correlation ^{31}P MAS experiment on **1** is shown in Figure 2.

The F2 projection in Figure 2, corresponding to the 1Q ^{31}P MAS spectrum of **1**, is labeled with the assignment of the ^{31}P resonances A−F to the crystallographic P sites P1−P6 as derived from inspection of the 2Q−1Q correlation pattern in comparison with the distance connectivities from the X-ray structure (see Table 1). The strongest "self-correlation" along the diagonal is found for ^{31}P C, identifying C as P1 in the structure. C is also strongly correlated with F, hence ^{31}P F = P5 in the structure. The strongest correlation is between A and B, so that ^{31}P A/B can be assigned to the shortest P−P distance, namely P2−P3. C = P1 is more strongly correlated with D than with E, allowing assignment of ^{31}P D to P4. Since D is more strongly correlated with B than with A, it is clear that ^{31}P B = P2 and ^{31}P A = P3. This leaves ^{31}P E to be assigned to P6. This assignment of all ^{31}P resonances for **1** from purely qualitative inspection of Figure 2 is fully confirmed by quantitative analysis of further 2D ^{31}P zero-quantum spin-diffusion MAS experiments[19] on **1**.[20] Note that unique assignment of resonances to specific crystallographic sites would otherwise only be possible from NMR experiments on oriented single crystals.
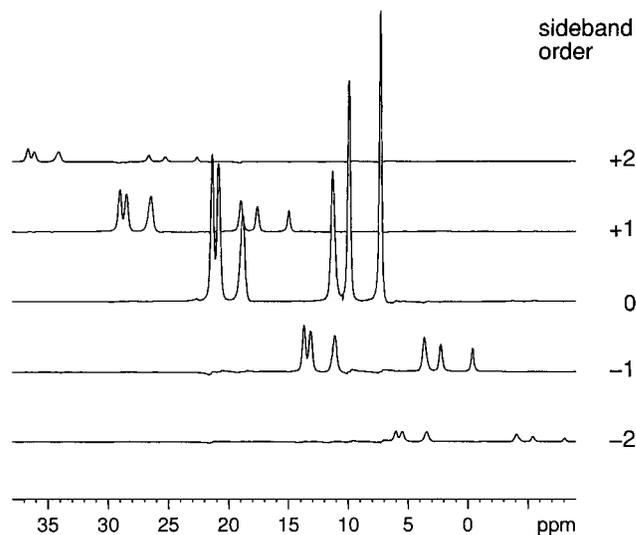
Figure 3. Stack plot of the 202.5-MHz ^{31}P 2D PASS spectrum of Cd$_3$(PO$_4$)$_2$.

Now that all ^{31}P resonances A−F of **1** have been assigned to the six independent crystallographic P sites P1−P6, it is desirable to precisely determine the ^{31}P shielding tensor components for these six resonances. In this way also empirical relationships between local geometries and bond strength arguments derived from diffraction data and δ_{iso} and/or the eigenvalues of the ^{31}P shielding tensors can be probed.[21] As mentioned above, the determination of the principal components of the ^{31}P shielding tensors for **1** presents two problems. First, the presence of multiple sites will lead to overlap problems in sufficiently slow spinning ^{31}P MAS spectra. Second, and more importantly, the small ^{31}P shielding tensors for the PO$_4{}^{3-}$ moiety at common magnetic field strengths of up to 7 T would require very low MAS frequencies of only a few hundred hertz in order to obtain a sufficient number of spinning sidebands for analysis of the spinning sideband patterns. In this very slow spinning MAS regime, however, it is no longer possible to ignore the contribution of homonuclear ^{31}P dipolar coupling to the line shape. This orthophosphate ^{31}P MAS NMR problem has also been pointed out in the literature where single-crystal NMR experiments[22] or the use of ^{31}P multiple pulse MAS (CRAMPS)[23] methods have been proposed as a remedy. Both methods are not generally applicable, in particular not for cases with multiple PO$_4{}^{3-}$ sites. Combining the use of very high external magnetic field strengths with a ^{31}P 2D sideband separation MAS experiment[2] eliminates both problems also for cases with multiple PO$_4{}^{3-}$ sites. Working at very high B_0 produces sufficiently intense spinning sideband patterns for determination of the principal components of the ^{31}P shielding tensors at MAS frequencies where contributions from homonuclear dipolar coupling may be safely ignored. For **1** also under those high-field MAS conditions there is severe overlap in the 1D ^{31}P MAS spectra, preventing spinning sideband analysis. The 2D PASS experiment,[2] which separates spinning sidebands by order, removes this overlap problem. In brief, the sideband separation is achieved by a judicious choice of timing of five π-pulses over one rotor period as a function of t_1 increments.[2] Since only a small number of spinning sidebands occurs in the ^{31}P MAS spectra of **1**, a fairly small number of t_1 increments is sufficient to achieve sideband separation. The stack plot of a

(19) Baldus, M.; Tomaselli, M.; Meier, B. H.; Ernst, R. R. *Chem. Phys. Lett.* **1994**, *230*, 329.
(20) Dusold, S.; Kümmerlen, J.; Schaller, T.; Sebald, A.; Dollase, W. A. *J. Phys. Chem.* Submitted for publication.

(21) Aime, S.; Digilio, G.; Gobetto, R.; Bigi, A.; Ripamonti, A.; Roveri, N.; Gazzano, M. *Inorg. Chem.* **1996**, *35*, 149.
(22) Eichele, K.; Wasylishen, R. E. *J. Chem. Phys.* **1994**, *98*, 3108.
(23) Harris, R. K.; Jackson, P.; Wilkes, P. J.; Belton, P. S. *J. Magn. Reson.* **1987**, *73*, 178.

Table 2.   ^{31}P MAS NMR Data for **1**[a]

crystallogr position	[31]P resonance	δ_{iso} [31]P (ppm)	σ_{11} (ppm)	σ_{22} (ppm)	σ_{33} (ppm)	η
P3	A	22.0	−34	−23	−9	0.85
P2	B	21.5	−33	−22	−9	0.88
P1	C	19.5	−34	−19	−5	1.00
P4	D	12.0	−23	−12	0	0.92
P6	E	10.6	−19	−11	−2	0.93
P5	F	7.9	−14	−9	−1	0.72

[a] Haeberlen's notation[25] is used to report shielding tensor components: $\delta_{iso} = -\sigma_{iso}$; $|\sigma_{33} - \sigma_{iso}| \geq |\sigma_{11} - \sigma_{iso}| \geq |\sigma_{22} - \sigma_{iso}|$; $\eta = (\sigma_{22} - \sigma_{11})(\sigma_{33} - \sigma_{iso})^{-1}$.
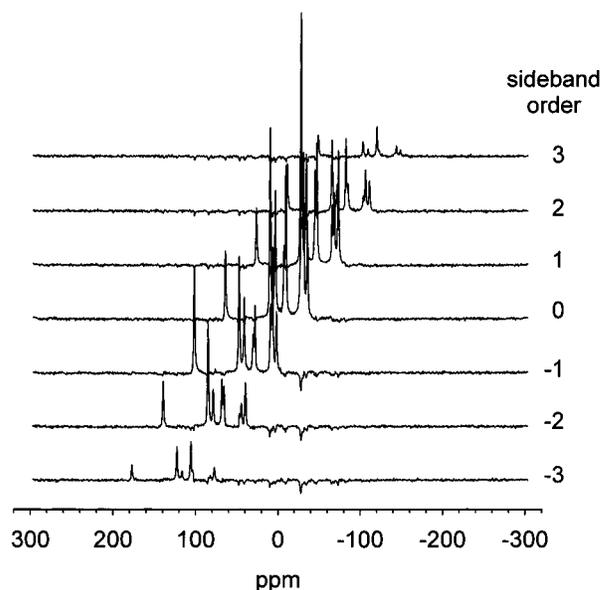
202.5-MHz [31]P 2D PASS experiment on **1** is shown in Figure 3. From the 2D PASS experiment the integrated intensities of each individual spinning sideband manifold of all six ^{31}P resonances can now be obtained free of overlap problems, and thus the principal shielding tensor components can be determined in the usual manner.[24] Table 2 lists the eigenvalues of the shielding tensors of all six ^{31}P resonances A−F determined from this experiment.

Similar considerations apply with respect to the determination of the [113]Cd shielding tensor components for **1**: while crowding and overlap in 1D [113]Cd MAS spectra of **1** is more severe than in the ^{31}P MAS spectra, it is not necessary to consider unwanted interference of homonuclear [113]Cd dipolar coupling. The [113]Cd shielding anisotropies are more expressed than for ^{31}P, so that a [113]Cd 2D PASS experiment on **1** at $B_0 = 7$ T and with a MAS frequency of 2.5 kHz is an appropriate choice of experimental conditions (which also ensure that heteronuclear [31]P−[113]Cd dipolar interactions need not be taken into account). Figure 4 displays a stack plot of this [113]Cd 2D PASS experiment on **1**, and the eigenvalues of the [113]Cd shielding tensors of **1** are given in Table 3. The [113]Cd shielding tensor eigenvalues determined from this 2D PASS experiment are in considerable disagreement with previously reported data on **1**,[21] which had been obtained from 1D [113]Cd MAS spectra with only very few and low-intensity spinning sidebands.

Conclusions

High-resolution multiple-quantum NMR spectroscopy is shown to be an applicable tool for the assignment of resonances to specific crystallographic sites in inorganic solids of complex known X-ray crystal structure, such as $Cd_3(PO_4)_2$. Assignments from this two-dimensional 2Q−1Q correlation experiment take advantage of the chemical-shift resolution in the fast MAS regime. In addition to the qualitative inspection of a single 2D spectrum such as that we have described here, the 2Q intensities are supposed to depend on the mutual internuclear distances in a more quantitative manner.

It is further demonstrated that ^{31}P spinning sideband intensities, unaffected by homonuclear dipolar couplings and overlap problems, and suitable to extract ^{31}P shielding tensor eigenvalues

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

(25) Haeberlen, U. High Resolution NMR in Solids. Selective Averaging. In *Adv. Magn. Reson., Suppl. 1* 1976.

Figure 4. Stack plot of the 66.6-MHz [113]Cd 2D PASS spectrum of $Cd_3(PO_4)_2$.

Table 3.   [113]Cd MAS NMR Data of **1**[a]

[113]Cd resonance	δ_{iso} [113]Cd (ppm)	σ_{11} (ppm)	σ_{22} (ppm)	σ_{33} (ppm)	η
A	64.5	−175	−88	70	0.65
B, B′	10.1	77	21	−128	0.48
C	3.8	79	12	−102	0.68
D	−6.8	144	47	−177	0.57
E	−9.1	80	33	−86	0.49
F	−27.9	−25	24	85	0.87
G	−30.5	−41	4	128	0.46
H	−35.1	122	61	−78	0.54

[a] Haeberlen's notation[25] is used to report shielding tensor components; see Table 2.

for solid orthophosphates, are obtained from ^{31}P PASS experiments at high B_0 and sufficiently high MAS frequencies. As in the case of ^{31}P, consideration of [113]Cd chemical shift tensor parameters alone (obtained by means of a [113]Cd PASS experiment) does not allow unique assignment of the [113]Cd resonances to the respective Cd sites in the structure of $Cd_3(PO_4)_2$. However, based on the full assignment of all six ^{31}P resonances from the above described two-dimensional [31]P 2Q−1Q MAS correlation experiment, it is now possible to exploit selective [31]P−[113]Cd double resonance MAS NMR experiments in order to also assign the [113]Cd resonances to the crystallographic Cd sites in **1**; results of such [31]P−[113]Cd double-resonance experiments will be reported elsewhere.[20]