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Article

Cobalt Phosphonates: An Unusual Polymeric Cobalt Phosphonate Containing a Clathrated Phosphonate Anion and a Layered Bisphosphonate

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Novel cobalt phosphonates $[Co(H_2O)_4(H_4L)][H_2L]\cdot 2H_2O$, **1**, and $Co_2(H_2O)_2(L)$, **2**, have been synthesized from 1,8-octylenediphosphonic acid (H_4L). **1** has been fully characterized by X-ray single-crystal data, TGA, IR spectroscopy, and chemical analysis. The compound crystallizes in the triclinic space group $P\bar{1}$ with $a = 5.5415(8)$ Å, $b = 8.6382(8)$ Å, $c = 16.794$ (2) Å, $\alpha = 87.694(2)°$, $\beta = 80.859(2)°$, $\gamma = 76.005(2)°$, $V = 770.11(19)$ Å^3, and $Z = 1$. A cobalt atom lies in the center of symmetry and is octahedrally coordinated by two oxygen atoms from two undissociated diphosphonic ligands H_4L and four molecules of water. The cobalt atom and undissociated ligand H_4L are combined to form polymeric chains along the *c*-axis, resulting in the formation of a one-dimensional framework. The positive charge on the cobalt atom remains upon coordination and is balanced by a negatively charged uncoordinated ligand (H_2L) found as a clathrate in the lattice. Two lattice water molecules, hydrogen-bonded with the coordinated and uncoordinated ligands, complete the structure. The metal phosphonate chains are held together and bridge the uncoordinated anionic ligands by a number of strong hydrogen bonds, which make the structure possible. Cobalt phosphonate **2** has been characterized by TGA measurements, IR spectroscopy, and chemical analysis. The compound has a layered structure with an interlayer spacing of 14.26 Å. Metal phosphonate layers are cross-linked by hydrocarbon chains. The water molecules are coordinated to the metal atom. According to IR data, compound **2** contains two equivalent PO bonds and one different PO bond, which may be a result of the different types of Co–O–P connectivity within one phosphonic group.

Introduction

Metal phoshonates represent an important class of organic–inorganic compounds with potential applications in catalysis and ion exchange.[1−3] Due to great interest in the molecular design of structures with such specific properties, a considerable variety of metal phosphonates have already been prepared.[4−10] Among them there are compounds with variable nuclearity[11] and linear one-dimensional[12] and layered[5,13] structures. It has been recently shown that polyvalent metals and diphosphonic acids can give porous materials, which can be utilized as catalysts in a number of organic reactions.[3,5] In this connection phosphonic acids with two phosphonate groups are very attractive for creation of new classes of such compounds. In the literature alkyldiphosphonic acids are well-known as a precursor of self-assembled monolayers (SAMs) and multilayer films on high surface area silica and gold surfaces.[14,15] In addition diphosphonic acids can be

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employed as building blocks in supramolecular chemistry. Thus, the acid with two members in alkyl chains forms hydrogen-bonded adducts with a pillar-layered framework.[16] On the other hand, transition metals, such as cobalt and nickel, are known to give coordination polymers with different organic ligands.[17] These interesting abilities can be used for design and construction of new supramolecular compounds with various structures and properties.

In this paper we report on the synthesis, characterization, and structural features of novel cobalt phosphonates derived from 1,8-octylenediphosphonic acid.

Experimental Section

Materials and Methods. The chemicals were purchased from commercial sources and used as received.

The IR spectra were recorded in KBr pellets on a Nicolet Nexus 470 FTIR spectrometer with a spectral resolution of 2.000 cm^{-1}. Thermogravimetric studies were carried out with a DuPont TGA 951 instrument and TA Instruments TGA Q-500 at a heating rate of 10 °C/min under compressed air and argon, respectively. The resulting TGA residue of compound **2**, cobalt pyrophosphate, was identified from the International Center for Diffraction Data (ICDD No. 34-1378). Microprobe analysis was performed at the Department of Geology & Geophysics, Texas A&M University, College Station, TX. The elemental analysis data were obtained from Galbraith Laboratories, Inc., Knoxville, TN, and Robertson Microlit Laboratories, Madison, NJ. BSE SEM images were taken at the Department of Geology & Geophysics, Texas A&M University.

Synthesis of 1,8-Octylenediphosphonic Acid (H_4L). The ligand was synthesized by an Arbuzov-type reaction.[14,18,19] 1,8-Dibromooctane (Aldrich, 37 mmol) was mixed with triethyl phosphite (Alfa Aesar, 93 mmol) with vigorous stirring under a nitrogen atmosphere. The solution was heated and left at 150 °C for 6−7 h. Then the temperature was lowered, and air was allowed into the flask. The final tetraethyl phosphonate was hydrolyzed by refluxing with concentrated hydrochloric acid (125 mL) for 7−8 h. The resulting yellow liquid was left at room temperature overnight. The stirring of this saturated solution resulted in the formation of a white solid. The solid was filtered off, washed thoroughly with deionized water and acetone, and air-dried (6.7 g, 67%). IR: $\nu_{as}(CH_2)$ 2930 cm^{-1} (s); $\nu_s(CH_2)$ 2851 cm^{-1} (s); ν(PO−H); 2δ(POH) 2800−2100 cm^{-1} (m, mw, w); $\delta_s(CH_2)$ 1466 cm^{-1} (mw); $\delta(CH_2P)$ 1403 cm^{-1} (w); $\tau(CH_2)$, $\omega(CH_2)$ 1339−1298 cm^{-1} (w); ν(P═O) 1238, 1216 cm^{-1} (s); δ(POH) 1082 cm^{-1} (s); ν(P−OH) 1008, 949 cm^{-1} (vs).

Synthesis of $[Co(H_2O)_4(H_4L)][H_2L]\cdot 2H_2O$ (1). A 0.37 mmol sample of cobalt(II) acetate tetrahydrate (Aldrich) was dissolved in 5 mL of deionized water. Diphosphonic acid H_4L (0.36 mmol) was suspended in 10 mL of H_2O, and the stirred suspension was slightly heated. HF (EM science, 48%) was added dropwise to dissolve the diphosphonic acid. Then the hot clear solution was mixed with previously prepared cobalt acetate under stirring. The reaction mixture was heated for an additional 15−20 min, maintaining the temperature below the boiling point. Then the resulting pink solution was held at room temperature for 2 days. Pink crystals were collected, washed with water, and air-dried (0.13 g, 51%). Anal. Found: C, 27.03; H, 6.87; P, 18.21; Co, 8.66. Calcd for $C_{16}H_{50}O_{18}P_4Co$: C, 26.94; H, 7.06; P, 17.37; Co, 8.26. IR: $\nu_{as}(OH)$, $\nu_s(OH)$ 3525−3117 cm^{-1} (ms); $\nu_{as}(CH_2)$, $\nu_s(CH_2)$ 2922−2846 cm^{-1} (s, ms); ν(PO−H), 2δ(POH) 2800−2100 cm^{-1} (mw, w); δ(HOH) 1638 cm^{-1} (mw); $\delta_s(CH_2)$ 1466 cm^{-1} (mw), $\delta(CH_2P)$ 1414 cm^{-1} (w); $\tau(CH_2)$, $\omega(CH_2)$ 1334−1185 cm^{-1} (w); ν(P═O) 1129 cm^{-1} (s); δ(POH) 1070 cm^{-1}; ν(P−OH) 1000, 942 cm^{-1} (vs).

Synthesis of $Co_2(H_2O)_2(L)$ (2). H_4L (3.68 mmol) was suspended in 40 mL of water under vigorous stirring. The solution of cobalt acetate tetrahydrate (Aldrich, 7.37 mmol) in 12 mL of H_2O was added to the suspension. The pH value was lowered to 2.5−2.7 by addition of acetic acid. The final mixture was transferred into a medium-sized Teflon-lined pressure vessel and left for 3 days at 125 °C. The purple solid was filtered off, washed with water, and dried at 60 °C (1.44 g, 79%). Anal. Found: C, 22.67; H, 4.58; P, 14.85; Co, 27.87. Calcd for $C_8H_{20}O_8P_2Co_2$: C, 22.66; H, 4.75; P, 14.61; Co, 27.80. IR: $\nu_{as}(OH)$ 3456 cm^{-1} (s); $\nu_s(OH)$ 3414 cm^{-1} (ms); $\nu_{as}(CH_2)$, $\nu_s(CH_2)$ 2940−2847 cm^{-1} (ms); δ(HOH) 1626 cm^{-1} (mw); $\delta_s(CH_2)$ 1466 cm^{-1} (mw), $\delta(CH_2P)$ 1411 cm^{-1} (w); $\tau(CH_2)$, $\omega(CH_2)$ 1333−1188 cm^{-1} (w); $\nu(PO_3)$ 1108, 999, 942 cm^{-1} (s, vs).

Crystallography. Data collection for the compound $[Co(H_2O)_4(H_4L)][H_2L]\cdot 2H_2O$ (**1**) was carried out on a Bruker SMART 1000 CCD platform diffractometer equipped with monochromated Mo Kα radiation and an OXFORD cool stream low-temperature control unit. Data collection and reduction were performed with a Bruker CCD SMART 5.4 and SAINT+ 6.0 from Bruker AXS.[20] Crystallographic computing was performed using the SHELXTL 5.10 package.[21]

A pink crystal of compound **1**, of dimensions 0.42 × 0.40 × 0.18 mm^3, was mounted on a Bruker AXS CCD platform diffractometer with Mo Kα ($\lambda = 0.71073$ Å) radiation at −163 °C. A full sphere of data with 2424 frames was collected with a scan width of 0.3° in ω and an exposure time of 20 s. Final cell parameters were obtained by refining the *xyz* centroids of 7101 strong reflections with $I/\sigma > 10$ to yield $a = 5.5415(8)$ Å, $b = 8.6382(8)$ Å, $c = 16.794\ (2)$ Å, $\alpha = 87.694(2)°$, $\beta = 80.859(2)°$, $\gamma = 76.005(2)°$, and $V = 770.11(19)$ Å^3. An absorption correction was performed with SADABS and led to a transmission parameter between 1 and 0.93. Of the 8725 reflections collected, 3485 are unique ($R_{int} = 0.0153$). A summary of crystallographic data is given in Table 1.

Structure Solution and Refinement. Structure solution was performed in space group $P\bar{1}$ (No. 2) with SHELXTL.[21] The positions of Co and P atoms were located by Patterson methods XS.[21] All other atoms were located from successive different Fourier synthesis. All non-hydrogen atoms were anisotropically refined by full-matrix least squares on F^2 using the XL program.[21] Hydrogen atoms were located from a difference Fourier map and set to idealized positions.

The X-ray powder data were collected with a Bruker Advance powder unit by the step scan method with Cu Kα radiation ($\lambda = 1.5418$ Å).

Results and Discussion

Crystal Structure of $[Co(H_2O)_4(H_4L)][H_2L]\cdot 2H_2O$ (1). The representation of the unit cell of the compound is shown

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Table 1. Crystal Data and Structure Refinement of Compound **1**

empirical formula	$C_{16}H_{50}O_{18}P_4Co$	V, Å^3	770.11(19)
fw	713.37	Z	1
temp, K	110(2)	D_{calcd}, Mg/m^3	1.538
λ(Mo Kα), Å	0.71073	μ, mm^{-1}	0.838
cryst syst	triclinic	no. of reflns collected/unique	8725/3485 (R_{int} = 0.0153)
space group	$P\bar{1}$	no. of data/restraints/params	3485/0/180
a, Å	5.5415(8)	GOF on F^2	1.123
b, Å	8.6382(13)	R1, wR2^a ($I > 2\sigma(I)$)	0.0356, 0.0929
c, Å	16.794(2)	R1, wR2 (all data)	0.0365, 0.0937
α, deg	87.694(2)		
β, deg	80.859(2)		
γ, deg	76.005(2)		

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$. $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$.

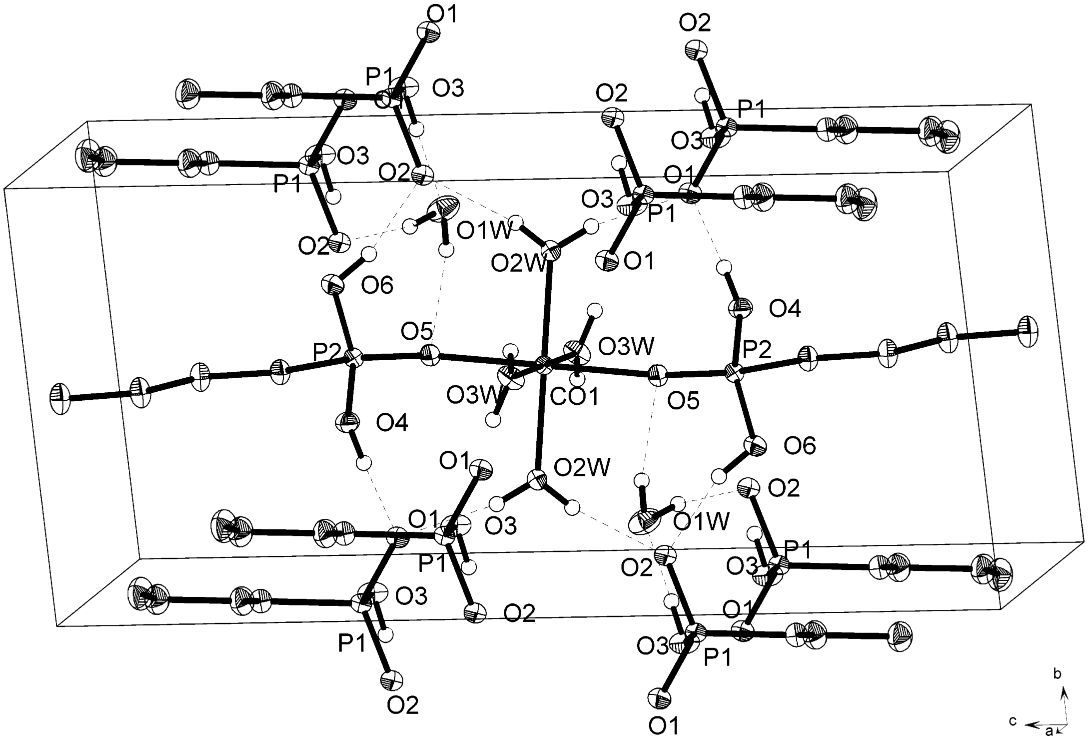

Figure 1. Unit cell representation of compound **1**.

in Figure 1. The cobalt phosphonate crystallizes in the P-1 space group (Table 1). The cobalt atom (Co1) lies on the center of symmetry and is octahedrally coordinated with two oxygen atoms (O5) from two undissociated phosphonate ligands H_4L and four molecules of water (O2W, O3W). The O5 oxygen atoms occupy the axial positions of the octahedron. The Co1−O5 bonds are slightly longer (2.138(1) Å) than the Co−OW equatorial bonds (Table 2). In the neutral phosphonate ligand H_4L the P2−O5 bond length (1.514(1) Å) is shorter than the other two (1.550(1) and 1.562(1) Å), indicating that oxygens O4 and O6 are protonated. It should be noted that the second uncoordinated diphosphonate ligand H_2L was found as a clathrate in the structure. The charge on the cobalt ion is satisfied by a proton displacement from each acid group in the clathrated ligand. This arrangement is evident from the fact that the P1−O3 bond distance (1.571(1) Å) is significantly longer than the other two P−O interatomic distances (1.504(1) and 1.531(1) Å) in the P1 tetrahedron.

Table 2. Selected Bond Lengths (Å) and Bond Angles (deg) of Compound **1**^{a}

Co(1)−O(2W) (2×)	2.0350(12)	O(1)−P(1)−O(2)	113.72(7)
Co(1)−O(3W) (2×)	2.1116(13)	O(1)−P(1)−O(3)	108.32(7)
Co(1)−O(5) (2×)	2.1379(12)	O(2)−P(1)−O(3)	109.81(7)
P(1)−O(1)	1.5043(12)	O(1)−P(1)−C(1)	109.04(8)
P(1)−O(2)	1.5312(12)	O(2)−P(1)−C(1)	108.65(8)
P(1)−O(3)	1.5710(13)	O(3)−P(1)−C(1)	107.10(8)
P(1)−C(1)	1.7999(18)	O(5)−P(2)−O(6)	114.26(7)
P(2)−O(5)	1.5135(12)	O(5)−P(2)−O(4)	113.23(7)
P(2)−O(6)	1.5498(13)	O(6)−P(2)−O(4)	104.68(7)
P(2)−O(4)	1.5624(13)	O(5)−P(2)−C(8)	110.41(8)
P(2)−C(8)	1.7866(17)	O(6)−P(2)−C(8)	106.07(8)

O(2W)−Co(1)−O(2W)#1	180.00(7)	O(4)−P(2)−C(8)	107.68(8)
O(2W)−Co(1)−O(3W) (2×)	91.73(5)	P(2)−O(5)−Co(1)	133.66(7)
O(2W)#1−Co(1)−O(3W) (2×)	88.27(5)		
O(2W)−Co(1)−O(5) (2×)	90.19(5)		
O(2W)#1−Co(1)−O(5)	89.81(5)		
O(3W)#1−Co(1)−O(5) (2×)	86.77(5)		
O(3W)−Co(1)−O(5) (2×)	93.23(5)		
O(2W)−Co(1)−O(5)#1	89.81(5)		

[a] Symmetry transformations used to generate equivalent atoms: #1, $-x + 1, -y + 1, -z + 1$; #2, $-x, -y + 1, -z$; #3, $-x + 1, -y, -z$.

Cobalt atoms, together with coordinated phosphonic ligands H_4L form infinite polymeric chains, running parallel to the c-axis at $^1/_2b$ (Figure 1). A network of hydrogen bonds connects the infinite chains to water molecules and uncoordinated clathrated ligands H_2L (Table 3). The charge-

Table 3. Hydrogen Bond Distances (Å) and Angles (deg) for Compound **1**[a]

D−H···A	*d*(D−H)	*d*(H...A)	*d*(D···A)	∠(DHA)
O(4)−H(4)···O(1)#4	0.84	1.73	2.561(2)	169.3
O(2W)−H(2WA)···O(1)#5	0.84	1.85	2.669(2)	166.3
O(2W)−H(2WB)···O(2)#6	0.84	1.92	2.748(2)	169.0
O(6)−H(6)···O(2)#6	0.84	1.71	2.516(2)	160.8
O(3W)−H(3WA)···O(5)#6	0.84	2.13	2.967(2)	177.3
O(3W)−H(3WB)···O(3)#7	0.84	2.04	2.873(2)	174.9
O(3)−H(3)···O(1W)#8	0.84	1.73	2.565(2)	172.8
O(1W)−H(1WB)···O(2)	0.84	1.96	2.773(2)	164.2
O(1W)−H(1WA)···O(5)	0.84	2.19	3.014(2)	168.6

[a] Symmetry transformations used to generate equivalent atoms: #1, $-x + 1, -y + 1, -z + 1$; #2, $-x, -y + 1, -z$; #3, $-x + 1, -y, -z$; #4, $x, y + 1, z$; #5, $-x + 1, -y, -z + 1$; #6, $x + 1, y, z$; #7, $x + 1, y + 1, z$; #8, $x - 1, y, z$.

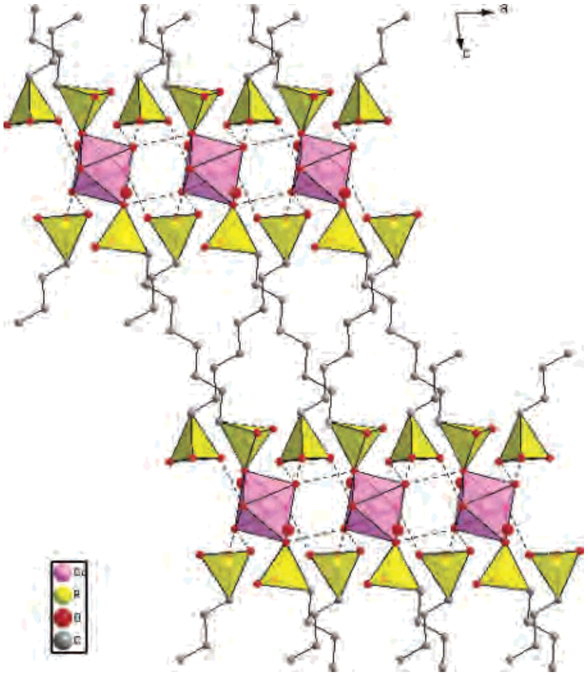

Figure 2. Polyhedral representation of the crystal structure of compound **1** along the *b*-axis.

compensating H_2L ligands are located at $b = 0$ with the midpoint of the alkyl chain at $c = 0$. Figure 2 is a view down the *b*-axis direction and shows that the alkyl chains of the clathrated uncoordinated ligands slope in the direction opposite those of the infinite chains. Furthermore, the two types of alkyl chains alternate in the *b*-axis direction.

The hydrogen bonds between the infinite chains and the uncoordinated phosphonic acid dianions are O4−H···O1 (2.561(2) Å) and O6−H···O2 (2.516(2) Å). These O···O distances are quite short because O1 and O2 may share the negative charge resulting from displacing a proton from the P1 phosphonic acid groups. The hydrogen-bonded lattice water molecules are located above and below the (020) planes (Figure 3) and are related by $\bar{1}$ symmetry. These molecules are hydrogen bonded to O5 of the infinite chains and O2 of the anionic phosphonate groups. Additionally the water molecules coordinated to cobalt also act as hydrogen donors to the phosphonate oxygens (Figures 1 and 3).

Such an arrangement results in the formation of a one-dimensional framework in which the clathrated uncoordinated ligand H_2L acts as a counterion to the positively charged $[Co(H_2O)_4(H_4L)]^{2+}$ motif. Similar behavior of diphosphonic acids has been observed in the 1:1 adduct of piperazine and 1,2-ethylenediphosphonic acid $[C_4H_{12}N_2]^{2+}$-$[HO_3P(CH_2)_2PO_3H]^{2-}$.[16] In the adduct anionic diphosphonic ligands are linked together and with the corresponding cations by hydrogen bonding. It should be noted that the bond distances and angles in C−PO_3 moieties of the adduct are very close to those observed in the compound $[Co(H_2O)_4$-$(H_4L)][H_2L]·2H_2O$ (Table 2), even though no metal is involved in the adduct.[16]

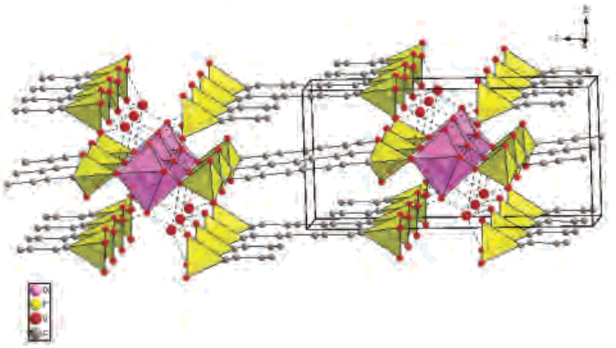

Figure 3. View of the crystal structure of compound **1** along the *a*-axis.

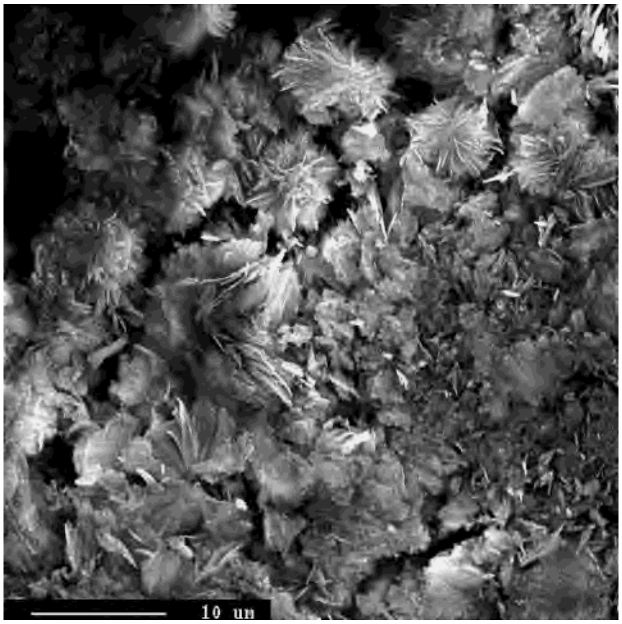

Figure 4. BSE SEM image of compound **2**.

$Co_2(H_2O)_2(L)$ (2). According to the SEM photographs, this compound crystallizes as thin platelets (Figure 4). The X-ray powder pattern yields an interlayer spacing of 14.26 Å (Figure 5). It is very likely that metal layers are cross-linked by hydrocarbon chains. It has been reported that copper phosphonates, $Cu_2(H_2O)_2(O_3P(CH_2)_nPO_3)·xH_2O$ ($n = 2-5$), with similar composition, have an average increase of 1.32 Å in interlayer spacing per carbon.[22] Assuming similarity of the structures, we compare the calculated value for an eight-carbon chain (15.29 Å) with the experimental result in cobalt phosphonate **2** (14.26 Å). It is possible that

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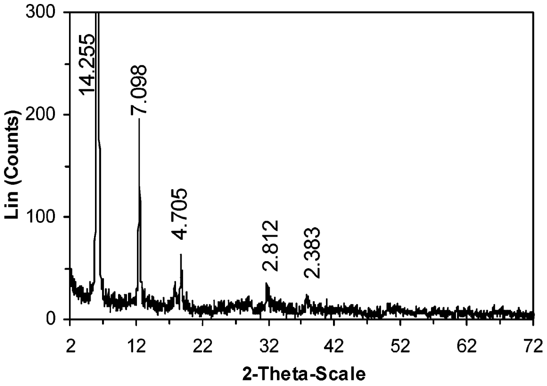

Figure 5. X-ray powder pattern of compound **2**.

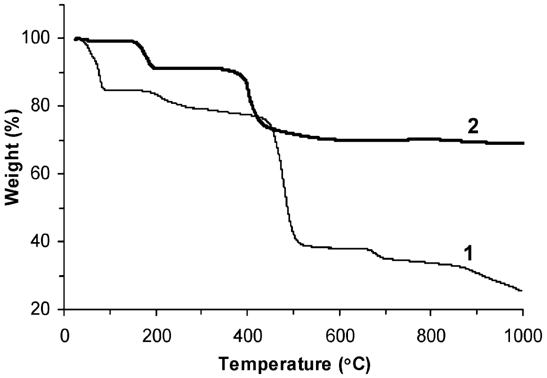

Figure 6. TGA curves for compounds **1** and **2**.

the chains in **2** are slightly tilted to account for the 1 Å difference. However, the *Pmn*2$_1$ space group, reported for another layered metal phosphonate, $Co(O_3PCH_3)(H_2O)$,[23] seems to be more reasonable for cobalt phosphonate **2**, because of the spectral identity of both compounds. The compound is not crystalline enough to solve its structure from the X-ray powder pattern data, but some structural features of compound **2** can also be revealed from TGA and IR data (see the following sections).

Thermogravimetric Study. The thermogravimetric studies of **1** demonstrate a number of weight losses, indicating a complex process of the decomposition (Figure 6, curve 1). According to the structural data, there are lattice and coordinated water molecules in the compound. The TGA diagram shows that the stepwise dehydration begins at 24 °C. The first step (5.9%) corresponds to a loss of two lattice molecules of water. Then the release of four water molecules coordinated to the metal atom at higher temperature takes place (9.3%) (Figure 6, curve 1). The total weight loss for the whole process (15.2%) is in good agreement with the value of 15.1% for $6H_2O$ calculated from the formula $C_{16}H_{50}O_{18}P_4Co$. Surprisingly this process is complete at around 90 °C, a temperature much lower than expected for coordinated water. There are several small weight losses (7.1%) in the temperature range 175−390 °C. They can probably be assigned to a condensation of the hydroxyl groups in both phosphonate ligands with a theoretical weight loss value of 7.6%. The burning of organic chains and transformation of phosphonic moieties occur at 390−542 °C.[13a] The observed weight loss (39.2%) is higher than the theoretical value of 31.45%, indicating some loss of P_2O_5. Assuming the final end product is $Co(PO_3)_2$, the total weight loss should be 69.59% as opposed to an observed value of 66.40% at 800 °C. This could result from the retention of P_2O_5 at this temperature as shown by further loss of weight to 1000 °C.

The TGA curve of layered **2** exhibits two weight losses (Figure 6, curve 2). First, the metal phosphonate loses its water at 140−207 °C. This high temperature of dehydration shows the thermal stability of the compound, which can be attributed to a strong bonding of water molecules with the metal atom.[13a,24−26] The observed weight loss (8.3%) is in agreement with the calculated value of 8.5% for two water molecules. The second loss occurs at 360−600 °C. It can be assigned to the decomposition of the organic part and phosphonic group condensation.[24−26] The process is complete with a total weight loss value of 30.9%. The blue residue was determined to be cobalt pyrophosphate, $Co_2P_2O_7$. The formula weight calculated from these results is 422.0. The ideal formula weight of 423.9 (the expected total weight loss is 31.2%), calculated for $C_8H_{20}O_8P_2Co_2$, is in good agreement with the TGA result.

IR Study. The IR studies of the starting ligand H_4L demonstrate all characteristic vibrations typical of anhydrous phosphonic acids with hydrocarbon chains (Figure 7). The spectrum shows a number of bands with strong to very strong intensities in the PO stretching vibration region. Thus, the strong band near 1216 cm^{-1} indicates the presence of the hydrogen-bonded P═O group in H_4L.[27] A number of broad and weak bands observed in the 2800−2100 cm^{-1} region can be assigned to the ν(PO−H) and 2δ(POH) vibrations.[28] Symmetrical and asymmetrical stretching vibrations of P−OH groups (ν(P−OH)) appear at 1008 and 949 cm^{-1}, respectively.[29] The band around 1082 cm^{-1} probably belongs to the POH bending vibration ((δ(POH)).[27] The corresponding stretching (2922−2846 cm^{-1}) and bending (1466−1185 cm^{-1}) vibrations of CH_2 groups have also been detected.[30]

Solid-state IR spectra of the synthesized compound **1** are in good agreement with single-crystal data and TGA studies. According to X-ray data cobalt phosphonate **1** crystallizes with two molecules of water in the lattice. Additionally four molecules of water are present in the coordination sphere of cobalt. The high-frequency broad bands at 3225−3117 cm^{-1} can be attributed to the stretching vibrations of hydrogen-bonded lattice water molecules superimposed with symmetrical and asymmetrical vibrations in coordinated water

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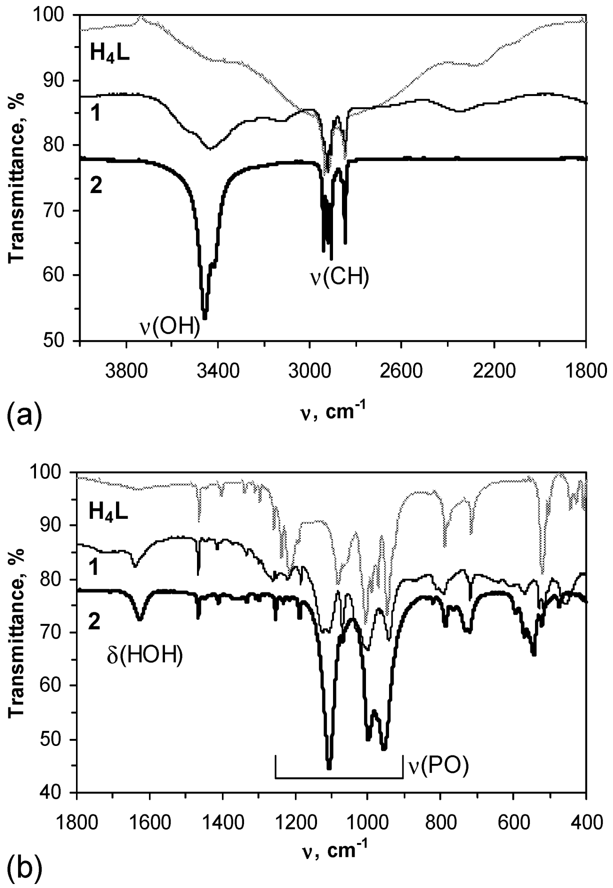

Figure 7. IR spectra in the ν(OH), ν(CH) (a) and ν(PO) (b) ranges.

(Figure 7a). The corresponding δ(HOH) band appears at 1638 cm^{-1}. Very important changes occur in the PO stretching vibration region. Thus, the ν(P=O) band (1216 cm^{-1}) is low-frequency-shifted ($\Delta\nu = 87$ cm^{-1}) due to coordination of the oxygen atom with cobalt. Indeed the P=O bond of the H_4L ligand elongates upon coordination (see the single-crystal data). The insignificant low-frequency shift and broadening of the ν(P−OH) bands (1000 and 942 cm^{-1})[29] are expected due to a number of strong hydrogen bonds in the system. Such a broadening can also be explained by the presence of P−OH groups in both coordinated (H_4L) and uncoordinated clathrated (H_2L) ligands. The ν(P−O$^-$) vibration was not identified as a separate band in the IR spectra because of probable overlap with ν(P−OH) vibrations. The bands at 2800−2100 and 1070 cm^{-1} can be attributed to ν(PO−H), 2δ(POH), and δ(POH) vibrations, respectively, since the POH groups remain protonated upon reaction with cobalt (Figure 7b).[28,29]

TGA studies of the layered compound **2** reveal the presence of a water molecule *coordinated* to the metal atom. The IR data support these results (Figure 7a). Indeed the IR spectra dramatically changed with the formation of **2**. First, a sharp band appeared at 3456 cm^{-1} with a shoulder at 3414 cm^{-1}. These bands can undoubtedly be attributed to the stretching vibrations of *coordinated* water molecules (ν_{as}(OH), ν_s(OH)) (Figure 7).[13a,24,31,32] Second, the sharpening of all other bands is observed. This fact can be explained by the absence of *lattice* water, which contributes some disorder in the structure due to a number of hydrogen bonds. The ν(PO) range exhibits three sharp vibrations at 1108, 999, and 942 cm^{-1} ($\Delta\nu$ is 109 and 57 cm^{-1}). Two bands at lower frequency can probably be assigned to the symmetrical and asymmetrical stretching vibrations of the equivalent PO bonds in compound **2**. The high-frequency band at 1108 cm^{-1} corresponds to a PO bond different from those mentioned above (Figure 7b). Such a variation in P−O distances occurs probably due to the different Co−O−P connectivity within the PO_3 group in the compound. As has been noted, the IR spectrum of **2** is very similar to that reported for $Co(O_3PCH_3)(H_2O)$, especially in the ν(PO) region.[23] Assuming similar symmetry of C−PO3 moieties and close composition of both compounds, we could suggest the $Pmn2_1$ space group for cobalt phosphonate **2**.

Conclusion

New metal phosphonates **1** and **2** have been synthesized from H_4L and characterized by TGA measurements, IR spectroscopy, and chemical analysis. The structure of compound **1** has been solved from X-ray single-crystal data. It has been demonstrated that the octahedrally coordinated cobalt atom and undissociated H_4L ligands form a one-dimensional framework, in which uncoordinated ligand H_2L is clathrated and acts as a counterion to the positively charged $[Co(H_2O)_4(H_4L)]^{2+}$ motif. Co−H_4L polymeric chains and counterions $[H_2L]^{2-}$ are held together by strong hydrogen bonding.

The layered character of the compound **2** structure has been revealed from the X-ray powder pattern data. It has been shown that the compound crystallizes with one water molecule coordinated to each metal atom, and the presence of nonequivalent PO bonds has been exhibited by IR spectroscopy. Most striking is the similarity of the IR spectrum to that of $Co(O_3PCH_3)(H_2O)$. All of these features plus the space group strongly indicate that compound **2** has the same layer structure as $M(O_3PC_6H_5)(H_2O)$.[33a,b]

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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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