Inorg. Chem. **2004**, *43*, 5360–5367

Inorganic Chemistry
Article

A Chain of Changes: Influence of Noncovalent Interactions on the One-Dimensional Structures of Nickel(II) Dicarboxylate Coordination Polymers with Chelating Aromatic Amine Ligands

YongBok Go, Xiqu Wang, Ekaterina V. Anokhina, and Allan J. Jacobson*

Department of Chemistry, University of Houston, Houston, Texas 77204-5003

Received May 19, 2004

Five one-dimensional coordination polymers, Ni(BDC)(1,10-phen) (**1**), Ni(BDC)(2,2′-bipy)·0.75H_2BDC (**2**), Ni(BDC)(1,10-phen)(H_2O) (**3**), Ni(BDC)(1,10-phen)(H_2O)·0.5H_2BDC (**4**) and Ni(BDC)(2,2′-bipy)(H_2O) (**5**) [where BDC = 1,4-benzenedicarboxylate, 2,2-bipy = 2,2′-bipyridine, and 1,10-phen = 1,10-phenanthroline] that have the same topology but markedly different geometry and packing of the chains have been synthesized by hydrothermal reactions. The results of variations of synthesis conditions and substitutions of 1,10-phenanthroline with 2,2′-bipyridine indicate that incorporation of the coordinating water molecule, which affects the degree of bending of the chain, is primarily influenced by the amine ligand size, suggesting a substantial structural role of aromatic–aromatic interactions and amine ligand steric effects. The incorporation of the guest H_2BDC molecules was found to be favored by lower pH conditions. Crystal data: **1**, monoclinic, space group $P2_1/n$, $a = 9.5589(6)$ Å, $b = 12.6776(8)$ Å, $c = 13.5121(9)$ Å, $\beta = 95.437(1)°$, $Z = 4$; **2**, monoclinic, space group $P2_1/c$, $a = 20.532(3)$ Å, $b = 21.505(3)$ Å, $c = 18.872(3)$ Å, $\beta = 93.86(1)°$, $Z = 16$; **3**, triclinic, space group $P\bar{1}$, $a = 8.618(3)$ Å, $b = 10.058(4)$ Å, $c = 11.353(4)$ Å, $\alpha = 115.31(1)°$, $\beta = 92.33(1)°$, $\gamma = 94.03(1)°$, $Z = 2$; **4**, triclinic, space group $P\bar{1}$, $a = 9.7682(12)$ Å, $b = 10.6490(13)$ Å, $c = 11.2468(14)$ Å, $\alpha = 76.685(2)°$, $\beta = 65.309(2)°$, $\gamma = 85.612(2)°$, $Z = 2$; **5**, monoclinic, space group $P2_1/c$, $a = 13.9683(9)$ Å, $b = 17.4489(11)$ Å, $c = 13.7737(9)$ Å, $\beta = 99.12(1)°$, $Z = 8$.

Introduction

Inorganic−organic hybrid materials have been studied for potential applications in gas storage, catalysis, separations, and molecular recognition.[1] The organic components containing N- or O-donors in the framework offer great potential for chemical and structural diversity.[2] Polycarboxylates are widely used as bridging ligands for designing new inorganic−organic hybrid materials. As a rigid and versatile bridging ligand, 1,4-benzenedicarboxylate (BDC) has been studied extensively.[3] Polycyclic aromatic bidentate ligands such as 2,2′-bipyridyl (2,2′-bipy) and 1,10-phenanthroline (1,10-phen) are frequently used in combination with polycarboxylates, leading to novel architectures where they facilitate supramolecular self-assembly through aromatic−aromatic ($\pi-\pi$ and CH$-\pi$) interactions.[4] Compared to face-to-face $\pi-\pi$ stacking interactions that, until recently, were the primary focus in the descriptions of aromatic supramolecular contacts, edge-to-face CH$-\pi$ interactions did not receive significant attention. In the past decade, however, their comparable importance in the crystal chemistry of coordination compounds is becoming more recognized.[5] Several

---

* To whom correspondence should be addressed: E-mail: ajjacob@uh.edu. Telephone: (713) 743-2785. Fax: (713) 743-2787.

(1) (a) Chae, H. K.; Siberio, D. Y.; Kim, J.; Go, Y.; Eddaoudi, M.; Matzger, A. J.; O'Keeffe, M.; Yaghi, O. M. *Nature* **2004**, *427*, 523. (b) Seo, J. S.; Whang, D.; Lee, H.; Jun, S. I.; Oh, J.; Jeon, Y. J.; Kim, K. *Nature* **2000**, *404*, 982 (c) Kahn, O.; Martinez, C. *Science* **1998**, *279*, 44. (d) Janiak, C. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1431. (e) Zaworotko, M.; Rogers, R. D. In *Synthesis of New Materials by Coordination Chemistry Self-Assembly and Template Formation*; ACS Symposium, Anaheim, CA, 1999.

(2) (a) Eddaoudi, M.; Moler, D. B.; Li, H.; Chen, B.; Reineke, T. M.; O'Keeffe, M.; Yaghi, O. M. *Acc. Chem. Res.* **2001**, *34*, 319. (b) Hagraman, P. J.; Hagraman, D.; Zubieta, J. *Angew. Chem., Int. Ed.* **1999**, *38*, 2639. (c) Kitagawa, S.; Kondo, M. *Bull. Chem. Soc. Jpn.* **1998**, *71*, 1739. (d) Batten, S. R.; Robson, R. *Angew. Chem., Int. Ed.* **1998**, *37*, 1460.

(3) (a) Li, H.; Eddaoudi, M.; Yaghi, O. M. *Nature* **1999**, *402*, 276. (b) Groenman, R. H.; MacGillivaray, L. R.; Atwood, J. L. *Chem. Commun.* **1998**, 2735. (c) Zhang, Y.; Li, J. M.; Zhu, M.; Wang, Q. M.; Wu, X. T. *Chem Lett.* **1998**, 1051. (d) Hong, C. S.; Do, Y. *Inorg. Chem.* **1998**, *37*, 4470. (e) Franesconi, L. C.; Corbin, D. R.; Clauss, A. W.; Hendrickson, D. N.; Stucky, G. D. *Inorg. Chem.* **1981**, *20*, 2078.

(4) (a) Chen, X. M.; Liu, G. F. *Chem. Eur. J.* **2002**, *8*, 4811. (b) Liu, G. F.; Ye, B. H.; Ling, Y. H.; Chen, X. M. *Chem. Commun.* **2002**, 1442. (c) Yao, J.-C.; Huang, W.; Li, B.; Gou, S.; Xu, Y. *Inorg. Chem. Commun.* **2002**, *5*, 711.

10.1021/ic049341u CCC: $27.50

coordination polymers with BDC and 2,2-bipy or 1,10-phen ligands, most of which are one-dimensional, have been reported for divalent cations Mn^{2+}, Co^{2+}, Cu^{2+}, Zn^{2+}, and Cd^{2+},[6−8] but in the case of Ni^{2+}, only mono- or dinuclear molecular complexes containing a combination of these ligands have been described to date.[9,10] Herein, we present the syntheses and structures of five new one-dimensional coordination polymers of Ni^{2+}: Ni(BDC)(1,10-phen) (**1**), [Ni(BDC)(2,2′-bipy)]·0.75H_2BDC (**2**), Ni(BDC)(1,10-phen)(H_2O) (**3**), [Ni(BDC)(1,10-phen)(H_2O)]·0.5H_2BDC (**4**), and Ni(BDC)(2,2′-bipy)(H_2O) (**5**).

This new series of coordination polymers is based on topologically identical chains where the nickel centers chelated by amine ligands are linked by BDC bridges. The coordination modes of the BDC ligands, geometry of the chains (zigzag vs crankshaft configuration as well as the angles between the individual links), and chain packing, however, are substantially different among these compounds and were found to be primarily influenced by noncovalent interactions.

Experimental Section

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

Synthesis of Ni(BDC)(1,10-phen) (1). A mixture of $NiCl_2·6H_2O$ (0.42 mmol, 100 mg), 1,4-benzenedicarboxylic acid (0.63 mmol, 104.7 mg), KOH (1.68 mmol, 94.3 mg), 1,10-phenanthroline (0.42 mmol, 75.8 mg), and H_2O (0.5 mL) was heated in a 23 mL stainless steel reactor with a Teflon liner at 170 °C for 48 h. The blue crystalline product was filtered and washed with water and acetone. Yield: 57% based on Ni. Anal. Calcd for $C_{20}H_{12}N_2NiO_4$: C, 59.60; H, 3.00; N, 6.95. Found: C, 59.68; H, 3.13; N, 7.04. IR (KBr): 3367.05m(br), 3079.78w, 3056.63w, 1623.77w, 1585.20w, 1552.42s, 1536.99s, 1506.14s, 1425.14m, 1400.07s, 1340.29w, 1315.12w, 1299.79w, 1253.51w, 1222.65w, 1195.65w, 1141.65m, 1103.09w, 1085.73w, 1020.16m, 889.02w, 869.74w, 850.45s, 842.74s, 779.10w, 750.17m, 728.96s, 646.04m, 549.61w, 536.11m, 499.47m, 482.11w, 453.19w, 428.12w cm^{-1}.

Synthesis of [Ni(BDC)(2,2′-bipy)]·0.75H₂BDC (2). A mixture of $NiCl_2·6H_2O$ (0.42 mmol, 100 mg), 1,4-benzenedicarboxylic acid (0.50 mmol, 84.0 mg), KOH (0.76 mmol, 42.5 mg), 2,2′-bipyridine (0.42 mmol, 65.4 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. The green rod-shaped crystals were filtered and washed with water and acetone. Yield: 51% based on Ni. Anal. Calcd for $C_{24}H_{16.5}N_2NiO_7$: C, 57.24; H, 3.30; N, 5.56. Found: C, 56.83; H, 3.23; N, 5.53. IR (KBr): 3430.76m(br), 3068.21m, 1695.13s, 1604.49w, 1575.56w, 1533.14s, 1509.99m, 1473.35w, 1456.00w, 1407.78s, 1278.58m, 1176.37w, 1132.01w, 1105.01w, 1054.87w, 1018.23w, 923.74w, 902.52w, 881.31w, 846.60m, 765.60m, 730.89m, 671.11m, 651.82w, 532.26m 474.40w, 441.62w, 418.47w cm^{-1}.

Synthesis of Ni(BDC)(1,10-phen)(H₂O) (3). This compound was prepared under the same conditions as **1** except for lower synthesis temperature (160 °C). The product in the form of blue crystals was filtered and washed with water and acetone. Yield: 57% based on Ni. Anal. Calcd for $C_{20}H_{14}N_2NiO_5$: C, 57.05; H, 3.35; N, 6.65. Found: C, 56.62; H, 3.41; N, 6.64. IR (KBr): 3363.26m(br), 3060.49w(br), 1689.34w, 1625.7w, 1583.28m, 1548.56s, 1513.85m, 1496.49w, 1423.21m, 1403.93s, 1380.79s, 1295.93w, 1222.65w, 1143.58w, 1103.09w, 1085.73w, 1049.09w, 1014.38m, 885.17w, 871.61w, 848.53m, 838.88m, 794.53m, 765.60w, 744.39m, 727.03m, 644.11w, 541.90m, 516.83m cm^{-1}.

Synthesis of [Ni(BDC)(1,10-phen)(H₂O)]·0.5H₂BDC (4). This compound was prepared similarly to **2** except for the use of 1,10-phen instead of 2,2′-bipy and the reaction temperature of 180 °C. The blue crystalline product was filtered and washed with water and acetone. Yield: 57% based on Ni. Anal. Calcd for $C_{27}H_{17}N_2NiO_7$: C, 57.18; H, 3.40; N, 5.56. Found: C, 57.01; H, 3.41; N, 5.64. IR (KBr): 3377.73m(br), 3066.76m(br), 1688.86s, 1586.17w, 1542.30vs, 1516.74m, 1507.52m, 1425.62m, 1404.89s, 1378.38s, 1260.00w, 1246.76w, 1147.44w, 1123.82w, 1105.5w, 1088.62w, 1016.79w, 853.35s, 796.46m, 774.28m, 744.39m, 726.07s, 603.13m, 534.67m, 516.83m cm^{-1}.

Synthesis of Ni(BDC)(2,2′-bipy)(H₂O) (5). This compound was prepared as deep-blue crystals under the same reaction conditions as **1** except for the use of 2,2′-bipy instead of 1,10-phen. Yield: 69% based on Ni. Anal. Calcd for $C_{18}H_{14}N_2NiO_5$: C, 54.46; H, 3.55; N, 7.06. Found: C, 54.34; H, 3.58; N, 7.16. IR (KBr): 3316m(br), 3104.85m, 1577.49w, 1570.23w, 1548.56s, 1523.49w, 1506.14m, 1475.28m, 1444.43s, 1411.64s, 1378.86s, 1311.36w, 1253.51w, 1174.44w, 1153.23w, 1056.80w, 1027.87w, 1016.30w, 098.31w, 887.1w, 844.67s, 806.10m, 759.82s, 734.75w, 653.75w, 634.46w, 522.61m, 441.62w, 418.47w cm^{-1}.

Crystallographic Studies. Single crystals of suitable dimensions for **1**−**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 by 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 by use of the Siemens SAINT program,[11] with the intensities corrected for 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 with SHELXTL.[12] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined isotro-

---

(5) (a) Janiak, C. *J. Chem. Soc., Dalton Trans.* **2000**, 3885. (b) Waters, M. L. *Curr. Opin. Chem. Biol.* **2002**, *6*, 736. (c) Hunter, C. A.; Sanders, K. M. *J. Am. Chem. Soc.* **1990**, *112*, 5525. (d) Suezawa, H.; Yoshida, T.; Umezawa, Y.; Tsuboyama, S.; Nishio, M. *Eur. J. Inorg. Chem.* **2002**, 3148.

(6) (a) Sun, D.; Cao, R.; Liang, Y.; Shi, Q.; Su, W.; Hong, M. *J. Chem Soc., Dalton Trans.* **2001**, 2335. (b) Cano, J.; De Munno, G.; Sanz, J.; Ruiz, R.; Lloret, F.; Faus, J.; Julve, M. *J. Chem. Soc., Dalton Trans.* **1994**, 3465. (c) Zhu, L. G.; Xiao, H. P.; Lu, J. Y. *Inorg. Chem. Commun.* **2004**, *7*. 94. (d) Zhang, L. J.; Zhao, X. L.; Cheng, P.; Xu, J. Q.; Tang, X.; Cui, X. B.; Xu, W.; Wang, T. G. *Bull. Chem. Soc. Jpn.* **2003**, *76*, 1179. (e) Shi, X.; Zhu, G.; Fang, Q.; Wu, G.; Tian, G.; Wang, R.; Zhang, D.; Xue, M.; Qiu, S. *Eur. J. Inorg. Chem.* **2004**, 185.

(7) Zhang, X.-M.; Tong, M.-L.; Gong, M.-L.; Chen, X.-M. *Eur. J. Inorg. Chem.* **2003**, 138.

(8) Xu, H. B.; Su, Z. M.; Shao, K. Z.; Zhao, Y. H.; Xing, Y.; Liang, Y. C.; Zhang, H. J.; Zhu, D. X. *Inorg. Chem. Commun.* **2004**, *7*, 260.

(9) Deng, Z. L.; Shi, J.; Jiang, Z. H.; Liao, D. Z.; Yan, S. P.; Wang, G. L.; Wang, H. G.; Wang, R. J. *Polyhedron* **1992**, *11*, 885.

(10) Xiao, H. P.; Shi, Z.; Zhu, L. G.; Xu, R. R.; Pang, W. Q. *Acta Crystallogr.* **2003**, *C59*, m82.

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

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

Table 1. Crystallographic Data for Compounds **1**−**5**

	1	**2**	**3**	**4**	**5**
chemical formula	$C_{20}H_{12}N_2NiO_4$	$C_{24}H_{16.5}N_2NiO_7$	$C_{20}H_{14}N_2NiO_5$	$C_{24}H_{17}N_2NiO_7$	$C_{18}H_{14}N_2NiO_5$
FW	403.03	503.19	421.04	504.11	397.02
cryst syst	monoclinic	monoclinic	triclinic	triclinic	monoclinic
space group	$P2_1/n$	$P2_1/c$	$P\bar{1}$	$P\bar{1}$	$P2_1/c$
a, Å	9.5589(6)	20.532(3)	8.618(3)	9.768(1)	13.9683(9)
b, Å	12.6776(8)	21.505(3)	10.058(4)	10.649(1)	17.449(1)
c, Å	13.5121(9)	18.872(3)	11.353(4)	11.247(1)	13.7737(9)
α, deg			115.31(1)	76.685(2)	
β, deg	95.437(1)	93.86(1)	92.33(1)	65.309(2)	99.12(1)
γ, deg			94.03(1)	85.612(2)	
V, Å^3	1630.1(2)	8314(2)	884.7(6)	1034.1(2)	3314.6(4)
Z	4	16	2	2	8
temp, K	223(2)	293(2)	223(2)	293(2)	293(2)
ρ_c, g cm^{-3}	1.642	1.604	1.580	1.570	1.591
μ(Mo Kα), mm^{-1}	1.221	0.986	1.133	0.991	1.204
R1, wR2 [$I > 2\sigma(I)$][a]	0.0289, 0.0700	0.0573, 0.1032	0.0454, 0.0984	0.0306, 0.0790	0.0291, 0.0747
R1, wR2 (all data)[a]	0.0403, 0.0744	0.2134, 0.1465	0.0699, 0.1072	0.0349, 0.0817	0.0404, 0.0798

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

pically with geometric constrains. Crystal data for the compounds **1**−**5** are summarized in Table 1.

Results

Crystal Structures. Compounds **1**−**5** are all formed by one-dimensional chains where octahedrally coordinated Ni(II) centers are linked by BDC bridges. These structures significantly differ, however, in coordination modes of the BDC ligands, geometry of the chains (Table 2), and chain packing (Table 3).

Structures of Individual Chains in 1−5. The simplest coordination pattern is observed in compounds **1** and **2** (Table 2), where each nickel atom has an octahedral environment formed by three chelating bidentate ligands: one aromatic amine ligand (1,10-phen in **1** and 2,2′-bipy in **2**) and two carboxylic groups from two BDC ligands. As generally found in complexes with chelating carboxylate ligands, the nickel octahedra are highly distorted [O−Ni−O angles formed by chelating carboxylate range between 62.11(5) and 63.2(1)] due to the short O−O separation in the carboxylate group [2.182(5)−2.199(5) Å]. The angles between the “blades” (Ni−O−C−O and Ni−N−C−C−N planes) in these propellerlike units, however, are closer to the ideal value of 120° (108−128° for **1** and 115−125° for **2**). The Ni−O bond distances range from 2.038(1) to 2.211(2) Å in **1** and from 2.054(4) to 2.128(3) Å in **2**, and Ni−N bond distances are 2.045(2) and 2.059(2) Å in **1** and range from 2.040(5) to 2.065(5) Å in **2**, which are typical values for the corresponding Ni−L distances. Each BDC ligand connects two nickel centers leading to a zigzag chain where the Ni−Ni−Ni angles, defined by the orientation of the two BDC ligands in the $Ni(BDC)_2L$ building units (L = 1,10-phen in **1** and 2,2′-bipy in **2**), are close to the ideal value of 120° [121.52(1)° in **1** and 126.30(1) and 127.19(1)° in **2**]. The Ni−Ni distances within the chains are 10.647(3) Å for **1** and 10.535(2) and 10.576(2) Å for **2**. A chain similar to that in **2** with M−M−M angles of 128.52(1)° is found in Zn(BDC)(2,2′-bipy)·(2,2′-bipy).[7]

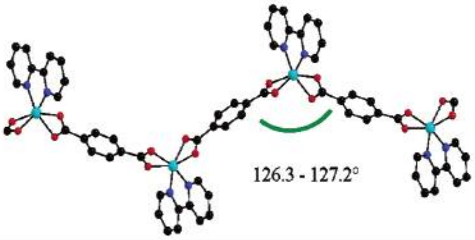
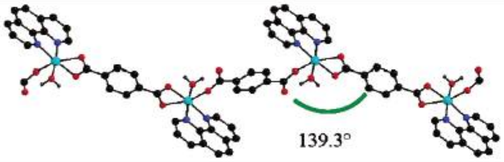
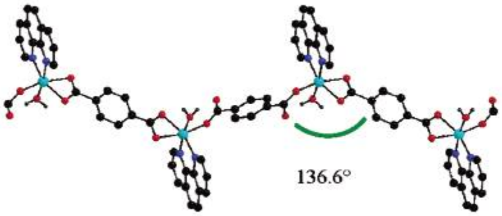
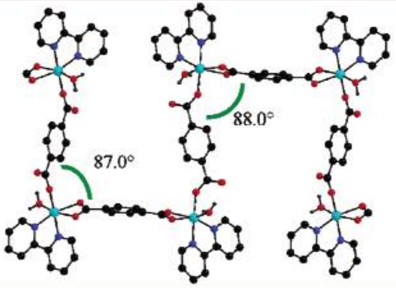
In compounds **3** and **4**, the environment of nickel atoms is modified by incorporation of a coordinating water molecule into a *trans* position to one of the nitrogen atoms, resulting in change of a coordination mode of one of the two BDC ligands from chelating to monodentate (Table 2). A simultaneous presence of chelating and monodentate coordination modes of BDC ligands is quite rare and is found, to our knowledge, in only two recent examples: $[Ni(BDC)(py)_3]_6\cdot(DMF)_6\cdot(H_2O)_9$,[13] where the bis-chelating and bis-monodentate BDC ligands alternate throughout the chain as in **3** and **4**, and $[Cd(BDC)(2,2'\text{-bipy})]\cdot H_2O$,[8] where one carboxylic group in each BDC ligand is chelating and the other is monodentate. Compared to the chains in **1** and **2**, the incorporation of the water molecule in **3** and **4** causes an increase in the Ni−Ni−Ni angle to an idealized value of 135°, leading to less bent chains. The observed Ni−Ni−Ni angles within the chains are 139.26(1)° in **3** and 136.57(1)° in **4**. The Ni−Ni distances for nickel atoms bridged by bis-chelating BDC ligands [10.663(5) Å in **3** and 10.63(1) Å in **4**] are similar to those in **1** and **2**, while bis-monodentate BDC bridges lead to longer Ni−Ni distances [11.23(4) Å in **3** and 11.37(1) Å in **4**].

Similarly to **3** and **4**, compound **5** is based on $Ni(BDC)(L)(H_2O)$ chains where the nickel atoms are bridged by alternating bis-chelating and bis-monodentate ligands (Table 2). The orientation of the coordinating water molecule with respect to the amine ligand in **5** (*cis* to both nitrogens), however, is different from that in **3** and **4** (*trans* to one of the nitrogens and *cis* to the other) and leads to a more bent chain with idealized Ni−Ni−Ni angle of 90° as opposed to 135°. The observed Ni−Ni−Ni angles in **5** are 87.05(1)° and 88.01(1)°. The Ni−Ni distances [10.657(4) Å for bis-chelating and 11.305(4), 11.151(1) for bis-monodentate BDC-bridged pairs, respectively] are similar to those in **3** and **4**. In contrast to compounds **1**−**4** and most other 1D coordination polymers with BDC bridges, the chain configuration in **5** is crankshaft rather than zigzag. This feature is not a direct result of a different local environment around the nickel atoms, since the alternative zigzag configuration (derived from the crankshaft chain by 180° rotations around the bis-chelating BDC bridges) does not lead to any steric

---

(13) Ohmura, T.; Mori, W.; Hasegawa, M.; Takei, T.; Ikeda, T.; Hasegawa, E. *Bull. Chem. Soc. Jpn.* **2003**, *76*, 1387.

Table 2. Structures of the Chains and Synthesis Conditions Summary for Compounds **1**−**5**

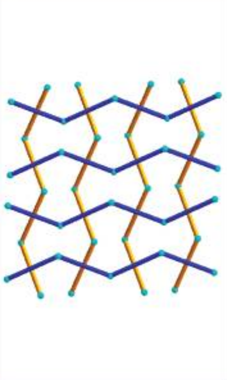
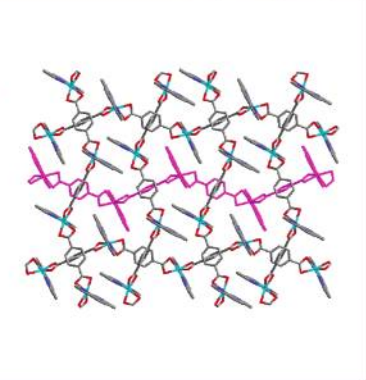
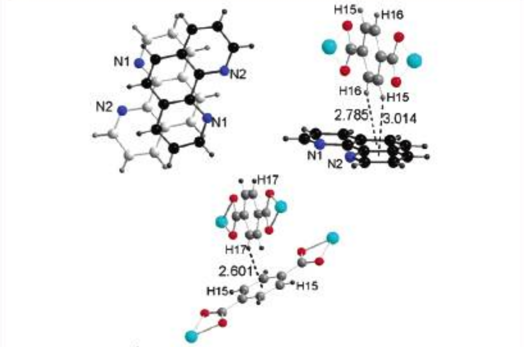
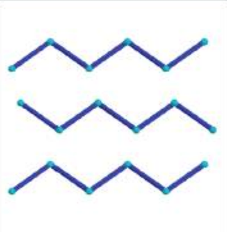
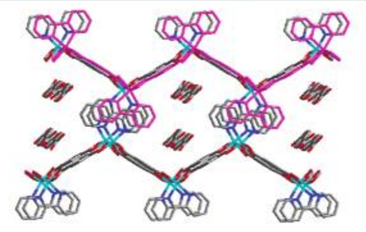
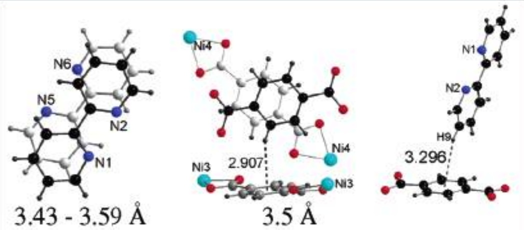
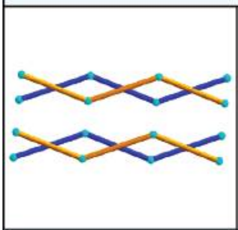
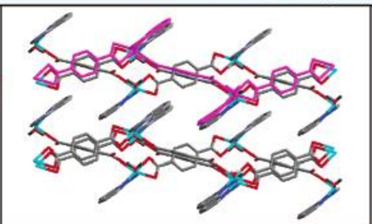
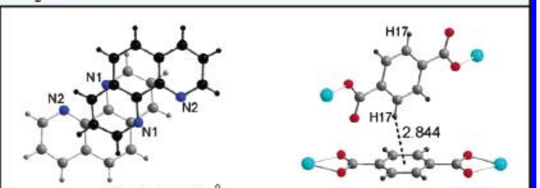
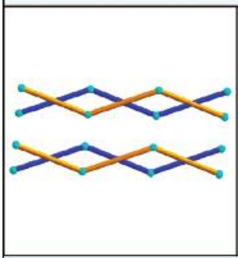
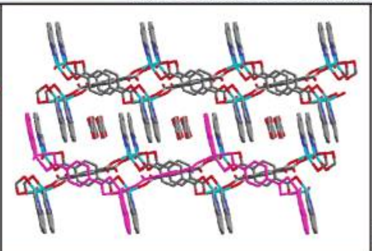
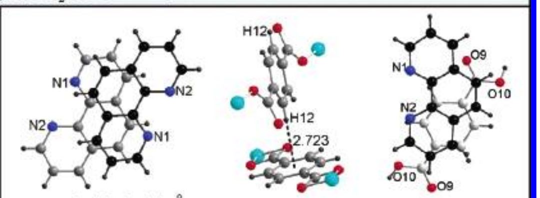
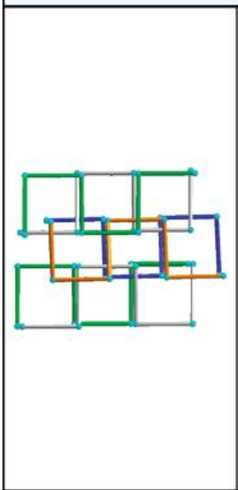
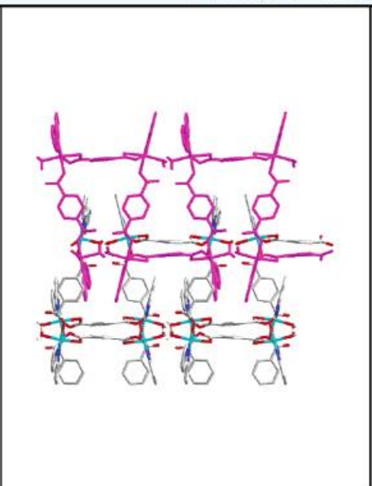
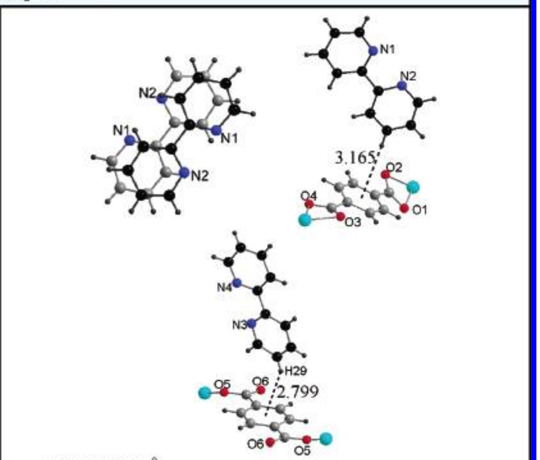
	1-D chain[a]	Reaction conditions
Ni(BDC)(1,10-phen) **1**		1 : 1.5 : 4 : 1[b] 165-210 °C[c] pH 8[d]
Ni(BDC)(2,2'-bipy)·0.75H_2BDC **2**		1 : 1.2 : 1.8 : 1 160 °C pH 5
Ni(BDC)(1,10-phen)(H_2O) **3**		1 : 1.5 : 4 : 1 150-165 °C pH 8.5
Ni(BDC)(1,10-phen)(H_2O)· 0.5H_2BDC **4**		1 : 1.2 : 1.8 : 1 140-200 °C pH 4
Ni(BDC)(2,2'-bipy)(H_2O) **5**		1 : 1.5 : 4 : 1 150-200 °C pH 8.5

[a] Angles shown in the figures correspond to Ni−Ni−Ni angles. [b] Molar ratio of reactants ($NiCl_2$:H_2BDC:KOH:amine). [c] Temperature range for the formation of the compound. Optimized synthesis temperatures are given in the Experimental Section. [d] Final pH.

hindrance within the individual chain, suggesting that the less common crankshaft configuration in **5** is preferred on the basis of optimization of interchain noncovalent interactions and packing considerations.

Chain Packing and Supramolecular Interactions in 1−5. The structures of individual chains in compounds **1** and **2** are essentially the same and differ only in the size of the amine ligand (Table 2). The chain packing in these structures, however, is significantly different (Table 3). In compound **1**, the chains form two types of layers so that the chain axes in adjacent layers are almost perpendicular to each other. Each 1,10-phen ligand is involved in face-to-face $\pi-\pi$ interactions with a 1,10-phen ligand from the closest layer of the same type. The 1,10-phen planes are parallel displaced as typically found in coordination polymers with aromatic nitrogen-containing ligands.[4,5a] In addition, two rings of each 1,10-phen ligand form close contacts with two hydrogens from one of the two crystallographically distinct BDC ligands (BDC-1) that is oriented almost perpendicular (ca. 88°) to the 1,10-phen plane. Since these BDC ligands are located at inversion centers, their other two hydrogens have equivalent CH−π interactions with another 1,10-phen ligand, so that each BDC-1 ligand is sandwiched between two parallel 1,10-phen planes. The rings of the BDC-1 ligands, in turn, have π−CH interactions with hydrogens from two BDC-2 ligands. Each of these BDC-2 ligands interacts with two BDC-1 rings,

Table 3. Chain Packing[a] and Details of Aromatic−Aromatic Interactions ($\pi-\pi$ and CH−π) in Compounds **1**−**5**

Ni(BDC)(1,10-phen) 1		
		 3.34 - 3.37 Å[a]
Ni(BDC)(2,2'-bipy)·0.75H_2BDC 2		
		 3.43 - 3.59 Å 3.5 Å
Ni(BDC)(1,10-phen)(H_2O) 3		
		 3.46-3.49 Å
Ni(BDC)(1,10-phen)(H_2O)·0.5H_2BDC 4		
		 3.42-3.44 Å 3.44 Å
Ni(BDC)(2,2'-bipy)(H_2O) 5		
		 3.33-3.49 Å

[a] Schematic representations of the Ni−BDC backbones and the corresponding full structure views are shown, with purple lines highlighting single chains. [b] Interplanar distances.

leading to the formation of columns of edge-to-face stacked aromatic rings in the direction perpendicular to the chains.

In contrast to **1**, the chains in compound **2** are arranged in layers with the same directions of the chain axes (Table 3). The layers are stacked so that the 2,2′-bipy ligand planes form columns with face-to-face $\pi-\pi$ interactions where each 2,2′-bipy ligand interacts with two 2,2′-bipy ligands from adjacent layer. This stacking leads to the formation of channels where the guest H_2BDC molecules are located. The guest H_2BDC molecules form an extensive network of aromatic−aromatic interactions with the chains: face-to-face $\pi-\pi$ stacking with BDC ligands, CH−π interactions with BDC ligands, and π−CH interactions with 2,2′-bipy ligands. In addition, the H_2BDC molecules are linked to each other through hydrogen bonding to form linear planar chains as found in all polymorphs of pure terephthalic acid.[14] A closely similar packing of M(BDC)(2,2′-bipy) chains is found in Zn(BDC)(2,2′-bipy)·(2,2′-bipy).[7] In contrast to **2**, however, the guest 2,2-bipy planes in this structure are oriented perpendicular to the channel axes.

Compounds **3** and **4**, which are based on almost identical Ni(BDC)(1,10-phen)(H_2O) chains (Table 2) and differ in the presence of guest H_2BDC molecules, have similar chain packing (Table 3) and hydrogen-bonding patterns (Figure 1a,b). The water molecules in both compounds are hydrogen-bonded to two noncoordinating carbonyl oxygen atoms from bis-monodentate BDC ligands: an adjacent ligand from the same chain [Ow−O distance 2.66(1) Å in **3** and 2.65(1) Å in **4**] and that from a neighboring chain [Ow−O distance 2.86(1) Å in **3** and 2.81(1) Å in **4**]. The interchain hydrogen bonding leads to the formation of layers of chains (Table 3). Additional interactions within the layers occur through CH−π contacts between BDC ligands that form edge-to-face stacked columns similar to those found in **1**. The layers interact through $\pi-\pi$ contacts between the 1,10-phen ligands. In compound **3**, the 1,10-phen planes are inclined toward the layers at ca. 65°, leading to a compact packing. In compound **4**, on the other hand, the 1,10-phen planes are almost perpendicular (ca. 99°) to the layers, which increases the interlayer separation and creates space to accommodate the guest H_2BDC molecules. Each H_2BDC molecule has $\pi-\pi$ interactions with two 1,10-phen ligands and is hydrogen-bonded to two other H_2BDC molecules to form chains similar to those in **2**.

In compound **5**, the chains are parallel to each other and form a compact packing with a complex three-dimensional network of aromatic−aromatic interactions (Table 3) and hydrogen bonding (Figure 1c). One of the two crystallographically distinct water molecules (Ow9) is hydrogen-bonded to two noncoordinating carbonyl oxygen atoms from bis-monodentate BDC ligands: an adjacent ligand from the same chain [a strong hydrogen bond with an Ow9−O6 distance of 2.561(2) Å] and that from a neighboring chain [Ow9−O8 distance 2.844(2) Å]. The other water molecule (Ow10) forms hydrogen bonds with a carbonyl oxygen from the same chain [Ow10−O8 distance 2.812(2) Å] and with a water molecule Ow9 from an adjacent chain [Ow10−Ow9 distance 3.057(2) Å]. Each 2,2′-bipy ligand has $\pi-\pi$ interactions with one 2,2′-bipy ligand and CH−π interactions with a BDC ligand. In addition, one of the two crystallographically independent 2,2′-bipy ligands has π−CH interactions with a BDC ligand.

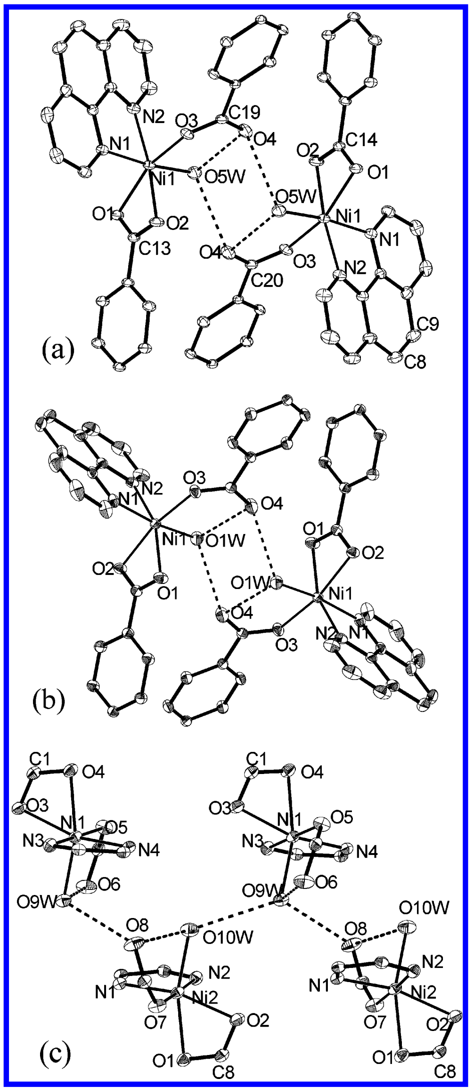


Figure 1. Perspective view of the Ni^{2+} coordination environment including the H-bonds (dotted lines) for **3** (a), **4** (b), and **5** (c). Hydrogen atoms are omitted for clarity, and thermal ellipsoids are at the 30% probability level.

Characterization: (a) Vibrational Spectra. The IR spectra of **1** and **2** show typical chelating carboxylate antisymmetric and symmetric stretching bands at 1536 and 1400 cm^{-1} for **1** and 1533 and 1407 cm^{-1} for **2**, respectively. A strong $\nu(CO_2)$ band at 1695 cm^{-1} in the spectrum of **2** confirms that the BDC guest molecule resides in the channel in a protonated form. In the IR spectra of **3** and **4**, $\nu_{asym}(CO_2)$ and $\nu_{sym}(CO_2)$ stretching vibrations at 1548 and 1404, 1380 cm^{-1} for **3** and 1542 and 1404, 1378 cm^{-1} for **4**, respectively, show that the BDC ligand adopts both monodentate and chelating coordination modes. A strong band at 1692 cm^{-1} in the spectrum of **4** is assigned to the guest H_2BDC molecule. The IR spectrum of **5** shows an unusually complex pattern in the region of the characteristic bands for the

---

(14) (a) Bailey, M.; Brown, C. J. *Acta Crystallogr.* **1967**, *22*, 387. (b) Sledz, M.; Janczak, J.; Kubiak, R. *J. Mol. Struct.* **2001**, *595*, 77.

dicarboxylate unit. The antisymmetric stretching bands around 1550(vs) cm^{-1} appear as a broad septet instead of the more usual single or double strong bands, and the symmetric stretching bands appear at 1411 and 1378 cm^{-1}. The splitting of $\nu_{asym}(CO_2)$ arises from a complex network of hydrogen bonds as shown in Figure 1c. A broad band at 3316m cm^{-1} is assigned to OH stretching vibration from the coordinated water molecule involved in relatively strong hydrogen bonding.

(b) Thermal Analysis. Compound **1**, Ni(BDC)(1,10-phen), is stable up to 350 °C, above which it decomposes to NiO in a single step (observed weight loss 80.43%; calcd 81.46%). Compound **3,** Ni(BDC)(1,10-phen)(H_2O), first loses its coordinated water molecule (onset at 115 °C, completion at 140 °C; obsd 4.12%, calcd 4.29%) to form **1**, as was identified by powder diffraction. Its further decomposition behavior is, therefore, analogous to that of **1** [single-step loss of organic ligands (obsd 79.75%, calcd 77.92%) starting at 350 °C]. In contrast to **3**, compound **5**, Ni(BDC)(2,2′-bipy)(H_2O), dehydrates at a significantly higher temperature (onset at 205 °C, completion at 220 °C; obsd 4.84%, calcd 4.54%). Its subsequent single-step decomposition to NiO begins at 350 °C (obsd 76.23%, calcd 76.74%) and is completed at 400 °C.

The decomposition of compounds containing guest H_2BDC molecules is somewhat unusual. For compound **2**, Ni(BDC)(2,2′-bipy)·0.75H_2BDC, the weight loss corresponding to the removal of the guest H_2BDC is expected to be 24.75%. The observed weight loss in the first decomposition step (onset at 300 °C, completion at 330 °C), however, is significantly larger (34.56%). Consequently, the second weight loss of 50.50% between 350 and 420 °C is lower than the expected value for the removal BDC and 2,2′-bipy ligands (60.42%). The overall weight loss (obsd 85.06%; calcd 85.17%) and the chemical analysis data indicate that the composition of the compound is correct. The discrepancy in the two steps suggests that the loss of the guest H_2BDC molecules is accompanied by a partial decomposition of the framework, in contrast to Zn(BDC)(2,2′-bipy)·(2,2′-bipy),[7] which loses its 2,2′-bipy guests with the framework being intact. For compound **4**, Ni(BDC)(1,10-phen)(H_2O)·0.5H_2BDC, the expected weight losses for the removal of coordinated water and H_2BDC guests are 3.63%, and 15.08%, respectively. The observed first weight-loss step between 210 and 270 °C corresponds to 11.47%, while the loss in second step between 275 and 340 °C is 6.94%. The sum of the two observed values (18.41%), however, is close to the expected 18.71%. The weight loss in the third decomposition step between 340 and 410 °C is consistent with the removal of the organic ligands (obsd 67.42%, calcd 65.12%). Decreasing the heating rate to 0.1 °C/min did not lead to significant changes in the values of weight losses, indicating that the discrepancy between the calculated and observed values for the first two steps is not due to the diffusion effects.

Discussion

Comparative analysis of the structures of a new series of one-dimensional Ni^{2+} coordination polymers indicates that the incorporation of a coordinating water molecule plays a major role in determining the coordination mode of BDC ligands (chelating vs monodentate) and the degree of bending of the chain. Analysis of the relationships between the synthesis conditions and the product composition suggests, however, that the presence of a coordinated water molecule is predominantly determined by the size of the amine ligand (Table 2). Under the range of the synthesis conditions studied, substitution of 1,10-phenanthroline with 2,2′-bipyridine leads to products with different water content, with the exception of compounds **3**, Ni(BDC)(1,10-phen)(H_2O), and **5**, Ni(BDC)(2,2′-bipy)(H_2O), that form from the same reactant ratio ($NiCl_2$:H_2BDC:KOH:amine = 1:1.5:4:1) at temperatures below 160 °C. Even though these two compounds have the same composition, Ni(BDC)(L)(H_2O), the pronounced differences in the corresponding chain structures (stretched zigzag chain in **3** and bent crankshaft chain in **5**) clearly illustrate the influence of the amine ligand size. Considering the ligand steric effects alone, however, one might expect that the substitution of 1,10-phen in **3** with smaller 2,2′-bipy would lead to a similar structure with layered stacking of the chains (Table 3) and smaller interlayer separation, as usually observed when the size of a ligand is varied in the case of layered compounds pillared by aliphatic ligands.[15] Therefore, the substantial structural differences between **3** and **5** can be attributed primarily to the effects of aromatic−aromatic interactions. Moreover, as the synthesis temperature increases above 165 °C, compound **3**, Ni(BDC)(1,10-phen)(H_2O), transforms to the anhydrous phase **1**, while the 2,2′-bipyridine derivative **5**, Ni(BDC)(2,2′-bipy)(H_2O), remains the only product up to 200 °C. The significant difference in the stability of the hydrated products with 2,2′-bipy and 1,10-phen ligands (**3** and **5**) can be also seen in the contrast between their dehydration temperatures (115 and 205 °C, respectively). While one of the reasons for this difference could be a more hydrophobic nature of 1,10-phen ligand compared to that of 2,2′-bipy, it is not a predominant factor, since a reverse combination, a hydrated derivative for 1,10-phen, Ni(BDC)(1,10-phen)(H_2O)·0.5H_2BDC (**4**), and an anhydrous one for 2,2′-bipy, Ni(BDC)(2,2′-bipy)·0.75H_2BDC (**2**), results from a reactant ratio corresponding to a lower pH ($NiCl_2$:H_2BDC:KOH:amine = 1:1.2:1.8:1). The lower pH conditions seem to favor the incorporation of the guest H_2BDC molecules due to the stabilization of their neutral diprotonated state.

Conclusions

Five new one-dimensional coordination polymers with the general formula $Ni(BDC)L(H_2O)_x \cdot yH_2BDC$ ($x = 0, 1$; $y = 0, 0.5, 0.75$; L = 1,10-phenanthroline or 2,2′-bipyridine) have been prepared and characterized, and their structural relationships have been investigated. These polymers are based on

---

(15) Clearfield, A. *Prog. Inorg. Chem.* **1998**, *47*, 371.

topologically identical chains where the nickel centers chelated by amine ligands are linked by BDC bridges. Substitution of 1,10-phenanthroline with 2,2′-bipyridine resulted in significant differences in the composition of the compounds and geometry and packing of the chains, which indicates the predominant structural role of aromatic−aromatic interactions and the steric effects of these ligands. While the energy of each individual $\pi-\pi$ or CH-π interaction is low, their cooperative effects in compounds with polycyclic ligands can become a decisive factor in the choice between alternative structures with energetically close but different patterns of covalent bonding. The high degree of flexibility of the chains (Ni−Ni−Ni angles of ca. 90°, 120°, and 135°), which allows them to adapt to the changes in the amine ligand size, is achieved by the versatility of coordination modes of the BDC bridges: a switch from a chelating to a monodentate coordination mode accompanied by incorporation of a coordinating water molecule provides a means to change the Ni−Ni−Ni angle from 120° to 90° or 135° without a significant perturbation in the geometry of the nickel coordination environment. Another pathway to adjust the M−M−M angles within the chains by modifying the coordination number and/or coordination geometry around the metal center is found in related one-dimensional $M(BDC)L(H_2O)_x$ ($x = 0, 1$; L = 1,10-phenanthroline or 2,2′-bipyridine) compounds with divalent transition metal cations that have less specific coordination preferences than nickel (Co^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}).[6,8]

Acknowledgment. We thank the National Science Foundation (DMR-0120463) and the R. A. Welch Foundation.

Supporting Information Available: X-ray crystallographic data, in CIF format, for the structure determination of **1**−**5**. This material is available free of charge via the Internet at http://pubs.acs.org.

IC049341U