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Influence of the Reaction Temperature and pH on the Coordination Modes of the 1,4-Benzenedicarboxylate (BDC) Ligand: A Case Study of the Ni^{II}(BDC)/2,2′-Bipyridine System

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Three new Ni(BDC)/2,2′-bipy compounds, $Ni_2(BDC)(HBDC)_2(2,2'\text{-bipy})_2$ (**2**), $Ni_3(BDC)_3(2,2'\text{-bipy})_2$ (**3**), and Ni(BDC)-$(2,2\text{-bipy})_2 \cdot 2H_2O$ (**5**), in addition to the previously reported $Ni(BDC)(2,2'\text{-bipy}) \cdot 0.75H_2BDC$ (**1**) and Ni(BDC)(2,2′-bipy)(H_2O) (**4**) [BDC = 1,4-benzenedicarboxylate; 2,2′-bipy = 2,2′-bipyridine], have been synthesized by hydrothermal reactions. A systematic investigation of the effect of the reaction temperature and pH resulted in a series of compounds with different compositions and dimensionality. The diverse product slate illustrates the marked sensitivity of the structural chemistry of polycarboxylate aromatic ligands to synthesis conditions. Compound **1**, which has a channel structure containing guest H_2BDC molecules, is formed at the lowest pH. The guest H_2BDC molecules are connected by hydrogen bonds and form extended chains. At a slightly higher pH, a dimeric molecular compound **2** is formed with a lower number of protonated carboxylate groups per nickel atom and per BDC ligand. Reactions at higher temperature and the same pH lead to the transformation of **1** and **2** into the two-dimensional, layered trinuclear compound **3**. As the pH is increased, a one-dimensional polymer **4** is formed with a water molecule coordinated to Ni^{2+}. Bis-monodentate and bischelating BDC ligands alternate along the chain to give a crankshaft rather than a regular zigzag arrangement. A further increase of the pH leads to the one-dimensional chain compound **5**, which has two chelating 2,2′-bipy ligands. Crystal data: **2**, triclinic, space group $P\bar{1}$, $a = 7.4896(9)$ Å, $b = 9.912(1)$ Å, $c = 13.508(2)$ Å, $\alpha = 86.390(2)^\circ$, $\beta = 75.825(2)^\circ$, $\gamma = 79.612(2)^\circ$, $Z = 2$; **3**, orthorhombic, space group *Pbca*, $a = 9.626(2)$ Å, $b = 17.980(3)$ Å, $c = 25.131(5)$ Å, $Z = 4$; **5**, orthorhombic, space group *Pbcn*, $a = 14.266(2)$ Å, $b = 10.692(2)$ Å, $c = 17.171(2)$ Å, $Z = 8$.

Introduction

Aromatic polycarboxylates are widely used as bridging ligands in the construction of inorganic/organic hybrid nanoporous materials[1] because they are sterically rigid and chemically robust, leading to frameworks of high thermal stability approaching that of purely inorganic zeolites.[2] The presence of two potentially coordinating oxygen atoms in the carboxylic acid group, on the one hand, is beneficial for thermal stability and, on the other hand, leads to several possible coordination modes (monodentate, bridging, chelating), resulting in a low degree of structure predictability compared to aromatic nitrogen-donor ligands. Multiple coordination modes are often observed within the same structure, and several examples have been reported where as many as three different coordination modes occur within the same polycarboxylate ligand.[3] Moreover, the multiple coordination modes are conducive to structural isomerism, as illustrated by the two polymorphs of $Co(dcbp)(H_2O)_2$ (dcbp = 4,4′-dicarboxylato-2,2′-bipyridine).[4] The two polymorphs have three-dimensional frameworks of remarkably

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different topologies as a result of different coordination modes of the dcbp ligand: in the first polymorph, both carboxylic groups are monodentate, while in the second polymorph, one is bridging and the other is noncoordinating. Another feature that distinguishes polycarboxylic ligands from aromatic nitrogen-donor ligands is a much wider variation in the degree of protonation and deprotonation, which affects not only the ligand coordination ability but also its charge and, therefore, the metal-to-ligand ratio and, consequently, the resulting topology. Furthermore, carboxylate groups are much more actively involved in hydrogen bonding, as both acceptors (especially noncoordinating oxygens of monodentate carboxylates) and donors (in the case of protonated carboxylic groups). The optimization of hydrogen-bonding interactions can become one of the principal structure-determining factors. Many supramolecular hydrogen-bonding patterns characteristic of carboxylate anions and carboxylic acids are often encountered in coordination polymers. For example, in purely organic crystals, a ubiquitous "dicarboxylic dimer" connects coordination polymer chains in a nickel 1,2,3-benzenetricarboxylate.[5] Other examples of these synthons are found in several 1,4-benzenedicarboxylates (BDCs) containing neutral H_2BDC as guest molecules: these molecules are located in one-dimensional channels and form linear flat hydrogen-bonded chains, which effectively become extended one-dimensional templates.[6]

These diverse aspects of the structural chemistry of polycarboxylate aromatic ligands are markedly sensitive to synthesis conditions requiring a thorough systematic study of the influence of each individual factor, such as the pH, temperature, and solvent, on coordination modes and protonation states of these ligands. This information is especially valuable because, once the conditions for the formation of a specific building block are identified, it occasionally becomes possible to expand the structure while preserving the framework topology by increasing the ligand length and generate "isoreticular" materials with much larger pores.[7] Over the years of intensive studies of transition-metal mono- and polycarboxylates, a vast amount of data have been acquired, but systematic investigations focusing on the influence of a particular synthesis parameter, while keeping numerous other factors constant, are still very rare. For example, two recent systematic studies of the effect of temperature on the structure of cobalt succinates and divalent transition-metal diglycolates and iminodiacetates clearly illustrated the trend of an increase of the degree of condensation of metal polyhedra and an increase of the density of carboxylic groups as a result of temperature increase.[8] To our knowledge, in the case of aromatic polycarboxylates, however, no new studies of comparable scope have been performed, and previously reported information has not been critically systematized.

We have conducted a systematic study on the Ni(BDC)/2,2′-bipyridine system. The introduction of 2,2′-bipyridine, which has predictable coordination properties and almost exclusively acts as a "terminal" chelating bidentate ligand, confines the propagation of M/BDC/M linkages to one or two dimensions and limits the extent of structural changes that occur upon movement by a given increment in temperature or pH, thus facilitating a more detailed study of the effect of a particular synthesis parameter. The choice of a terminal diamine ligand, for example, between 2,2′-bipyridine or 1,10-phenanthroline, has additional structural consequences because of the influence on aromatic/aromatic interactions[6] and was not varied in this study. The nature of the transition metal in these systems is very important;[9] therefore, all of our experiments in this work were limited to nickel, which, compared to other divalent transition metals under these conditions, has the least likely probability of variations in its coordination geometry. In the present work, the pH and temperature effects on the Ni(BDC)/2,2′-bipy system have been further studied, and here we report the syntheses and structures of three new Ni^{2+} coordination compounds: one dimer, $Ni_2(BDC)(HBDC)_2(2,2'\text{-bipy})_2$ (**2**), and two polymers, $Ni_3(BDC)_3(2,2'\text{-bipy})_2$ (**3**) and $Ni(BDC)(2,2'\text{-bipy})_2\cdot 2H_2O$ (**5**).

Experimental Section

Materials and Methods. All of the reactants were reagent grade and were used as purchased without further purification. The IR spectra were measured on a Galaxy series FTIR 5000 spectrometer with pressed KBr pellets. Thermal analyses were performed on a thermogravimetric analysis V5.1A Du Pont 2100 instrument from room temperature to 600 °C with a heating rate of 3 °C/min in air.

Synthesis. All compounds were prepared by a hydrothermal reaction. A mixture of $NiCl_2\cdot 6H_2O$ (100 mg, 0.42 mmol), 1,4-benzenedicarboxylic acid (69.9 mg, 0.42 mmol), KOH (0−118 mg, 0−2.1 mmol), 2,2′-bipyridine (65.7 mg, 0.42 mmol), and H_2O (0.5 mL) was heated in a 23-mL stainless steel reactor with a Teflon liner at 150−210 °C for 48 h. The crystals obtained were filtered and washed with water and acetone (compounds **1**−**4**) or with ethanol and acetone (dark purple block-shaped compound **5**). Compound **5** decomposes slowly in water. The results from a series of experiments are summarized in Figure 1. The diagram shows the appearance of compounds **1**−**5** as a function of temperature and the amount of KOH added. Optimized syntheses of compounds **2**, **3**, and **5** are given below.

$Ni_2(BDC)(HBDC)_2(2,2'\text{-bipy})_2$ (2). A mixture of $NiCl_2\cdot 6H_2O$ (0.42 mmol, 100 mg), 1,4-benzenedicarboxylic acid (0.42 mmol, 69.9 mg), KOH (0.84 mmol, 47.1 mg), 2,2′-bipyridine (0.42 mmol, 65.7 mg), and H_2O (0.5 mL) was heated in a 23-mL stainless steel reactor with a Teflon liner at 150 °C for 48 h. The green block-shaped crystals were filtered and washed with water and acetone. Yield: 45% based on Ni. Anal. Calcd for $C_{44}H_{15}N_4Ni_2O_{12}$: C, 56.94; H, 3.69; N, 6.04. Found: C, 56.88; H, 3.33; N, 5.99. IR (KBr): 3100.99m, 3070.13w, 1710.56s, 1606.56w, 1598.70w, 1585.20m, 1563.99w, 1515.78s, 1471.42w, 1407.78m (multiple), 1349.33w, 1313.29w, 1297.86w, 1226.51m, 1170.58w, 1153.28w, 1143.58w,

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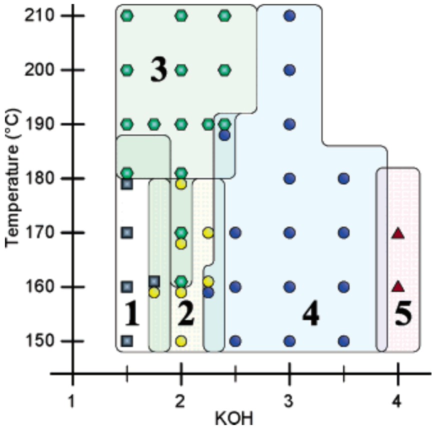

Figure 1. Composition diagram for the $NiCl_2{\cdot}6H_2O/H_2BDC/KOH$/2,2′-bipy system. The scale on the *x* axis represents the molar ratio of KOH to $NiCl_2{\cdot}6H_2O$. The symbols correspond to individual reactions and the colors to specific compounds. Grey squares: **1**. Yellow circles: **2**. Green hexagons: **3**. Blue circles: **4**. Red triangles: **5**.

1110.80w, 1052.94w, 970.02w, 892.88w, 865.88w, 856.24m, 823.46w, 802.24w, 786.82m, 769.46m, 748.24m, 539.97m, 520.68w, 503.33m cm^{-1}.

$Ni_3(BDC)_3(2,2'\text{-bipy})_2$ (3). This compound was produced as a mixture with compound **3** at temperatures 155−180 °C from the same reactant ratio as **3**. At temperatures above 180 °C, the reaction mixture gives a pure phase of this compound. The green hexagonal crystals were filtered and washed with water and acetone. Yield: 63% based on Ni. Anal. Calcd for $C_{44}H_{28}N_4Ni_3O_{12}$: C, 53.88; H, 2.87; N, 5.71. Found: C, 53.33; H, 3.00; N, 5.74. IR (KBr): 3396.23w (br), 3108.70w, 3077.85w, 1617.99m, 1604.49m, 1562.06m, 1500.35m, 1475.28w, 1442.50w, 1380.79s, 1315.22w, 1249.65w, 1155.25w, 1097.30w, 1054.87w, 883.24w, 846.60w, 823.46m, 769.46m, 759.82m, 744.39m, 538.04m cm^{-1}.

$Ni(BDC)(2,2'\text{-bipy})_2{\cdot}2H_2O$ (5). To achieve the high yield and purity, a mixture of $NiCl_2{\cdot}6H_2O$ (0.42 mmol, 100 mg), 1,4-benzenedicarboxylic acid (0.63 mmol, 104.7 mg), KOH (1.68 mmol, 94.3 mg), 2,2′-bipyridine (0.84 mmol, 130.8 mg), and H_2O (0.5 mL) was heated in a 23-mL stainless steel reactor with a Teflon liner at 160 °C for 48 h. Yield: 75% based on Ni. Anal. Calcd for $C_{56}H_{48}N_8Ni_2O_{12}$: C, 58.88; H, 4.23; N, 9.81. Found: C, 58.87; H, 4.28; N, 9.84. IR (KBr): 3316m (br), 3104.85m, 1604.01s, 1587.18s, 1573.15s, 1493.60w, 1473.35m, 1442.02s, 1377.41s, 1307.02w, 1283.40w, 1248.20w, 1223.13w, 1172.99w, 1152.26m, 1187.18w, 1056.32m, 1040.89w, 1022.09m, 890.95ww, 817.19m, 772.35m, 753.55m, 737.16m, 653.27w, 632.54w, 548.17w, 497.54w, 416.55w cm^{-1}.

Crystallographic Studies. Single crystals of suitable dimensions for **2**, **3**, and **5** were used for the structure determinations. All measurements were made with a Siemens SMART platform diffractometer equipped with a 1K CCD area detector. A hemisphere of data (1271 frames at 5-cm detector distance) was collected for each phase using a narrow-frame method with scan widths of 0.3° in ω and an exposure time of 30−40 s/frame. The first 50 frames were remeasured at the end of data collection to monitor instrument and crystal stability, and the maximum correction applied to the intensities was <1%. The data were integrated using the Siemens SAINT program,[10] with the intensities corrected for the Lorentz factor, polarization, air absorption, and absorption due to variation in the path length through the detector faceplate. The structures were solved by direct methods and refined on F^2 by full-matrix least squares using SHELXTL.[11] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined isotropically with geometric constraints. Crystal data for compounds **2**, **3**, and **5** are summarized in Table 1.

Table 1. Crystallographic Data for Compounds **2**, **3**, and **5**

	2	**3**	**5**
chemical formula	$C_{22}H_{15}N_2NiO_6$	$C_{44}H_{28}N_4Ni_3O_{12}$	$C_{28}H_{24}N_4NiO_6$
fw	462.07	980.83	571.22
cryst syst	triclinic	orthorhombic	orthorhombic
space group	$P\bar{1}$	*Pbca*	*Pbcn*
a, Å	7.4896(9)	9.626(2)	14.266(2)
b, Å	9.912(1)	17.980(3)	10.692(2)
c, Å	13.508(2)	25.131(5)	17.171(2)
α, deg	86.390(2)		
β, deg	75.825(2)		
γ, deg	79.612(2)		
V, Å^3	956.1(2)	4349.1(4)	2619.0(6)
Z	2	4	4
temp, K	273(2)	293(2)	293(2)
ρ_c, g cm^{-3}	1.605	1.498	1.449
μ(Mo Kα), mm^{-1}	1.060	1.352	0.791
R1, wR2 [$I > 2\sigma(I)$]^a	0.0490, 0.1021	0.0353, 0.0716	0.0306, 0.0815
R1, wR2 (all data)^a	0.0762, 0.1120	0.0590, 0.0786	0.0402, 0.0883

^{a} $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. $wR2 = [\sum w(F_o^2 - F_c^2)_2/\sum w(F_o^2)^2]^{1/2}$.

Results and Discussion

Synthesis. The hydrothermal reactions of $NiCl_2{\cdot}6H_2O$ and H_2BDC with 2,2′-bipy and KOH gave compounds **1**−**5**, which formed under similar reaction conditions but with different amounts of KOH and at different temperatures (Figure 1). The syntheses and structures of compounds **1** and **4** were reported previously.

The initial molar ratio of the reactants, $Ni^{2+}/H_2BDC/KOH/$2,2′-bipy, from which one-dimensional coordination polymer **1** with diprotonated H_2BDC guest molecules was synthesized was 1:1:1.5:1. A large amount of unreacted H_2BDC (ca. 10% of the original amount) was found in the raw product. In an effort to minimize the amount of unreacted H_2BDC, the reactant ratio was varied to 1:1:2:1, providing more base for the completion of deprotonation but still keeping the pH low. A mixture of the dimeric molecular complex, **2**, and the two-dimensional coordination polymer, **3**, was obtained at temperatures below 180 °C. Compound **2** was the dominant product, with a few crystals of **3** as an impurity when the temperature was 160 °C but was obtained as a pure phase at 150 °C. Compound **3** could be isolated as a pure phase from the same reactant mixture above 180 °C. Compound **3** also began to form from the reactant ratio of 1:1:1.5:1, from which compound **1** was synthesized when the synthesis temperature exceeded 180 °C and became the only product above 190 °C.

A pure phase of **3** could also be obtained by reaction of $NiCl_2{\cdot}6H_2O$, 1,4-dicyanobenzene (DCB), and 2,2-bipy in H_2O (Ni^{2+}:DCB:2,2′-bipy:H_2O = 1:1:1:132). This method was previously used to synthesize one-dimensional polymers of M(BDC)(1,10-phen)$(H_2O)_x$ for Co^{2+}, Cu^{2+}, and Zn^{2+} and three-dimensional polymers of M(BDC)(1,10-phen)Cl_x for

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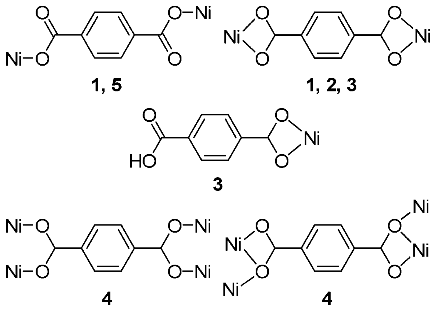
(10) *SAINT, Program for Data Extraction and Reduction*; Siemens Analytical X-ray Instruments Inc.: Madison, WI, 1996.

(11) *SHELXTL, Program for Refinement of Crystal Structures*; Siemens Analytical X-ray Instruments Inc.; Madison, WI, 1994.

Chart 1. Versatile Coordination Modes of BDC Ligands in Compounds **1**−**5**



Mn^{2+} and Cd^{2+}. Compared to these cations, Ni^{2+} formed a different one-dimensional coordination polymer with 1,10-phen, $\mathrm{Ni(BDC)(1,10\text{-}phen)(H_2O)\cdot 0.5H_2BDC}$,[6] under these conditions.

An increase of KOH corresponding to the ratio 1:1:2.5:1 results in one-dimensional coordination polymer **4**. A further increase in the pH lowers the yield of **4**, and pink plate-shaped crystals, which were identified as $\mathrm{[Ni(2,2'\text{-}bipy)_3]Cl_2}$ by X-ray crystallography, begin to appear.[12] When the reactant ratio is increased to 1:1:4:1, compound **5** forms with a large amount of $\mathrm{[Ni(2,2'\text{-}bipy)_3]Cl_2}$. A higher yield of **5** could be obtained when the reactant ratio was adjusted to 1:1.5:4:2, as described in the Experimental Section.

Crystal Structures. Compounds **1**−**5** all contain a combination of BDC and 2,2′-bipy ligands but have a remarkable structural and compositional diversity that is achieved in part by the versatile connectivity of the BDC ligands as shown in Chart 1.

The structures of the compounds **1**, **4**, and **5** are formed by infinite one-dimensional chains where octahedrally coordinated Ni(II) centers are linked by BDC bridges. On the other hand, compound **2** is based on a discrete dimeric molecule where the two nickel centers are bridged by one BDC ligand (Figure 3), and **3** is a two-dimensional polymer formed by trinuclear Ni(II) units linked by BDC bridges. These compounds were synthesized from the same reactants and solvent but different reactant ratios. The crystal structures of compounds **1** and **4** (Figure 2) were described in our previous work.[6]

Compound 2. The environment of the Ni centers in **2** is identical with that in **1** (Figure 3). The Ni−O bond distances range from 2.056(10) to 2.160(7) Å, and the Ni−N bond distances are 2.004(11) and 2.076(11) Å. However, compound **2** has a molecular rather than a polymeric structure because only one of the two BDC ligands coordinating to each nickel atom bridges two nickel centers in bischelating coordination mode while the other BDC has monochelating and one-protonated, noncoordinating carboxylic groups, resulting in the formation of discrete dimeric molecules. The dimers form layers by face-to-face $\pi-\pi$ interactions between 2,2′-bipy ligands, and these layers are stacked through CH−π interactions [$d_{\mathrm{H8-centroid}} = 3.418(4)$ Å] between the HBDC ligands. The hydrogen atom from a noncoordinating carboxylic group is hydrogen-bonded to the chelating oxygen atom of a neighboring molecule [$d_{\mathrm{O6\cdots O2}} = 2.682(5)$ Å]. A similar molecular compound, $\mathrm{[Ni_2(BDC)(2,2'\text{-}bipy)_4][ClO_4]_2}$, has been synthesized at room temperature. This ionic compound has only one BDC ligand, which connects two Ni centers, and the remaining octahedral sites around each Ni atom are occupied by two chelating 2,2′-bipy ligands.[13]

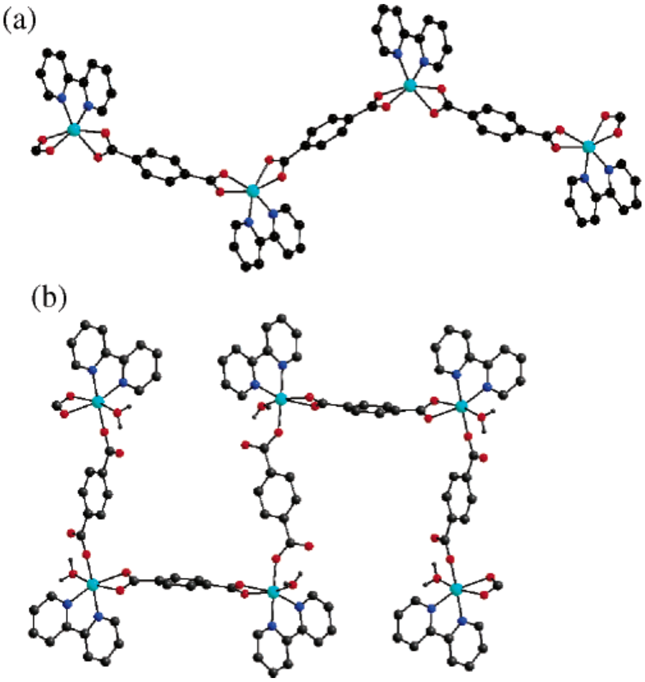


Figure 2. One-dimensional chain structures of compounds **1** (a) and **4** (b).

Compound 3. As shown in Figure 4, in compound **3**, three Ni^{2+} atoms are clustered by BDC ligands in bridging coordination mode. The coordination environment around Ni1, which is on the inversion center, is octahedral. The ligands coordinated to the Ni2 atom form a distorted octahedron, frequently found in compounds with chelating BDC and 2,2′-bipy ligands. The Ni1−Ni2 distance is 3.443(1) Å, and the Ni2−Ni1−Ni2 angle is 180°. Each $\mathrm{Ni1O_6}$ octahedron shares its opposite O1 corners with two $\mathrm{Ni2O_4N_2}$ octahedra. Each trinuclear $\mathrm{Ni_3(BDC)_3(2,2'\text{-}bipy)_2}$ unit is connected to six other trinuclear units by sharing each of its six BDC ligands, resulting in the formation of a two-dimensional (6,3) net with a thickness of the trinuclear unit. The chelating 2,2′-bipy ligands are located on both sides of the layer. The layers are stacked by $\pi-\pi$ interactions of each 2,2′-bipy ligand with one ring from each of its two neighboring 2,2′-bipy ligands from an adjacent layer.

A trimeric building unit similar to that in **3** is also found in several compounds[14] including MOF-3, $\mathrm{Zn_3(BDC)_3(CH_3OH)_4\cdot 2(CH_3OH)}$[15] (Figures 4 and 5) which is a three-dimensional porous network instead of a two-dimensional

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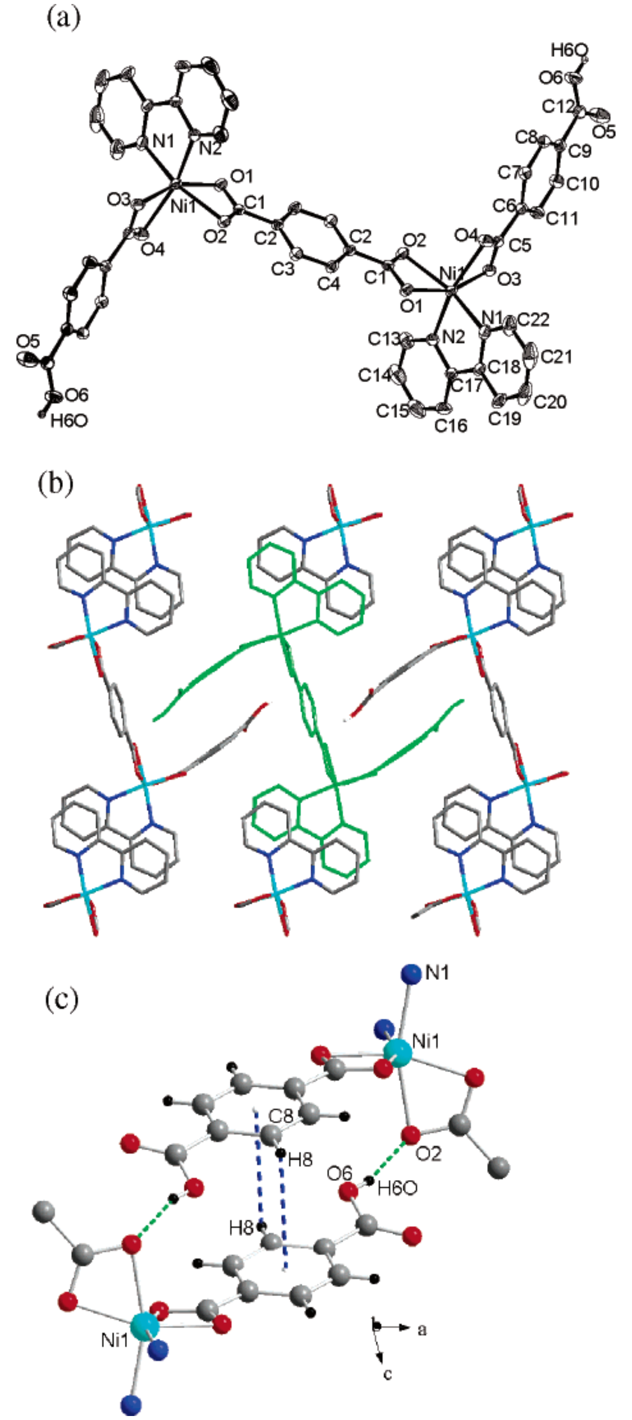

Figure 3. (a) Perspective view of the dimeric molecule of **2**. Hydrogen atoms except for the carboxylic acid proton are omitted for clarity, and thermal ellipsoids are at the 30% probability level. (b) Packing diagram of **2** showing $\pi-\pi$ stacking of the 2,2′-bipy ligands. One discrete molecule is highlighted by a green line. (c) CH$-\pi$ interaction between two HBDC ligands (blue dotted line) and hydrogen bonding (green dotted line).

sheet. As in **3**, each trimer in MOF-3 is linked to six adjacent trimers, but unlike **3**, where the centers of all six neighbors are located in the same plane leading to a layered structure, in MOF-3, four of the neighbors are displaced (two above and two below), resulting in a three-dimensional framework.

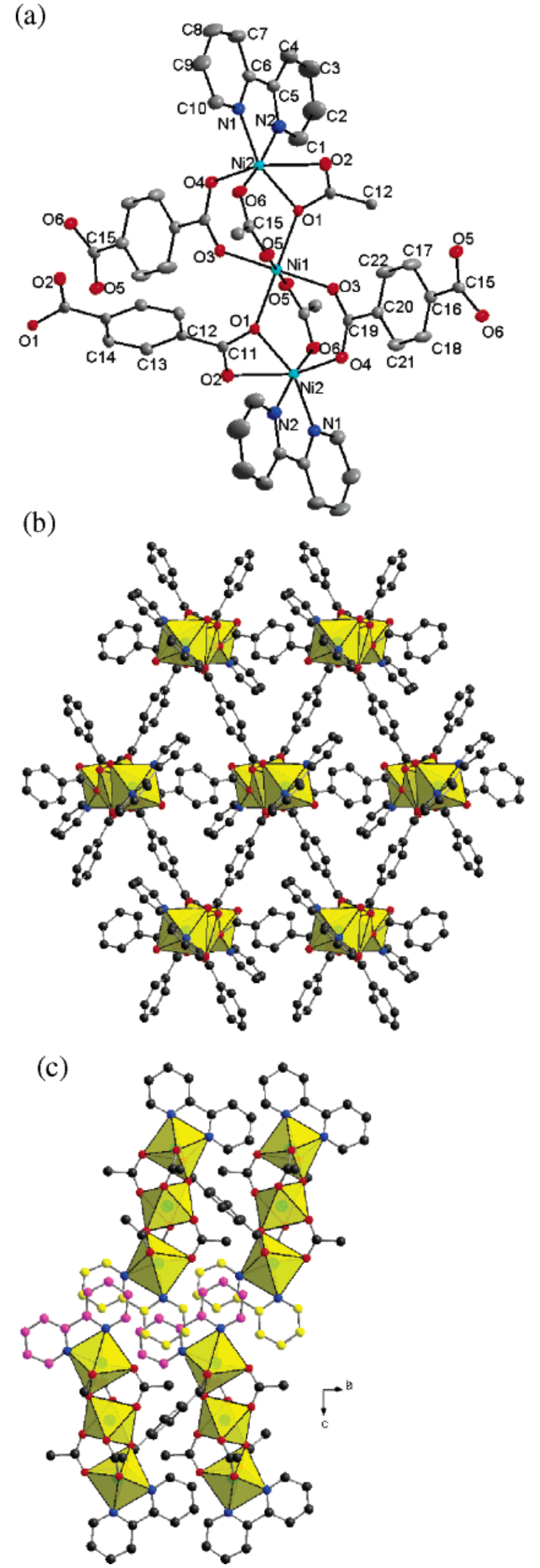

Figure 4. (a) Perspective view of the main building unit of **3**. Hydrogen atoms are omitted for clarity, and thermal ellipsoids are at the 50% probability level. (b) Top view of a two-dimensional layer in **3** showing connectivity of the trinuclear Ni(II) building units. A chelating 2,2′-bipy ligand coordinates to each trimer on each side of the plane. (c) Interlayer $\pi-\pi$ interactions through sandwiched 2,2′-bipy ligands. Each 2,2′-bipy shown in purple is sandwiched between two 2,2′-bipy ligands shown in yellow and vice versa.

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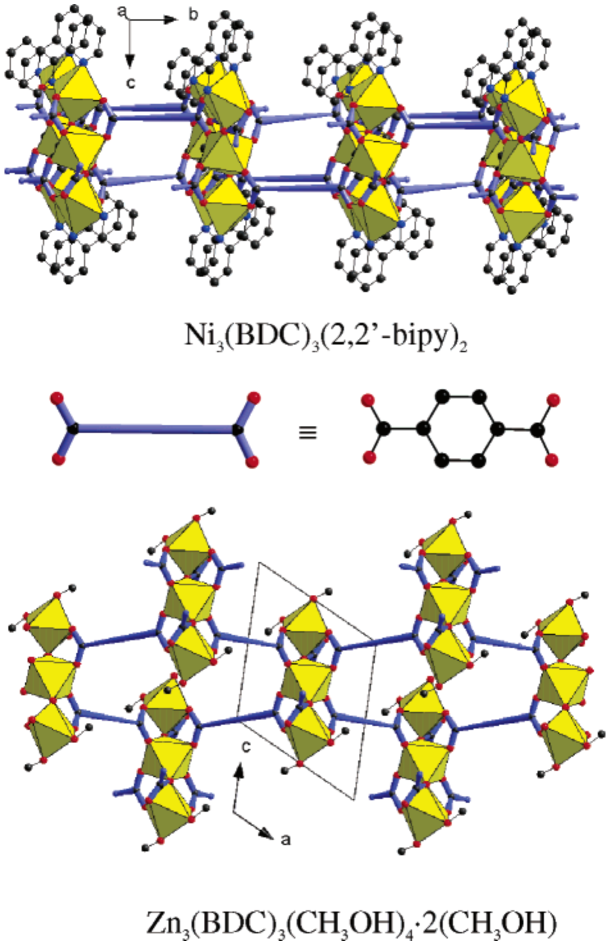

Figure 5. Schematic views of connectivity between trimeric M(II) units in two-dimensional compound **3** (top) and three-dimensional compound MOF-3 (bottom). The BDC linkers are schematically shown in blue. The connectivity between trimers in the direction of the view is identical in the two compounds.

Compound 5. Compound **5** (Figure 6) is based on infinite zigzag chains where nickel centers chelated by two 2,2-bipy ligands are bridged by bis-monodentate BDC ligands. The monodentate oxygen atoms, O2, are in cis positions, as found in all Ni(2,2′-bipy)$_2$L$_2$ octahedral complexes leading to the idealized Ni−Ni−Ni angle of 90°. The observed Ni−Ni−Ni angle in **5** is 98.24(6)°, while the angle in compound **4** is 87 or 88°. The Ni−Ni distance, 11.355(1) Å, is similar to that found in compound **4** for nickel atoms bridged by bis-monodenate BDC ligands [11.305(4) and 11.151(1) Å]. This distance is longer than that in other compounds where two nickel atoms are bridged by bischelating BDC ligands: 10.535(2) and 10.576(2) Å in **1**, 10.652(10) Å in **2**, and 10.572(1) Å in **3**. The guest water molecule (O1w) in compound **5** is hydrogen-bonded to a noncoordinating carbonyl oxygen (O1) atom from the bis-monodentate BDC ligand [$d_{\mathrm{O1}\cdots\mathrm{O1w}} = 2.745(3)$ Å].

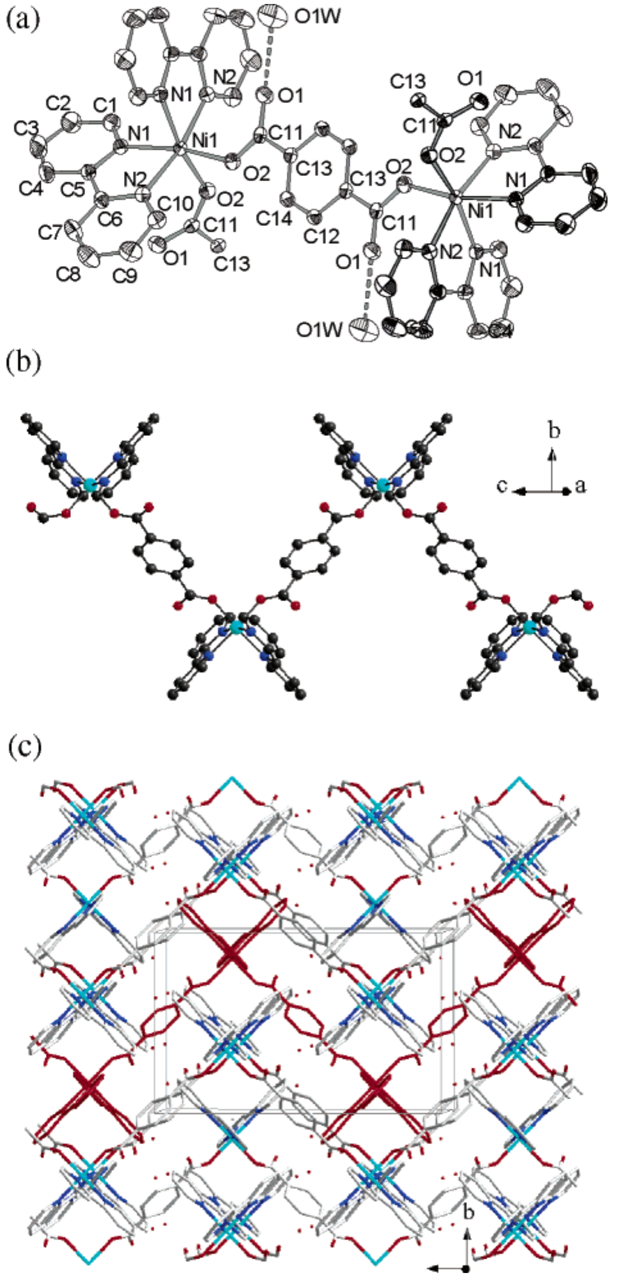

Figure 6. (a) Perspective view of the Ni^{2+} coordination environment in **5** showing hydrogen bonds with guest H$_2$O molecules (dotted line). Hydrogen atoms are omitted for clarity, and thermal ellipsoids are at the 30% probability level. (b) Fragment of the one-dimensional single-chain structure. (c) Chain-packing diagram of **5** with a red line highlighting a single chain.

Characterization. (i) Vibrational Spectra. In the IR spectrum of **2**, the strong band at 1710 cm^{-1} indicates the presence of a protonated carboxylic group, which confirms the X-ray crystal structure. The ν_{asym}(CO$_2$) and ν_{sym}(CO$_2$) stretching vibrations at 1515 and 1407 cm^{-1}, respectively, show that all other carboxylic groups are chelating. The ν_{asym}(CO$_2$) stretching band at 1604 cm^{-1} in the IR spectrum of **3** is relatively weak compared to that of most compounds containing BDC ligands. In the IR spectrum of **5**, the ν_{asym}(CO$_2$) and ν_{sym}(CO$_2$) stretching vibrations at 1587 and 1377 cm^{-1} show that all BDC ligands adopt monodentate coordination modes. The splitting of the antisymmetric stretching band around 1587(vs) cm^{-1} is due to the hydrogen bonding between the carbonyl oxygen of the BDC ligand and the guest water molecule, and a similar pattern was observed in compound **4**.

(ii) Thermal Analysis. Compound **3** is stable nearly up to 400 °C and decomposes to NiO, as identified by X-ray powder diffraction, in one step (onset at 400 °C, completion at 450 °C; obs 76.80%, calcd 77.15%). Compound **2** shows an unexpected two-step decomposition to NiO from 310 to 400 °C (total weight loss: obs 85.55%, calcd 83.83%). The intermediate product was identified as compound **3** by X-ray powder diffraction and IR spectroscopy, and the first weight loss was in agreement with the corresponding loss of $^1/_2$H$_2$BDC and $^1/_3$(2,2′-bipy) molecules per nickel (obs 30.12%, calcd 29.25%). The second weight loss was consistent with decomposition of **3** to NiO (obs 55.43%, calcd 54.58%). This, at first sight surprising, condensation of the dimeric molecules **3** to a polymer containing trinuclear clusters, **3**, was in agreement with the temperature effect in the synthesis of these compounds: the reactant ratio that gives a mixture of **2** and **3** below 180 °C results in a pure phase **3** when heated above 180 °C. In a similar way, compound **1** showed an unexpected decomposition profile in our previous report [calculated weight losses for 0.75H$_2$BDC per Ni^{2+} and 1.0(BDC + 2,2′-bipy) per Ni^{2+} were 27.75% and 60. 42%]. The new information on the structural properties and thermal behavior of Ni-BDC/2,2′-bipy coordination polymers allowed the identification of the previously unknown product of the partial decomposition of the framework of **1** as compound **3**, which was confirmed by X-ray power diffraction and FTIR spectroscopy. Consequently, the first observed weight loss of 34.56% corresponded to the loss of 0.75 of guest H$_2$BDC and $^1/_3$ of 2,2′-bipy (calcd 35.08%) to form the trinuclear compound **3**, and the second weight loss was due to the decomposition of the framework to NiO (obs 50.50%, calcd 50.76%). Similar to the transformation of **2** to **3**, the thermal transformation of **1** to **3** also paralleled the effect of increasing the synthesis temperature. Compound **5** lost its guest water molecules slowly until 150 °C (obs 5.24%, calcd 6.31%) followed by a two-step decomposition to NiO (obs 28.23% and 53.79%). The second weight loss starting at 250 °C was consistent with the loss of one of the two 2,2′-bipy ligands (obs 28.23%, calcd 27.34%). The final weight loss of 53.79% was in agreement with the decomposition of Ni(BDC)(2,2′-bipy) to NiO (calcd 53.27%).

Conclusion

Our investigation of the NiCl$_2$/BDC/KOH/2,2′-bipy system resulted in a series of compounds ranging from a dimeric molecular compound to a two-dimensional polymer. At 160 °C, the reactant ratio of 1:1:1.5:1 (pH 4) led to a one-dimensional coordination polymer **1**. The guest H$_2$BDC molecules were connected by hydrogen bonds and formed extended chains. A ratio 1:1:2:1 corresponding a slightly higher pH of 4.75 led to a molecular compound **2** that has, overall, a lower amount of protonated carboxylic groups per nickel and per BDC ligand. The same reactant ratio, but higher synthesis temperature, led to the transformation of compound **2** to the layered compound **3**, where all BDC ligands were deprotonated and bridging, resulting in the formation of trinuclear Ni$_3$(BDC)$_6$(2,2′-bipy)$_2$ units, was built by corner-sharing nickel octahedra. Similarly, compound **3** formed from a mononuclear coordination polymer **1** at higher synthesis temperature. The increase of the condensation of metal polyhedra as a result of a synthesis temperature increase is quite common in coordination polymers and has been especially well-documented in the case of cobalt succinates.[8a] The transformations of **1** and **2** to **3** also occur as solid-state reactions at 300−310 °C, as shown in thermogravimetric analysis experiments.

A further increase of the pH to 5.25 (reactant ratio 1:1:2.5:1) led to the previously reported one-dimensional polymer **4**, which forms at a wide range of temperatures, 150−210 °C. Increasing either the pH to 8.5 (reactant ratio 1:1:4:1) or the 2,2′-bipy content in this mixture led to incorporation of the second chelating 2,2′-bipy into the chain and the formation of a one-dimensional polymer **5**. In contrast, in the case of a zinc coordination polymer with an overall M/BDC/2,2′-bipy ratio of 1:1:2, Zn(BDC)(2,2′-bipy)·(2,2′-bipy),[16] half of the 2,2′-bipy ligands are present as guest molecules. The examples above further illustrate the structural and compositional diversity in metal/organic hybrid materials that can be achieved by adjustment of the reactant ratio as well as by the versatile connectivity of the BDC ligands.

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Supporting Information Available: X-ray crystallographic data, in CIF format, for the structure determination of **2**, **3**, and **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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