DALTON
FULL PAPER

# Synthesis and characterization of two new cadmium phosphonocarboxylates $Cd_2(OH)(O_3PC_2H_4CO_2)$ and $Cd_3(O_3PC_2H_4CO_2)_2 \cdot 2H_2O$ †

**Florence Fredoueil,[a] Michel Evain,[b] Dominique Massiot,[c] Martine Bujoli-Doeuff,[b] Pascal Janvier,[a] Abraham Clearfield[d] and Bruno Bujoli *[a]**

[a] *Laboratoire de Synthèse Organique, UMR CNRS 6513, 2 Rue de la Houssinière, BP92208, 44322 Nantes Cedex 03, France. E-mail: bujoli@chimie.univ-nantes.fr*
[b] *Institut des Matériaux Jean Rouxel, UMR CNRS 6502, 2 Rue de la Houssinière, BP92208, 44322 Nantes Cedex 03, France*
[c] *CRMHT UPR CNRS 4212, 1D Avenue de la Recherche Scientifique, 45071 Orléans Cedex 02, France*
[d] *Department of Chemistry, Texas A&M University, College Station, Texas 77843, USA*

***Received 9th November 2001, Accepted 21st January 2002***
***First published as an Advance Article on the web 6th March 2002***

The coordination chemistry of 2-carboxyethylphosphonic acid with cadmium salts is described, leading to two new pillared layered phosphonates that were fully characterized using $^{31}P$ and $^{113}Cd$ solid state NMR spectroscopy. A densely packed arrangement is observed for $Cd_2(OH)(O_3PC_2H_4CO_2)$, exhibiting structural features uncommon in metal phosphonates: a triply bridging OH, a (222) connectivity for the $PO_3$ groups and a mixed 5-fold and 6-fold coordination for the metal.

## Introduction

The field of metal phosphonates has grown very large,[1] with various examples of applications,[2] among which catalysis has retained a particular interest for our group.[3] Since our pioneering work showing that the access to pillared layered phosphonates is not restricted to the use of bis-phosphonic acids but is also possible starting from functional phosphonic acids, namely $H_2O_3P–R–Z$ [Z = $NH_2$, $CO_2H$],[4] many metal phosphonocarboxylates have been reported.[5] The coordination chemistry of functional phosphonic acids is indeed of great interest because it offers a possible route for the construction of robust metal–organic frameworks with permanent porosity, potentially applicable for example in catalysis, gas and liquid separations or organic molecule sorption. This strategy is a good complement to other studies involving organic polycarboxylates as secondary building units[6] since the richness of the coordination mode of the $PO_3$ units permits access to comparatively new types of architectures. In this study, we report the synthesis of two new cadmium phosphonocarboxylates $Cd_2(OH)(O_3PC_2H_4CO_2)$ (**1**) and $Cd_3(O_3PC_2H_4CO_2)_2 \cdot 2H_2O$ (**2**) with two major goals: (*i*) as the two main building blocks forming the inorganic framework in cadmium phosphonates (Cd and $PO_3$) contain NMR-observable nuclei, it was interesting to know if solid state NMR gives access to detailed structural information in such compounds, (*ii*) we were also expecting the coordination behaviour of 2-carboxyethylphosphonic acid with cadmium to be different from the well-documented case of zinc, owing to the effect of size, considering the radius of $Cd^{2+}$ compared to $Zn^{2+}$.

## Experimental

### Materials and methods

All starting materials were purchased from Aldrich Chemical Co. and were used as received. The chemical analyses were performed by the C.N.R.S. Analysis Laboratory (Vernaison). FTIR spectra were obtained in the 500–4000 $cm^{-1}$ range, on a Bruker Vector22 FT-IR spectrometer using KBr pellets containing *ca.* 2% of the sample. A Perkin-Elmer TGS2 thermogravimetric analyzer was used to obtain TGA thermograms, that were run in an air atmosphere from room temperature to 250 °C at a scan rate of 5 °C $min^{-1}$. Nuclear magnetic resonance solid state $^{31}P$ and $^{113}Cd$ spectra have been acquired on a Bruker DSX300 spectrometer operating at 7.0 T, using CP-MAS $\{^1H\}$-$^{31}P$ and $\{^1H\}$-$^{113}Cd$ excitation, as previously described[7] with typical contact time of 1.5 ms and 1 s recycle time. Spectra were simulated using a modified version of the Bruker Winfit program.[8]

### X-Ray data collection

**Structure determination of $Cd_2(OH)(O_3PC_2H_4CO_2)$ (1).** Step-scanned X-ray powder data for the sample were collected at ambient temperature on the finely ground sample introduced into a quartz capillary (0.3 mm diameter). The X-ray source was the X7a beam at the National Synchrotron Light Source (Brookhaven National Laboratory, USA) with a double Si(111) crystal monochromator ($\lambda$ = 0.79904(1) Å). The sample was rotated to reduce preferred orientation. Data were collected between 2 and 66° in $2\theta$ with a step size of 0.005°. The powder pattern was indexed by the TREOR program[9] on the basis of the first 20 observed lines. The best solution which indexed all the peaks indicated a monoclinic cell with lattice parameters $a$ = 10.67 Å, $b$ = 6.67 Å, $c$ = 5.02 Å, $\beta$ = 103.37°. The systematic absences were consistent with the space group $P2_1/m$.

---

† Electronic supplementary information (ESI) available: main crystallographic data, position and equivalent isotropic displacement parameters and bond lengths and angles for $Cd_2(OH)(O_3PC_2H_4CO_2)$. See http://www.rsc.org/suppdata/dt/b1/b110275n/

DOI: 10.1039/b110275n

**Structure refinement for $Cd_2(OH)(O_3PC_2H_4CO_2)$.** The raw pattern data were transferred to the GSAS program package.[10a] The powder pattern was refined with the Le Bail technique using the following parameters: unit cell constants, scale factor, background (shifted Chebyshev function, 12 variables), profile (pseudo-Voigt with Finger–Cox–Jephcoat asymmetry: 6 variables including line width, strain broadening, sample shift, and FCJ asymmetry). Integrated intensities were extracted from the profile over the range $2° < 2\theta < 66°$. A direct methods calculation was then computed using this data set in the SHELXTL V5.0 program.[11] The position of the Cd, P, O (except O(5)) and C atoms were derived from this calculation and refined with soft constraints. No constraints were applied to either Cd–O bonds or O ··· O nonbonded distances in the cadmium polyhedra. In the initial stages of refinement, the P–O and P–C bond distances were held to 1.53(2) and 1.80(2) Å, respectively. The phosphonate groups were constrained to the tetrahedral geometry by giving appropriate values for O ··· O (2.53(2) Å) and O ··· C (2.73(2) Å) nonbonded contacts. The carbon–carbon distances in the alkyl chains were constrained to a distance of 1.50(2) Å. To obtain constraint on the bond angles, the distances between the two atoms bonded to the carbon whose angle is to be constrained were held to values of 2.46(2) Å (for C ··· C) and 2.69(2) Å (for P ··· C). Constrained refinement of the carboxyl moieties was carried out by assigning a value of 1.30(1) Å for the C–O bonds and 2.22(2) Å for the O ··· O nonbonded distance. A Fourier-difference map was used to find the remaining oxygen O(5). Neutral atomic scattering factors were used for all atoms. A correction was made for the preferred orientation effect by using the March–Dollase model[10b] implemented in the GSAS suite of programs. The diffraction vector in the present case is along the *a** axis. The refined parameter was the ratio (0.907) of the effect along this axis to that along the perpendicular plane. No correction was made for absorption effects. The cadmium atoms were refined anisotropically, all others isotropically. The positions of the hydrogen atoms of the alkyl chains were introduced in calculated position (C–H: 1.07 Å). The weight of the constraints was progressively reduced as the refinement progressed and finally completely removed in the last stage (except for the C–H bond lengths). The final cycle of refinement, based upon 66 variable parameters for 1288 reflections, smoothly converged with agreement factors of $R_p = 0.045$, $wR_p = 0.040$, and $R(F^2) = 0.024$. A final Rietveld refinement plot is given in Fig. 1. Selected bond distances and angles are listed in Table 1.

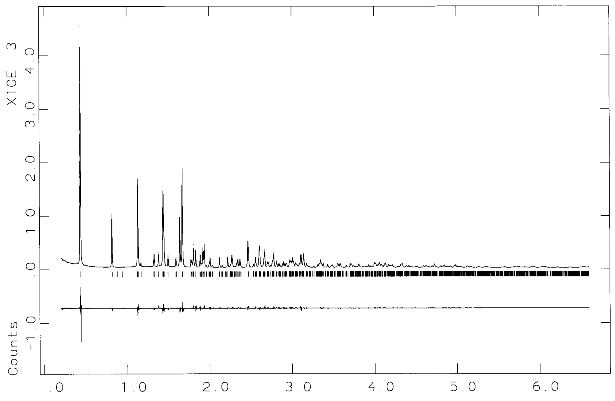

**Fig. 1** Observed (•) and calculated (−) profiles for the Rietveld refinement of $Cd_2(OH)(O_3PC_2H_4CO_2)$. The difference plot is on the same intensity scale.

**Crystallographic data.** $Cd_2(OH)(O_3PC_2H_4CO_2)$, monoclinic $P2_1/m$; $a = 10.6650(1)$, $b = 6.66527(5)$, $c = 5.02277(5)$ Å, $\beta = 103.3372(6)°$, $V = 347.416(6)$ Å$^3$, $Z = 2$, $M = 392.86$.

CCDC reference number 169517.

**Table 1** Selected bond lengths (Å) and angles (°) for the non-hydrogen atoms in $Cd_2(OH)(O_3PC_2H_4CO_2)$

| | | | |
|---|---|---|---|
| Cd(1)–O(2)$^a$ | 2.299(6) | Cd(2)–O(3)$^e$ | 2.244(4) |
| Cd(1)–O(3)$^a$ | 2.192(5) | Cd(2)–O(5)$^f$ | 2.369(4) |
| Cd(1)–O(4) | 2.192(5) | Cd(2)–O(5)$^b$ | 2.369(4) |
| Cd(1)–O(5)$^a$ | 2.256(5) | P–O(1) | 1.536(5) |
| Cd(1)–O(5)$^b$ | 2.256(4) | P–O(5)$^d$ | 1.551(4) |
| Cd(2)–O(1)$^c$ | 2.288(4) | P–O(5)$^g$ | 1.551(4) |
| Cd(2)–O(1)$^d$ | 2.288(4) | P–C(2) | 1.812(5) |
| Cd(2)–O(3) | 2.244(4) | | |
| | | | |
| O(2)$^a$–Cd(1)–O(3)$^a$ | 90.8(2) | O(1)$^c$–Cd(2)–O(3)$^e$ | 98.5(2) |
| O(2)$^a$–Cd(1)–O(4) | 86.2(2) | O(1)$^d$–Cd(2)–O(3) | 98.5(2) |
| O(2)$^a$–Cd(1)–O(5)$^a$ | 113.1(1) | O(1)$^c$–Cd(2)–O(5)$^f$ | 95.6(2) |
| O(2)$^a$–Cd(1)–O(5)$^b$ | 113.1(1) | O(1)$^d$–Cd(2)–O(5)$^b$ | 95.6(2) |
| O(3)$^a$–Cd(1)–O(4) | 177.1(2) | O(1)$^c$–Cd(2)–O(5)$^b$ | 84.4(2) |
| O(3)$^a$–Cd(1)–O(5)$^a$ | 96.4(1) | O(1)$^d$–Cd(2)–O(5)$^f$ | 84.4(2) |
| O(3)$^a$–Cd(1)–O(5)$^b$ | 96.4(1) | O(3)–Cd(2)–O(3)$^e$ | 180.0(2) |
| O(4)–Cd(1)–O(5)$^a$ | 84.7(1) | O(3)–Cd(2)–O(5)$^f$ | 91.0(2) |
| O(4)–Cd(1)–O(5)$^b$ | 84.7(1) | O(3)$^e$–Cd(2)–O(5)$^b$ | 91.0(2) |
| O(5)$^a$–Cd(1)–O(5)$^b$ | 131.7(2) | O(3)–Cd(2)–O(5)$^b$ | 89.0(2) |
| O(1)$^c$–Cd(2)–O(1)$^d$ | 179.9(2) | O(3)$^e$–Cd(2)–O(5)$^f$ | 89.0(2) |
| O(1)$^c$–Cd(2)–O(3) | 81.5(2) | O(5)$^f$–Cd(2)–O(5)$^b$ | 180.0(2) |
| O(1)$^d$–Cd(2)–O(3)$^e$ | 81.5(2) | | |

Atom related by: $^a$ $x, y, -1 + z$; $^b$ $2x, -y, -1 + 2z$; $^c$ $-1 + x, y, -1 + z$; $^d$ $1 - x, -1/2 + y, 1 - z$; $^e$ $-x, -1/2 + y, -z$; $^f$ $-x, -1/2 + y, 1 - z$; $^g$ $1 - x, 1 - y, 1 - z$.

### Synthesis of $Cd_2(OH)(O_3PC_2H_4CO_2)$ (1)

A mixture of cadmium nitrate (1 mmol), 2-carboxyethylphosphonic acid (1 mmol) and DABCO (3 mmol) in 15 mL water was placed in the PTFE cell of an autoclave, which was sealed and kept at 170 °C in a drying oven for 2 weeks. **1** was obtained as a white crystalline powder that was collected by filtration, washed with water and acetone and dried at room temperature (yield: 97%). IR (KBr, cm$^{-1}$) 3011 (m), 1540 (vs), 1449 (m), 1401 (m), 1321 (m), 1069 (s), 1035 (vs), 978 (s). TGA: no weight loss within the 25–300 °C range. Found: P, 7.70; C, 9.32; H, 1.30. Calc. for $Cd_2PO_6C_3H_5$: P, 7.88; C, 9.17; H, 1.28%.

### Synthesis of $Cd_3(O_3PC_2H_4CO_2)_2\cdot 2H_2O$ (2)

A mixture of cadmium nitrate (1 mmol), 2-carboxyethylphosphonic acid (1 mmol) and DABCO (1 mmol) in 15 mL water was placed in the PTFE cell of an autoclave, which was sealed and kept at 170 °C in a drying oven for 5 days. **2** was obtained as a white crystalline powder that was collected by filtration, washed with water and acetone and dried at room temperature (yield: 85%). IR (KBr, cm$^{-1}$) 3488 (m), 1546 (vs), 1413 (s), 1399 (s), 1102 (m), 1051 (s), 1025 (vs), 1007 (s), 980 (s). TGA room temperature to 300 °C, 5.1% weight loss between 40 and 130 °C [$-2H_2O$, calculated 5.3%]. Found: P, 8.99; C, 10.88; H, 1.88. Calc. for $Cd_3P_2O_{12}C_6H_{12}$: P, 9.17; C, 10.67; H, 1.79%. XRD: $a = 8.7928(6)$ Å, $b = 9.5002(7)$ Å, $c = 9.1846(7)$ Å, $\beta = 113.614(2)°$.

## Results

### Crystal structure of $Cd_2(OH)(O_3PC_2H_4CO_2)$ (1)

The crystal packing is presented in Fig. 2 and 3, showing a pillared layered structure (stacking axis: *a*). In the middle of each slab (*bc* plane), half of the Cd atoms [Cd(2)] are octahedrally coordinated by four oxygen atoms of phosphonate groups and two hydroxo units. The second type of Cd sites [Cd(1)] corresponds to a trigonal bipyramid made up of two phosphonate oxygen atoms, one hydroxo group and two oxygen atoms coming from carboxyethyl chains of the upper and lower layers. The carboxylate units are linking two distinct Cd(1) atoms according to a bridging mode. In this structure, two

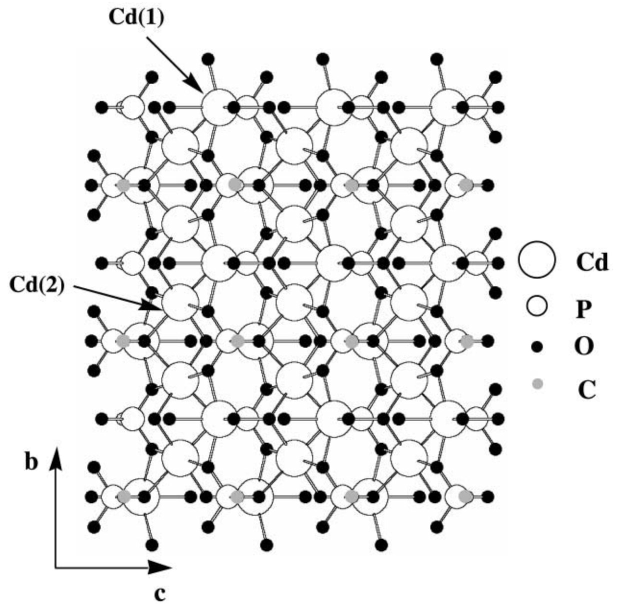

**Fig. 2** Schematic representation of a layer of $Cd_2(OH)(O_3PC_2H_4CO_2)$ as seen perpendicular to the *a* axis. The carbon atoms that are not bound to phosphorus have been omitted for clarity.

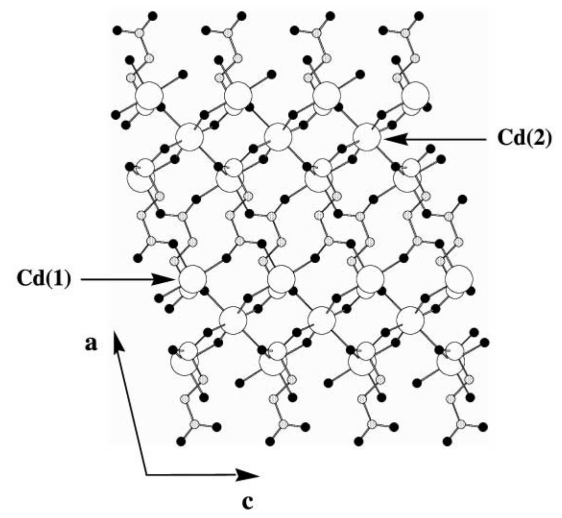

**Fig. 3** Schematic representation of the pillared layered arrangement in $Cd_2(OH)(O_3PC_2H_4CO_2)$ viewed down the *b* axis.

important features are noteworthy: (*i*) the three phosphonate oxygen atoms are each bridging two adjacent cadmium atoms, leading to the first example of a (222) $PO_3$ connectivity ever observed in metal phosphonates, (*ii*) the hydroxo groups exhibit a triply bridging geometry [2 Cd(2) and 1 Cd(1)] that is somewhat uncommon.

## Discussion

Various zinc 2-carboxyethylphosphonates have been reported showing 3-D arrangements comprised of inorganic layers pillared by the functional phosphonic acid units: $Zn_3(O_3PC_2H_4CO_2)_2$, $Zn(O_3PC_2H_4CO_2H)\cdot 1.5H_2O$ and $Zn_3(O_3PC_2H_4CO_2)_2\cdot 3H_2O$.[4a,12] One common feature in these three products is the presence of zinc atoms, at least partially, in a tetrahedral geometry. Such coordination for cadmium (due to its size) is highly unlikely. An overview of the literature shows that examples of cadmium phosphonates are relatively limited, with one layered structure $Cd(O_3PR)\cdot H_2O$ [R = $CH_3$, $C_6H_5$],[13] one pillared layered structure $Cd(O_3PC_2H_4NH_2)$[14] and one 1-D polymeric network ($Cd_4$(**1**$NH\cdot H_2O)_3(H_2O)_6(NO_3)_4)(NO_3)$ [macrocyclic leaflets with **1**$NH_2$ = *N*-(phosphonomethyl)-aza-18-crown-6].[15] In all cases, the cadmium atoms were found to occupy only octahedral sites, except for the latter compound where one 7-coordinate cadmium site is also present. For this reason, some new structural types were expected to arise from the reaction of 2-carboxyethylphosphonic acid with cadmium salts. According to the experimental conditions two new compounds, $Cd_2(OH)(O_3PC_2H_4CO_2)$ (**1**) and $Cd_3(O_3PC_2H_4CO_2)_2\cdot 2H_2O$ (**2**), have been obtained and isolated, both as polycrystalline products. Despite all our efforts however, all attempts to refine the structure of (**2**) from its X-ray powder diffraction pattern failed. Nevertheless, the FTIR spectrum of (**2**) [$\nu_{C\text{–}O}$ 1546 cm$^{-1}$] clearly shows that the carboxylate moiety is coordinated to cadmium, suggesting again a pillared layered structure as in the case of (**1**). The coordination of the carboxylic acid units is consistent with our previous experience in the zinc series that showed that the only way to achieve layered compounds with non-coordinated $CO_2H$ groups was to perform the synthesis in organic solvents mixed with water (*e.g.* 5% water in acetone).[4a] Solid state $^{113}$Cd NMR data of (**2**) (Fig. 4) show the presence of three resonances in a 1 : 1 : 1 ratio (at 159.8, 67.6 and 46.0 ppm) corresponding to three different cadmium sites. Attempts to correlate the $^{113}$Cd NMR parameters with the structure have been made to allow the assignment of the different metal environments.[16] From the wide range of oxo–Cd compounds examined in the solid state, Ellis[17] found a general pattern between $^{113}$Cd chemical shifts and the coordination number, where compounds with 6-coordinate Cd give shifts in the range 150 to −60 ppm whereas 7- and 8-coordinate Cd compounds give shifts in the range 0 to −60 ppm and 0 to −100 ppm, respectively. Ellis *et al.*[18] also pointed out that the isotropic shifts of the Cd–oxo compounds examined to date are not sufficiently discriminating to allow structure–shift correlations since the coordination polyhedra around the Cd ion can be very irregular. For compound (**1**) however, a clear difference is observed for the isotropic chemical shifts of $CdO_5$ (≈220 ppm) and $CdO_6$ (≈140 ppm) (Fig. 5). This assignment is in agreement with the values observed for $CdO_6$ environments in other cadmium phosphonates (Table 2; $150 < \delta_{iso} < 165$ ppm), and we can thus reasonably assume that the line observed at 159.8 ppm in compound (**2**) also corresponds to a $CdO_6$ site. The two other upfield signals suggest the presence of more distorted coordination polyhedra with strong Cd–O bonds and additional weaker interactions as reported for β′-tricadmium phosphate;[19] in this compound eight $^{113}$Cd resonances were observed in the [65–165 ppm] range for cadmium sites tightly bound to five oxygen atoms along with one or two supplementary Cd–O contacts of various lengths (2.55 to 3.1 Å). Then the chemical shift anisotropy of the P sites in compound (**2**) was determined; in fact, in the zinc phosphonate series a correlation was shown to exist between the κ parameter (indicative of the

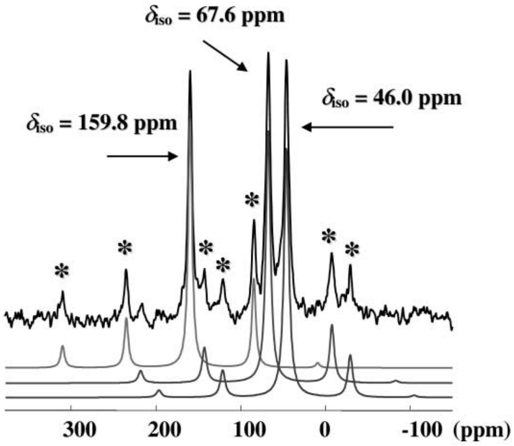

**Fig. 4** $^{113}$Cd MAS NMR spectrum (7 kHz) of $Cd_3(O_3PC_2H_4CO_2)_2\cdot 2H_2O$. Asterisks denote spinning sidebands.

**Table 2** Experimental values for $^{113}$Cd chemical shift and for $^{31}$P chemical shift tensor, for compounds (**1**) and (**2**) compared to other cadmium phosphonates from the literature

| Compound | $^{113}$Cd | $^{31}$P | $PO_3$ connectivity |
|---|---|---|---|
| $Cd_2(OH)(O_3PC_2H_4CO_2)$<br>(**1**) | $\delta_{iso}{}^a = 220.2$ ppm<br>Site 1 (50%)<br>**[$CdO_5$]**<br>$\delta_{iso}{}^a = 140.2$ ppm<br>Site 2 (50%)<br>**[$CdO_6$]** | $\delta_{iso}{}^b = 32.6$ ppm<br>$\kappa^c = -1.0$<br>$\Omega^d = 67.5$ ppm | (**222**) |
| $Cd_3(O_3PC_2H_4CO_2)_2{\cdot}2H_2O$<br>(**2**) | $\delta_{iso}{}^a = 159.8$ ppm<br>Site 1 (33%)<br>$\delta_{iso}{}^a = 67.6$ ppm<br>Site 2 (33%)<br>$\delta_{iso}{}^a = 46.0$ ppm<br>Site 3 (33%) | $\delta_{iso}{}^b = 38.7$ ppm<br>$\kappa^c = -0.5$<br>$\Omega^d = 75.0$ ppm<br>Site 1 (50%)<br>$\delta_{iso}{}^b = 34.4$ ppm<br>$\kappa^c = -0.3$<br>$\Omega^d = 88.2$ ppm<br>Site 2 (50%) | **unknown** |
| $Cd(O_3PC_2H_4NH_2)$<br>[from ref. 5] | $\delta_{iso}{}^a = 163.4$ ppm<br>**[$CdNO_5$]** | $\delta_{iso}{}^b = 27.9$ ppm<br>$\kappa^c = -0.2$<br>$\Omega^d = 115.9$ ppm | (**122**) |
| $Cd(O_3PCH_3){\cdot}H_2O$<br>[from ref. 5] | $\delta_{iso}{}^a = 151.6$ ppm<br>**[$CdO_6$]** | $\delta_{iso}{}^b = 34.4$ ppm<br>$\kappa^c = 0.0$<br>$\Omega^d = 89.4$ ppm | (**122**) |
| $Cd(O_3PC_2H_5){\cdot}H_2O$ | $\delta_{iso}{}^a = 153.4$ ppm<br>**[$CdO_6$]** | $\delta_{iso}{}^b = 37.8$ ppm<br>$\kappa^c = 0.0$<br>$\Omega^d = 62.5$ ppm | (**122**) |

[a] Chemical shifts are referenced to the $^{113}$Cd resonance in $Cd(NO_3)_2{\cdot}4H_2O$. [b] Chemical shifts are referenced to the $^{31}$P resonance in 85% $H_3PO_4$. [c] Chemical shift skew defined as $3(\delta_{22} - \delta_{iso})/\Omega$. [d] Chemical shift span defined as $\delta_{11} - \delta_{33}$ with $\delta_{11} \geq \delta_{22} \geq \delta_{33}$.

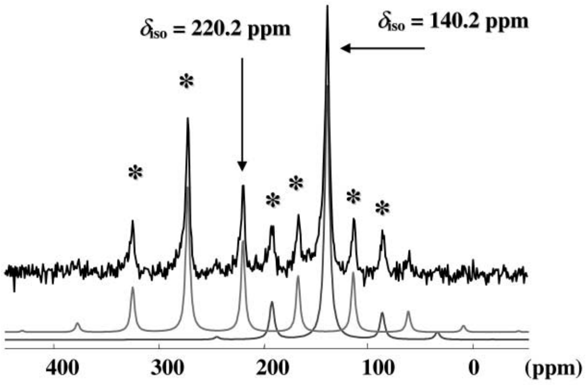

**Fig. 5** $^{113}$Cd MAS NMR spectrum (3.5 kHz) of $Cd_2(OH)(O_3PC_2H_4CO_2)$. Asterisks denote spinning sidebands.

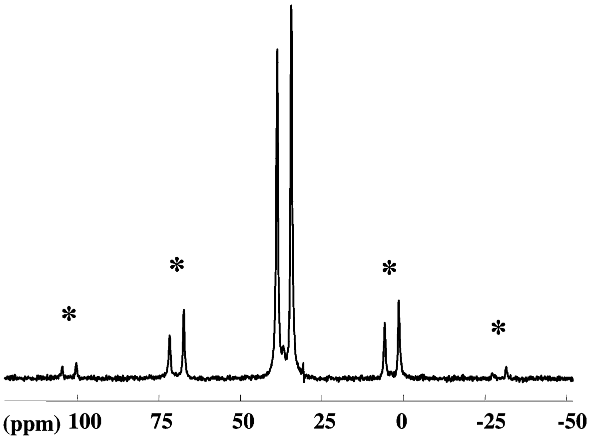

**Fig. 6** $^{31}$P MAS NMR spectrum (4 kHz) of $Cd_3(O_3PC_2H_4CO_2)_2{\cdot}2H_2O$. Asterisks denote spinning sidebands.

chemical shift asymmetry) and the connectivity of the $PO_3$ groups.[7] It was thus of interest to know if such a trend was also present in the case of the cadmium phosphonates. The data collected in Table 2 seem to indicate different ranges of variation for the $\kappa$ parameter according to the connectivity: −1.0 for a (222) coordination mode and [−0.2, 0.0] for a (122) connectivity. The $\kappa$ value observed for the two phosphorus sites present in compound (**2**) are −0.3 and −0.5 respectively (Fig. 6), the latter being notably different from that observed in the reference compounds. As the number of model cadmium phosphonates available is however very limited, no conclusive interpretation can be made about the coordination mode adopted by the $PO_3$ blocks present in compound (**2**). In addition, a two-dimensional $^{31}$P exchange experiment was performed to confirm the monophasic character of (**2**) (see Fig. 7). Two types of experiments were carried out, with and without proton decoupling during the mixing period.[20] When proton decoupling was applied, the two sites of (**2**) show up along the diagonal line. For a 250 ms mixing time, an exchange figure (off-diagonal cross peaks in the two-dimensional contour plots in which the two sites are involved) was present when proton decoupling was turned off during the mixing time. The exchange process is driven by $^1$H spin diffusion and this unambiguously shows that the two observed phosphorus species are intimately mixed at the molecular scale, thus confirming that compound (**2**) is a single phase. The chemical formula of $Cd_3(O_3PC_2H_4CO_2)_2{\cdot}2H_2O$ [$a$ = 8.7928(6) Å, $b$ = 9.5002(7) Å, $c$ = 9.1846(7) Å, $\beta$ = 113.614(2)°] is very close to that of two pillared layered zinc phosphonates: $Zn_3(O_3PC_2H_4CO_2)_2$[4a] and $Zn_3(O_3PC_2H_4CO_2)_2{\cdot}3H_2O$.[12] For the latter compound, the repeating structure unit along the layering direction is $Zn(O_3PC_2H_4CO_2)/Zn(H_2O)_3/Zn(O_3PC_2H_4CO_2)$, in which the $Zn(H_2O)_3$ units are bonded to two oxygen atoms of two carboxyl groups from two neighboring layers. This results in a large interlayer spacing (14.3 Å), ruling out any structural similitude with our compound. On the other hand, although the cell parameters of product (**2**) are close to that observed in $Zn_3(O_3PC_2H_4CO_2)_2$ [$a$ = 8.126(1) Å, $b$ = 9.237(1) Å, $c$ = 8.587(2) Å, $\beta$ = 106.26(3)°], only one phosphorus site and two zinc sites are reported in the structure of this zinc phosphonate, while the infrared spectra of the two compounds differ notably in the $PO_3$ region. For these reasons the nature of the metal/$PO_3$ arrangement in (**2**) is expected to be different from that present in $Zn_3(O_3PC_2H_4CO_2)_2$.

In conclusion, we have shown in this paper that the reaction of 2-carboxyethylphosphonic acid with cadmium salts led to

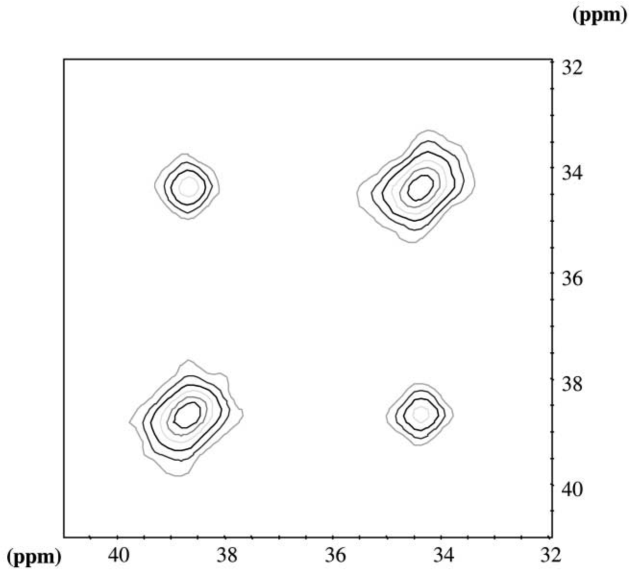

**Fig. 7** $[^{31}P]^{31}P$ proton-mediated two-dimensional MAS NMR exchange spectrum (10 kHz) of $Cd_3(O_3PC_2H_4CO_2)_2{\cdot}2H_2O$.

pillared layered structures radically different from that observed in the zinc series. This confirms that the presence of tetrahedral sites for the metal in known zinc 2-carboxyethylphosphonates is the limiting factor responsible for this phenomenon; the larger $Cd^{2+}$ (compared to $Zn^{2+}$) is not stable in such 4-fold geometry.

## References

1 See for example: A. Clearfield, in *Progress in Inorganic Chemistry*, ed. K. D. Karlin, John Wiley & Sons, Inc., New York, 1998, vol. 47, pp. 371–510.

2 See for example: (*a*) M. Graetzel, O. Kohle, M. K. Nazzeruddin, P. Pechy, F. P. Royzinger, S. Ruile and S. M. Zakeeruddin, *PCT Int. Appl.*, WO 95 29,924 (Cl. CO7F9/58), 9 Nov 1995, 52 pp.; (*b*) L. C. Brousseau III and T. Mallouk, *Anal. Chem.*, 1997, **69**, 679–687; (*c*) L. C. Brousseau III, D. J. Aurentz, J. Benesi and T. Mallouk, *Anal. Chem.*, 1997, **69**, 688–694; (*d*) G. Will, J. Sotomayor, S. N. Rao and D. Fitzmaurice, *J. Mater. Chem.*, 1999, **9**, 2297–2299; (*e*) M. J. Heeg and S. S. Jurisson, *Acc. Chem. Res.*, 1999, **32**, 1053–1060; (*f*) M. Felderhoff, S. Heinen, N. Molisho, S. Webersinn and L. Walder, *Helv. Chim. Acta*, 2000, **83**, 181–192.

3 (*a*) D. Deniaud, B. Schöllhorn, D. Mansuy, J. Rouxel, P. Battioni and B. Bujoli, *Chem. Mater.*, 1995, **7**, 995–1000; (*b*) D. Deniaud, G. A. Spyroulias, J. F. Bartoli, P. Battioni, D. Mansuy, C. Pinel, F. Odobel and B. Bujoli, *New J. Chem.*, 1998, **22**, 901–905; (*c*) V. Pénicaud, C. Maillet, P. Janvier, M. Pipelier and B. Bujoli, *Eur. J. Org. Chem.*, 1999, 1745–1748; (*d*) C. Maillet, P. Janvier, M. Pipelier, T. Praveen, Y. Andres and B. Bujoli, *Chem. Mater.*, 2001, **13**, 2879–2884; (*e*) I. O. Benitez, B. Bujoli, L. J. Camus, C. M. Lee, F. Odobel and D. R. Talham, *J. Am. Chem. Soc.*, 2002, in press.

4 (*a*) S. Drumel, P. Janvier, P. Barboux, M. Bujoli-Doeuff and B. Bujoli, *Inorg. Chem.*, 1995, **34**, 148–156; (*b*) S. Drumel, P. Janvier, D. Deniaud and B. Bujoli, *J. Chem. Soc., Chem. Commun.*, 1995, 1051–1052; (*c*) P. Janvier, S. Drumel, Y. Piffard and B. Bujoli, *C. R. Acad. Sci.,, Ser. IIb: Mec., Phys., Chim., Astron.*, 1995, **320**, 29–35; (*d*) S. Drumel, M. Bujoli-Doeuff, P. Janvier and B. Bujoli, *New J. Chem.*, 1995, **19**, 239–242.

5 (*a*) A. Distler and S. C. Sevov, *Chem. Commun.*, 1998, 959–960; (*b*) N. Stock, G. D. Stucky and A. K. Cheetham, *Chem. Commun.*, 2000, 2277–2278; (*c*) N. Stock, S. A. Frey, G. D. Stucky and A. K. Cheetham, *J. Chem. Soc., Dalton Trans.*, 2000, 4292–4296; (*d*) M. Riou-Cavellec, M. Sanselme, J. Grenèche and G. Ferey, *Solid State Sci.*, 2000, **2**, 717–724; (*e*) S. J. Hartman, E. Todorov, C. Cruz and S. C. Sevov, *Chem. Commun.*, 2000, 1213–1214; (*f*) J. Zhu, X. Bu, P. Feng and G. D. Stucky, *J. Am. Chem. Soc.*, 2000, **122**, 11563–11564 and references therein.

6 M. Eddaoudi, D. B. Moler, H. Li, B. Chen, T. M. Reineke, M. O'Keeffe and O. M. Yaghi, *Acc. Chem. Res.*, 2001, **34**, 319–330.

7 D. Massiot, S. Drumel, P. Janvier, M. Bujoli-Doeuff and B. Bujoli, *Chem. Mater.*, 1997, **9**, 6–7.

8 D. Massiot, F. Fayon, M. Capron, I. King, S. Le Calvé, B. Alonso, J. Durand, B. Bujoli, Z. Gan and G. Hoatson, *Magn. Reson. Chem.*, 2002, **40**, 70–76.

9 P. E. Werner, L. Erikson and M. J. Westdahl, *J. Appl. Crystallogr.*, 1985, **18**, 367.

10 (*a*) A. Larson and R. B. von Dreele, *GSAS: Generalized Structure Analysis System*, Los Alamos National Laboratory, Los Alamos, NM, 1985; (*b*) W. A. Dollase, *J. Appl. Crystallogr.*, 1986, **19**, 267.

11 G. M. Sheldrick, SHELXTL V5.0, Analytical X-ray Instruments Inc., Madison, WI, USA, 1995.

12 G. Cao, L. K. Rabenberg, C. M. Nunn and T. E. Mallouk, *Chem. Mater.*, 1991, **3**, 149–156.

13 G. Cao, V. M. Lynch and L. N. Yacullo, *Chem. Mater.*, 1993, **5**, 1000–1006.

14 F. Fredoueil, D. Massiot, P. Janvier, F. Gingl, M. Bujoli-Doeuff, M. Evain, A. Clearfield and B. Bujoli, *Inorg. Chem.*, 1999, **38**, 1831–1833.

15 C. V. K. Sharma and A. Clearfield, *J. Am. Chem. Soc.*, 2000, **122**, 1558–1559.

16 M. F. Summers, *Coord. Chem. Rev.*, 1988, **86**, 43–134.

17 P. D. Ellis, *Science*, 1983, **221**, 1141–1146.

18 R. S. Honkonen, P. S. Marchetti and P. D. Ellis, *J. Am. Chem. Soc.*, 1986, **108**, 912–915.

19 S. Aime, G. Digilio, R. Gobetto, A. Bigi, A. Ripamonti, N. Roveri and M. Gazzano, *Inorg. Chem.*, 1996, **35**, 149–154.

20 K. W. Schmidt-Rohr and H. Spiess, *Multidimensional Solid-State NMR and Polymers*, Academic Press, New York, 1994.