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Reactions and Reactivity of Co−bpdc Coordination Polymers (bpdc = 4,4′-biphenyldicarboxylate)

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By choosing a suitable metal center, ligand, and solvents, we have revealed several structural transformations involving a polymer precursor. ${}^{1}_{\infty}[Co(bpdc)(H_2O)_2]\cdot H_2O$ (**1**) was prepared by reaction of Na_2bpdc and $Co(NO_3)_2$ in aqueous solution. Immersing **1** in pyridine/water solutions of (2:1) and (8:1) ratios yielded a second one-dimensional structure ${}^{1}_{\infty}[Co(bpdc)(py)_2(H_2O)_2]\cdot 2py$ (**2**) and a two-dimensional structure ${}^{2}_{\infty}[Co(bpdc)(py)_2]\cdot H_2O$ (**3**), respectively. After heating **1** under N_2 to remove all water within the structure, the compound Co(bpdc) ($\mathbf{I_R}$) was obtained. When $\mathbf{I_R}$ was immersed in solutions of pyridine/water (5:4) and in pure pyridine (in air), a third one-dimensional structure of ${}^{1}_{\infty}[Co(bpdc)(py)_2(H_2O)_2]\cdot 2py\cdot H_2O$ (**4**) and **3**, respectively, were obtained. Compounds **2**−**4** easily transformed to **1** when immersed in water. Crystal data for **1**: monoclinic, space group *C*2/*c* with $a = 6.950(1)$, $b = 31.585(6)$, and $c = 6.226(1)$ Å, $\beta = 95.84(3)°$, $Z = 4$. Crystal data for **2**: triclinic, space group $P\bar{1}$ with $a = 9.646(2)$, $b = 10.352(2)$, and $c = 17.031(3)$ Å, $\alpha = 79.02(3)°$, $\beta = 86.88(3)°$, $\gamma = 77.16(3)°$, $Z = 2$. Crystal data for **3**: triclinic, space group $P\bar{1}$ with $a = 9.137(2)$, $b = 10.480(2)$, and $c = 12.254(2)$ Å, $\alpha = 102.10(3)°$, $\beta = 100.80(3)°$, $\gamma = 99.43(3)°$, $Z = 2$. Crystal data for **4**: orthorhombic, space group *Pbcn* with $a = 13.468(3)$, $b = 16.652$ (3), and $c = 14.977(3)$ Å, $Z = 4$.

Introduction

Self-assembled infinite metal coordination complexes formed through the deliberate selection of metals and multifunctional exodentate ligands, based upon their coordination habits, have so far spawned tremendous interests in the areas of materials chemistry. The fascinating structures of these complexes, coupled with their specific functionality, have made them highly promising in various applications, particularly absorption, catalysis, and molecular magnetization.[1]

While an enormous amount of current research is being focused on the synthesis and structure characterization, studies of chemical reactivity of coordination polymers are largely limited to absorption−desorption processes of the guest molecules. Unlike many well-studied molecular species, which generally dissolve in one or more solvents,[2] the vast majority of coordination polymers are insoluble in most common organic or inorganic solvents, which makes any further characterization and reactivity studies difficult. It is, therefore, not surprising to observe the striking imbalance on the synthetic activities compared to other activities involving chemical reactions of these coordination networks.

Chemical reactivity of a templated phosphate complex has been briefly discussed in a recent paper.[3] By eliminating organic templates in a basic solution, crystals of a new inorganic compound with a different structure can be grown. This study not only suggests that certain chemical reactions of coordination polymers are possible but also shows that under appropriate conditions they may act as precursors toward the synthesis of new compounds. In this paper, we report the systematic study focused on the chemical reactivity of a cobalt−biphenyldicarboxylate (bpdc)-based polymer precursor and several new coordination polymers resulting from its reactions.

Our primary reason for choosing a bpdc-based coordination polymer as a precursor and water as a reaction medium is based on the following considerations: (a) High reactivity is essential for any effective precursor. Our preliminary studies on bpdc-based systems have shown that this ligand is highly reactive in aqueous solutions. (b) Water molecules interact actively with the bpdc molecules via hydrogen bonds. Such interactions play a significant role in the crystal structure formation process.

Experimental Section

All chemicals purchased are of reagent grade or better and were used without purification. The disodium biphenyldicarboxylate (Na_2-bpdc, 1.08 g, 3.8 mmol) was prepared by gently heating biphenyldicarboxylic acid (1.0 g, 4.1 mmol) and sodium hydroxide (0.33 g, 8.2 mmol) in deionized water. Elemental (C, H, N) microanalyses were performed by Schwarzkopf Microanalytical Lab, Inc. Powder X-ray diffraction (PXRD) data of samples were collected on a Rigaku D/M-2200 T automated diffraction system (U1tima$^+$) at an operating powder of 40 kV/40 mA. All structural transformation products were identified by comparing the observed and calculated PXRD patterns.

Synthesis of ${}^{1}_{\infty}[Co(bpdc)(H_2O)_2]\cdot H_2O$ (1). Addition of an aqueous solution (10 mL) of $Co(NO_3)_2$ (0.2910 g, 1 mmol) to an aqueous

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Table 1. Crystallographic Data for **1**−**4**

	1	**2**	**3**	**4**
empirical formula	$C_{14}H_{14}CoO_7$	$C_{34}H_{32}CoN_4O_6$	$C_{24}H_{20}CoN_2O_5$	$C_{34}H_{34}CoN_4O_7$
fw	353.18	651.57	475.35	669.58
space group	*C*2/*c* (No. 15)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	*Pbcn* (No. 60)
a (Å)	6.950(1)	9.646 (2)	9.137 (2)	13.468 (3)
b (Å)	31.585(6)	10.352 (2)	10.480 (2)	16.652 (3)
c (Å)	6.226(1)	17.031 (2)	12.254 (2)	14.977(3)
α, (deg)	90	79.02(3)	102.10(3)	90
β, (deg)	95.84(3)	86.88(3)	100.80(3)	90
γ (deg)	90	77.16(3)	99.43(3)	90
V (deg) (Å^3)	1359.6(4)	1627.6 (5)	1101.5 (4)	3358.9(12)
Z	4	2	2	4
T (K)	293(2)	293(2)	293(2)	293(2)
λ (Å)	0.71073	0.71073	0.71073	0.71073
ρ_{calc} (gcm^{-3})	1.725	1.329	1.433	1.324
μ (mm^{-1})	1.297	0.577	0.817	0.563
R^a ($I > 2\sigma(I)$)	0.0409	0.0646	0.0595	0.0470
$R_w{}^b$	0.0880	0.0860	0.1116	0.0843

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum[w(|F_o^2| - |F_c^2|)^2]/\sum w(F_o^2)^2]^{1/2}$. Weighting: **1**, $w = 1/[\sigma^2(F_o^2) + (0.01P)^2 + 8.0P]$, where $P = (F_o^2 + 2F_c^2)/3$; **2**, $w = 1/[\sigma^2(F_o^2) + 1.00\ P]$; **3**, $w = 1/[\sigma^2(F_o^2) + 1.20\ P]$; **4**, $w = 1/[\sigma^2(F_o^2) + 3.50\ P]$.

Table 2. Non-hydrogen Atomic Coordinates and Equivalent Isotropic Temperature Factors (Å^2) for **1**[a]

atoms	*x*	*y*	*z*	U_{eq}
Co	0.5000	0.5000	0	0.023(1)
O(1)	0.4864(4)	0.4385(1)	0.0708(4)	0.032(1)
O(2)	0.6007(5)	0.0830(1)	0.1229(5)	0.042(1)
O(3)	0.2919(4)	0.5123(1)	0.2234(4)	0.025(1)
O(4)	0	0.4571(1)	0.2500	0.036(1)
C(1)	0.5000	0.4204(2)	0.2500	0.023(1)
C(2)	0.5000	0.3728(2)	0.2500	0.022(1)
C(3)	0.4530(6)	0.3511(1)	0.0597(7)	0.029(1)
C(4)	0.4509(6)	0.3071(1)	0.0613(7)	0.030(1)
C(5)	0.5000	0.2847(2)	0.2500	0.025(1)
C(6)	0.5000	0.2375(2)	0.2500	0.027(1)
C(7)	0.5583(6)	0.2148(1)	0.0777(7)	0.029(1)
C(8)	0.5617(6)	0.1712(1)	0.0791(7)	0.030(1)
C(9)	0.5000	0.1490(2)	0.2500	0.026(1)
C(10)	0.5000	0.1014(2)	0.2500	0.032(1)

[a] U_{eq} defined as one third of the trace of the orthogonalized **U** tensor.

Table 3. Non-hydrogen Atomic Coordinates and Equivalent Isotropic Temperature Factors (Å^2) for **2**[a]

atoms	*x*	*y*	*z*	U_{eq}
Co(1)	0.5000	0.5000	0	0.033(1)
Co(2)	1.5000	1.0000	0.5000	0.040(1)
O(1)	0.6305(3)	0.5622(3)	0.0704(2)	0.040(1)
O(2)	0.5095(3)	0.5698(3)	0.1848(2)	0.054(1)
O(3)	1.3616(3)	0.9686(3)	0.4204(2)	0.050(1)
O(4)	1.4991(4)	0.9333(4)	0.3139(2)	0.061(1)
O(5)	0.6661(3)	0.4764(3)	−0.0849(2)	0.047(1)
O(6)	1.3364(3)	1.0105(3)	0.5870(2)	0.051(1)
N(1)	0.4269(4)	0.7098(3)	−0.0559(2)	0.043(1)
N(2)	1.4305(4)	1.2193(4)	0.4618(2)	0.051(1)
N(3)	0.8173(5)	0.6852(5)	−0.1179(3)	0.067(1)
N(4)	1.1891(5)	0.8006(5)	0.6228(3)	0.071(1)
C(1)	0.6131(5)	0.5872(4)	0.1398(3)	0.037(1)
C(2)	0.7251(5)	0.6436(4)	0.1708(2)	0.033(1)
C(3)	0.7242(5)	0.6572(5)	0.2495(3)	0.045(1)
C(4)	0.8292(5)	0.7097(5)	0.2770(3)	0.048(1)
C(5)	0.9383(5)	0.7444(4)	0.2276(2)	0.037(1)
C(6)	0.9386(5)	0.7304(4)	0.1486(2)	0.045(1)
C(7)	0.8327(4)	0.6795(4)	0.1208(2)	0.041(1)
C(8)	1.0517(5)	0.7980(4)	0.2582(2)	0.039(1)
C(9)	1.0201(5)	0.8848(5)	0.3123(3)	0.049(1)
C(10)	1.1278(5)	0.9303(4)	0.3424(3)	0.049(1)
C(11)	1.2667(5)	0.8929(4)	0.3175(2)	0.037(1)
C(12)	1.2975(5)	0.8096(4)	0.2614(2)	0.040(1)
C(13)	1.1917(5)	0.7605(4)	0.2324(3)	0.043(1)
C(14)	1.3866(5)	0.9366(5)	0.3528(3)	0.041(1)
C(15)	0.4132(5)	0.7444(5)	−0.1354(3)	0.051(1)
C(16)	0.3786(5)	0.8751(5)	−0.1738(3)	0.065(2)
C(17)	0.3565(6)	0.9761(5)	−0.1320(4)	0.072(2)
C(18)	0.3665(6)	0.9444(5)	−0.0510(4)	0.071(2)
C(19)	0.4011(5)	0.8090(5)	−0.0147(3)	0.059(2)
C(20)	1.4289(6)	1.2794(6)	0.3865(3)	0.071(2)
C(21)	1.3902(7)	1.4164(7)	0.3607(4)	0.088(2)
C(22)	1.3447(7)	1.4944(7)	0.4166(4)	0.096(2)
C(23)	1.3426(7)	1.4360(6)	0.4952(4)	0.082(2)
C(24)	1.3872(6)	1.2990(5)	0.5153(3)	0.063(2)
C(25)	0.9457(7)	0.6267(6)	−0.0910(3)	0.075(2)
C(26)	1.0436(6)	0.6932(8)	−0.0763(4)	0.086(2)
C(27)	1.0104(8)	0.8287(8)	−0.0912(4)	0.097(2)
C(28)	0.8797(8)	0.8936(6)	−0.1197(4)	0.100(2)
C(29)	0.7845(6)	0.8170(6)	−0.1325(4)	0.086(2)
C(30)	1.1395(7)	0.8018(6)	0.5537(4)	0.092(2)
C(31)	1.0353(9)	0.7359(9)	0.5439(4)	0.134(3)
C(32)	0.9790(8)	0.6695(8)	0.6083(5)	0.114(3)
C(33)	1.0312(8)	0.6631(7)	0.6813(4)	0.102(2)
C(34)	1.1355(7)	0.7322(6)	0.6849(4)	0.090(2)

[a] U_{eq} defined as one third of the trace of the orthogonalized **U** tensor.

solution (5.5 mL) of Na$_2$(bpdc) (0.1431 g, 0.055 mmol) immediately resulted in white-grey precipitate of **1** which was then washed by distill water (10 mL). Compound **1** was isolated in high yield (0.1625 g, 92%). Anal. Calcd: C, 47.61; H, 3.93. Found: C, 47.13; H, 4.13. Single crystals of **1** were grown by diffusion method. An aqueous solution of Na$_2$(bpdc) (0.1 M, 1 mL) was allowed to diffuse slowly through ethylene glycol to react with aqueous Co(NO$_3$)$_2$ (0.1 M, 1 mL). Transparent, pale amber crystals of **1** (0.0272 g, 77%) emerged after 7 days. Anal. Calcd: C, 47.61; H, 3.93. Found: C, 47.13; H, 4.22.

Synthesis of $^{1}_{\infty}$[Co(bpdc)(py)$_2$(H$_2$O)$_2$]·2py (2). Compound **1** (6.7 mg) was immersed in 0.3 mL of a pyridine solution (pyridine/water = 2:1). Single crystals of **2** grew out of solution after several hours. They were collected after filtration (∼8.6 mg, 70%).

Synthesis of $^{2}_{\infty}$[Co(bpdc)(py)$_2$]·H$_2$O (3). A 6.7 mg powder sample of **1** was immersed in 0.45 mL of a pyridine solution (pyridine/water = 8:1) for several hours to produce the pink powder of **3** (9.9 mg, 78%). Anal. Calcd: C, 60.64; H, 4.24; N, 5.89. Found: C, 61.20; H, 4.37; N, 5.93. Single crystals of **3** were synthesized by the hydro(solvo)-thermal method. Co(NO$_3$)$_2$·6H$_2$O (0.1453 g, 0.5 mmol) and H$_2$bpdc (0.0612 g, 0.25 mmol) (mole ratio = 2:1) were reacted in a pyridine (5 mL) and water (5 mL) solution in a digestion bomb at 120 °C for 3 days. The single-phased magenta crystals of **3** were isolated in a yield of 79% (0.095 g).

Synthesis of $^{1}_{\infty}$[Co(bpdc)(py)$_2$(H$_2$O)$_2$]·2py·H$_2$O (4). A 22.8 mg of **1** was heated under nitrogen gas to 220 °C to give out all uncoordinated and coordinated water molecules (confirmed by TGA weight loss data). This resulted in an intermediate, **I$_R$** (found 19.3 mg; cal 19.3 mg). **I$_R$** was then immersed in 0.18 mL of a pyridine solution (pyridine/water

Table 4. Non-hydrogen Atomic Coordinates and Equivalent Isotropic Temperature Factors (Å^2) for **3**^{a}

atoms	*x*	*y*	*z*	U_{eq}
Co	0.6079(1)	0.8851(1)	0.6207(1)	0.037(1)
O(1)	0.7002(4)	0.8668(3)	0.7947(2)	0.059(1)
O(2)	0.7248(4)	0.7254(3)	0.6441(2)	0.056(1)
O(3)	0.5502(3)	0.8201(3)	0.4493(2)	0.045(1)
O(4)	0.4948(4)	0.9614(3)	0.3425(2)	0.047(1)
O(5)	0.6822(10)	1.0090(8)	1.0147(5)	0.208(4)
N(1)	0.8165(4)	1.0183(4)	0.6267(3)	0.049(1)
N(2)	0.4030(4)	0.7539(3)	0.6280(3)	0.042(1)
C(1)	0.7447(5)	0.7637(5)	0.7502(4)	0.051(1)
C(2)	0.8202(6)	0.6867(5)	0.8253(4)	0.053(1)
C(3)	0.8347(6)	0.5595(5)	0.7803(4)	0.055(1)
C(4)	0.9048(6)	0.4873(5)	0.8495(4)	0.055(1)
C(5)	0.9624(6)	0.5385(5)	0.9627(4)	0.062(2)
C(6A)^b	0.9059(17)	0.6481(14)	1.0135(11)	0.067(4)
C(6B)^b	0.9930(16)	0.6835(15)	0.9993(11)	0.061(4)
C(7A)^b	0.8426(17)	0.7240(16)	0.9447(13)	0.065(4)
C(7B)^b	0.9181(18)	0.7581(17)	0.9327(14)	0.059(4)
C(8)	0.5158(5)	0.8493(4)	0.3558(3)	0.036(1)
C(9)	0.5042(5)	0.7441(4)	0.2494(3)	0.038(1)
C(10A)^b	0.4382(15)	0.7554(14)	0.1446(15)	0.040(3)
C(10B)^b	0.5046(16)	0.7827(16)	0.1444(15)	0.046(4)
C(11A)^b	0.5099(16)	0.6843(18)	0.0473(13)	0.058(4)
C(11B)^b	0.4285(15)	0.6630(17)	0.0472(12)	0.054(4)
C(12)	0.5014(6)	0.5508(4)	0.0524(3)	0.051(1)
C(13)	0.5318(5)	0.5268(4)	0.1588(3)	0.046(1)
C(14)	0.5342(5)	0.6211(4)	0.2561(3)	0.046(1)
C(15)	0.9486(7)	1.0317(6)	0.7030(5)	0.074(2)
C(16)	1.0820(7)	1.1171(7)	0.7034(5)	0.087(2)
C(17)	1.0821(7)	1.1889(6)	0.6243(6)	0.081(2)
C(18)	0.9488(7)	1.1770(6)	0.5468(5)	0.076(2)
C(19)	0.8194(6)	1.0913(5)	0.5517(4)	0.058(1)
C(20)	0.3543(6)	0.6323(4)	0.5572(4)	0.049(1)
C(21)	'0.2355(6)	0.5397(5)	0.5635(4)	0.058(1)
C(22)	0.1569(6)	0.5725(6)	0.6473(5)	0.067(1)
C(23)	0.3255(6)	0.7853(5)	0.7101(4)	0.054(1)
C(24)	0.2047(7)	0.6971(6)	0.7225(5)	0.069(2)

[a] U_{eq} defined as one third of the trace of the orthogonalized **U** tensor. [b] Site occupancy factor = 0.5.

Table 5. Non-hydrogen Atomic Coordinates and Equivalent Isotropic Temperature Factors (Å^2) for **4**^{a}

atoms	*x*	*y*	*z*	U_{eq}
Co	0	0	0	0.039(1)
O(1)	−0.1366(2)	0.0266(1)	−0.0534(2)	0.046(1)
O(2)	−0.2387(2)	−0.0234(2)	0.0498(2)	0.057(1)
O(3)	−0.0628(2)	−0.0081(2)	0.1283(2)	0.051(1)
O(4)	0	−0.1234(2)	0.2500	0.068(1)
N(1)	0.0251(2)	0.1270(2)	0.0268(2)	0.052(1)
N(2)	−0.1607(3)	−0.2272(3)	0.2222(3)	0.082(1)
C(1)	−0.2204(2)	0.0033(2)	−0.0260(2)	0.039(1)
C(2)	−0.3041(2)	0.0077(2)	−0.0925(2)	0.036(1)
C(3)	−0.3967(3)	−0.0217(2)	−0.0712(2)	0.044(1)
C(4)	−0.4738(2)	−0.0187(2)	−0.1324(2)	0.044(1)
C(5)	−0.4591(2)	0.0134(2)	−0.2167(2)	0.038(1)
C(6)	−0.3658(2)	0.0432(2)	−0.2380(3)	0.049(1)
C(7)	−0.2895(3)	0.0414(2)	−0.1763(3)	0.050(1)
C(8)	−0.0046(4)	0.1831(2)	−0.0293(3)	0.064(1)
C(9)	0.0109(5)	0.2639(2)	−0.0144(4)	0.089(2)
C(10)	0.0563(4)	0.2874(3)	0.0615(5)	0.107(2)
C(11)	0.0856(4)	0.2307(3)	0.1203(5)	0.102(2)
C(12)	0.0689(4)	0.1509(3)	0.1012(4)	0.086(2)
C(13)	−0.1733(5)	−0.3055(5)	0.2412(5)	0.113(2)
C(14)	−0.2363(6)	−0.3521(4)	0.1925(6)	0.130(3)
C(15)	−0.2859(5)	−0.3218(5)	0.1290(6)	0.132(3)
C(16)	−0.2738(4)	−0.2443(5)	0.1081(5)	0.114(2)
C(17)	−0.2116(4)	−0.2002(3)	0.1568(4)	0.083(2)

[a] U_{eq} defined as one third of the trace of the orthogonalized **U** tensor.

Table 6. Selected Bond Lengths (Å) and Angles (deg) for **1**^{a}

Co−Co^{ii}	3.1130(5)	Co−O(3)	2.142(2)
Co−O(1)	1.998(2)	Co−O(3)^{ii}	2.168(3)
Co−O(1)^{i}	1.998(2)	Co−O(3)^{iii}	2.168(3)
Co−O(3)^{i}	2.142(2)	O(3)−O(2)^{v}	2.640(4)
O(1)−Co−O(1)^{i}	180.0	O(3)^{i}−Co−O(3)^{ii}	96.23(10)
O(1)−Co−O(3)^{i}	90.94(10)	O(3)−Co−O(3)^{ii}	83.77(10)
O(1)^{i}−Co−O(3)^{i}	89.06(10)	O(1)−Co−O(3)^{iii}	87.58(10)
O(1)−Co−O(3)	89.06(10)	O(1)^{i}−Co−O(3)^{iii}	92.42(10)
O(1)^{i}−Co−O(3)	90.94(10)	O(3)^{i}−Co−O(3)^{iii}	83.77(10)
O(3)^{i}−Co−O(3)	180.0	O(3)−Co−O(3)^{iii}	96.23(10)
O(1)−Co−O(3)^{ii}	92.42(10)	O(3)^{ii}−Co−O(3)^{iii}	180.0
O(1)^{i}−Co−O(3)^{ii}	87.58(10)	Co−O(3)−Co^{ii}	92.47(10)

[a] Symmetry transformations used to generate equivalent atoms: i -x+1,-y+1,-z; ii -x+1,y,-z+1/2; iii x,-y+1,z-1/2; iv -x, y, -z+1/2; v x-1/2, y+1/2, z.

Table 7. Selected Bond Lengths (Å) and Angles (deg) for **2**^{a}

Co(1)−O(1)	2.063(3)	Co(2)−O(3)^{ii}	2.071(3)
Co(1)−O(1)^{i}	2.063(3)	Co(2)−O(3)	2.071(3)
Co(1)−O(5)	2.104(3)	Co(2)−O(6)^{ii}	2.104(3)
Co(1)−O(5)^{i}	2.104(3)	Co(2)−O(6)	2.104(3)
Co(1)−N(1)	2.174(4)	Co(2)−N(2)	2.198(4)
Co(1)−N(1)^{i}	2.174(4)	Co(2)−N(2)^{ii}	2.198(4)
O(5)−O(2)^{i}	2.640(4)	O(6)−O(4)^{ii}	2.605(4)
O(1)−Co(1)−O(1)^{i}	180.0	O(3)^{ii}−Co(2)−O(3)	180.000(1)
O(1)−Co(1)−O(5)	89.23(11)	O(3)^{ii}−Co(2)−O(6)^{ii}	89.55(12)
O(1)^{i}−Co(1)−O(5)	90.77(11)	O(3)−Co(2)−O(6)^{ii}	90.45(12)
O(1)−Co(1)−O(5)^{i}	90.77(11)	O(3)^{ii}−Co(2)−O(6)	90.45(11)
O(1)^{i}−Co(1)−O(5)^{i}	89.23(11)	O(3)−Co(2)−O(6)	89.55(12)
O(5)−Co(1)−O(5)^{i}	180.0	O(6)^{ii}−Co(2)−O(6)	180.0
O(1)−Co(1)−N(1)	88.18(13)	O(3)^{ii}−Co(2)−N(2)	89.57(14)
O(1)^{i}−Co(1)−N(1)	91.82(13)	O(3)−Co(2)−N(2)	90.43(14)
O(5)−Co(1)−N(1)	90.67(13)	O(6)^{ii}−Co(2)−N(2)	91.97(14)
O(5)^{i}−Co(1)−N(1)	89.33(13)	O(6)−Co(2)−N(2)	88.03(14)
O(1)−Co(1)−N(1)^{i}	91.82(13)	O(3)^{ii}−Co(2)−N(2)^{ii}	90.43(14)
O(1)^{i}−Co(1)−N(1)^{i}	88.18(13)	O(3)−Co(2)−N(2)^{ii}	89.57(14)
O(5)−Co(1)−N(1)^{i}	89.33(13)	O(6)^{ii}−Co(2)−N(2)^{ii}	88.03(14)
O(5)^{i}−Co(1)−N(1)^{i}	90.67(13)	O(6)−Co(2)−N(2)^{ii}	91.97(14)
N(1)−Co(1)−N(1)^{i}	180.0	N(2)−Co(2)−N(2)^{ii}	180.000(1)

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

= 5:4) to give brownish, block single crystals of **4** and an unknown powder after several hours. When $\mathbf{I_R}$ (7.8 mg) was immersed in pyridine (1 mL) overnight, the product of **3** (11.3 mg, 91%) was isolated by vacuum evaporation of the solution. Anal. Calcd for **3**: C, 60.64; H, 4.24; N, 5.89. Found: C, 60.02; H, 4.35; N, 5.86.

When $\mathbf{I_R}$, **2**, **3**, and **4** were immersed in distilled water for a few hours, each of these compounds was converted to **1** in high yields (>90%). Unless otherwise specified, all reactions were performed at room temperature.

Crystallographic Studies. Single-crystal structure analyses for all four compounds were performed on an Enraf-Nonius CAD4 diffractometer equipped with graphite monochromatized Mo Kα radiation (λ = 0.71073 Å). Single crystals with dimensions of 0.32 × 0.16 × 0.01 mm (**1**), 0.35 × 0.30 × 0.25 mm (**2**), 0.35 × 0.10 × 0.10 mm (**3**), and 0.35 × 0.30 × 0.20 mm (**4**) were selected for the crystal structure analyses. Each crystal was mounted on the tip of a glass fiber and placed onto the goniometer head. Unit cells were obtained and refined by 20 well-centered reflections with $8.79 \le \theta \le 10.99°$ (**1**), $8.23 \le \theta \le 14.73°$ (**2**), $7.85 \le \theta \le 12.84°$ (**3**), and $8.62 \le \theta \le 15.46°$ (**4**), respectively. All data were collected at 293(2) K with ω-scan method within the limits $2° < \theta < 26°$. All data collections were monitored by three standards every 4 h, and raw intensities were corrected for Lorentz and polarization effects and for absorption by empirical method based on ψ-scan data.[4] Direct phase determination yielded the positions of cobalt atoms and some non-hydrogen atoms. The remaining non-hydrogen atoms were located from the subsequent difference Fourier synthesis. Hydrogen atoms were located from difference Fourier maps

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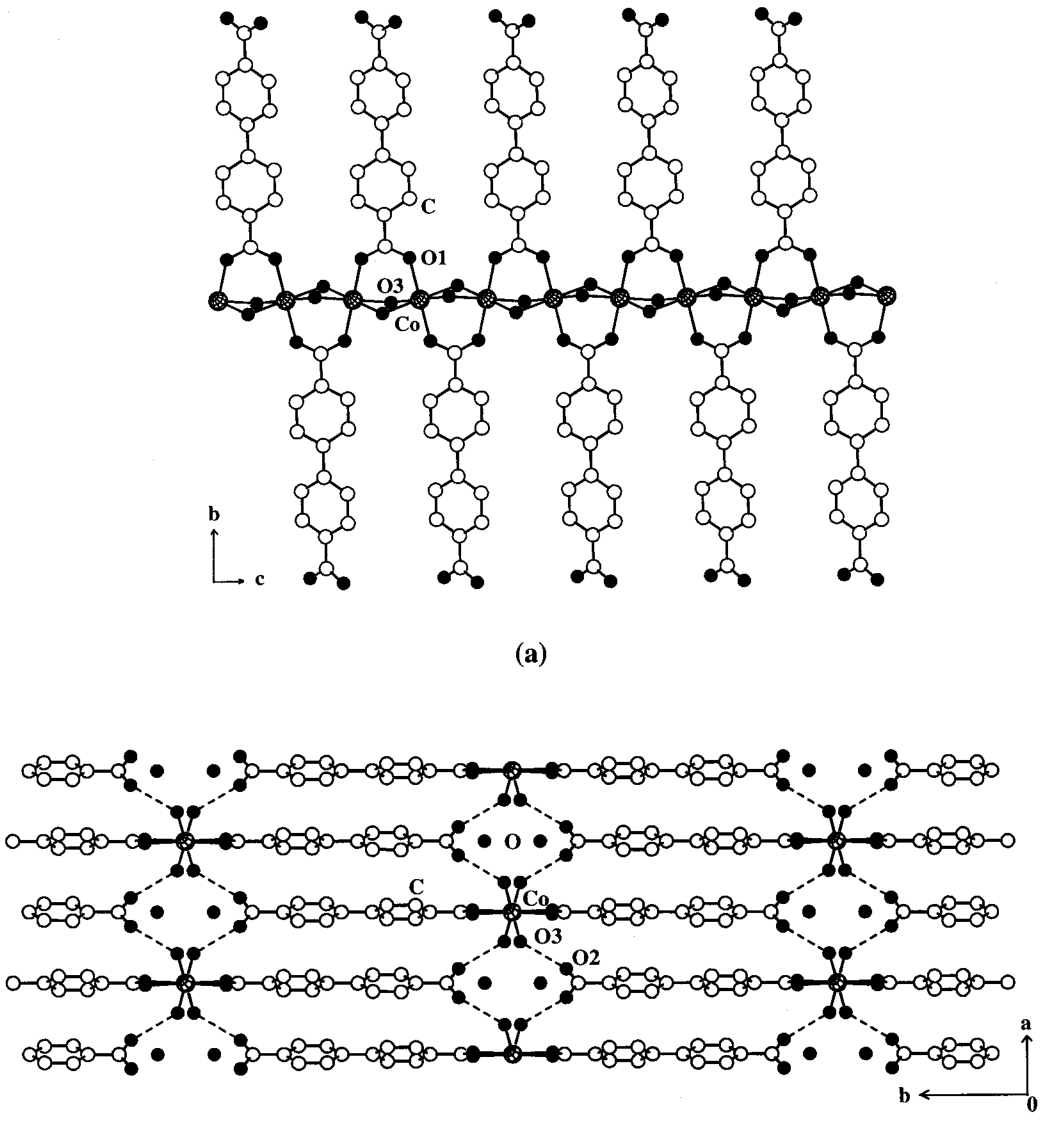
(4) Kopfmann, G.; Hubber R. *Acta Crystallogr.* **1968**, *A24*, 348.



(a)

(b)

Figure 1. Crystal structure of $^{1}_{\infty}$[Co(bpdc)(H_2O)$_2$]·H_2O (**1**). (a) View showing a single chain extending along the *c* axis. (b) View along the *c* axis showing interchain hydrogen bonding (O(3)···O(2)^{v} 2.640(4) Å). The cross-shaded circles represent Co, open circles C, and solid circles O atoms. The uncoordinated water molecules are also shown in the figure. All H atoms are omitted for clarity.

Table 8. Selected Bond Lengths (Å) and Angles (deg) for **3**[a]

Co−O(4)^{i}	2.005(3)	Co−N(2)	2.163(4)
Co−O(3)	2.005(3)	Co−O(2)	2.167(3)
Co−N(1)	2.149(4)	Co−O(1)	2.201(3)
O(4)^{i}−Co−O(3)	105.40(11)	N(1)−Co−O(2)	92.18(14)
O(4)^{i}−Co−N(1)	91.35(14)	N(2)−Co−O(2)	86.92(13)
O(3)−Co−N(1)	95.26(14)	O(4)^{i}−Co−O(1)	100.25(11)
O(4)^{i}−Co−N(2)	88.13(13)	O(3)−Co−O(1)	153.56(11)
O(3)−Co−N(2)	88.87(13)	N(1)−Co−O(1)	90.37(14)
N(1)−Co−N(2)	175.83(13)	N(2)−Co−O(1)	85.65(14)
O(4)^{i}−Co−O(2)	159.93(11)	O(2)−Co−O(1)	59.98(11)
O(3)−Co−O(2)	93.94(11)		

[a] Symmetry transformations used to generate equivalent atoms: i -*x*+1,-*y*+2,-*z*+1; ii -*x*+2,-*y*+1,-*z*+2; iii -*x*+1,-*y*+1,-*z*.

Table 9. Selected Bond Lengths (Å) and Angles (deg) for **4**

Co−O(1)^{i}	2.054(2)	Co−O(3)	2.103(2)
Co−O(1)	2.054(2)	Co−N(1)^{i}	2.178(3)
Co−O(3)^{i}	2.103(2)	Co−N(1)	2.178(3)
O(2)−O(3)	2.656(3)	O(3)−O(4)	2.780(4)
O(4)−N(2)	2.801(5)		
O(1)^{i}−Co−O(1)	180.0	O(3)^{i}−Co−N(1)^{i}	87.51(11)
O(1)^{i}−Co−O(3)^{i}	90.52(9)	O(3)−Co−N(1)^{i}	92.49(11)
O(1)−Co−O(3)^{i}	89.48(9)	O(1)^{i}−Co−N(1)	89.90(11)
O(1)^{i}−Co−O(3)	89.48(9)	O(1)−Co−N(1)	90.10(11)
O(1)−Co−O(3)	90.52(9)	O(3)^{i}−Co−N(1)	92.49(11)
O(3)^{i}−Co−O(3)	180.0	O(3)−Co−N(1)	87.51(11)
O(1)^{i}−Co−N(1)^{i}	90.10(11)	N(1)^{i}−Co−N(1)	180.0
O(1)−Co−N(1)^{i}	89.90(11)		

[a] Symmetry transformations used to generate equivalent atoms: i -*x*,-*y*,-*z*; ii -*x*-1,*y*,-*z*-1/2; iii -*x*, *y*, 1/2-*z*.

but were not refined, and their thermal parameters were set equal to 1.2U_{eq} of the parent non-hydrogen atoms. All of the non-hydrogen atoms were subjected to anisotropic refinement. Data collections were controlled by the CAD4/PC program package. Computations were performed using the SHELX97 program package.[5] Analytic expressions of atomic scattering factors were employed, and anomalous dispersion corrections were incorporated.[6] The final full-matrix least-squares refinement on F^2 was applied to the data. Details of data collection and structure refinement, along with unit cell parameters for **1**−**4** can

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(5) Sheldrick, G. M. SHELX-97: program for structure refinement; University of Goettingen: Germany, 1997.

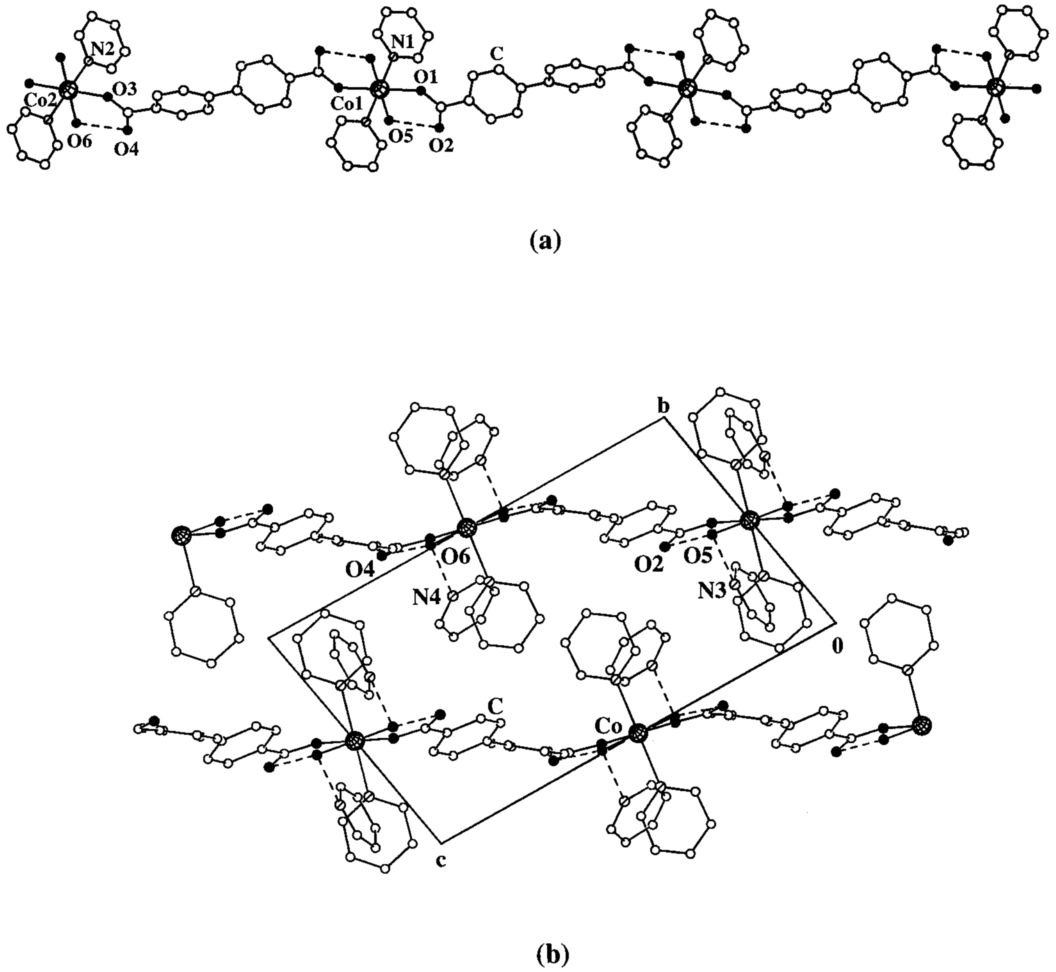
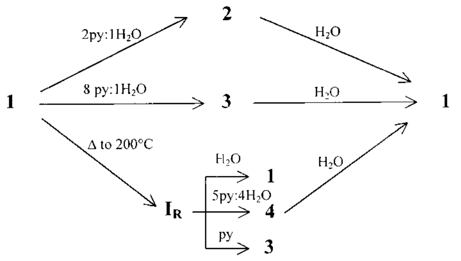


Figure 2. Crystal structure of $^{1}_{\infty}[\mathrm{Co(bpdc)(py)_2(H_2O)_2}]\cdot 2\mathrm{py}$ (**2**). (a) View showing a single chain. The hydrogen bonds between the uncoordinated carboxylic oxygen and coordinated water molecules are indicated by dashed lines. (b) View showing the stacking pattern of the chains. The uncoordinated pyridine molecules are also shown. The cross-shaded circles represent Co, open circles C, solid circles O, and singly shaded circles N. All H atoms are omitted for clarity.

Scheme 1



be found in Table 1. Selected bond distances and angles are listed in Tables 2−5, respectively.

Results and Discussion

Synthesis and Reactivity. Pyridine was the ligand of choice for reactions with **1**. As a *reactive* solvent, it acts both as a preferable medium and a suitable ligand of attack. Previous studies have shown that it is highly reactive toward transition metals.[7] More importantly, it exhibits a similar bonding habit and binding power compared to that of water. Coordination of this ligand onto **1** will indubitably alter the bpdc−H_2O H-bonding structure, resulting in crystal structure reorganization. While **1** showed no signs of reactions in pure pyridine and water, it dissolved in py−H_2O solutions with appropriate ratios. Single crystals of transparent light-pink **2** were produced in quantitative yield with a molar ratio of py/H_2O = 2:1. Further reactions of **1** in highly concentrated pyridine solutions (e.g., molar ratio of py/H_2O = 8:1) converted it to magenta compound **3** with a novel 2D structure. Upon heating to 200 °C, the uncoordinated and two coordinated water molecules (15.3%) were evolved from **1** giving rise to amorphous purple-blue intermediate $\mathbf{I_R}$ (see Scheme 1). Structure **1** recovered rapidly and fully by immersing $\mathbf{I_R}$ in water. Crystals of transparent, orange **4** formed upon exposure of $\mathbf{I_R}$ in a py/H_2O solution of a 5:4 molar ratio. Immersion of $\mathbf{I_R}$ in nearly pure pyridine (containing a very small amount of water) overnight followed by drying in air converted it completely to **3**. Attempts to synthesize **2** and **4** via hydrothermal and diffusion reactions were not successful. Further experiments showed that the reactions of **1** leading to **2**−**4** were fully *reversible*. Upon addition of water, **2**−**4** rapidly converted back to **1** (Scheme 1). No reactions were observed when placing **1** in acetone, acetonitrile, benzene or ether.

Structures. The crystal structure of **1** contains one-dimensional chains of $^{1}_{\infty}[\mathrm{Co(bpdc)(H_2O)_2}]$ which are parallel to crystallographic *c* axis, as shown in Figure 1a.[8] Each chain is

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(6) *International Tables for X-ray Crystallography*: Kluwer Academic Publishers: Dordrecht, 1989; Vol. C, Tables 4.2.6.8 and 6.1.1.4.

(7) (a) D'Alfonso, G.; Pasini, A. *J. Chem. Soc., Dalton. Trans.* **1993**, 1231. (b) Yaghi, O. M.; Li. G.; Li. H. *Nature* **1995**, *378*, 703. (c) Cendrowski-Guillaume, S. M.; O'Loughlin, J. L.; Pelczer, I.; Spencer, J. T. *Inorg. Chem.* **1995**, *34*, 3935.

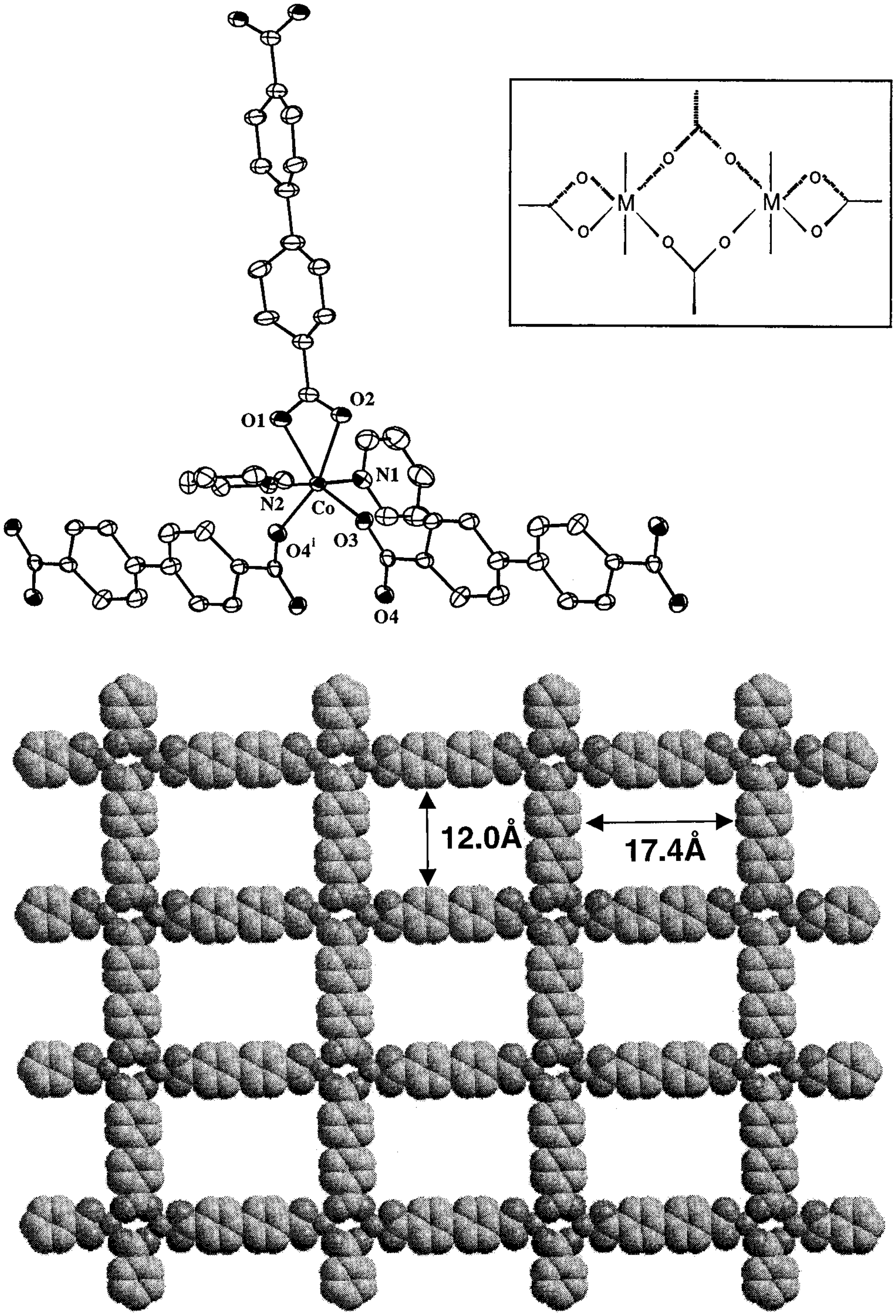

Figure 3. Crystal structure of $^2_\infty$[Co(bpdc)(py)$_2$]·H_2O (**3**). Top: ORTEP drawing of Co(bpdc)$_3$(py)$_2$ with thermal vibrational ellipsoids (30%). Bottom: Space-filling model of the noninterpenetrating two-dimensional network of rectangular grids. The size of the grid is 17.4 × 12 Å. Pyridine, water molecules, and hydrogen atoms are omitted for clarity. (The building block unit is shown in the insert.)

formed by connection of six-coordinated Co metals through the four μ_2-H_2O with Co−O distances of 2.142(2) and 2.168(3) Å, and two trans μ_2-bpdc with a Co−O distance of 1.998(2) Å. The Co atoms are located on an inversion center with an octahedral geometry. The O(1)−Co−O(1)^i, O(3) ^{i}−Co−O(3), and O(3)^{ii}−Co−O(3)^{iii} angles are 180.0°. Other O−Co−O angles around Co centers range from 83.77(10) to 96.23(10)°. The central structural motif of the chain is an edge-sharing octahedron of $CoO_2O'_4$ where O is a carboxylic oxygen of μ_2-bpdc and O′, oxygen from μ_2-H_2O. The intermetallic Co−Co distance is 3.1130(5) Å. Hydrogen bonding between the uncoordinated carboxylate ions and aqua-hydrogen from the adjacent chains facilitates the primary interchain interactions (Figure 1b). The uncoordinated (guest) water molecules are also indicated in the Figure.

The crystal structure of **2** is also a one-dimensional polymeric chain containing octahedrally coordinated Co metal centers (see Figure 2a). Each metal ion is bonded to two terminal water molecules, two μ_2-bpdc via monodentate carboxylic oxygen, and two pyridines. There are two crystallographically indepen-

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(8) A similar structure has been reported recently: Deakin, L.; Arif, A. M.; Miller, J. S. *Inorg. Chem.* **1999**, *38*, 5072.

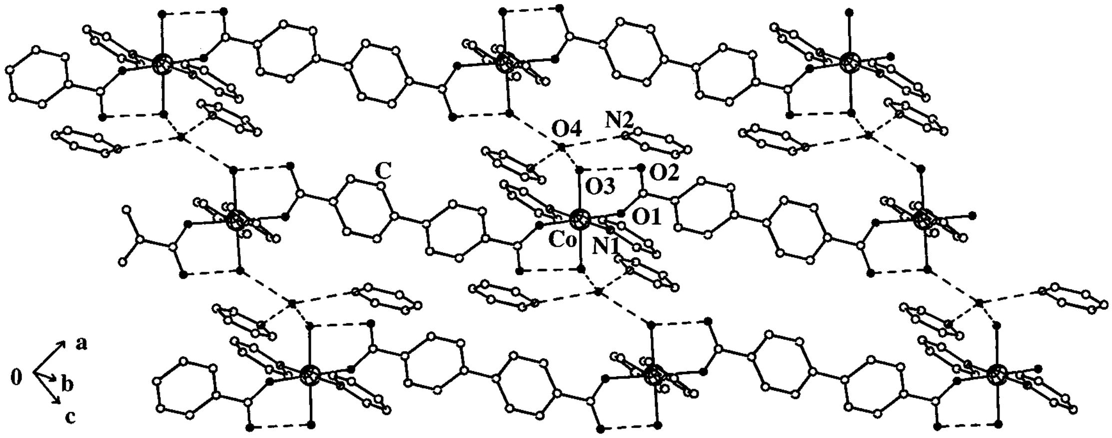

Figure 4. View of $^{1}_{\infty}$[Co(bpdc)(py)$_2$(H$_2$O)$_2$]·2py·H$_2$O (**4**). The same labeling scheme as Figure 2 is used. Both uncoordinated pyridine and water are shown in the figure. Hydrogen bonds are indicated by dashed lines. All H atoms are omitted for clarity.

dent Co atoms in the structure with slight differences in their local geometry. All O−Co−N and O−Co−O angles (for O atoms at cis-positions) around the Co1 center range from 88.18(13) to 91.82(13)°, whereas the corresponding angles around the Co2 center range from 88.03(14) to 91.97(14)°. The metal carboxylate oxygen distances are 2.063(3) Å (Co1) and 2.071(3) Å (Co2). The metal and water oxygen distance is 2.104(3) Å for both Co centers. The Co2−N of 2.198(4) Å is slightly longer than Co1−N, 2.174(4) Å. The Co1−Co2 distance is 15.501(4) Å. The hydrogen bonds between the uncoordinated carboxylic oxygen and hydrogen atoms of the coordinated water molecules, the positions of the two uncoordinated pyridine molecules, and their hydrogen bonds with coordinated water molecules are indicated in Figure 2.

The structure of **3**, as illustrated in Figure 3, contains noninterpenetrating two-dimensional networks of rectangular grids, constructed by octahedrally bonded Co interconnected through chelating and μ_2-bridging carboxylate ions of bpdc. All Co metal atoms are equivalent and coordinate to one chelate carboxylate ion of a bpdc with Co−O distances of 2.167(3) and 2.201(3) Å, two μ_2-bridging carboxylate ions of the two different bpdc with a Co−O distances of 2.005(3) Å, and two pyridine at trans-positions (above and below the 2D network, with Co−N distances of 2.149(4), 2.163(4) Å), as shown in Figure 3 (top). The nitrogen atoms are located in the axial position with N−Co−N angles of 175.83(13)°, whereas the O−Co−O angles around the Co center range from 59.98(11) to 159.93(11)°. The two Co metals bridged by the same two μ_2-bridging carboxylate form a dimer [Co$_2$]$^{4+}$ as a secondary building block[9] with a Co−Co distance of 4.56 Å (Figure 3, bottom). The rectangular-shaped grid formed by four Co and four bpdc gives rise to the largest rectangular void among the noninterpenetrating structures, with approximate dimensions of the cavity 17.4 × 12.0 Å (cross-section) and 15.7 × 10.3 Å based on the van der Waals volumes (Figure 3, bottom). There are also two lattice waters located at opposite corners within each rectangular void. Upon stacking, the nearest-neighboring layers shift by $^1/_2(a + b)$ so that the pyridine molecules from one layer fall in the center of the rectangular voids of the other layer.

The structure of **4** is closely related to **2**. The one-dimensional chains formed by six-coordinated Co atoms connected through bpdc are almost identical to those in **2**. The Co center coordinates to two monodentate oxygen atoms in the trans positions with a Co−O distance of 2.054(2) Å. The other four sites are occupied by two terminal waters with Co−O a distance of 2.103(2) Å and by pyridine with a Co−N distance of 2.178(3) Å. The Co−Co separation through the bpdc ligand is 15.4 Å. However, the structure also contains an additional lattice water molecule, giving rise to a rather different H-bonding network, thereby a different packing scheme and crystal structure system from **2**. A view of **4** showing the stacking pattern of the chains is depicted in Figure 4.

A comparison among the four structures shows that the Co(II) ions in **1**, **2**, and **4** are located in the inversion center, whereas the Co(II) ions in **3** are not. It appears that the octahedral geometry of Co(II) in **3** is highly distorted. A coordination environment of Co(II) similar to **3** can be found in Co(4,4′-bpy)(CH$_3$COO)$_2$.[9d] All bond lengths and angles in the title compounds are comparable with those previously reported.[10] A close look at the crystal structures of **1**−**3** also reveals some important features regarding their structure formation and relationships. **1** was crystallized in aqueous solution. In this structure, two oxygen from the same carboxylate ion form chelate bonds with the metals while the other two oxygen from the remaining carboxylate ion on the opposite site of the bpdc form hydrogen bonds with coordinated water molecules to achieve a stable configuration. Compound **2** formed upon dissolving **1** in pyridine−water solution of an appropriate ratio. The consequence of ligand−ligand competition was breakage of metal−μ_2-H$_2$O bonds and replacement of metal−pyridine bonds. This, in turn, deprived some of the hydrogen bonds between bpdc and bridging water molecules and altered their bonding modes. The structure reorganization led to **2**. Continuing addition of a sufficient amount of pyridine caused a full superseding of coordinated water and deprivation of their hydrogen bonds with the carboxylate, thereby allowing a new structure **3**, where all carboxylic oxygen are coordinated to metals, to form.

In summary, **1** is a reactive supramolecular precursor. By a controlled synthesis with suitable choice of ligand and solvent, its solubility and chemical reactivity are greatly enhanced and

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[9] (a) Randall, C. R.; Shu, L.; Chiou, Y.-M.; Hagen, K. S.; Ito, M.; Kitajima, N.; Lachicotte, R. J.; Zang Y.; Junior, L. Q. *Inorg. Chem.* **1995**, *34*, 1036. (b) Seo, J. S.; Whang, D.; Lee, H.; Jun, S. I.; Oh, J.; Jeon, Y. J.; Kim, K. *Nature* **2000**, *404*, 982. (c) Reineke, T. M.; Eddaoudi, M.; Moler, D.; O'Keeffe, M.; Yaghi, O. M. *J. Am. Chem. Soc.* **2000**, *122*, 4843. (d) Lu, J.; Yu, C.; Niu, T.; Paliwala, T.; Crisci, G.; Somosa, F.; Jacobson, A. J. *Inorg. Chem.* **1998**, *37*, 4637.

[10] (a) Nadzhafov, G. N.; Shnulin, A. N.; Mamedov, Kh. S. *Zh. Strukt. Khim.* **1981**, *22*, 124. (b) Blake, A. J.; Gilby, L. M.; Parsons, S.; Rawson, J. M.; Reed, D.; Solan, G. A.; Winpenny, R. E. P. *J. Chem. Soc., Dalton Trans.* **1996**, 3575.

its reactions lead to new compounds that are not accessible by other methods. Both **2** and **4** can only be synthesized via **1**. The nanoscale pores found in **3** (17.4 × 12.0 Å) represents the largest rectangular-shaped void without interpenetration reported thus far. The reversible conversion between **1** and **3** is intriguing in that structure reorganization between two seemingly unrelated structures can occur under such mild conditions. Further experiments are currently being conducted to investigate and to understand the mechanism involved in these reactions. The work presented here has demonstrated that the deliberate synthesis of supramolecular precursors and their further reactions may not only be possible, but also effective, with a suitable choice of ligands and solvents. The reactive precursor approach may provide a new route to the rational synthesis and crystal engineering of coordination polymers.

Acknowledgment. We thank the National Science Foundation for its generous support via Grant DMR-9553066 and the REU supplemental funds.

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

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