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Structural characterization of $\text{Cd}_3(\text{O}_3\text{PC}_2\text{H}_4\text{CO}_2)_2 \cdot 2\text{H}_2\text{O}$ from in-house X-ray powder data and NMR

The title compound poly[[bis(μ -2-carboxylatoethylphosphonato)cadmium] dihydrate], $\text{Cd}_3(\text{O}_3\text{PC}_2\text{H}_4\text{CO}_2)_2 \cdot 2\text{H}_2\text{O}$, was prepared by a hydrothermal reaction and its crystal structure determined from in-house powder data. The structure was solved in both $P2_1/c$ and $P2_1$ space groups. The refinement converged with $R_p = 0.1046$, $R_{wp} = 0.1378$ and $R_f = 0.0763$ in $P2_1/c$. However, the solid-state NMR data could not be explained. The structure was then solved in $P2_1$ and the refinement converged with $R_p = 0.0750$, $R_{wp} = 0.1022$ and $R_f = 0.0409$ and satisfied the NMR requirements.

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1. Introduction

Metal phosphonates are often obtained as crystalline powders and their structures are determined *ab initio* utilizing in-house or synchrotron data. The space-group determination is one of the most sensitive steps in the structure determination from powder data. The selection of the space group is usually accomplished through examination of the systematic absences of reflections. In powder diffraction, this process is complicated owing to the overlap of reflections, especially at higher angles, and to the background noise-to-signal ratio, since some of the reflections can be hidden by the background. This can lead to ambiguous space-group determination; in such cases the structure should be attempted using each possible space group to determine which is the most correct. Physical characterization techniques such as solid-state NMR are also very useful to determine the correctness of the structure and may help in choosing the correct space group. An example is provided in the cadmium phosphonate structure determined here where NMR data was used to determine the correct space group.

Metal phosphonates have been extensively studied because of their potential applications in catalysis (Clearfield, 1996, 1998*a*, 2002; Sharma & Clearfield, 2000; Sharma *et al.*, 2001; Clearfield & Wang, 2002; Maillet *et al.*, 2001), ion exchange (Alberti, 1996; Alberti *et al.*, 1997, 1999; Clearfield, 1984, 1988, 1995), proton conductivity (Alberti *et al.*, 1992; Bujoli *et al.*, 1990; Le Bideau *et al.*, 1994; Fredoueil *et al.*, 1998; Odobel *et al.*, 2001; Stein *et al.*, 1996), gas and liquid separations (Riou *et al.*, 1998, 2000; Riou & Ferey, 1998; Serpaggi & Ferey, 1998; Adair *et al.*, 2001), biology (Nonglaton *et al.*, 2004), and organic molecule sorption (Clearfield & Wang, 2002; Yang, 1986; Clearfield, 1998*b*). The choice of the ligand is very important to accomplish the desired properties. Several examples of cadmium phosphonates were published in the literature by Cao *et al.* (1988), Sun *et al.* (2003), Clearfield *et al.* (2001) (see Mao & Clearfield, 2002; Mao *et al.*, 2002; Cabeza *et al.*, 2002) and Bujoli *et al.* (1990) (see Fredoueil *et al.*, 1999,

2002). These structures are generally layered and the Cd atom is five-, six- or seven-coordinated.

In a previous paper Fredoueil *et al.* (2002) presented the synthesis and physical properties of $\text{Cd}_2(\text{OH})(\text{O}_3\text{PC}_2\text{H}_4\text{CO}_2)$ and $\text{Cd}_3(\text{O}_3\text{PC}_2\text{H}_4\text{CO}_2)_2 \cdot 2\text{H}_2\text{O}$ ($\text{Cd}_3\text{L}_2 \cdot 2\text{H}_2\text{O}$). The solid-state NMR spectra provided detailed structural information of these compounds, but only the structure of the first compound was determined; the second structure could not be solved at that time. In this paper we present the crystal structure of $\text{Cd}_3(\text{O}_3\text{PC}_2\text{H}_4\text{CO}_2)_2 \cdot 2\text{H}_2\text{O}$ determined *ab initio* from the X-ray powder diffraction pattern.

2. Structure solution

The compound was synthesized as described by Fredoueil *et al.* (2002). A mixture of cadmium nitrate (1 mmol), 2-carboxyethylphosphonic acid (1 mmol) and bicyclo(2,2,2)-1,4-diazaoctane (DABCO, 1 mmol) in 15 ml of water was kept in a Teflon-lined pressure vessel at 443 K for 5 d. The white crystalline powder which was collected by filtration, washed with water and acetone and dried at room temperature (yield: 85%) was characterized as being $\text{Cd}_3\text{L}_2 \cdot 2\text{H}_2\text{O}$.

The structure was determined from in-house X-ray data (Fig. 1). The X-ray source was a rotating anode with a copper target operating at 50 kV and 180 mA, and equipped with a graphite monochromator. Quantitative intensity data were collected using a Rigaku computer-automated diffractometer operating in the step scan reflection mode using 0.5° divergence and scattering slits; the step size was 0.01° in 2θ for each data set. For cell indexing the $K\alpha_2$ contribution was stripped from the data using the program *powderX* (Dong, 1998) to achieve higher resolution; however, this information was

included in the structure solution and refinement. The data were recorded between 5 and 95° in 2θ , with a step size of 0.01° and a count time of 30 s per step.

The cell parameter determination was made using the *Treor90* program (Werner *et al.*, 1985). The indexing yielded the cell dimensions $a = 9.1812$ (28), $b = 9.4989$ (20), $c = 8.8798$ (18) Å, $\beta = 113.58$ (2) $^\circ$ and $V = 702.55$ Å³ as the best solution [M (20) = 35]. The structure was first determined in $P2_1/c$ based upon the systematic absences. The refinement of the structure converged with $R_p = 0.1046$, $R_{wp} = 0.1378$ and $R_f = 0.0763$. However, several problems remained:

- (i) not all the water molecules could be detected;
- (ii) only two types of Cd atoms were located, one in a general position and one in a special position;
- (iii) one of the carboxyl O atoms was disordered.

Such sitting would require two resonances in the NMR spectrum in a 2:1 ratio. The ^{113}Cd solid-state MAS NMR spectrum, shown in Fig. 2, contains three different chemical shifts in a 1:1:1 ratio corresponding to three Cd atoms in different environments with equal multiplicity factors. The ^{31}P NMR spectrum (Fig. 3) contained two distinct chemical shifts near each other, implying two P atoms that exist in slightly different environments. A finer analysis of the powder pattern allowed the localization if there was a violation to the reflection condition of $P2_1/c$ ($h0l, l = 2n$); the 103 reflection should be absent if the symmetry was $P2_1/c$, however, this reflection appears with a very low intensity (Fig. 1). The presence of this peak allowed the determination of the symmetry as $P2_1$. All the atoms were located and the structure was solved in the space group $P2_1$ and refined with the following reliability indexes $R_p = 0.0750$, $R_{wp} = 0.1022$ and $R_f = 0.0409$.

The program *EXPO* (Altomare *et al.*, 1995) was used to solve the structure. Three Cd atoms, two P atoms and most of the O atoms were localized by direct methods. The refinement strategy using the *GSAS* program (Larson & Von Dreele, 1986) consisted of a first step which involved the Le Bail-method refinement for the background (using 12 terms of a Chebychev function), zero shift, cell parameters and peak-profile function, considering a dummy H atom and maintaining a scale factor which was constant and equal to 1. Once these parameters were deemed to be satisfactory ($R_p = 0.056$) they were fixed, the known atoms were entered into the program and the scale factor refined. By successive refinement and Fourier difference maps, all the atoms were located. The following bond

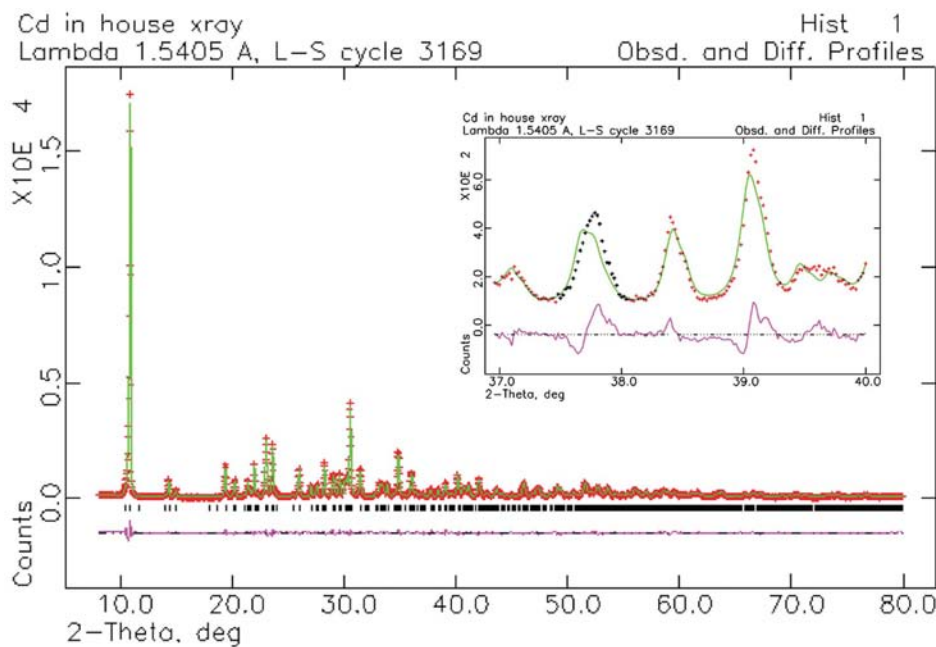


Figure 1

Observed (+), calculated (–) and difference profiles for the Rietveld refinement of $\text{Cd}_3\text{L}_2 \cdot 2\text{H}_2\text{O}$. The second peak in the insert at 37.7° in 2θ corresponds to the 212, 040 and 103 reflections shown in black.

constraints were applied: Cd—O (2.0 Å), P—O (1.52 Å), P—C (1.80 Å), C—O (1.35 Å), C—C (1.54 Å) and C—H (1.0 Å) prior to the position refinement of the atoms. The bond angles around the P atom were constrained to idealized tetrahedral angles by applying the constraints to the non-bonded O···O (2.5 Å) and O···C (2.7 Å) distances. The positions for the H atoms bonded to the C atoms were calculated and a final Fourier difference map allowed us to localize the remaining H atoms. The constraint parameter was first fixed to 500 in the initial refinement cycles and totally released in the last cycle of the refinement. The atomic positions were first refined, then the temperature factors and finally all the parameters were refined simultaneously. Fig. 1 shows the observed powder pattern, the calculated and the difference curve after the last refinement cycle.

3. Results and discussion

Table 1 presents the crystallographic data. The atomic positions have been deposited,¹ and the bond lengths and angles are represented in Table 2. Three crystallographically independent Cd atoms are coordinated to six O atoms in a distorted octahedral environment due to the bridging mode of the layers. Fig. 4 shows the connectivity of these atoms, which produces the layers. Cd1 is bonded to four O atoms from the phosphonate groups (O1 and O7 from P1; O2 and O10 from P2), one O atom (O5) from the carboxylic acid group and one water molecule (O9). Cd2 is bonded to three O atoms from the phosphonate groups (O1 and O3 from P1 and O4 from P2), two water molecules (O9 and O11) and one water from one of the carboxylic groups (O8 which is also bonded to C6). The bonding around Cd3 is very constrained due to the double bridging with P2 (O2 and O10) and C5 (O5 and O6); Cd3 is also bonded to two other O atoms from the phosphonate groups, respectively, O3 from P1 and O4 from P2. P2 and C5 are also constrained by their tetrahedral and planar geometry, respectively. There are two distinct P atoms. For P1 two of its O atoms bond to two Cd ions each, the third is bonded to only one Cd ion. In P2 two of the O atoms bridge the same Cd atom (Cd3) and are also bonded to another Cd ion (Cd1). The last O atom is bonded to Cd2 and Cd3. Each P atom is coordinated to five Cd atoms through two μ_3^- oxygen bridges and one μ_2^- bonded oxygen. This connectivity builds the layers and is similar in structure to the phosphonate-carboxylate ligands. All the O atoms; except the two water O atoms (O9 and O11), O7 (from the phosphonate group P1) and O6 (from the carboxylic group and bonded to C5), are shared by two Cd atoms simultaneously.

The structure is layered with the ligand cross-linking the layers between them (Fig. 5); one side of the layer is bridged by the phosphonate groups, the other by the carboxylic groups in an alternating fashion.

¹ Supplementary data for this paper are available from the IUCr electronic archives (Reference: BS5017). Services for accessing these data are described at the back of the journal.

Table 1

Experimental data.

Crystal data	
Chemical formula	C ₆ Cd ₃ O ₁₂ P ₂
<i>M_r</i>	663.23
Cell setting, space group	Monoclinic, <i>P</i> 2 ₁
<i>a</i> , <i>b</i> , <i>c</i> (Å)	8.7743 (3), 9.4828 (3), 9.1670 (3)
β (°)	113.609 (2)
<i>V</i> (Å ³)	698.89 (4)
<i>Z</i>	2
<i>D_x</i> (Mg m ⁻³)	3.151
Radiation type	<i>K</i> α ₁ , <i>K</i> α ₂
Temperature (K)	296
Specimen form, colour	Powder, colourless
Specimen preparation temperature (K)	296
Data collection	
Diffractometer	Rigaku RU200
Data collection method	Step scan method
2 θ (°)	2 θ _{min} = 7.56823, 2 θ _{max} = 80.14822, increment = 0.01
Refinement	
Refinement on	Full-matrix least-squares on <i>F</i> ²
<i>R</i> -factors and goodness of fit	<i>R_p</i> = 0.075, <i>R_{wp}</i> = 0.102, <i>R_{exp}</i> = 0.060, <i>S</i> = 1.89
<i>R_F</i>	0.041
Wavelength of incident radiation (Å)	1.5418
Excluded region(s)	None
Profile function	CW profile function number 4 with 21 terms†
No. of parameters	91
Weighting scheme	LOOPARRAY
(Δ/σ) _{max}	5.46

† Pseudovoigt profile coefficients as parameterized by Thompson *et al.* (1987). Asymmetry correction by Finger *et al.* (1994); microstrain broadening by Stephens (1999). #1(GU) = 64.419, #2(GV) = -24.294, #3(GW) = 5.301, #4(GP) = 0.331, #5(LX) = 0.000, #6(ptec) = 0.00, #7(trns) = 8.70, #8(shift) = 0.0000, #9(sfec) = 0.00, #10(S/L) = 0.0285, #11(H/L) = 0.0248, #12(eta) = 0.9820, #13(S400) = 2.1E-01, #14(S040) = 8.4E-02, #15(S004) = 2.7E-01, #16(S220) = 8.3E-02, #17(S202) = 3.7E-01, #18(S022) = 1.1E-01, #19(S301) = 1.7E-01, #20(S103) = 3.7E-01, #21(S121) = 3.9E-02. Peak tails are ignored where the intensity is below 0.0100 times the peak Anisotropic broadening axis: 0.0 0.0 1.0

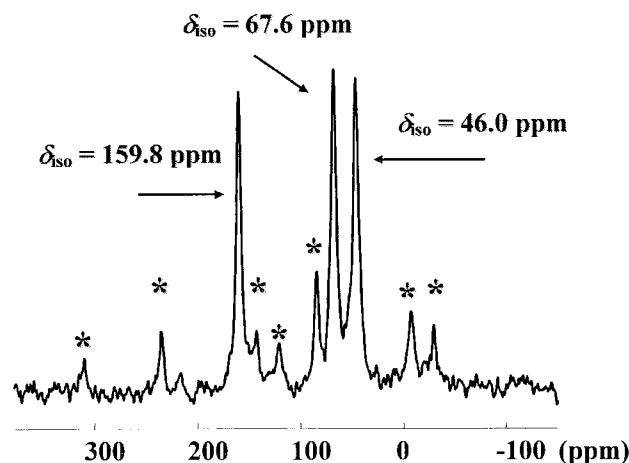


Figure 2

¹¹⁵Cd MAS NMR spectrum (7 kHz) of Cd₃(O₃PC₂H₄CO₂)₂·2H₂O as presented by Fredoueil *et al.* (2002). Asterisks denote spinning sidebands.

Table 2
Selected bond lengths (Å) and angles (°) for Cd₃L₂·2H₂O.

Cd1–O1 ⁱ	2.29 (4)	P1–O1 ⁱ	1.53 (5)
Cd1–O2 ⁱ	2.30 (4)	P1–O3	1.52 (4)
Cd1–O5 ⁱ	2.30 (4)	P1–O7	1.54 (2)
Cd1–O7 ⁱ	2.29 (3)	P1–C1 ⁱ	1.79 (5)
Cd1–O9 ⁱ	2.28 (4)	P2–O2	1.52 (5)
Cd1–O10 ⁱ	2.28 (4)	P2–O4 ⁱⁱ	1.51 (3)
Cd2–O1 ⁱⁱⁱ	2.31 (3)	P2–C2	1.80 (7)
Cd2–O3	2.30 (2)	P2–O10 ^{iv}	1.52 (3)
Cd2–O4	2.36 (3)	C1–C3	1.56 (5)
Cd2–O8	2.31 (4)	C2–C4	1.56 (7)
Cd2–O9 ⁱⁱⁱ	2.31 (3)	C3–C6 ^v	1.54 (4)
Cd2–O11 ⁱ	2.31 (3)	C4–C2	1.56 (7)
Cd3–O2	2.33 (3)	C4–C5 ^{vi}	1.54 (8)
Cd3–O3	2.31 (4)	C5–O5	1.32 (6)
Cd3–O4	2.27 (2)	C5–O6	1.35 (3)
Cd3–O5	2.30 (3)	OC5–C4 ^{vii}	1.54 (8)
Cd3–O6	2.21 (4)	C6–C3 ^{viii}	1.54 (4)
Cd3–O10 ^{iv}	2.31 (4)	C6–O8	1.38 (7)
		C6–O12 ^{vi}	1.36 (5)
O2–P2–O4 ⁱⁱ	111 (2)	O1 ⁱⁱⁱ –Cd2–O9 ⁱⁱⁱ	62.6 (6)
O2–P2–C2	109 (3)	O1 ⁱⁱⁱ –Cd2–O11 ⁱ	101 (1)
O2–P2–O10 ^{iv}	108 (2)	O3–Cd2–O4	80.2 (9)
O4 ⁱⁱ –P2–C2	110 (2)	O3–Cd2–O8	75.7 (8)
O4 ⁱⁱ –P2–O10 ^{iv}	110 (1)	O3–Cd2–O9 ⁱⁱⁱ	151 (6)
C2–P2–O10 ^{iv}	109 (2)	O3–Cd2–O11 ⁱ	87.8 (1)
O5–C5–O6	110 (2)	O4–Cd2–O8	58.3 (1)
O5–C5–C4 ^{vii}	107 (4)	O4–Cd2–O9 ⁱⁱⁱ	92.9 (9)
O6–C5–C4 ^{vii}	104 (2)	O4–Cd2–O11 ⁱ	142 (1)
O8–C6–C3 ^{viii}	105 (3)	O8–Cd2–O9 ⁱⁱⁱ	76.7 (1)
O8–C6–O12 ^{vi}	105 (3)	O8–Cd2–O11 ⁱ	83.5 (1)
C3 ^{viii} –C6–O12 ^{vi}	105 (2)	O9 ⁱⁱⁱ –Cd2–O11 ⁱ	80.2 (1)
O3–P1–C1 ⁱ	110 (2)	O2–Cd3–O3	64.8 (1)
O1 ⁱ –Cd1–O2 ⁱ	156 (9)	O2–Cd3–O4	109 (7)
O1 ⁱ –Cd1–O5 ⁱ	112 (9)	O2–Cd3–O5	80.2 (7)
O1 ⁱ –Cd1–O7 ⁱ	90.3 (1)	O2–Cd3–O6	135 (1)
O1 ⁱ –Cd1–O9 ⁱ	63.2 (7)	O2–Cd3–O10 ^{iv}	64.0 (1)
O1 ⁱ –Cd1–O10 ⁱ	86.7 (8)	O3–Cd3–O4	81.7 (9)
O2 ⁱ –Cd1–O5 ⁱ	80.8 (8)	O3–Cd3–O5	97.1 (1)
O2 ⁱ –Cd1–O7 ⁱ	69.2 (7)	O3–Cd3–O6	128 (1)
O2 ⁱ –Cd1–O9 ⁱ	104 (9)	O3–Cd3–O10 ^{iv}	110 (1)
O2 ⁱ –Cd1–O10 ⁱ	104 (1)	O4–Cd3–O5	169 (7)
O5 ⁱ –Cd1–O7 ⁱ	90.3 (9)	O4–Cd3–O6	116 (9)
O5 ⁱ –Cd1–O9 ⁱ	175 (1)	O4–Cd3–O10 ^{iv}	72.5 (1)
O5 ⁱ –Cd1–O10 ⁱ	120 (9)	O5–Cd3–O6	56.9 (1)
O7 ⁱ –Cd1–O9 ⁱ	89.7 (1)	O6–Cd3–O10 ^{iv}	123 (1)
O7 ⁱ –Cd1–O10 ⁱ	148 (1)	O5–Cd3–O10 ^{iv}	118 (1)
O9 ⁱ –Cd1–O10 ⁱ	61.0 (7)	O1 ⁱ –P1–O3	109 (2)
O1 ⁱⁱⁱ –Cd2–O3	146 (7)	O1 ⁱ –P1–O7	110 (2)
O1 ⁱⁱⁱ –Cd2–O4	110 (9)	O1 ⁱ –P1–C1 ⁱ	114 (3)
O1 ⁱⁱⁱ –Cd2–O8	137 (9)	O3–P1–O7	108 (1)
		O7–P1–C1 ⁱ	107 (2)

Symmetry codes: (i) $1-x, -\frac{1}{2}+y, 1-z$; (ii) $1-x, \frac{1}{2}+y, -z$; (iii) $x, -1+y, z$; (iv) $1-x, -\frac{1}{2}+y, -z$; (v) $-1+x, 1+y, z$; (vi) $1+x, y, z$; (vii) $-1+x, y, z$; (viii) $1+x, -1+y, z$.

In a previous paper Fredoueil *et al.* (2002) presented the solid-state NMR data for the title compound. The solid-state MAS ³¹P NMR spectrum (Fig. 3) exhibited two resonances of equal intensity at 38.7 and 34.4 p.p.m., which are attributed to P1 and P2. P1 and P2 are not bonded in the same way (Fig. 6); they exhibit two different chemical shifts as P1 is in a (2,2,1) coordination to the Cd ions and P2 is in a (2,2,2) coordination to the metal. The ¹¹³Cd NMR spectrum (Fig. 2) showed three resonances at 159.8, 67.6 and 46.0 p.p.m. in a 1:1:1 ratio, which are correlated to the three Cd ions present in the structure.

Fredoueil *et al.* (2002), in their attempt to determine the structure of the compound, mentioned the work by Ellis (1983) who tried to correlate the ¹¹³Cd NMR parameters with structure. He found that the positions of the peaks are related to Cd coordination and that for a six-coordinate Cd ion the peaks have chemical shifts in the range 150 to –60 p.p.m., for a seven-coordinate Cd ion of the order 0 to –60 p.p.m. and for an eight-coordinate Cd ion of the order 0 to –100 p.p.m. In the case of our compound the three Cd atoms are six-coordinate and the chemical shifts fall in the first interval. However, these

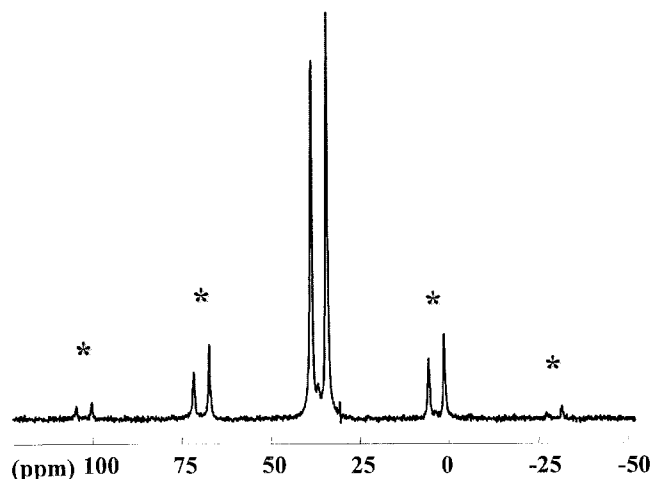


Figure 3
³¹P MAS NMR spectrum (4 kHz) of Cd₃(O₃PC₂H₄CO₂)₂·2H₂O as presented by Fredoueil *et al.* (2002). Asterisks denote spinning sidebands.

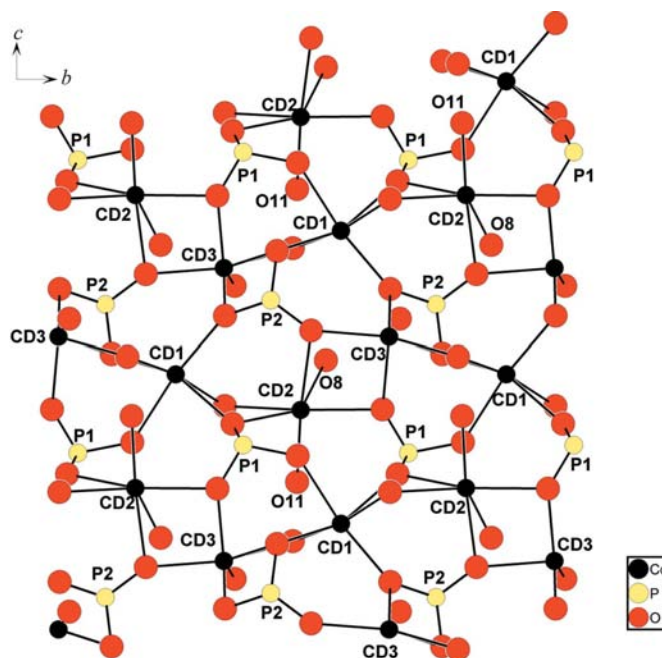


Figure 4
Ball and stick representation of the layers in Cd₃(O₃PC₂H₄CO₂)₂·2H₂O as viewed down the *a* axis.

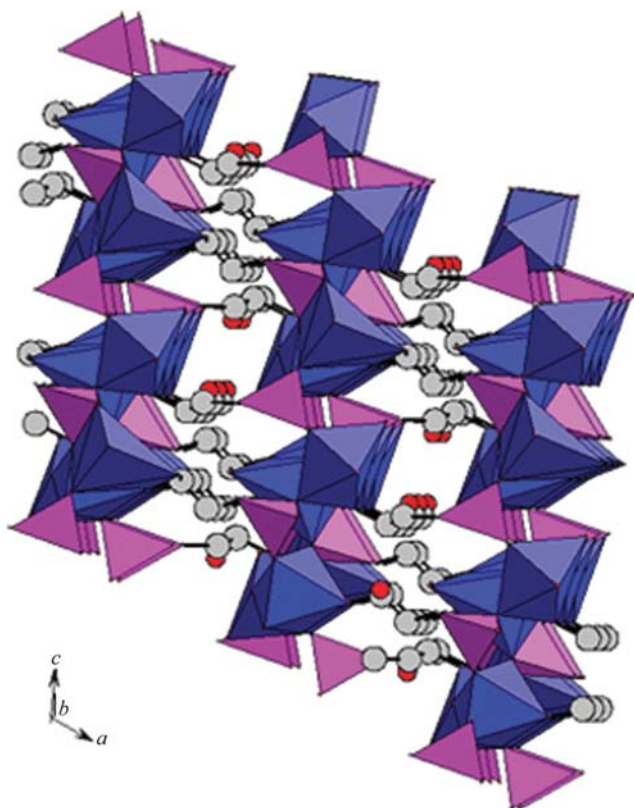


Figure 5
Polyhedral representation of the layer arrangement and cross-linking in $\text{Cd}_3\text{L}_2 \cdot 2\text{H}_2\text{O}$. The cadmium octahedra are dark grey with one face light grey, the phosphonate tetrahedra are a lighter shade of grey, the carbon connecting chains are light grey and the carboxyl oxygens darker grey than the carbons.

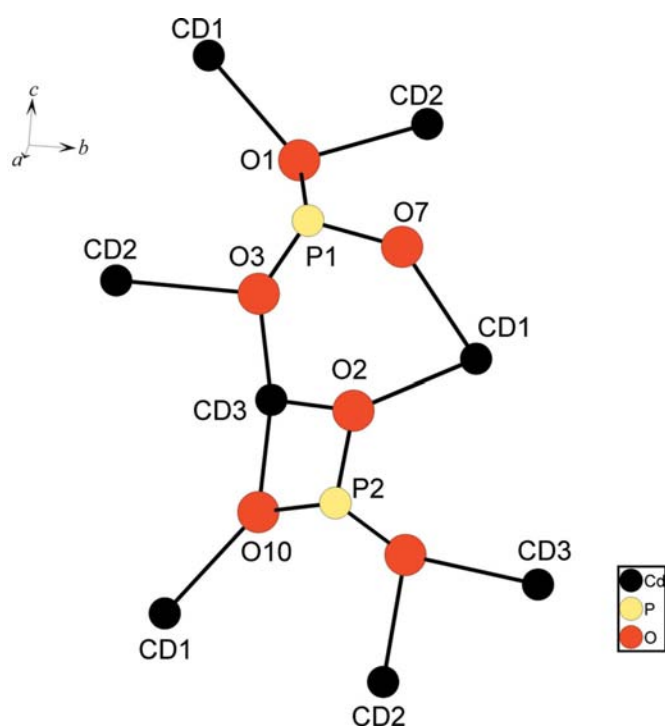


Figure 6
Connectivity of the P atoms with the three Cd atoms in a (2,2,2) type for P2 and (2,2,1) for P1.

atoms are not distorted in the same way. Aime *et al.* (1996) also reported the influence of longer and weaker bonds on Cd chemical shifts. A bond up to 3.1 Å could move the peak's chemical shift upfield. Fig. 7 shows the environment of the Cd atoms up to 3.15 Å. In the case of Cd1, an additional oxygen at 3.14 Å is observed. Cd2 has two extra weak bonds at 2.99 Å with O7 and 3.13 Å with O10. However, Cd3 does not have any additional atoms within this range. Based upon these arguments we can then assign the ^{113}Cd chemical shifts as follows: 159.8 p.p.m. corresponds to Cd3, 67.6 p.p.m. corresponds to Cd1 and 46.0 p.p.m. corresponds to Cd2. Various studies have been reported on the title ligand, in general, the reported structures are pillared where the carboxy groups bridge one of the layers and the phosphonate groups on the adjacent layer. This is the case for $\text{Mn}_3(\text{O}_3\text{P}(\text{CH}_2)_2\text{CO}_2)_2$ published by Stock *et al.* (2000), in which weak ferromagnetic and antiferromagnetic ordering was found. Zinc also shows this arrangement, in $\text{Zn}_3(\text{O}_3\text{PC}_2\text{H}_4\text{CO}_2)_2$, $\text{Zn}(\text{O}_3\text{PC}_2\text{H}_4\text{CO}_2\text{H}) \cdot 1.5\text{H}_2\text{O}$ and $\text{Zn}_3(\text{O}_3\text{PC}_2\text{H}_4\text{CO}_2)_2 \cdot 3\text{H}_2\text{O}$ (Drumel *et al.*, 1995; Cao *et al.*, 1991). In all these cases the zinc atoms are in a tetrahedral environment. In $\text{Cd}_2(\text{OH})(\text{O}_3\text{PC}_2\text{H}_4\text{CO}_2)$ (Fredoueil *et al.*, 2002), one of the Cd atoms is in a five-coordinate geometry and the other Cd atom is in a six-coordinate geometry. Carboxyethyl phosphonic acid was also reacted with aluminium and lead. The compounds obtained were $\text{Al}_3(\text{OH})_3(\text{O}_3\text{PCH}_2\text{CH}_2\text{CO}_2)_2 \cdot 3\text{H}_2\text{O}$, $\text{Pb}_5(\text{O}_3\text{PC}_2\text{H}_4\text{CO}_2)_2(\text{O}_3\text{PC}_2\text{H}_4\text{COOH})_2$ and $\text{Pb}_3(\text{O}_3\text{PC}_2\text{H}_4\text{CO}_2)_2$ (Gomez-Alcantara *et al.*, 2004). The structure of $\text{Al}_3(\text{OH})_3(\text{O}_3\text{PCH}_2\text{CH}_2\text{CO}_2)_2 \cdot 3\text{H}_2\text{O}$ was not solved but compared with $\text{Ga}_3(\text{OH})_3(\text{O}_3\text{PCH}_2\text{CH}_2\text{CO}_2)_2 \cdot 2\text{H}_2\text{O}$, which, based on ^{71}Ga and ^{31}P NMR and IR studies, suggested a very distorted GaO_6 environment, with a pillared layer structure where the organic chains are oriented perpendicular to the layers and with the carboxylate moieties coordinated to the Ga atoms. The crystal structure of $\text{Pb}_5(\text{O}_3\text{PC}_2\text{H}_4\text{CO}_2)_2(\text{O}_3\text{PC}_2\text{H}_4\text{COOH})_2$ was

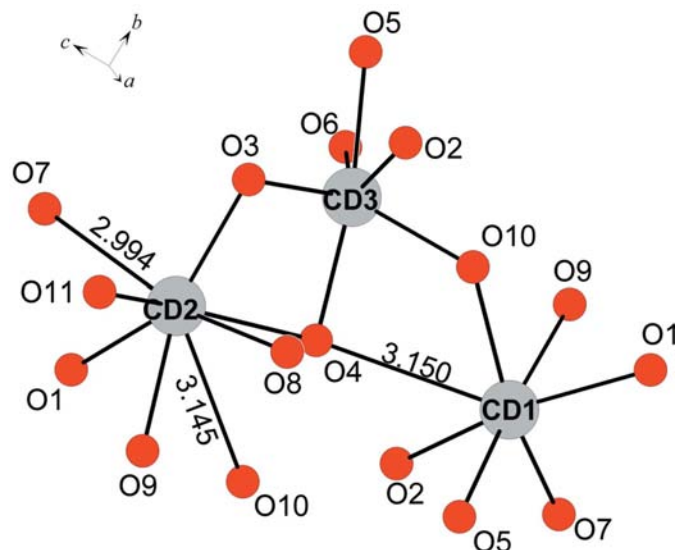


Figure 7
Oxygen environments around the Cd atoms, showing longer weaker bonds around Cd1 and Cd2.

solved from a single crystal and the structure showed three independent Pb atoms in a seven and eightfold coordination. In this case the ligand pillars two adjacent layers. $\text{Cd}_3(\text{O}_3\text{PC}_2\text{H}_4\text{CO}_2)_2 \cdot 2\text{H}_2\text{O}$ also presents the same kind of pillared structure where one layer is coordinated by the carboxylic group and the adjacent layer by the phosphonic group, as $\text{Ga}_3(\text{OH})_3(\text{O}_3\text{PCH}_2\text{CH}_2\text{CO}_2)_2 \cdot 2\text{H}_2\text{O}$. The sixfold coordination around the Cd atoms is very distorted.

4. Conclusions

The crystal structure of $\text{Cd}_3\text{L}_2 \cdot 2\text{H}_2\text{O}$ was solved in the space group $P2_1$. The structure contained three distinct Cd atoms in the octahedral environments of the O atoms and two P-atom environments, which is in accordance with the solid-state MAS NMR spectra. The required numbers of symmetrically independent Cd and P atoms in this structure can be provided only in the space group $P2_1$. Since there was just one weak reflection in violation of the requirements for the $P2_1/c$ symmetry, it was prudent to seek a solution in this space group. This is an example of how in X-ray structure determinations, especially with powder data where the space group is in doubt, one may be misled without the additional physical techniques of characterization.

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