Syntheses and Crystal Structures of Two Cobalt Carboxylate−Phosphonates with 4,4′-Bipyridine as a Secondary Metal Linker

Jun-Ling Song,[a] Andrey V. Prosvirin,[b] Han-Hua Zhao,[b] and Jiang-Gao Mao*[a]

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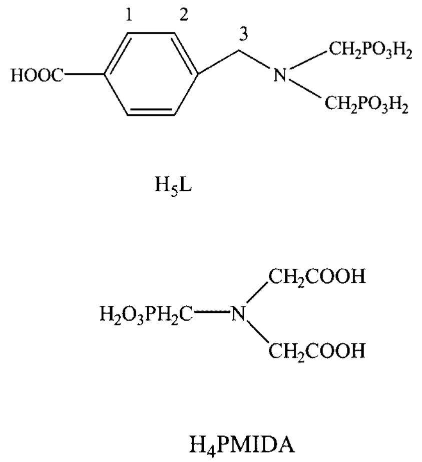
The hydrothermal syntheses and crystal structures of two novel cobalt carboxylate–phosphonates with 4,4′-bipyridine (4,4′-bipy) as the secondary metal linker are reported. Compound **1**, $[Co_3(H_2L)_2(H_2O)_4(4,4'\text{-bipy})]$, where H_5L = 4-$HO_2CC_6H_4CH_2N(CH_2PO_3H_2)_2$, crystallizes in the monoclinic space group $C2/c$ with a = 25.9281(5), b = 9.76310(10), c = 17.3671(5) Å, β = 103.290(2)°, V = 4278.6(2) Å^3, and Z = 4. Its structure contains a pillar-layered architecture in which Co^{II} octahedra are linked by carboxylate–phosphonate ligands to form a 2D layer and these layers are crosslinked further by 4,4′-bipy ligands to form a porous 3D network. Compound **2**, $[Co_2(PMIDA)(H_2O)_5(4,4'\text{-bipy})]\cdot 4H_2O$, where H_4PMIDA = $H_2O_3PCH_2N(CH_2CO_2H)_2$, crystallizes in the triclinic space group $P\bar{1}$ with a = 7.8009(7), b = 13.4560(12), c = 13.5453(12) Å, α = 65.207(2), β = 88.035(2), γ = 77.135(2)°, V = 1255.57(19) Å^3, and Z = 2. The crystal structure of compound **2** contains 1D zigzag chains in which two cobalt(II) ions are bridged by PMIDA ligand to form dimeric units, and these dimeric units are connected further by bridging 4,4′-bipy ligands.

Introduction

Recently, many research studies have been devoted to the synthesis of metal phosphonates with open-framework or microporous structures because of their potential applications in ion-exchange, catalysis and sensors.[1−6] Furthermore, interesting magnetic properties have been observed in some of these systems. For example, weak ferromagnetic or canted antiferromagnetic behavior has been observed in some Mn^{II}, Fe^{II}, Cu^{II} and Co^{II} compounds.[3,7−14] The strategy of attaching functional groups such as carboxylic acids, crown ethers and amines to the phosphonic acid molecule has been found to be an effective method for the preparation of metal phosphonates with open-framework and microporous structures. For example, a series of novel microporous materials has been synthesized by hydrothermal reactions of different metal salts with carboxylate-functionalised phosphonic acids $H_2O_3PCH_2CH_2CO_2H$ and $H_2O_3PCH_2CO_2H$.[15−17] The use of additional bidentate metal linkers, such as 1,10-phenanthroline, 2,2′-bipyridine, piperazine and 4,4′-bipyridine, results in various mixed-metal hybrids of V and Mo.[13,18] Reports regarding the corresponding divalent transition metal compounds are rare.[12,13] We selected two carboxylate−phosphonic acids, H_5L [H_5L = 4-$HOOCC_6H_5CH_2N(CH_2PO_3H_2)_2$] and H_4PMIDA [H_4PMIDA = $H_2O_3PCH_2N(CH_2COOH)_2$] (Scheme 1), in combination with 4,4′-bipyridine (4,4′-bipy) as the secondary metal linker. Zinc(II) and cobalt(II) compounds prepared from H_4PMIDA have been reported previously.[19] Hydrothermal reactions of the metal salts with the above phosphonic acids and 4,4′-bipy led to two new cobalt carboxylate−phosphonates, namely $[Co_3(H_2L)_2(H_2O)_4(4,4'\text{-bipy})]$ (**1**) and $[Co_2(PMIDA)(H_2O)_5(4,4'\text{-bipy})]\cdot 4H_2O$ (**2**). Herein we report their syntheses and crystal structures.



Scheme 1. The structure of H_5L and H_4PMIDA

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[a] State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, The Chinese Academy of Sciences,
Fuzhou 350002, P. R. China
[b] Department of Chemistry, Texas A&M University,
P. O. Box 30012, College Station, TX 77843-3012, USA
E-mail: mjg@ms.fjirsm.ac.cn

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Results and Discussion

Crystal Structure Descriptions for Compounds 1 and 2

As shown in Figure 1, the asymmetric unit of compound **1** contains two unique Co^{II} atoms. The Co(1) atom is octahedrally coordinated by the tridentate phosphonate ligand (1 N and 2 O), two phosphonate oxygen atoms from two other phosphonate ligands, and one nitrogen atom from a 4,4′-bipy ligand. The Co(1)−O bond lengths are in the range from 2.036(7) to 2.087(6) Å, and the Co(1)−N bond lengths are in the range from 2.154(8) to 2.348(8) Å. The O−Co−O and O−Co−N bond angles deviate from the values for an ideal octahedron (Table 1). The atom Co(2) lies on a twofold symmetry axis and is octahedrally coordinated to two phosphonate oxygen atoms from two Co(1)(H_2L) units, and four water ligands. The Co−O bond lengths fall between 2.049(6) and 2.152(7) Å, and the O−Co−O bond angles are in the range from 84.5(3) to 95.6(3)°. These bond lengths and angles are similar to those in $Co_2[PMIDA]_2(H_2O)_5{\cdot}H_2O$,[19] as well as for other cobalt(II) phosphonates.[13,14,20] The carboxylate−phosphonate ligand is hexadentate and occupies three coordination sites on one Co^{II} ion and also bridges three Co^{II} ions. The phosphonate group containing P(2) is tridentate, whereas the one containing the atom P(1) is bidentate. It should be noted that the benzoic acid moiety does not coordinate to metal ions and remains protonated (O2). The atom O(11) in the P(1)O_3 group is also noncoordinating. This PO_3 group is singly protonated based on P−O distances and charge balance. The noncoordinating carboxylate (O2) and phosphonate (O11) oxygen atoms are hydrogen-bonded to an aquo ligand (O1W) (Table 1). The [CoN_2O_4] and [CoO_6] octahedra are interconnected by bridging carboxylate−phosphonate ligands in the plane {400} (Figure 2). The interlayer distance is 12.9 Å (1/2*a*). The 2D layers are further crosslinked by 4,4′-bipy ligands

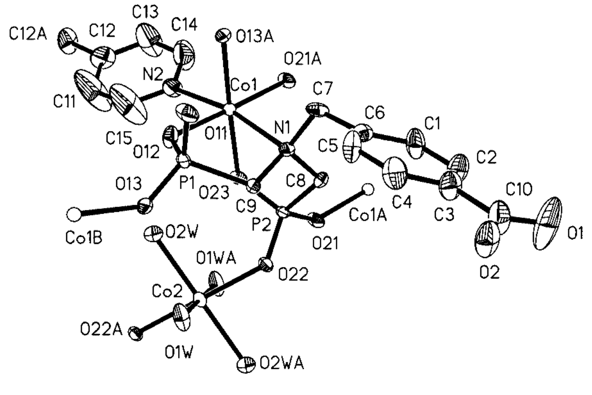

Figure 1. ORTEP representation of the asymmetric unit of compound **1**; thermal ellipsoids are drawn at the 50% probability level

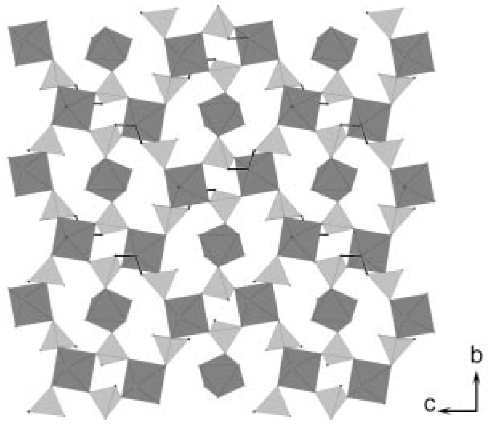

Figure 2. A <400> cobalt carboxylate−phosphonate layer in **1**; the CPO_3 tetrahedra and CoN_2O_4 octahedra are represented by medium and light gray, respectively; the $CH_2C_6H_5COOH$ moiety of the ligand has been omitted for clarity

Table 1. Selected bond lengths [Å] and angles [°] for compound **1**

Co(1)−O(12)	2.036(7)	Co(2)−O(22)#3	2.049(6)
Co(1)−O(23)	2.063(7)	Co(2)−O(2W)#3	2.121(7)
Co(1)−O(13)#1	2.082(6)	Co(2)−O(2W)	2.121(7)
Co(1)−O(21)#2	2.087(6)	Co(2)−O(1W)#3	2.152(7)
Co(1)−N(2)	2.154(8)	Co(2)−O(1W)	2.152(7)
Co(1)−N(1)	2.348(8)	C(10)−O(1)	1.209(15)
Co(2)−O(22)	2.049(6)	C(10)−O(2)	1.290(14)
Hydrogen bonds:			
O(1w)···O(1)#6	2.735(11)	O(1W)···O(11)#5	2.992(10)
O(12)−Co(1)−O(23)	92.2(3)	O(22)−Co(2)−O(22)#3	180.0(3)
O(12)−Co(1)−O(13)#1	90.0(3)	O(22)−Co(2)−O(2W)#3	84.5(3)
O(23)−Co(1)−O(13)#1	177.7(3)	O(22)#3−Co(2)−O(2W)#3	95.5(3)
O(12)−Co(1)−O(21)#2	178.0(3)	O(22)−Co(2)−O(2W)	95.5(3)
O(23)−Co(1)−O(21)#2	89.8(3)	O(22)#3−Co(2)−O(2W)	84.5(3)
O(13)#1−Co(1)−O(21)#2	88.0(3)	O(2W)#3−Co(2)−O(2W)	180.0(6)
O(12)−Co(1)−N(2)	87.9(3)	O(22)−Co(2)−O(1W)#3	91.8(3)
O(23)−Co(1)−N(2)	92.0(3)	O(22)#3−Co(2)−O(1W)#3	88.2(3)
O(13)#1−Co(1)−N(2)	88.7(3)	O(2W)#3−Co(2)−O(1W)#3	89.5(3)
O(21)#2−Co(1)−N(2)	92.0(3)	O(2W)−Co(2)−O(1W)#3	90.5(3)

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

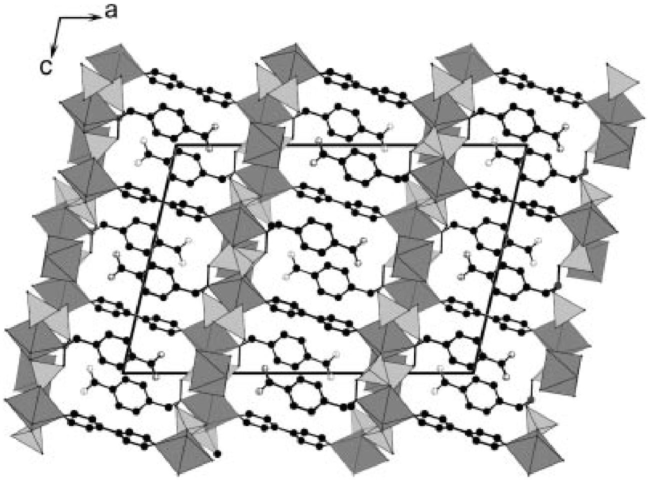

Figure 3. A view of the crystal structure of complex **1** along the *b* axis; the CPO_3 tetrahedra and CoN_2O_4 octahedra are represented by medium and light gray, respectively; C and O atoms are represented by black and crossed circles, respectively

to form a pillar-layered structure (Figure 3), which contains channels with a size of about 9 × 11 Å based on the crystal structure. The benzoic acid moieties are located in these channels.

Compound **2** features a 1D zigzag chain structure. There are two independent Co^{II} ions in the asymmetric unit of compound **2** (Figure 4). Co(1) is octahedrally coordinated to a tetradentate PMIDA ligand, an aquo ligand and a nitrogen atom from a 4,4′-bipy ligand, whereas Co(2) is octahedrally coordinated by one 4,4′-bipy N atom, one phosphonate oxygen atom from a neighboring Co(1)(PMIDA) chelating unit as well as four aquo ligands. The Co−O distances are in the range from 2.082(4) to 2.181(4) Å, and the Co−N distances fall in the range 2.115(3) to 2.156(4) Å. These bond lengths are similar to those in other Co^{II} complexes with O- and N-containing ligands.[13,14,19,20] The PMIDA ligand is pentadentate, occupying four sites on a Co^{II} ion (1 N, 3 O) and bridging to another Co^{II} ion. O(1) and O(3) atoms of the carboxylate groups remain noncoordinating. The phosphonate group adopts a bidentate and bridging coordination mode, with one oxygen atom (O11) not involved in metal coordination. This type of coordination mode is different from that for $Co_2[PMIDA]_2(H_2O)_5 \cdot H_2O$,[19] in which the phosphonate group is tridentate and one carboxylate group is bidentate. The PMIDA ligand in compound **1** has been fully deprotonated based on charge balancing.

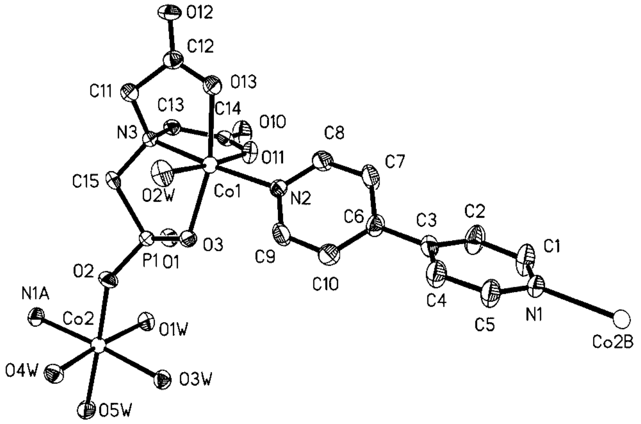

Figure 4. An ORTEP representation of the asymmetric unit of **2**; thermal ellipsoids are drawn at the 30% probability level

The two types of cobalt(II) octahedra are bridged by a PMIDA ligand to form a dimeric unit, and such dimeric units are further interconnected by bridging 4,4′-bipy ligands to form a 1D chain (Figure 5). These chains are held together by hydrogen bonds among noncoordinating carboxylate (O12 and O10) and phosphonate(O1) oxygen atoms as well as aquo ligands, resulting in a porous 3D network (Figure 6, Table 2). The lattice water molecules are located in the pores and are also involved in hydrogen bonding (Table 2, Figure 6).

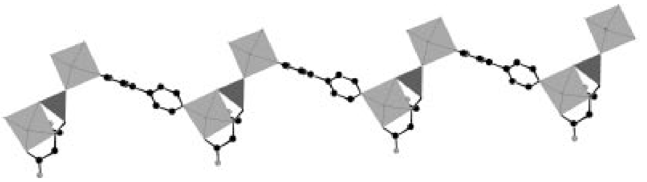

Figure 5. A 1D zigzag chain along the diagonal axis *b* and the −*c* axis in **2**; the CPO_3 tetrahedra and CoN_2O_4 octahedra are represented by medium and light gray, respectively

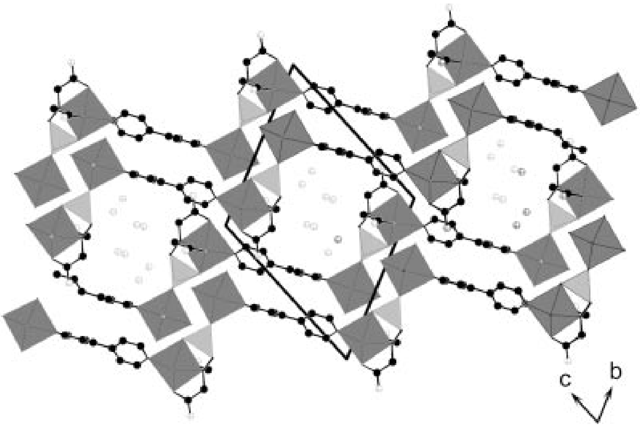

Figure 6. A view of the crystal structure of **2** along the *a* axis; the CPO_3 tetrahedra and CoN_2O_4 octahedra are represented by medium and light gray, respectively; C and O atoms are represented by black and crossed circles, respectively

TGA Studies

The TGA diagram of compound **1** shows three main stages of weight loss. The first stage begins at 138 °C and is complete at 342 °C, and corresponds to the loss of four water molecules. The observed weight loss of 6.4% is in good agreement with the calculated value of 6.7%. The second stage, occurring between 347 and 820 °C, corresponds to the combustion of 4,4′-bipy and diphosphonate ligands. The third stage, which overlaps with the second, continues up to 1000 °C and corresponds to further decomposition of the compound. Assuming the final product is a mixture

Table 2. Selected bond lengths [Å] and angles [°] for compound **2**

Co(1)−O(11)	2.082(4)	Co(2)−N(1)#1	2.148(4)
Co(1)−O(13)	2.085(4)	Co(2)−O(3W)	2.181(4)
Co(1)−N(2)	2.099(4)	Co(2)−O(5W)	2.075(4)
Co(1)−O(3)	2.115(3)	Co(2)−O(2)	2.091(4)
Co(1)−O(2W)	2.125(4)	Co(2)−O(1W)	2.120(4)
Co(1)−N(3)	2.156(4)	Co(2)−O(4W)	2.122(4)
Hydrogen bonds:			
O(1W)···O(1)	2.675(5)	O(2W)···O(10)#5	2.789(6)
O(1W)···O(3W)	2.973(5)	O(3W)···O(4W)	2.927(5)
O(3W)···O(4W)#2	2.756(5)	O(3W)···O(10)#3	2.865(6)
O(3W)···O(1)#3	2.628(5)	O(3W)···O(5W)	2.953(5)
O(4W)···O(2)	2.910(5)	O(4W)···O(5W)	2.936(5)
O(5W)···O(12)#4	2.747(5)	O(6W)···O(6W)#6	2.655(12)
O(6W)···O(8W)#6	2.611(13)	O(6W)···O(9W)	2.633(2)
O(7W)···O(8W)#7	2.786(9)	O(7W)···O(9W)#6	2.904(16)
O(8W)···O(1)#6	2.851(7)		
O(13)−Co(1)−N(3)	79.75(15)	O(2)−Co(2)−O(3W)	91.57(14)
N(2)−Co(1)−N(3)	171.75(17)	O(1 W)−Co(2)−O(3W)	87.46(14)
O(3)−Co(1)−N(3)	86.69(15)	O(4 W)−Co(2)−O(3W)	85.73(14)
O(2W)−Co(1)−N(3)	96.13(16)		

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

of $Co(PO_3)_2$ and $Co_2P_2O_7$ in a molar ratio of 1:1, the total weight loss should be 52.8%. On the other hand, if compound **1** completely decomposes to CoO, the total weight loss is calculated to be 79.2%. The observed weight loss (70.2%) is between these two theoretical values, and indicates the partial decomposition of $Co(PO_3)_2$ and $Co_2P_2O_7$ to CoO. The TGA weight loss curves of compound **2** also exhibit three stages. The first stage (24−269 °C) corresponds to loss of the four water molecules of crystallisation and five aquo ligands. The observed weight loss of 24.8% is in good agreement with the calculated value of 24.9% based on the loss of a total of nine H_2O molecules. The second loss occurs at 330−570 °C, and corresponds to the decomposition of the 4,4′-bipy and carboxylate−phosphonate ligand. The third stage, occurring between 620 and 1000 °C, corresponds to further decomposition of the organic groups. If the residue is assumed to be a mixture of CoO and $Co_2P_2O_7$ in a molar ratio of 2:1, the total weight loss is calculated to be 66.5%. On the other hand, if the final residue is CoO alone, the total weight loss is calculated to be 88.6%. The observed weight loss (74.8%) is between these two theoretical values, indicating that some $Co_2P_2O_7$ has decomposed to CoO.

Conclusion

In summary, the hydrothermal syntheses and crystal structures of two novel cobalt carboxylate−phosphonates containing 4,4′-bipy as the secondary metal linker have been described. The interconnection of the metal carboxylate−phosphonate layer in compound **1** by 4,4′-bipy leads to a pillar-layered architecture. In compound **2**, the dinuclear metal carboxylate−phosphonate units are crosslinked by 4,4′-bipy ligands resulting in a 1D chain. We believe that a wide range of new open-frameworks and microporous materials can be developed by self-assembly or by structure-directed synthesis of other metal phosphonate building blocks with secondary metal linkers such as 4,4′-bipy or acidic carboxylic acid. In the latter case, the carboxylate ligand may remain protonated and noncoordinated, in other words, it can act as an intercalated species between two metal phosphonate layers. Such compounds may have good ion-exchange properties and could exhibit proton conductivity.

Experimental Section

Materials and Instrumentation: All chemicals were obtained from commercial sources and used without further purification. Elemental analyses were performed with a Vario EL III elemental analyzer. Thermogravimetric analyses were carried out with a NETZSCH STA 449C unit at a heating rate of 15 °C/min under nitrogen. IR spectra were recorded with a Magna 750 FT-IR spectrophotometer on KBr pellets in the range 4000−400 cm^{-1}. ^{1}H and ^{31}P NMR spectra were recorded with a Varian Unity 500 NMR spectrometer using D_2O as solvent. H_3PO_4 (85%) was used as ^{31}P standard reference.

Preparation of H_5L and H_4PMIDA: H_5L was prepared by a Mannich-type reaction using 4-(aminomethyl)benzoic acid (15.1 g, 0.1 mol), hydrochloric acid (16 mL), deionized water (20 mL), phosphoric acid (32.8 g, 0.4 mol) and paraformaldehyde (9.0 g, 0.3 mol), according to known procedures.[16,21] The ^{31}P NMR spectrum shows a single peak at $\delta = 7.69$ ppm. ^{1}H NMR (D_2O) : $\delta =$ 3.50 (d, $J_{H,P} = 12.5$ Hz, 4 H, NCH_2PO_3), 4.74 (s, 2 H, 3-H), 7.73 (d, $J_{H,H} = 5.5$ Hz, 2 H, 2-H), 8.13 (d, $J_{H,H} = 5.5$ Hz, 2 H, 1-H) ppm (see Scheme 1 for atomic labeling). IR (KBr): $\tilde{\nu} = 3423$ (w), 2995 (m), 2771 (m), 2657 (m), 1720 (s), 1618 (w), 1583 (w), 1458 (m), 1435 (w), 1417 (w), 1327 (m), 1232 (m), 1138 (s), 1107 (s), 1022 (s), 939 (s), 862 (w), 810 (w), 746 (m), 710 (m), 580 (s), 519 (w), 494 (m), 451 (m) cm^{-1}. H_5L: $C_{10}H_{15}NO_8P_2$ (339.18): calcd. C 35.53, H 4.34, N 4.22; found C 35.41, H 4.46, N 4.13. H_4PMIDA

Table 3. Crystal data and structure refinements for compounds **1** and **2**

	1	**2**
Empirical formula	$C_{30}H_{40}Co_3N_4O_{20}P_4$	$C_{15}H_{32}Co_2N_3O_{16}P$
Formula mass	1077.33	659.27
Space group	$C2/c$	$P\bar{1}$
a [Å]	25.9281(5)	7.8009(7)
b [Å]	9.76310(10)	13.4560(12)
c [Å]	17.3671(5)	13.5453(12)
α [°]	90.0	65.207(2)
β [°]	103.290(2)	88.035(2)
γ [°]	90.0	77.135(2)
V [Å^3]	4278.55(15)	1255.57(19)
Z	4	2
$D_{\text{calcd.}}$ [g·cm^{-3}]	1.672	1.744
μ [mm^{-1}]	1.381	1.466
Measured reflections	6367	6417
Independent reflections	3699	4356
No. of parameters refined	279	335
GOF on F^2	1.214	1.066
R1, $wR2$ [$I > 2\sigma(I)$][a]	0.0728/0.1326	0.0533/0.1132
R1, $wR2$ (all data)	0.1326/0.2037	0.0828/0.1308

[a] $R1 = |F_o| - |F_c|/|F_o|$, $wR2 = \{w[(F_o)^2 - (F_c)^2]^2/w[(F_o)^2]^2\}^{1/2}$, $I > 4\sigma(I)$ for compound **1**.

was also synthesized by a Mannich-type reaction according to procedures described previously.[22]

Preparation of [$Co_3(H_2L)_2(H_2O)_4$(4,4′-bipy)] (1): A mixture of $CoCl_2{\cdot}6H_2O$ (0.24 g, 1.0 mmol), H_5L (0.17 g, 0.5 mmol) and 4,4′-bipy (0.09 g, 0.5 mmol) in distilled water (10 mL) was placed in a sealed hydrothermal reaction vessel equipped with a Teflon liner (25 mL), and then heated to 170 °C for 5 d. Pink crystals of **1** were collected. Yield: 0.09 g (ca. 26% based on cobalt). The initial and final pH values of this solution were 4.0 and 3.5, respectively. $C_{30}H_{40}Co_3N_4O_{20}P_4$ (1077.33): calcd. C 33.45, H 3.74, N 5.20; found C 33.65, H 3.56, N 5.26.

Preparation of [Co_2(PMIDA)$(H_2O)_5$(4,4′-bipy)]·$4H_2O$ (2): A mixture of $Co(CH_3COO)_2{\cdot}2H_2O$ (0.24 g, 1.0 mmol), H_4PMIDA (0.11 g 0.5 mmol) and 4,4′-bipyridine (0.09 g 0.5 mmol) in distilled water (10 mL) was placed in a sealed hydrothermal reaction vessel equipped with a Teflon liner (25 mL), and then heated to 80 °C for 5 d. The resulting orange-red solution was filtered and ethanol was allowed to diffuse slowly into the solution at room temperature. Orange-red crystals of **2** appeared after several days and were collected. Yield: 0.16 g (ca. 48% based on cobalt). The initial and final pH values of the solutions were 4.0 and 4.5, respectively. IR (KBr): $\tilde{\nu}$ = 3290 (s), 1668 (m), 1612 (s), 1578 (m), 1537 (m), 1433 (w), 1371 (m), 1335 (w), 1259 (w), 1119 (m), 1086 (s), 1070 (s), 960 (s), 814 (m), 769 (m), 735 (w), 636 (m), 575 (w), 515 (w), 488 (w). $C_{15}H_{32}Co_2N_3O_{16}P$ (659.27): calcd. C 27.33, H 4.89, N 6.37; found C 27.41, H 4.76, N 6.42.

X-ray Crystallographic Study: Single crystals of compounds **1** and **2** were mounted on a Siemens Smart CCD diffractometer equipped with a graphite-monochromated Mo-K_α radiation source (λ = 0.71073 Å). Intensity data were collected by the narrow-frame method at 293 K. A hemisphere of data (1271 frames at 5 cm detector distances) was collected with scan widths of 0.30° in ω and exposure time of 20 s per frame. The first 50 frames were collected again at 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%. Both data sets were corrected for Lorentz and polarization factors as well as for absorption using the SADABS program.[23] Both structures were solved by direct methods and refined by full-matrix least-squares fitting on F^2 using SHELX-97.[23] All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were located at geometrically calculated positions and refined with isotropic thermal parameters. Crystallographic data and structural refinements for compounds **1** and **2** are summarized in Table 3. Selected bond lengths and angles are listed in Tables 1 and 2, respectively. CCDC-233617 (**1**) and -233618 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

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