Inorg. Chem. **2002**, *41*, 2319–2324

Inorganic Chemistry
Article

Metal Carboxylate-Phosphonate Hybrid Layered Compounds: Synthesis and Single Crystal Structures of Novel Divalent Metal Complexes with *N*-(Phosphonomethyl)iminodiacetic Acid

Jiang-Gao Mao and Abraham Clearfield*

Department of Chemistry, Texas A&M University, College Station, Texas 77843-3255

Received October 22, 2001

Two novel divalent metal complexes with *N*-(phosphonomethyl)iminodiacetic acid, $H_2O_3PCH_2N(CH_2CO_2H)_2$ (H_4PMIDA), $[Co_2(PMIDA)(H_2O)_5]\cdot H_2O$, **1**, and $[Zn_2(PMIDA)(CH_3CO_2H)]\cdot 2H_2O$, **2**, have been synthesized and structurally characterized. The structure of complex **1** features two different kinds of Co(II) layers, namely, a cobalt phosphonate layer along the ⟨100⟩ plane and a cobalt carboxylate layer along the ⟨300⟩ plane. The Co(II) atoms in the phosphonate layer are octahedrally coordinated by 4 aqua ligands and 2 oxygen atoms from two phosphonic acid groups. Two Co(II) octahedra are bridged by a pair of phosphonic groups into a dimeric unit, and such dimers are interconnected into a layer through hydrogen bonding between aqua ligands. The Co(II) atoms in the carboxylate layer are octahedrally coordinated by a chelating PMIDA ligand, one aqua ligand, and one phosphonic oxygen atom from the neighboring PMIDA ligand. These Co(II) octahedra are interlinked by bridging carboxylic groups into a one-dimensional chain along the *c*-axis; such chains are held together by hydrogen bonds formed between carboxylic oxygen atoms and lattice water molecules, in such a way as to form a layer along the ⟨300⟩ direction. Two such layers are interconnected into a double layer via hydrogen bonding. These double layers are further interconnected with the Co(II) phosphonate layers through phosphonate tetrahedra along the *a* direction, resulting in the formation of a complicated three-dimensional network. The crystal structure of **2** contains a metal phosphonate and metal carboxylate hybrid layer along the ⟨202⟩ plane. One of the two zinc atoms in the asymmetric unit is tetrahedrally coordinated by four oxygen atoms from two phosphonic acid groups and two carboxylic groups; the other zinc atom is 5-coordinated by three oxygen atoms and a nitrogen atom from a chelating PMIDA ligand and one oxygen atom from the acetic acid. The above two types of zinc metal ions are interconnected by bridging carboxylic and phosphonic groups, resulting in the formation of a layered structure.

Introduction

Metal phosphonates have been a research field of rapid expansion in recent years, mainly because of their potential application in the areas of catalysis,[1] ion exchange,[2] proton conductivity,[3] intercalation chemistry,[4] photochemistry,[5] and materials chemistry.[6] Most of the compounds studied are layered species in which the metal octahedra are bridged by phosphonic acid tetrahedra to form two-dimensional layers that are separated by the hydrophobic regions of the organic moieties.[6] Studies from our group and from others have shown that a variety of metal ions, including group 4 and 14 elements and divalent and trivalent ions, form this type of layered compound.[6−9] To form the α-zirconium phosphate (α-ZrP) type layer structure, the size of the organic group

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* Author to whom correspondence should be addressed. E-mail: a-clearfield@mail.chem.tamu.edu.

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10.1021/ic011094w CCC: $22.00

should not exceed ~24 Å^2; our studies, however, have also shown that some new types of layer structures in zirconium phosphate/phosphonate compounds can be formed when the organic portion of the phosphonic acid is too large to fit the intermellar space.[10] Research on metal complexes with phosphonic acids attached with aza-crown ethers shows that those compounds have many unusual structural features.[9,11] One problem in metal phosphonate chemistry is that many metal phosphonates form poorly crystalline compounds. Phosphonic acids with additional carboxylic functional groups are interesting ligands because they provide more coordination sites that may increase the solubility of the metal phosphonates in water and improve the crystallinity of their metal complexes.[9,12] Earlier, we reported a mixed phosphate phosphonate layered zirconium compound with the ligand *N*-(phosphonomethyl)iminodiacetic acid (H_4PMIDA),[10] which was made by reacting a zirconium salt with a mixture of phosphoric acid and H_4PMIDA solutions. A linear chain compound was isolated when the reaction was carried out in the absence of phosphoric acid.[13] In both cases, the iminodiacetic moieties are only involved in hydrogen bonding. Thus, they are available for further metal complexing. Wood and co-workers obtained the canted antiferromagnet $\{K_2Co(PMIDA)\}_6 \cdot xH_2O$, whose crystal structure features a hexameric ring in the chair conformation.[14] In this paper, we report the synthesis and crystal structures of two novel divalent metal carboxylate−phosphonate hybrid layered compounds of H_4PMIDA, namely, $[Co_2(PMIDA)(H_2O)_5] \cdot H_2O$, **1**, whose structure contains double layers of Co(II) carboxylate interconnected by layers of Co(II) phosphonate, and $[Zn_2(PMIDA)(CH_3CO_2H)] \cdot 2H_2O$, **2**, whose crystal structure features a zinc carboxylate−phosphonate hybrid layer along the ⟨202⟩ plane.

Experimental Section

Preparation of $Co_2(PMIDA)(H_2O)_5 \cdot H_2O$, 1, and $Zn_2(PMIDA)(CH_3CO_2H) \cdot 2H_2O$, 2. Both complexes were synthesized by a similar method. Cobalt(II) acetate (Aldrich) or zinc(II) acetate (Fisher) (2 mmol) and *N*-(phosphonomethyl)iminodiacetic acid (H_4PMIDA, Aldrich, 1 mmol) were dissolved in distilled water (10 mL). Then, the mixture was heated for 30 min at 70 °C, and 2 mmol of urea was added to the solution to neutralize the acetic acid formed during the reaction. The resulting solution was filtered off. Single crystals of the target complexes were obtained by diffusing absolute alcohol into the filtrates. After 10 days, small pink crystals grew on the glass tube of the cobalt solution, and a voluminous pink gel formed. The pink gel was filtered off; results of elemental analysis and X-ray powder diffraction indicated that it has the same composition as that of the crystals, yield 45.8% (crystals and powder combined, 0.403 g). For the zinc complex, only colorless crystals were isolated, yield 37.5% (0.337 g). Elemental analysis for complex **1**: C, 13.01%; H, 3.95%; N, 3.20%; P, 7.21%. Calcd: C, 13.37%; H, 4.04%; N, 3.12%; P, 6.90%. Elemental analysis for complex **2**: C, 18.13%; H, 3.02%; N, 3.23%; P, 7.01%. Calcd: C, 18.69%; H, 3.14%; N, 3.11%; P, 6.88%.

Table 1. Crystal Data and Structure Refinement for **1** and **2**[a]

	1	**2**
empirical formula	$C_5H_{18}Co_2NO_{13}P$	$C_7H_{14}Zn_2NO_{11}P$
fw	449.03	449.90
space group	$P2_1/c$	$P2_1/n$
a, Å	14.172(3)	10.025(2)
b, Å	10.412(2)	8.949(1)
c, Å	9.814(2)	16.253(3)
β, deg	106.037(4)	90.155(3)
V, Å^3	1391.9(5)	1458.1(4)
Z	4	4
D_{calcd}, g cm^{-3}	2.143	2.050
temp (K)	110(2)	110(2)
μ, mm^{-1}	2.569	3.456
GOF	0.974	1.009
R1, wR2 ($I > 2\sigma(I)$)	0.0332, 0.0765	0.0464, 0.1174
R1, wR2 (all data)	0.0482, 0.0823	0.0673, 0.1309

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

Crystal Structure Determination. Single crystals were mounted on a Bruker Smart CCD using Mo Kα radiation ($\lambda = 0.71069$ Å) and the graphite monochromator at 110(2) K. The cell constants were indexed from reflections picked from 60 frames collected with 10 s exposure per frame. A hemisphere of data (1271 frames at 5 cm detector distances) was collected by the narrow-frame method with scan widths of 0.30° in ω and exposure time of 30 s per frame. The first 50 frames were recollected in the end of data collection to assess the stability of the crystal, and it was found that the decay in intensity was less than 1%. The data were corrected for Lorentz factor, polarization, air absorption, and absorption due to variations in the path length through the detector faceplate. An absorption correction based on either the ψ scan method or SADABS was also applied.[15a]

The space group was uniquely determined to be $P2_1/c$ (No. 14) for **1** and $P2_1/n$ (No. 14) for **2**. The structures were solved using direct methods (SHELXTL) and refined by the least-squares methods with atomic coordinates and anisotropic thermal parameters for all non-hydrogen atoms.[15b] All hydrogen atoms, except those for water molecules, were generated geometrically, assigned fixed isotropic thermal parameters, and included in the structure factor calculations. The hydrogen atoms for the water molecules in both complexes were located from difference Fourier maps and were refined isotropically. The final difference Fourier maps showed featureless residual peaks of 1.521 (for complex **1**, 0.83 Å from the C(3) atom) and 1.552 e$\cdot$Å^{-3} (for complex **2**, 0.04 Å from the Zn(1) atom), respectively. Some of the data collection and refinement parameters are summarized in Table 1, and important bond lengths and angles for the complexes are listed in Table 2. More details on the crystallographic studies as well as atom displacement parameters are given in the Supporting Information.

Results

1. Crystal Structure of $Co_2[O_3PCH_2N(CH_2COO)_2(H_2O)_5] \cdot H_2O$, 1.

An ORTEP drawing showing the coordination of the two independent cobalt atoms is presented in

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Table 2. Selected Bond Lengths [Å] and Angles [deg] for **1**[a]

Complex **1**				Complex **2**			
Co(1)−O(2)#1	2.053(2)	Co(1)−O(1W)	2.097(2)	Zn(1)−O(3)#1	1.927(3)	Zn(1)−O(2)	1.934(3)
Co(1)−O(2W)	2.097(2)	Co(1)−O(1)	2.101(2)	Zn(1)−O(4)#2	1.962(3)	Zn(1)−O(6)#3	1.987(3)
Co(1)−O(3W)	2.107(2)	Co(1)−O(4W)	2.158(2)	Zn(2)−O(1)	1.980(3)	Zn(2)−O(8)	1.991(3)
Co(2)−O(3)	2.073(2)	Co(2)−O(4)	2.075(2)	Zn(2)−O(5)	2.005(3)	Zn(2)−O(7)	2.020(3)
Co(2)−O(6)	2.079(2)	Co(2)−O(5)#2	2.096(2)	Zn(2)−N(1)	2.226(3)	P(1)−O(2)	1.524(3)
Co(2)−O(5W)	2.126(3)	Co(2)−N(1)	2.198(2)	P(1)−O(1)	1.531(3)	P(1)−O(3)	1.533(3)
P(1)−O(1)	1.526(2)	P(1)−O(2)	1.533(2)	P(1)−C(1)	1.822(5)	C(1)−C(2)	1.465(5)
P(1)−O(3)	1.535(2)	P(1)−C(1)	1.807(3)	N(1)−C(4)	1.475(5)	N(1)−C(1)	1.497(5)
C(1)−N(1)	1.496(4)	C(2)−N(1)	1.487(4)	C(2)−C(3)	1.530(6)	C(3)−O(5)	1.251(5)
C(2)−C(3)	1.530(4)	C(3)−O(5)	1.269(3)	C(3)−O(4)	1.260(5)	C(4)−C(5)	1.514(6)
C(3)−O(4)	1.270(3)	C(4)−N(1)	1.477(4)	C(5)−O(7)	1.254(5)	C(5)−O(6)	1.270(5)
C(4)−C(5)	1.534(4)	C(5)−O(7)	1.249(4)	C(6)−C(7)	1.326(6)	C(7)−O(8)	1.275(5)
C(5)−O(6)	1.273(4)	O(2)−Co(1)#1	2.053(2)	C(7)−O(9)	1.344(6)	O(3)−Zn(1)#3	1.927(3)
O(5)−Co(2)#3	2.096(2)			O(4)−Zn(1)#4	1.962(3)	C(6)−Zn(1)#1	1.987(3)
Co(1)···Co(1)#4	4.907(1)	Co(1)···Co(1)#5	4.907(1)	Zn(1)···Zn(1)#1	5.103(1)	Zn(1)···Zn(1)#3	5.103(1)
Co(1)···Co(1)#1	5.279(1)	Co(1)···Co(1)#6	5.327(1)	Zn(1)···Zn(2)	4.838(1)	Zn(1)···Zn(2)#1	5.061(1)
Co(1)···Co(2)#1	4.811(1)	Co(1)···Co(2)	5.487(1)	Zn(1)···Zn(2)#2	4.825(1)	Zn(1)···Zn(2)#3	5.081(1)
Co(2)···Co(2)#2	5.998(1)	Co(2)···Co(2)#3	5.998(1)	Zn(2)···Zn(2)#5	4.657(1)	Zn(2)···Zn(2)#6	5.675(1)
Co(2)···Co(2)#7	5.825(1)						
			Hydrogen Bonding				
O(1w)···O(2w)	2.864	O(1w)···O(2w)#5	2.870	O(1w)···O(3)	2.809	O(1w)···O(8)#3	2.931
O(2w)···O(4w)#6	2.831	O(2w)···O(6w)	2.713	O(2w)···O(6)	2.851	O(2w)···O(9)#7	2.949
O(2w)···O(3w)	2.800	O(3w)···O(4w)	2.845				
O(5w)···O(7)#8	2.620	O(6w)···O(7)	2.874				
O(2)#1−Co(1)−O(1W)	95.83(9)	O(2)#1−Co(1)−O(2W)	177.51(10)	O(3)#1−Zn(1)−O(2)	111.52(13)	O(3)#1−Zn(1)−O(4)#2	119.13(12)
O(1W)−Co(1)−O(2W)	86.15(10)	O(2)#1−Co(1)−O(1)	93.66(8)	O(2)−Zn(1)-O(4)#2	100.73(13)	O(3)#1−Zn(1)−O(6)#3	101.16(13)
O(1W)−Co(1)−O(1)	89.13(9)	O(2W)−Co(1)−O(1)	87.86(9)	O(2)−Zn(1)−O(6)#3	110.66(13)	O(4)#2−Zn(1)−O(6)#3	113.92(12)
O(2)#1−Co(1)−O(3W)	94.33(10)	O(1W)−Co(1)−O(3W)	167.88(10)	O(1)−Zn(2)−O(8)	104.27(13)	O(1)−Zn(2)−O(5)	117.05(13)
O(2W)−Co(1)−O(3W)	83.53(10)	O(1)−Co(1)−O(3W)	96.80(9)	O(8)−Zn(2)−O(5)	97.55(13)	O(1)−Zn(2)−O(7)	108.34(13)
O(2)#1−Co(1)−O(4W)	87.17(9)	O(1W)−Co(1)−O(4W)	90.21(10)	O(8)−Zn(2)−O(7)	89.81(12)	O(5)−Zn(2)−O(7)	130.24(13)
O(2W)−Co(1)−O(4W)	91.33(9)	O(1)−Co(1)−O(4W)	179.00(9)	O(1)−Zn(2)−N(1)	89.58(12)	O(8)−Zn(2)−N(1)	164.98(13)
O(3W)−Co(1)−O(4W)	83.70(10)	O(3)−Co(2)−O(4)	94.74(8)	O(5)−Zn(2)−N(1)	80.82(13)	O(7)−Zn(2)−N(1)	80.18(12)
O(3)−Co(2)−O(6)	96.58(9)	O(4)−Co(2)−O(6)	154.54(8)	O(2)−P(1)−O(1)	114.20(19)	O(2)−P(1)−O(3)	110.97(18)
O(3)−Co(2)−O(5)#2	87.73(8)	O(4)−Co(2)−O(5)#2	99.56(8)	O(1)−P(1)−O(3)	112.70(17)	O(2)−P(1)−C(1)	106.51(19)
O(6)−Co(2)−O(5)#2	103.60(8)	O(3)−Co(2)−O(5W)	176.86(9)	O(1)−P(1)−C(1)	104.91(18)	O(3)−P(1)−C(1)	106.90(18)
O(4)−Co(2)−O(5W)	85.20(10)	O(6)−Co(2)−O(5W)	84.70(10)	P(1)−O(1)−Zn(2)	113.08(17)	P(1)−O(2)−Zn(1)	129.4(2)
O(5)#2−Co(2)−O(5W)	89.19(10)	O(3)−Co(2)−N(1)	85.92(9)	P(1)−O(3)−Zn(1)#3	126.96(18)	C(3)−O(4)−Zn(1)#4	114.5(3)
O(4)−Co(2)−N(1)	79.07(8)	O(6)−Co(2)−N(1)	79.09(8)	C(3)−O(5)−Zn(2)	116.3(3)	C(5)−O(6)−Zn(1)#1	121.8(3)
O(5)#2−Co(2)−N(1)	173.36(9)	O(5W)−Co(2)−N(1)	97.14(10)	C(5)−O(7)−Zn(2)	117.3(3)	C(7)−O(8)−Zn(2)	125.3(3)
O(1)−P(1)−O(2)	113.09(12)	O(1)−P(1)−O(3)	112.14(12)	O(5)−C(3)−O(4)	124.4(4)	O(7)−C(5)−O(6)	123.5(4)
O(2)−P(1)−O(3)	113.64(12)	O(1)−P(1)−C(1)	106.01(13)	O(8)−C(7)−O(9)	119.4(4)		
O(2)−P(1)−C(1)	108.04(13)	O(3)−P(1)−C(1)	103.02(13)				
O(5)−C(3)−O(4)	122.4(3)	O(7)−C(5)−O(6)	123.6(3)				

[a] Symmetry transformations used to generate equivalent atoms. For complex **1**: #1, $-x + 2, -y + 1, -z + 2$; #2, $x, -y + {}^{3}/_{2}, z + {}^{1}/_{2}$; #3, $x, -y + {}^{3}/_{2}, z - {}^{1}/_{2}$; #4, $x, -y + {}^{1}/_{2}, z - {}^{1}/_{2}$; #5, $x, -y + {}^{1}/_{2}, z + {}^{1}/_{2}$; #6, $-x + 2, -y, -z + 2$; #7, $-x + 1, -y + 1, -z + 2$; #8, $-x + 1, y + {}^{1}/_{2}, -z + {}^{3}/_{2}$. For complex **2**: #1, $-x - {}^{1}/_{2}, y - {}^{1}/_{2}, -z + {}^{3}/_{2}$; #2, $x - {}^{1}/_{2}, -y + {}^{1}/_{2}, z + {}^{1}/_{2}$; #3, $-x - {}^{1}/_{2}, y + {}^{1}/_{2}, -z + {}^{3}/_{2}$; #4, $x + {}^{1}/_{2}, -y + {}^{1}/_{2}, z - {}^{1}/_{2}$; #5, $-x, -y, 1 - z$; #6, $-x, 1 - y, 1 - z$; #7, $-1 + x, y, z$.

Figure 1. The Co1 atom is octahedrally coordinated by four aqua ligands and two oxygens from two phosphonate groups. The phosphonate groups connect two cobalt atoms by O−P−O bridges, forming an eight-membered ring. The Co−O distances within these octahedra range from 2.053(2) to 2.158(2) Å. The third oxygen of the phosphonate groups bonds to Co2, as does the nitrogen of that PMIDA group. This arrangement results in the formation of a five-membered ring, consisting of Co2, N1, C1, P1, O3. The two carboxylate groups also form 5-membered chelate rings with Co2. These rings consist of atoms Co2, N1, C2, C3, O4 and Co2, N1, C4, C5, O6. Of the two remaining carboxylate oxygens, O5 bonds to another cobalt atom, forming a linear chain of Co2 octahedra, whereas O7 acts as acceptor of a hydrogen bond from a free water molecule, O6W. The sixth coordination site on Co2 is filled by a water molecule, O5W. The equatorial plane of Co2 consists of N1, O4, O5, O6, and the axial atoms are O3 and O5W. Figure 2 shows the arrangement of the zigzag chains along the *c*-axis direction connected through the O5 atoms. The Co2−O distances range from 2.073(2) to 2.126(2) Å, and the Co2−N bond length is 2.198(3) Å.

The Co1 octahedra forming dimers through phosphonate bridging are terminated by the four water molecules around the periphery of each octahedron. These water molecules bind the dimers together, through a network of hydrogen bonds, listed in Table 2 and shown in Figure 3. The dimers connect to the Co2 octahedra through O3 of the phosphonate group in both the positive and negative *a*-axis direction. The result is illustrated in Figure 4. The dimers are grouped about an *a*-axis value of zero and hydrogen bonded to each other in the *bc* plane. The dimers are connected to the chelated octahedra of Co2 at approximately +1/3*a* and −1/3*a* (Figure 4) and are, thus, sandwiched between the chains. The

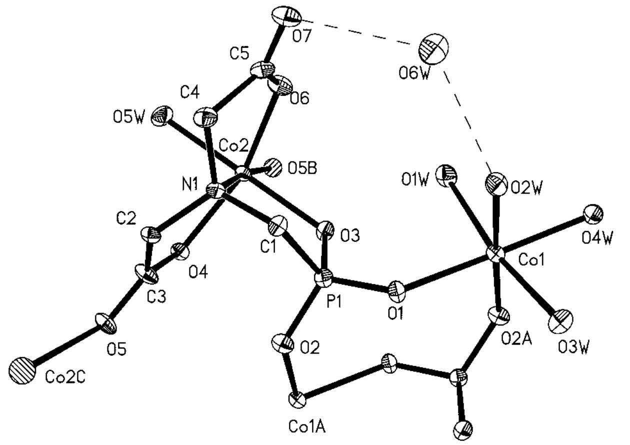

Figure 1. ORTEP representation of the asymmetry unit of complex **1**. Thermal ellipsoids are drawn at 50% probability. The dotted lines indicate hydrogen bonds.

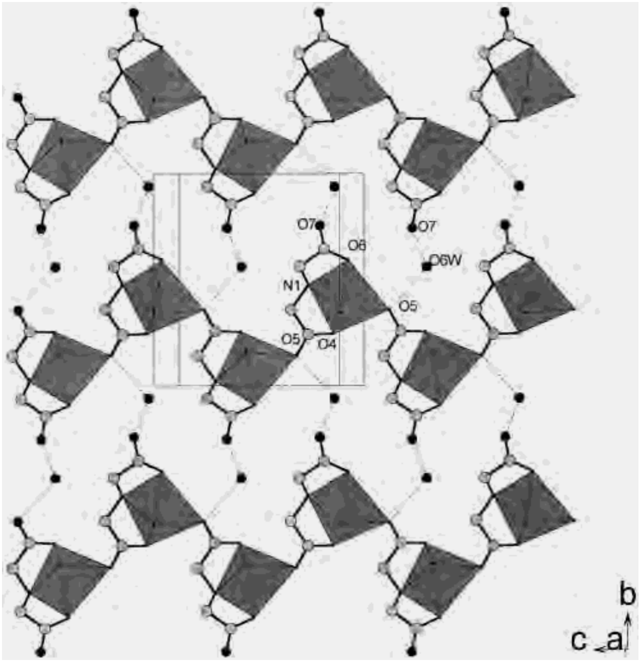

Figure 2. Polyhedral representation of a [300] cobalt carboxylate layer. C and O atoms are shown as gray and black circles, respectively. The phosphonic groups have been omitted for clarity. The dotted lines indicate hydrogen bonds.

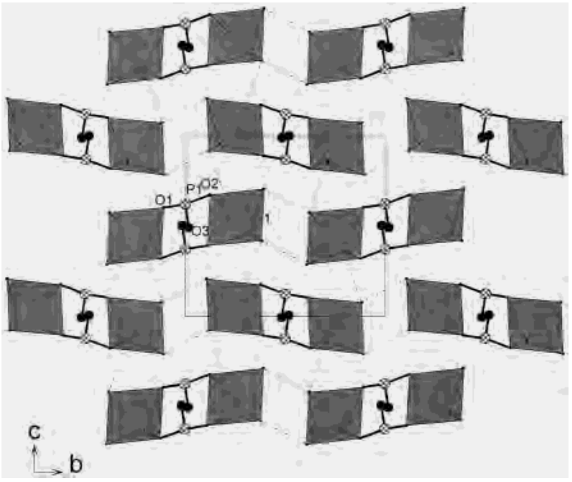

Figure 3. Polyhedral representation of a [100] cobalt phosphonate layer. P and O atoms are shown as crossed and black circles, respectively. The imino−diacetic acid moieties have been omitted for clarity. The dotted lines indicate hydrogen bonds.

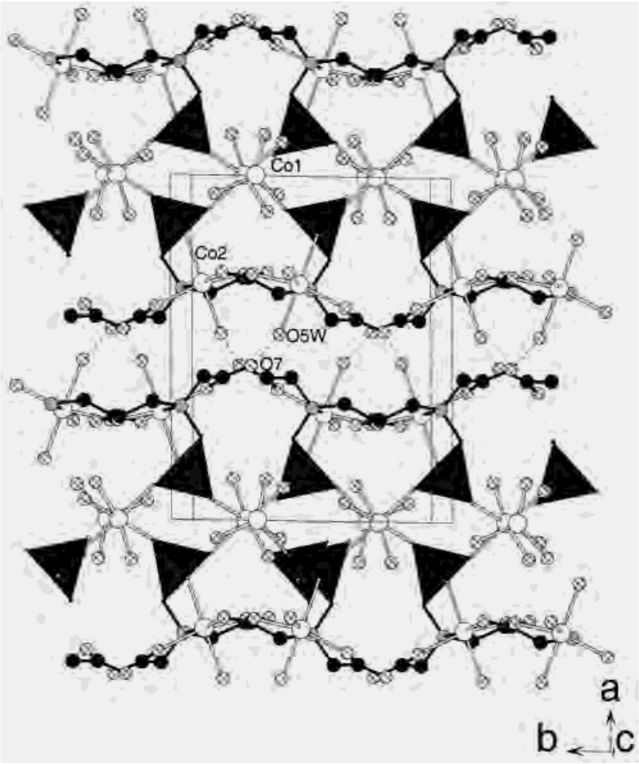

Figure 4. View of crystal structure of complex **1** along the *c* axis. The phosphonic groups are represented by tetrahedra. Co, N, O, and C atoms are shown as open, gray, crossed, and black circles, respectively.

hydrogen-bonding network ties the entire structure together three-dimensionally.

2. Crystal Structure of [Zn_2(PMIDA)(CH_3CO_2H)]·2H_2O, 2. The structure of the zinc compound is very different from that of the cobalt compound. It features a two-dimensional zinc carboxylate−phosphonate hybrid layer along the ⟨202⟩ plane.

There are two zinc atoms in each asymmetric unit (Figure 5). One zinc atom (Zn(1)) is tetrahedrally coordinated by two phosphonate oxygen atoms, O2, O3, and two carboxylic oxygen atoms (O4, O6) from four PMIDA ligands. The Zn−O (carboxylic) distances, 1.962(3) and 1.987(3) Å, are slightly longer than the Zn−O (phosphonate) bonds (1.927(3) and 1.934(3) Å). The second zinc atom is 5-coordinated by a chelating PMIDA with Zn2, O1, O5, O7, N1, and O8 from a neutral acetic acid molecule. Its coordination geometry can be best described as a trigonal bipyramid: O1, O5, and O7 atoms form a trigonal plane which is capped by N1 and O8 atoms (Figure 5). Unlike those in the cobalt compound, both carboxylic groups of PMIDA in the zinc compound are in the bridging coordination mode. The coordination about Zn2 arises from a single PMIDA group as represented in Figure 5 by P1. Two of the P1 phosphonate oxygen atoms bond to two Zn1 atoms. The third phosphonate oxygen, O1, bonds to a Zn2 and forms part of a five-membered ring Zn2−O1−P1−C1−N1. The second and third five-membered rings result from coordination by carboxylate oxygen atoms, viz.,

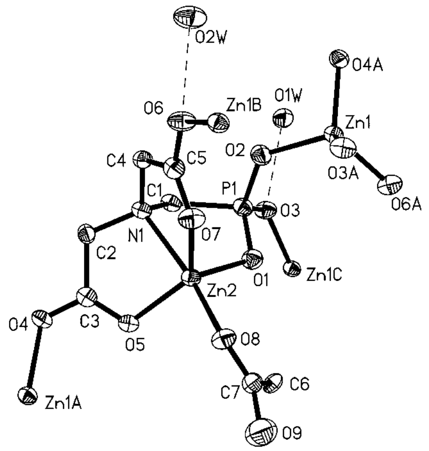

Figure 5. ORTEP representation of the asymmetry unit of complex **2**. Thermal ellipsoids are drawn at 50% probability. The dotted lines indicate hydrogen bonds.

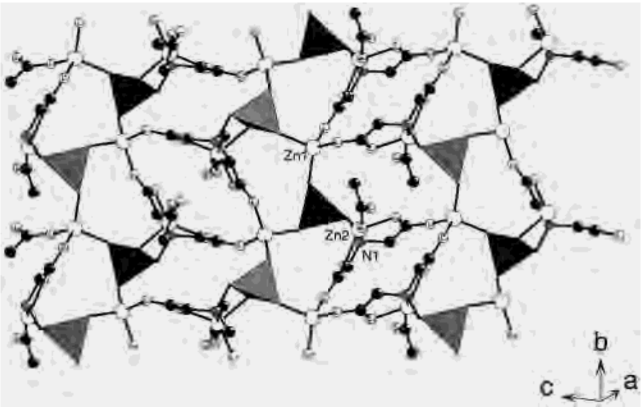

Figure 6. Zinc carboxylate−phosphonate hybrid layer parallel to the ⟨202⟩ plane. The phosphonate groups are shown in tetrahedra. Zn, O, C, and N atoms are represented by open, crossed, gray, and black circles, respectively.

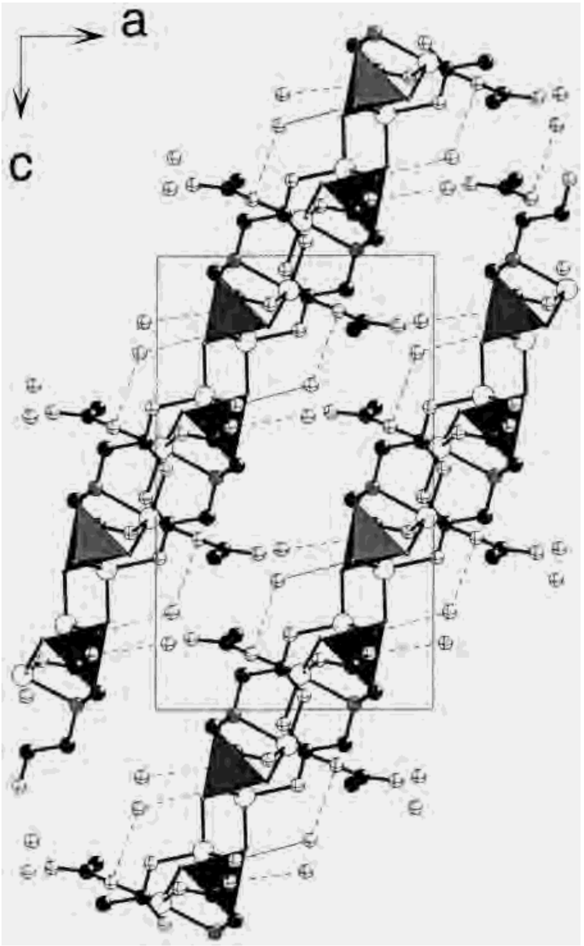

Figure 7. View of crystal structure of complex **2** along the *b* axis. The phosphonic groups are represented by tetrahedra. Zn, N, O, and C atoms are shown as open, gray, crossed, and black circles, respectively. The dotted lines indicate hydrogen bonds.

Zn2−N1−C2−C3−O5 and Zn2−N1−C4−C5−O7. The acetic acid molecule is neutral, because a PMIDA ligand carries four negative charges, which are compensated by two Zn(II) cations. Another strong indication of neutrality is that, among two C−O bonds in the acetic acid group, the C−O distance (C7−O9 1.344(6) Å) is significantly longer than that of the other oxygen bonded to zinc metal (C7−O8 1.275(5) Å); thus, the O(9) atom is most likely protonated. The O−C−O angle of this acetic acid group (O8−C7−O9 119.4(4)°) is also smaller than those of the bridging carboxylic groups of the PMIDA ligand in both complexes which range from 122.4(3)° to 124.4(4)° (Table 2). Apparently, insufficient time was allowed for sufficient hydrolysis of the urea to neutralize the acetic acid as the pH was in the NH_4Ac−Hac buffer region.

The two different kinds of zinc atoms are interconnected by bridging phosphonic and carboxylic groups, resulting in the formation of a zinc carboxylate−phosphonate hybrid layer along the ⟨202⟩ plane (Figure 6). Each Zn(1) atom is bridged to two Zn(1) and four Zn(2) atoms, while a Zn(2) atom is bridged by only two Zn(1) and two Zn(2) atoms. This connectivity forms a variety of rings with open spaces as shown in Figure 6. The nearest Zn···Zn separation is 4.825(1) Å. The lattice water molecules are hydrogen bonded to acetic groups; both acetic group and water molecules act as spacers between two zinc layers (Figure 7).

Discussion

Phosphonic acids containing one or two amine groups usually exist as Zwitter ions, as does H_4PMIDA.[16] Under acidic conditions, such acids do not act as chelating ligands; only the phosphonic group is coordinated to the metal ions, and carboxylic groups and nitrogen are only involved in hydrogen bonding. This is the case as in the Zr−PMIDA compounds.[10,12−13] The layered $Zr_2(PO_4)(H_2PMIDA)(HPMIDA)$ was obtained when a mixture of phosphoric acid and H_4PMIDA solution in the ratio of 1:1 was reacted with zirconyl chloride in the presence of HF;[12] without addition of phosphoric acid, a linear chain compound was isolated.[13] Each phosphonate group bridges with two and three Zr(IV) ions in the chain and layer Zr(IV) compounds, respectively.[12,13] The chelation coordination mode is adopted when the solution is less acidic and the metal ions used have

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an affinity for the nitrogen atom, such as Co(II) and Zn(II) ions. In the case of nitrilotris(methylenephosphonic acid), $NH^+[(CH_2PO_3H_2)_2(CH_2PO_3H^-)]$, the divalent metal complexes formed, which are formulated as $M\{NH(CH_2PO_3H)_3\}(H_2O)_3$ (M = Co, Mn, Zn), have a chain type structure, in which one phosphonate group and the nitrogen atom are only involved in hydrogen bonding.[17] A zinc phosphonate of the ligand $HOOCCH_2N(CH_2PO_3H_2)_2$ has also been isolated with a formula of $Zn_2\{O_2CCH_2NH(CH_2PO_3)_2\}$. Its structure features a three-dimensional network in which both carboxylic and phosphonate groups are in bridging coordination mode, and this work will be published subsequently.[18] We have initiated a study of the ion-exchange and additional complexing ability of metal−PMIDA complexes containing free carboxylate groups and will report on the results at a later date.

Acknowledgment. We acknowledge with thanks the financial support from the Robert A. Welch Foundation through Grant A673 and the Department of Energy, Basic Sciences Division, through Grant DOE 448071-00001.

Supporting Information Available: X-ray crystallographic files in CIF format for the structure determination of $Co_2(PMIDA)(H_2O)_5 \cdot H_2O$, **1**, and $Zn_2(PMIDA)(CH_3CO_2H) \cdot 2H_2O$, **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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