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A Novel Cadmium Aminophosphonate: X-ray Powder Diffraction Structure, Solid-State IR and NMR Spectroscopic Determination of the Fine Structure of the Organic Moieties

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A new divalent cadmium phosphonate, $Cd_2Cl_2(H_2O)_4(H_2L)$, has been synthesized from the ethylenediamine-*N*,*N′*-bis(methylenephosphonic acid) (H_4L). The obtained microcrystalline compound has been characterized by solid-state IR spectra and ^{13}C, ^{31}P, and ^{113}Cd CP MAS NMR. The static ^{13}P NMR spectra have been also recorded to give the δ_{11}, δ_{22}, and δ_{33} chemical shift parameters for both compounds. The spectral data, collected for $Cd_2Cl_2(H_2O)_4(H_2L)$, are in an agreement with its X-ray powder diffraction structure solved with the cell dimensions $a = 16.6105(10)$, $b = 7.1572(4)$, and $c = 6.8171(4)$ Å and $\beta = 98.327(4)°$. The octahedral coordination sphere of the cadmium atoms consists of two phosphonate oxygen atoms, two water oxygen atoms, and the two chlorine atoms. Cadmium atoms are bridged by the chlorine atoms forming four-membered rings. The phosphorus atoms exhibit a tetrahedral coordination with two oxygen atoms bonded to the cadmium atoms with P–O distances of 1.503(10) and 1.504(10) Å. The third oxygen atom, showing a longer P–O distance (1.546(9) Å), is not bonded to the metal center, nor is it bonded to a proton. The combined IR and NMR proton–phosphorus cross-polarization kinetic data together with the X-ray data confirm that the cadmium phosphonate has the zwitterionic structure ($NH_2^+CH_2P(O_2Cd_2)O^-$) similar to the initial aminophosphonic acid H_4L.

Introduction

The chemistry of layered metal phosphates and phosphonates is undergoing rapid expansion because of their potential activity in catalysis and ion exchange.[1−3] For this reason, a great number of these compounds have been prepared in the past decade.[2,4−10] Among them, there are organic−inorganic exchangers based upon the α-zirconium phosphate structure.[11] Another group of interesting zirconium aminophosphonates has been reported to behave as anion exchangers.[3,12] Great interest has been attracted by metal phosphonates derived from aminobis- and trisphosphonic acids.[13] The diphosphonic acids with diamino groups attached to phosphonic moieties are known to be good chelating agents. In fact the complexing ability of ethylenediamine-*N*,*N′*-bis(methylenephosphonic acid) (H_4L) with different metal cations in solution has recently been demonstrated.[14] In addition, its zwitterionic character[15] is very attractive for the

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synthesis of new metal phosphonates, the layered structure of which can provide potential ion exchanger activity. In this context the understanding of the structural features of these compounds is very important.

Commonly, metal phosphonates in many cases represent microcrystalline systems insoluble in water and organic solvents, and this circumstance complicates their structural analysis. Characterizations of such systems are usually carried out by X-ray powder diffraction[16] and solid-state NMR.[17] Although the X-ray powder patterns can often be solved, the problem of proton localization still remains and does not allow drawing conclusions about the fine structure of the organic ligands. For example, in the zirconium compounds $Zr(O_3PCH_2(NHCH_2CH_2)_nNHCH_2PO_3)$, capable of anion exchange, some of nitrogen atoms must be protonated with the associated anion being exchangeable.[12] However, these zirconium compounds are poorly crystalline and spectroscopic methods are not definitive. Therefore, we have undertaken to prepare similar phosphonates with divalent metals where the probability of obtaining crystalline products is more likely.

In this paper we report on the synthesis and structure of the cadmium aminophosphonate $Cd_2Cl_2(HPO_3CH_2NHCH_2CH_2NHCH_2PO_3H)\cdot 4H_2O$. The protons could reside as placed on the oxygen atoms or on the amino nitrogens.

Experimental Section

Materials and Methods. All chemicals were obtained from commercial sources and used without further purification.

The $^{31}P\{^1H\}$, $^{13}C\{^1H\}$, and $^{113}Cd\ \{^1H\}$CP MAS NMR spectra were collected with a Bruker MSL-300 spectrometer using H_3PO_4, TMS, and $Cd(NO_3)_2\cdot 4H_2O$ as external references, respectively. The δ^{iso} ^{31}P and ^{113}Cd values were determined at different MAS rates. The kinetic cross-polarization NMR measurements were carried out by determinations of intensities of the corresponding NMR resonances as functions of contact times in the standard cross-polarization pulse sequences. These measurements provide 10% errors in determinations of parameters T_{HX} and $T_{1\rho}(H)$ (see eq 1), which are well reproduced. For example, two independent H−P CP experiments on ethylenediamine-*N*,*N*′-bis(methylenephosphonic acid) gave the T_{HP} and $T_{1\rho}(H)$ values of 0.12 and 8.7 ms or 0.13 and 9.4 ms, respectively. The IR spectra were recorded on a Nicolet Nexus 470 FTIR spectrometer with spectral resolution of 2 cm^{-1} in KBr pellets.

Thermogravimetric analysis was carried out with a DuPont TGA 951 instrument at a heating rate of 10 °C/min under compressed air.

Elemental and microprobe analyses were performed in Galbraith Laboratories, Inc., Knoxville, TN, and at the Department of Geology & Geophysics, Texas A&M University, College Station, TX.

Synthesis of Ethylenediamine-*N*,*N*′-bis(methylenephosphonic acid) (H_4L). The diphosphonic acid was prepared as described in ref 18. A 50 mmol amount of paraformaldehyde (Aldrich) was gradually added to a stirring mixture of ethylenediamine (EM Science, 25 mmol) and diethyl phosphite (Aldrich, 50 mmol), maintaining the temperature at 70 °C. Then the reaction mixture was heated for 1 h at 85 °C. The resulting brown liquid was extracted with diethyl ether. The extract was dried with sodium sulfate, and the ether was evaporated. Concentrated hydrochloric acid (10 mL) was added to the residue. The solution was refluxed for 7 h. The excess of HCl was removed by addition of silver oxide. Deionized water and ethanol were added to precipitate the final compound. Recrystallization was carried out from diluted hydrochloric acid. Anal. Found: C, 16.70; H, 6.50; N, 10.19. Calcd for $C_4H_{18}N_2O_8P_2$: C, 16.91; H, 6.38; N, 9.86. $^{31}P\{^1H\}$ CP MAS NMR: 10.5 ppm (s). $^{13}C\ \{^1H\}$ CP MAS NMR: 44.4 ppm (bs). IR: ν(OH) 3501 cm^{-1} (ms), 3771 cm^{-1} (ms), 3300 cm^{-1} (m); $\nu(NH_2^+)$ ∼3006 cm^{-1} (m); $\nu(CH_2)$, ν(PO−H), 2δ(POH) 2900−2400 cm^{-1} (m, mw); δ(HOH) 1647 cm^{-1} (mw); $\delta(NH_2^+)$ 1513 cm^{-1} (mw); $\delta(CH_2)$ 1478−1380 cm^{-1} (mw); $\omega(CH_2)$ 1278 cm^{-1} (mw); $\nu_{as}(PO_2)$ 1156 cm^{-1} (s); $\nu_s(PO_2)$ 1029 cm^{-1} (s); ν(P−OH) 939 cm^{-1} (s).

Synthesis of $Cd_2Cl_2(H_2O)_4(H_2L)$. Aminophosphonic acid H_4L (3.5 mmol) was suspended in 20 mL of deionized water. A solution of cadmium chloride (Fisher, 7.0 mmol) in 20 mL of water was added to the suspension under vigorous stirring. The pH was then adjusted to 2 with 5 M HCl. The mixture was placed into a Teflon-lined pressure vessel and held at 150 °C for 3 days. A white solid was filtered off and washed with water. The dried solid was suspended in 20 mL of water and retreated with cadmium chloride solution (7.0 mmol in 20 mL of H_2O) as described above, and the hydrothermal reaction was repeated at 150 °C for 3.5 days. The final product was filtered off, washed with water, and dried at 60 °C (0.86 g, 40%). Anal. Found: C, 8.00; H, 3.35; N, 4.61; P, 9.91; Cl, 11.90; Cd, 36.84. Calcd for $C_4H_{20}N_2O_{10}P_2Cl_2Cd_2$: C, 7.83; H, 3.28; N, 4.56; P, 10.09; Cl, 11.56; Cd, 36.63. $^{31}P\ \{^1H\}$ CP MAS NMR: 8.7 ppm (s). $^{13}C\ \{^1H\}$ CP MAS NMR: 46.7 ppm (s). IR: ν(OH) 3431 cm^{-1} (ms), 3362 cm^{-1} (m); $\nu(NH_2^+)$ 3069 cm^{-1} (m); $\nu(CH_2)$ 2810 cm^{-1} (mw); δ(HOH) 1684 cm^{-1} (w); δ (NH_2^+) 1566 cm^{-1} (m); $\delta(CH_2)$ 1464−1384 cm^{-1} (mw); $\omega(CH_2)$ 1268 cm^{-1} (mw); $\nu_{as}(PO_2)$ 1131 cm^{-1} (s); $\nu_s(PO_2)$ 1087 cm^{-1} (s); $\nu_{as}(P{-}O^-)$ 996 cm^{-1} (ms).

X-ray Data Collection. An initial data set at high resolution was collected on a Bruker D8 Advance diffractometer with Bragg−Brentano $\theta-2\theta$ geometry (40 kV, 50 mA) using Ge monochromator with Cu Kα_1 radiation ($\lambda = 1.54056$ Å). The data were recorded between 5 and 95° in 2θ, with a step size of 0.01° and a count time of 30 s/step. The sample was packed into a flat plastic holder and was allowed to rotate at 15.00 rpm during the data collection. Intensity data were recorded on a Bruker D8 diffractometer with graphite monochromator in the $\theta-2\theta$ mode between 5 and 60° in 2θ, with a step size of 0.01° and a count time of 20 s/step, and between 50 and 100° in 2θ, with a step size of 0.01° and a count time of 25 s/step. The data were then merged into one powder pattern, using the software Eva.[19] A second data set was obtained on a new sample at ambient temperature on beam line X3B1 at the National Synchrotron Light Source at Brookhaven National Laboratory. X-rays of wavelength 0.70226(1) Å were selected by a double-

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crystal Si(111) monochromator. The sample was sealed in a capillary, which was continuously rotated during data collection. The data collection time increased from 2 s/point at 2 deg 2θ to 12 s at 34.997°, with a step size of 0.003°. The diffracted X-rays were selected by a Ge(111) analyzer crystal on a detector arm and detected using a commercial NaI scintillation counter; the measured X-ray counts were normalized to the signal from an ionization chamber between the monochromator and the sample to correct for decay and fluctuations of the incident beam intensity.

Structure Determination. A first determination of cell parameters was made using the Treor90 program[20] on the in-house data. The indexing yielded the cell dimensions $a = 16.985(4)$, $b = 7.140(2)$, and $c = 6.802(2)$ Å, $\beta = 105.00(3)°$, and $V = 796.77$ Å^3 as the best solution ($M(20) = 17$) and giving as reduced cell $a = 16.581$, $b = 7.139$, and $c = 6.802$ Å, $\beta = 98.34°$, and $V = 796.77$ Å^3. The analyses of the systematic absences were consistent with the space group $P2_1/n$.

The structure was solved using the in-house data by direct methods with the program EXPO.[21] Five of the 11 atoms of the asymmetric unit were located in the initial *E*-map. A series of Rietveld refinements alternated with Fourier difference maps, using the GSAS Program,[22] revealed the positions of the remaining atoms. The refinement strategy consisted in a first step of a Lebail method refinement for the background (using 12 terms of a Chebychev function), zero shift, cell parameters, and peak profile function, considering a dummy hydrogen atom and maintaining the scale factor constant and equal to 1. Once these parameters were satisfactory ($R_p = 7.94\%$), 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 bond restraints Cd−O (2.3 Å), Cd−Cl (2.6 Å), P−O (1.52 Å), P−C (1.80 Å), C−N (1.34 Å), and C−C (1.54 Å) were applied prior to position refinements of the atoms. The bond angles around the phosphorus atoms were restrained to ideal tetrahedral angles by applying restraints to the nonbonded O⋯O (2.5 Å) and O⋯C (2.7Å) distances and tetrahedral angles around the carbon. The restraint parameter was first fixed to 1000 and then lowered to 100 in the last cycles of the refinement. Preferred orientation along [110] and [10$\bar{1}$] was refined using the March−Dollase model.[23] The atomic positions were refined first and then the temperature factors, and finally all the parameters were refined simultaneously. The last set of refinement yielded a value of $R_p = 0.0862$, $R_{wp} = 0.1111$, and $R(F) = 0.0410$. At this point we calculated a final Fourier difference map and we were able to locate all the hydrogen atoms; these atoms were then included into the structure, and a final refinement of the structure was performed without restraint on the distances and by maintaining the hydrogen atoms at fixed positions. The final set of refinement converged with $R_p = 0.0794$, $R_{wp} = 0.1034$, and $R(F) = 0.0297$. We also solved and refined the synchrotron data of the sample. These data revealed the presence of a small impurity. The refinement of the structure was performed by the same method. The final set of refinement (without the hydrogen atoms) was obtained with $R_p = 0.0664$, $R_{wp} = 0.0871$, and $R(F) = 0.0512$. The structure was found to be identical to the one obtained by the in-house data. The impurity proved to be AgCl as a residue from the silver oxide reaction used to remove excess chlorine in the synthesis of the ligand.

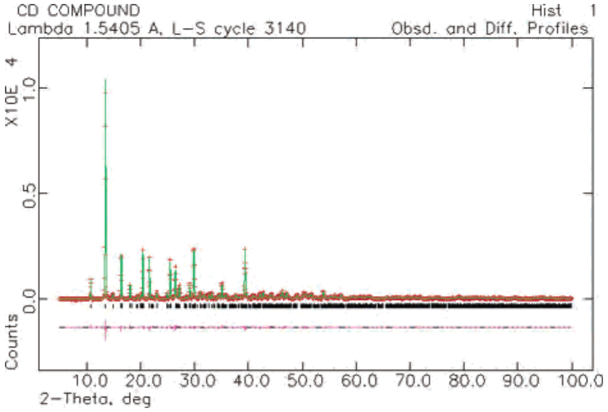

Figure 1. Observed (+), calculated (−), and difference profiles for the Rietveld refinement of $Cd_2Cl_2(H_2O)_4(H_2L)$. Tic marks indicate positions of calculated reflections.

Table 1. Crystallographic Data for $Cd_2Cl_2(H_2O)_4(H_2L)$

empirical formula	$Cd_2Cl_2P_2N_2O_{10}C_4H_{20}$
fw	613.88
space group	$P2_1/n$
a, Å	16.6105(10)
b, Å	7.1572(4)
c, Å	6.8171(4)
β, deg	98.327(4)
V, Å^3	801.9(2)
D_{calc}, Mg/m^3	2.543
Z	2
μ, cm^{-1}	102.25
λ, Å	1.540 56
R_{wp}[a]	0.1024
R_p[b]	0.0794
R_F[c]	0.0297

[a] $R_{wp} = (\sum w(I_o - I_c)^2/\sum wI_0^2)^{0.5}$ (w = weighting factor). [b] $R_p = \sum|I_o - I_c|/\sum I_o$. [c] $R_F = \sum|F_o - SF_c|/\sum|F_o|$($S$ = scale factor).

Figure 1 shows the observed and calculated powder patterns and the difference curve after the last refinement, from the in-house data. Table 1 presents the crystallographic data for the in-house data set with the final refined unit cell parameters. The atomic positions are given in the Supporting Information, and the bond lengths and angles from the in-house data are presented in Table 2.

Results and Discussion

The cadmium phosphonate $Cd_2Cl_2(H_2O)_4(H_2L)$ was obtained by the hydrothermal reaction of aminophosphonic acid H_4L and cadmium chloride (Experimental Section). The described first step of the procedure usually resulted in a white solid, which was found to be a $Cd_2Cl_2(H_2O)_4(H_2L)$/H_4L mixture. The amount of unreacted ligand H_4L significantly depended upon the conditions (reagent ratio, temperature, and reaction time). In fact, the presence of H_4L can be explained by the combination of the reaction mixture acidity and high temperature: the starting phosphonic acid crystallizes well and even gives large single crystals under these conditions. At the same time the cadmium phosphonate remains as a finely powdered compound. Thus, the hydrothermal technique leads to the formation of a recrystallized H_4L resulting in low yields of the desired reaction product. However the reaction can be successfully completed by the

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Table 2. Selected Bond Lengths (Å) and Angles (deg) for $Cd_2Cl_2(H_2O)_4(H_2L)$ from In-House Data

Cd1−Cl2	2.706(6)	Cl2−Cd−Cl2a	88.51(18)
Cd1−Cl2a	2.682(5)	Cl2−Cd1−O5	83.0 (4)
Cd1−O5	2.213(9)	Cl2−Cd1−O6w	175.6(4)
Cd1−O6w	2.300(9)	Cl2−Cd1−O7	83.2(4)
Cd1−O7	2.224(9)	Cl2−Cd1−O8w	85.5(4)
Cd1−O8w	2.359(10)	Cl2a−Cd1−O5	93.0(4)
P3−O4	1.546(9)	Cl2a−Cd1−O6w	97.3(4)
P3−O5	1.504(10)	Cl2a−Cd1−O7	93.6(5)
P3−O7	1.503(10)	O5−Cd1−O7	164.5(4)
P3−C11	1.789(9)	O5−Cd1−O8w	91.4(5)
O6−H16	1.037(19)	O6w−Cd1−O7	98.2(6)
O6−H17	1.039(19)	O6w−Cd1−O8w	98.8(5)
O8−H14	1.069(19)	O7−Cd1−O8w	127.7(26)
O8−H15	1.122(16)	C10−N9−C11	119.0(11)
N9−C10	1.459(11)	N9−C10−C10	114.4 (13)
N9−C11	1.406 (12)	P3−C11−N9	112.9(8)
N9−H12	0.885(26)	Cd1−Cl2−Cd1a	91.49(18)
N9−H13	0.881(15)	C11−N9−H12	89.3(17)
C10−C10	1.506(13)	C11−N9−H13	113.3(10)
C10−H20	1.090(18)	C10−N9−H12	78.3(16)
C10−H21	0.960(33)	C10−N9−H13	127.2(10)
C11−H18	1.109(23)	H12−N9−H13	109.3(24)
C11−H19	1.069(14)	C10−C10−H20	103.8(17)
O4−P3−O5	110.3(8)	C10−C10−H21	86.5(25)
O4−P3−O7	109.4(8)	H20−C10−H21	74.8(20)
O4−P3−C11	109.8(6)	N9−C11−H18	88.3(14)
O5−P3−O7	107(6)	N9−C11−H19	73.7(11)
O5−P3−C11	109.2(8)	H18−C11−H19	96.2(20)
O7−P3−C11	110.6(8)		

reheating of the $Cd_2Cl_2(H_2O)_4(H_2L)/H_4L$ suspension in water with an additional amount of $CdCl_2$. It should be noted that the crystallinity of the pure cadmium phosphonate was definitely improved by this repeat of the reaction.

Thermogravimetric Study. The TGA curve of $Cd_2Cl_2(H_2O)_4(H_2L)$ shows two major weight losses. The first step corresponds to a water loss at 100−183 °C. It should be noted that the dehydration process begins at quite high temperature and reveals a strong bonding of water molecules with the metal atom.[24−27] The observed weight loss (11.11%) compares suitably to a value calculated for a loss of four molecules of water (11.73%). A complicated stepwise process of the hydrogen phosphonate group condensation, burning of organic moieties, and the formation of oxychloro derivatives occurs between 266 and 830 °C. The transformation is completed at 830 °C, resulting in a white solid after a total weight loss of 33.22%. The residue was determined to be cadmium pyrophosphate, $Cd_2P_2O_7$, by its X-ray powder pattern; the expected weight loss (35.04%) is comparable with the calculated results.

Structure of $Cd_2Cl_2(H_2O)_4(H_2L)$. In the structure of $Cd_2Cl_2(H_2O)_4(H_2L)$ the cadmium atoms are in octahedral coordination bonded to two phosphonate oxygen atoms (O5 and O7), two water oxygen atoms (O6w and O8w), and the two chlorine atoms (Cl2, 2×). The Cd−O bond lengths are 2.213(9) and 2.224(9) Å for the phosphonate oxygen atoms, and for the water oxygens they are slightly longer (2.300(9) and 2.359(10) Å). The cadmium atoms are bridged by the chlorine atoms forming four-membered rings as shown in Figure 2. These entities assemble into infinite double chains in the *c*-axis direction through the bridging of the cadmium atoms by the phosphonic acid groups (−Cd−O5−P−O7−Cd−O5−P−). These chains are connected to each other in the *b*-axis direction by the organic chain of the ligand. This connectivity results in formation of layers (Figure 3), which are similar to the layers defined by the chlorinated ligand: ethylenediaminediisopropylphosphonic acid dichloride.[15]

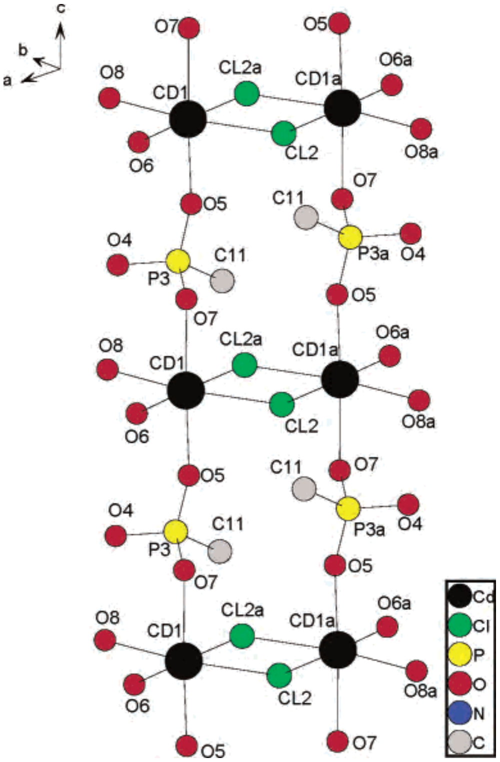

Figure 2. Representation of cadmium octahedra dimers sharing an edge through chloride ion bridging. The dimers form infinite double chains running parallel to the *c*-axis through phosphonate group linkage.

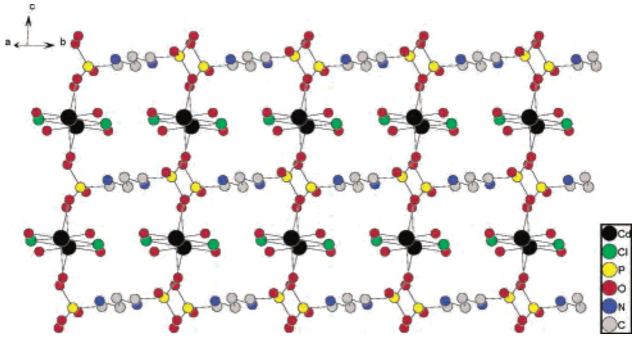

Figure 3. Representation of the layers formed by cross-linking of the double chains by the aminophosphonate groups.

The phosphorus atoms exhibit tetrahedral coordination with P−O distances of 1.504(10) and 1.503(10) Å for the two oxygen atoms (P−O7 and P−O5, respectively) bonded to the cadmium atoms. The third oxygen atom (O4) has a longer bond distance of 1.546(9) Å and is nonbonded. Nevertheless, this atom forms hydrogen bonds O4···O8W (2.69 Å) and O4···O6W (2.68 Å) as shown in Table 3. This connectivity occurs between adjacent layers which are shifted along the *c*-axis relative to each other by 1/2*c*. The

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Table 3. Hydrogen Bonds (Å, deg) in $Cd_2Cl_2(H_2O)_4(H_2L)$

bond	X−Y	X−H	H···Y	X−H···Y
N9−H12···Cl2	3.47	0.885(26)	2.60	164.5
N9−H13···O5	2.95	0.885(26)	2.17	146.8
N9−H13···O7	3.05	0.885(26)	2.49	121.5
O6w−H17···O8w	2.90	1.039(19)	2.25	118.9
O8w− H14···O6w	2.90	1.069(19)	1.87	162.5
O4···H16−O6w	2.68	1.037(19)	2.00	119.8
O4···H15−O8w	2.69	1.122(16)	2.10	109.1

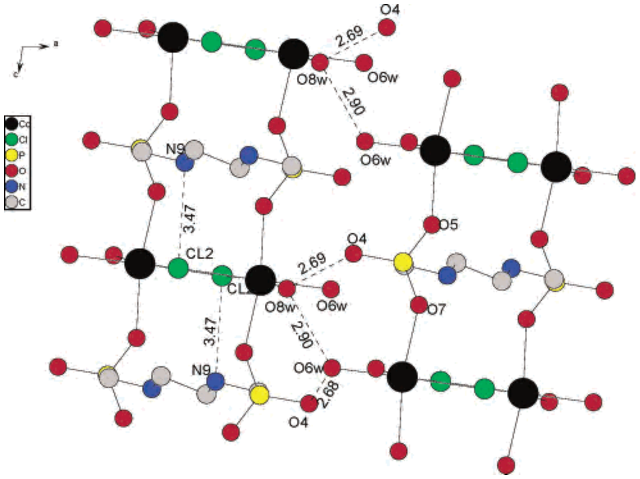

Figure 4. Hydrogen bonding in the structure. This structure is hold together through hydrogen bonding. The free oxygen of the phosphonic group is hydrogen bonded to two water molecules. The nitrogen is hydrogen bonded to the chlorine, showing its protonated nature.

coordinated water molecules are also hydrogen bonded, and their oxygen atoms are separated by a short interlayer distance of 2.90 Å. These hydrogen bonds are sufficiently strong to maintain the stability of the structure.

The localization of the hydrogen atoms allowed us to characterize the hydrogen-bonding network in the structure and led to a better understanding of the structure. The C10−N9−C11 angle is 119.0(11)°, closer to 120° than 109.5°; however, we observe the presence of two hydrogen atoms bonded to the nitrogen atom and showing its protonated nature. This nitrogen atom is hydrogen bonded to the chlorine atom, through H12, with a distance H···Cl of 2.6 Å, the N···Cl distance is 3.47 Å, and the angle around the hydrogen is 164.5°. The second hydrogen atom (H13) points toward the two phosphonate oxygen atoms bonded to Cd, at a distance of 2.17 Å for O5 and 2.49 Å for O7, and the distances N9···O5 and N9···O7 are both around 3 Å. The protonation of the nitrogen allows us to conclude that the non-metal-bonded phosphonate oxygen is negatively charged. This atom is also involved in hydrogen bonding to maintain the stability of the structure. Thus, the betaine structure of the ligand is maintained after bonding with the cadmium. The layers are maintained by the hydrogen bonds between O4···O6w, O4···O8w, and O6w···O8w, as presented in Table 3 and Figure 4. Because the water molecules are bonded to the cadmium atoms, the bond angles around the hydrogen interacting with O4 (<O4···H16−O6w = 109.1° and <O4···H15−O8w = 119.8°) are small compared to the angles formed in case of free water.

Each cadmium octahedron binds to two phosphorus tetrahedra through the oxygens in the axial positions. Such a bonding mode results in alternation between octahedra and tetrahedra along the chains. This ensemble defines cavities where the organic part of the phosphonic group fits. Note that conformations of the aminophosphonic units in the Cd compound and aminophosphonic acid H_4L^{15} are similar. The alternation of cadmium octahedra and phosphonate tetrahedra define the infinite chains, and the connection with the organic part of the ligand defines the layer in the (*b*, *c*) plane. Finally, we emphasize that at the time of this writing the literature contained only a few examples of structurally characterized cadmium phosphonates.[17d,28]

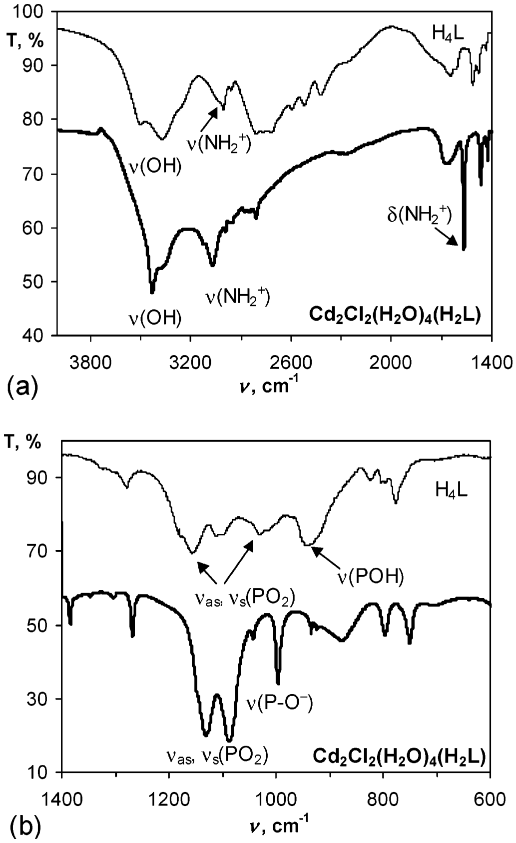

Figure 5. IR spectra of $Cd_2Cl_2(H_2O)_4(H_2L)$, compared to aminophosphonic acid H_4L in the *ν*(OH), *ν*(NH), and *δ*(NH) ranges (a) and *ν*(PO) range (b).

Infrared Spectroscopic Study. The crystal structure of H_4L^{15} clearly shows both nitrogen atoms to be protonated that is typical of compounds of this type. The IR spectrum of this zwitterion is shown in Figure 5 together with that of the cadmium phosphonate. The range of PO stretching vibrations in the IR spectrum of H_4L, prepared by us, supports the betaine structure. The spectrum exhibits three strong bands at 1156, 1029, and 939 cm^{-1}, assigned to $\nu_{as}(PO_2)$, $\nu_s(PO_2)$, and $\nu(P-OH)$, respectively, indicating clearly the presence of PO_3H groups.[15,29,30] Furthermore, all the PO bands are low-frequency shifted due to the strong intra- and intermolecular hydrogen bonds with lattice water molecules and NH_2^+ groups.[15] The NH_2^+ groups are expected to give

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two bands between 3000 and 2700 cm^{-1}, which are usually broad, unresolved, and extended to 2273 cm^{-1}.[31] Indeed, the IR spectrum of H_4L shows a broad band at 3006 cm^{-1} revealing the presence of the protonated NH groups. Broad and shallow bands at 2800−2400 cm^{-1} have been attributed to ν(PO−H) and 2δ(POH).[32,33] Finally, the high-frequency bands at 3501, 3371, and 3300 cm^{-1} and the absorption near 1647 cm^{-1} can undoubtedly be assigned to OH stretching and HOH bending vibrations in the hydrogen-bonded lattice molecules of water (Figure 4a,b).[34]

The IR spectrum has dramatically changed with the formation of the cadmium phosphonate. Moreover, the sharpening of all lines and a good resolution allowed us to carry out more complete band assignments and to make some conclusions about the structural features of the compound. Thus, the broad ν(OH) bands of the starting H_4L disappear upon coordination and a new band appears at 3431 cm^{-1} with a shoulder at 3362 cm^{-1} (Figure 5a). The latter is sharp and indicates that the water molecules are coordinated to the metal.[25,26,35,36] This fact explains the quite high temperature of dehydration, in the 100−183 °C range (see TGA Studies).

According to the IR data, NH groups are protonated in the cadmium phosphonate. Actually the IR spectrum in the ν(NH) range exhibits a new band at 3069 cm^{-1}, which is shifted to a higher frequency ($\Delta\nu = 63$ cm^{-1}) and assigned to $\nu(NH_2^+)$. The strong sharp band at 1566 cm^{-1} lies in the range typical of protonated secondary amines and undoubtedly belongs to the bending vibrations $\delta(NH_2^+)$.

The changes of the IR spectra in the ν(PO) region (Figure 5b) show the coordination of oxygen atoms in phosphonic group with cadmium atoms. For instance, the broad PO_2 stretching vibration bands (ν_{as}, ν_s) are shifted to 1131 and 1087 cm^{-1} with $\Delta\nu = 44$ cm^{-1}. A new sharp band is observed at 996 cm^{-1}. Notice that the broad band at 939 cm^{-1} (ν(P−OH)) disappears. Moreover, all vibrations in which the POH group participates (ν(PO−H), 2δ(POH)) are no longer present in the spectrum of the cadmium phosphonate. Such changes indicate the deprotonation of phosphonate moieties. Two bands at higher frequency are located closer to each other, and they can be assigned to the asymmetrical and symmetrical stretching vibrations of PO_2 groups bonded to the metal atoms. A low-frequency band (996 cm^{-1}) can be attributed to $\nu(P-O^-)$ since each phosphonic group loses its proton but is uncoordinated to the metal. Note that, the P−O groups for nonbonded oxygens show much longer bond distances (1.546(9) Å) than the other two bonded to the cadmium atoms (1.504(10), 1.503(10) Å). This agrees well with the higher position of the corresponding ν_{as}- and ν_s-(PO_2) bands in the IR spectrum (Figure 5b).

Table 4. Room-Temperature ^{13}C, ^{31}P, and ^{113}Cd Solid-State NMR Data (δ, ppm; $\Delta\nu$, Hz)

compd	$_{iso}\delta(^{13}C)$ ($\Delta\nu$)	$_{iso}\delta^{31}(P)$ ($\Delta\nu$)	Δ^a	$\delta 11$	$\delta 22$	$\delta_{33}{}^b$	η^c
H_4L	44.4 (420)	10.5 (260)	67	−50	3	78	0.8
$Cd_2Cl_2(H_2O)_4(H_2L)^d$	46.7 (440)	8.7 (70)	80	−32	−32	90	0.0

[a] $\Delta = \delta_{33} - {}^{iso}\delta$. [b] $\delta_{33} > \delta_{22} > \delta_{11}$. [c] $\eta = |\delta_{22} - \delta_{11}|/|\Delta|$. [d] $^{iso}\delta^{113}(Cd) = 180.3$ ppm.

Thus, according to the IR spectra the cadmium compound remains a zwitterionic structure as in the starting H_4L, confirming the X-ray evidence. Similar changes in IR spectra have been observed for the Fe(III)−$NH_3^+CH_2PO_3^{2-}$ system in which the band at higher frequency was attributed to ν-(P═O).[29]

NMR Study. Table 4 lists the solid-state NMR data collected for the phosphonic acid H_4L. The ^{13}C CP MAS NMR spectrum of H_4L shows a singlet resonance remarkably broadened ($\Delta\nu = 420$ Hz) due to the presence of unresolved J_{PC} constants of 140−160 Hz.[37] The line is symmetrical, and its shape does not change with the variation of contact times in the standard cross-polarization pulse sequences. Thus, chemical shifts of all the carbon atoms in H_4L are identical despite their chemical nonequivalency. The ^{31}P CP MAS NMR spectrum also exhibits a single resonance, which agrees well with the single-crystal X-ray structure. Principal components of the ^{31}P chemical shift tensor (Table 4), determined from the static ^{31}P NMR spectrum, show the anisotropy of 68 ppm, typical of aminophosphonic acids: 40−80 ppm.[37] The asymmetry parameter ($\eta = 0.8$) is also typical and corresponds well to a completely asymmetric environment of ^{31}P in the PO_3H groups where all the P−O bond lengths are different due to the presence of strong H-bonds[15] found in the crystal structure and IR data. It is important also that the high asymmetry rules out a fast migration of acidic protons on the NMR time scale.[38] Thus, all the solid-state data are in good agreement and support the zwitterionic nature of aminophosphonic acid H_4L.

The ^{31}P and ^{113}Cd CP MAS NMR spectra of $Cd_2Cl_2(H_2O)_4(H_2L)$ exhibit only one resonance in each case (Table 3) in full accordance with the powder X-ray diffraction structure. The ^{113}Cd CP MAS NMR spectrum is collected rapidly due to the effective H−Cd cross-polarization through protons of water molecules coordinated with the cadmium atoms. This is also in good agreement with the structural, IR, and analytical data.

The isotropic ^{113}Cd shifts in cadmium phosphonates with octahedral CdO_6 environments commonly lie between 150 and 165 ppm.[17d,28] Lower-field signals are expected when the Cd coordination number is reduced.[39] For example, $Cd_2(OH)(O_3PC_2H_4CO_2)$ with a trigonal bipyramid CdO_5 coordination shows a ^{113}Cd resonance at ≈220 ppm.[17d] Therefore, the appearance of the low-field ^{113}Cd signal in

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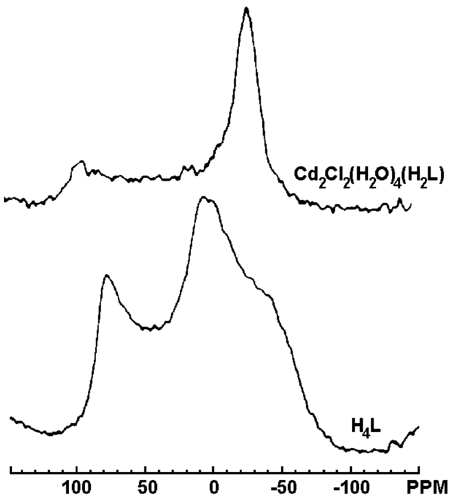

Figure 6. Static ^{31}P CP MAS NMR spectra of aminophosphonic acid H_4L (a) and $Cd_2Cl_2(H_2O)_4(H_2L)$ (b).

$Cd_2Cl_2(H_2O)_4(H_2L)$ (180.3 ppm), untypical of the octahedral Cd atoms, can be explained by the presence of two Cl atoms in the coordination sphere.

The isotropic ^{13}C chemical shift does not practically change in going from H_4L (44.4 ppm) to compound $Cd_2Cl_2(H_2O)_4(H_2L)$ (46.7 ppm); the resonance remains symmetrical and undergoes no additional broadening. Thus, the ^{13}C CP MAS NMR spectra are insufficient for structural conclusions. On the other hand, there is no clear evidence for deprotonation of the nitrogen atoms in the compound. The isotropic ^{31}P chemical shift in phosphonic groups, usually sensitive to the M−O coordination,[17c,28] again changes very slightly from H_4L to $Cd_2Cl_2(H_2O)_4(H_2L)$ (Table 3), and thus, the MAS NMR provide no additional information about the structure of the organic moieties in the cadmium phosphonate.

According to ref 17b, structural conclusions and even determinations of types of the metal coordination can be made on the basis of static ^{31}P NMR spectra. In accord, the static ^{31}P spectra of H_4L and compound $Cd_2Cl_2(H_2O)_4(H_2L)$ differ strongly: all the elements, δ_{11}, δ_{22}, and δ_{33}, change (Table 4), leading to an axial symmetry of the $\delta^{31}P$ tensor in the Cd compound (Figure 6, NMR). This axial symmetry could be attributed to dynamic processes in the solid state: rapid C_3 reorientations of the PO_3 groups and/or proton migrations which could average the P−O bonds. For example, such averaging of the P−O bonds was established in $CH_3(CH_2)_5P(O)(OH)_2$.[37,38] However, this can be ruled out due to the remarkable increase of the $\delta(^{31}P)$ anisotropy from H_4L to the cadmium phosphonate. Moreover, the compound, after being frozen in liquid nitrogen and rapidly transferred into the NMR probe (the spectrum was obtained in <1 min), showed the same line shape. In the absence of the dynamics, the observed $\delta(^{31}P)$ tensor could be assigned to a 111 connectivity in the PO_3 group when each O atom is binding to one metal atom.[17b] However this spectroscopic test, being probably uncommon, contradicts the powder X-ray diffraction structure. We believe that this unusual behavior reflects the structural features of $Cd_2Cl_2(H_2O)_4(H_2L)$: two O atoms coordinate with two Cd to give the *equal* and *shortened* P−O bonds (1.504(10) and 1.503(10) Å versus 1.493 and 1.504 Å in H_4L) with an angle of 109.9° between them. Then, orientations of components δ_{11} and δ_{22} practically along these two bonds could produce the axial-symmetrical tensor. It should be noted that such orientations have been established in zirconium α-carboxymethylphosphonate, $Zr(O_3PCH_2COOH)_2$.[17a] Thus, the traditional CP MAS and static NMR spectra collected for $Cd_2Cl_2(H_2O)_4(H_2L)$ agree with the structure and do not contradict the IR spectra. However, they provide no evidence for the zwitterionic nature of the cadmium phosphonate, as established by the IR spectra. Add that the simple comparison of the X-ray structures of zwitterionic H_4L and the compound also does not help to detail the structure of the organic moieties. Note that the angles CNC in both compounds are similar and were determined as 112.8(3)° (H_4L)[15] and 119.0(11)° ($Cd_2Cl_2(H_2O)_4(H_2L)$).

Chart 1. Possible Proton−Phosphorus Interactions Bearing on Cross-Polarized ^{31}P Spectra

1a 1b

Additional structural information in the solid state can be obtained from dynamics of the NMR proton−nucleus cross-polarization (CP), providing to determine the kinetic parameters, such as the CP rates, T_{HX}^{-1}, and relaxation times, $T_{1\rho}(H)$.[40] These parameters are available from an analysis of the CP kinetic curves in variable-contact-time CP experiments. Magnitudes of the cross-polarization times, T_{HX}, are dictated by molecular mobility in the solid state and the dipolar coupling ($D = \mu_0\gamma_H\gamma_X h/(8\pi^2 r^3)$).[40] At equal molecular mobility, the T_{HX} values will depend on the number of protons, involved in the cross-polarization, and internuclear distances. Thus, the proton−phosphorus CP rates, T_{HP}^{-1}, could potentially distinguish the structures in Chart 1: three protons, closest to ^{31}P (CH_2 and POH), are involved in magnetization transfer in structure **1b** versus two protons (CH_2) in **1a** (see the corresponding arrows). Note that distances (C)H···P and (O)H···P in zwitterionic H_4L are very similar and measured as 2.37 and 2.34 Å, respectively.[15]

The kinetic H−P CP NMR data, collected for H_4L ligand and the cadmium phosphonate, are presented in Table 4. The cadmium phosphonate was additionally characterized by the CP experiments on nuclei ^{13}C and ^{113}Cd. The H−P CP data were treated in the framework of a classical spin I−S model[35] valid for weak heteronuclear dipolar interactions when the cross-polarization goes through remote protons.[41] Figure 7 demonstrates the pattern's ^{31}P-intensity versus contact time reflecting the simple double-exponential behavior. This behavior corresponds to the above spin model and reveals the absence of various domains (crystalline or amorphous)

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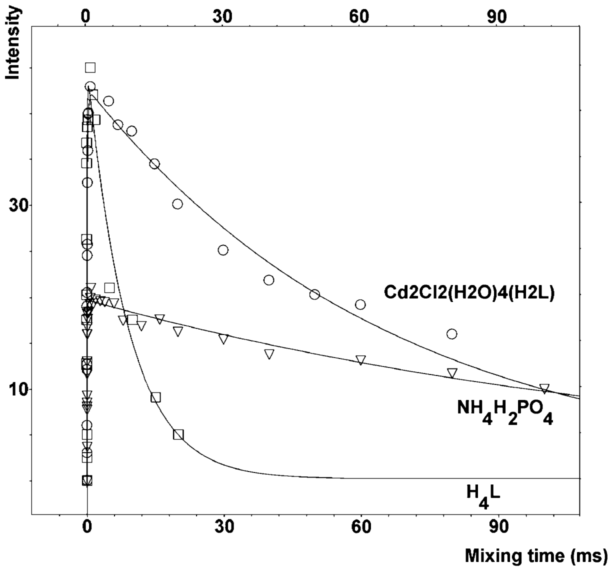

Figure 7. Kinetic NMR proton−phosphorus CP curves: ^{31}P signal intensity versus contact time (ms) in variable-contact-time CP experiments on $Cd_2Cl_2(H_2O)_4(H_2L)$, $NH_4H_2PO_4$, and H_4L.

in the investigated materials.[42,43] The effective cross-polarization time constants, T_{HP}, and the effective proton relaxation times in the rotating coordinate system, $T_{1\rho}(H)$, were obtained by fitting procedures of the experimental data to

$$I(t) = I_0(1 - T_{HP}/T_{1\rho}(H))^{-1}(\exp(- t/T_{1\rho}(H)) - \exp(-t/T_{HP})) \qquad (1)$$

where t is the contact time. The same approach was applied to determine the T_{HC} and T_{HCd} times in $Cd_2Cl_2(H_2O)_4(H_2L)$.[44] The data in Table 5 show that the experimental T_{HX} times in the cadmium phosphonate change as

$$T_{HCd} > T_{HP} > T_{HC} \qquad (2)$$

This order agrees well with the dipolar coupling to account for the closest H−X distances: H−C (1 Å), H−P (2.3−2.4 Å), and H−Cd (3 Å) in groups CH_2, CH_2P (and POH), and $Cd{\cdot}H_2O$, respectively. In addition, rapid spin diffusion in the standard CP experiments leads to the action of different protons as a single spin system.[40] Therefore the CP experiments on the different nuclei show similar $T_{1\rho}(H)$ values, lying between 43 and 70 ms.

According to the X-ray and spectral data, the aminophosphonic acid, H_4L, represents a zwitterion, where distances H−P in the $CH_2{-}PO_3H^-$ fragments are practically identical. Hence the short T_{HP} time of 0.12 ms in H_4L can be attributed to the cross-polarization through *three* closest protons. Comparison of H_4L and $Cd_2Cl_2(H_2O)_4(H_2L)$ in Table 5 reveals a *1.5-fold elongation* of T_{HP} in the case of the cadmium compound. The X-ray, IR, and NMR data showed that the aminophosphonic acid H_4L forms numerous intra- and intermolecular hydrogen bonds. In turn, the cadmium compound gives a network containing the different bridging atoms and hydrogen bonds with the participation of water molecules. Therefore, higher molecular mobility in the cadmium phosphonate seems to be unlikely. In accord, the proton $T_{1\rho}(H)$ time increases remarkably on going from H_4L to the cadmium phosphonate confirming its more rigid structure. Thus, the above-mentioned elongating T_{HP} effect can undoubtedly be attributed to a removal of the P−OH proton from a cross-polarization sphere of ^{31}P in fragments $CH_2{-}PO_3^-$ of the Cd phosphonate. This conclusion is in a good agreement with the IR data. To check independently the reliability of CP measurements, we have studied the room-temperature H−P CP kinetics in solid $[NH_4]^+[H_2PO_4]^-$ (Figure 7) versus $([NH_4]^+)_2[HPO_4]^{2-}$ reported in the literature.[40] Again, the T_{HP} value, measured in $[NH_4]^+[H_2PO_4]^-$ as 0.092 ms,[45] is shorter than that in $([NH_4]^+)_2[HPO_4]^{2-}$ (0.134 or 0.142 ms in the conventional H−P CP or TORQUE experiment, respectively[40]) Theoretically, these compounds should show a 2-fold difference in T_{HP}. In reality this difference is less due to participation of the remote protons (NH_4) in the CP process.

Table 5. T_{HP} and $T_1\rho(H)$ Values Calculated from the Room-Temperature Kinetic Proton−Phosphorus Cross-Polarization (ms)

compd	T_{HP}	$T_{1\rho}(H)$
H_4L	0.12	8.7
$Cd_2Cl_2(H_2O)_4(H_2L)$	0.17	73
	1.5 (H−Cd)	43
	0.075 (H−C)	50

Summarizing all the data, we conclude that in the PO_3-Cd_2 bonding modes the uncoordinated PO oxygens do not bond to protons (the HP NMR cross-polarization and IR data) but the nitrogen atoms are protonated (the X-ray and IR data) and hence the cadmium phosphonate has a zwitterionic structure (Chart 1, **1a**). A similar structural motif has been reported for aminophosphonate $(NH_4)Zr(F_2)[H_3\{O_3PCH_2NH(CH_2CO_2)_2\}_2]{\cdot}3H_2O{\cdot}NH_4Cl$, where the O atom, uninvolved in the metal bonding, is also deprotonated.[46]

One of the reasons for synthesizing this cadmium compound and several zinc analogues (to be published) was to prepare pillared compounds in which all the phosphonate oxygens would be utilized in layer formation. Protonation of the amino groups would then be accompanied by insertion of an anion in the interlamellar space imparting anion exchange capability to the compound. Use of $CdCl_2$ as the source of metal ion lead instead to the presence of chloride-bridged Cd dimers and a novel layer formation through the phosphonate connectivity. Although the amino groups are protonated, the charge is balanced by the formation of $P{-}O^-$ groups. The chloride ions are not available for exchange and are not required in view of this novel structure. More recently, we have carried out the synthesis in a nitrate system, and in this case, we obtained a poorly crystalline solid but what appears to be a layered structure with three orders of

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(45) The fitting procedure gave the $T_{1\rho}(H)$ value of 130 ms.

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reflections with $d_{001} = 24$ Å. This compound may be the type we envision forming a layer of the type expected with mobile anions. Further investigations as to the ion exchange behavior of these compounds are in progress.

Conclusions

A new divalent cadmium phosphonate $Cd_2Cl_2(H_2O)_4(H_2L)$ has been synthesized from the ethylenediamine-*N*,*N*′-bis(methylenephosphonic acid), H_4L, and characterized by solid-state IR spectra and ^{13}C, ^{31}P, and ^{113}Cd CP MAS NMR. The spectral data are in a good agreement with the X-ray powder diffraction structure of the Cd phosphonate solved with the cell dimensions $a = 16.6105(10)$, $b = 7.1572(4)$, and $c = 6.8171(4)$ Å and $\beta = 98.327(4)°$. The octahedral coordination sphere of the cadmium atoms consists of two phosphonate oxygen atoms, two water oxygen atoms, and the two chlorine atoms. The coordinated water molecules are hydrogen bonded, and their oxygen atoms are separated by a short distance of 2.90 Å. The phosphorus atoms exhibit a tetrahedral coordination where two oxygen atoms are bonded to the cadmium atoms. The third oxygen atom, showing a longer P−O distance, is not binding to the metal center. According to the localization of the hydrogen atoms, the Cd compound has the zwitterionic structure ($NH_2^+CH_2P(O_2Cd_2)O^-$) similar to that of the initial ethylenediamine-*N*,*N*′-bis(methylene phosphonic acid). The IR spectra in combination with the NMR proton−phosphorus cross-polarization kinetics support independently this conclusion.

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Supporting Information Available: One X-ray crystallographic file, in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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