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Self-assembly of a Novel One-dimensional Zigzag Coordination Polymer

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Reaction of anhydrous $NiBr_2$ with pyrazine and disodium terephthalate in the presence of water results in the formation of a one-dimensional (1D) coordination polymer $[Ni(pyrazine)_2(H_2O)_4]\cdot$(terephthalate) 1 which demonstrates a linear zigzag coordination pattern running along the crystallographic *c*-axis. The title compound crystallizes in the monoclinic space group C2/c with $a = 16.833(2)$, $b = 9.173(1)$, $c = 11.107(1)$ Å, $\beta = 119.373(2)^\circ$, and $D_c = 1.667$ for $Z = 4$. Final refinement based upon 4345 observed reflections led to a final *R* value of 0.052 for the polymeric product. The included terephthalate anion participates in eight O—H···O hydrogen bonds to coordinated water molecules.

Keywords: Coordination polymer; Hydrogen bonding; Host-guest chemistry

In recent years, the design of coordination polymers that possess unique molecular structures (*i.e.*, brick [1], ladder [2], and diamondoid [3]) has received a great deal of attention in the area of crystal engineering. These novel frameworks come together in the solid state due to a combination of coordination and hydrogen bonds that can, in principle, give rise to functional solids that have unique and predictable molecular architectures. The ability to control structure at the molecular level provides an additional tool in the design of new materials that may have interesting inclusion properties. Our research group is particularly interested in the formation and inclusion properties of cavity-containing rectangular frameworks [4] based upon two unique bridging ligands.

In this contribution, we report the first example of a zigzag coordination polymer $[Ni(pyrazine)_2(H_2O)_4]\cdot$(terephthalate) 1 (where terephthalate = 1,4-benzenedicarboxylate) based on an aromatic bidentate ligand (*i.e.*, pyrazine), which gives rise to an one-dimensional network. The pyrazines are found *cis* around each nickel center, which allows the network to propagate in a zigzag coordination motif. To our knowledge, there have been no previous examples of an infinite zigzag (*i.e.*, *cis*) coordination polymer based on aromatic spacer units. The only reported examples of a *cis* coordination polymer have been based on bridging halides [5].

In the attempt to form a neutral rectangular grid based upon nickel, 1 was isolated as a *cis* coordination polymer. The unexpected zigzag

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*Corresponding author. Tel.: (573) 882-9606, Fax: (573) 884-9606, e-mail: atwoodj@missouri.edu structure of **1** was achieved by simply replacing the metal center with nickel, instead of the cobalt center found in the rectangular example [4b]. The formation of **1** over the anticipated rectangular analog is still unclear.

A hot, aqueous solution (3 mL) of anhydrous $NiBr_2$ (6.6 mg, 0.03 mmol) was added to a hot, aqueous solution (3 mL) containing both pyrazine (2.4 mg, 0.03 mmol) and disodium terephthalate (6.3 mg, 0.03 mmol) according to Eq. (1).

$$NiBr_2 + N_2C_4H_4 + Na_2(O_4C_8H_4) \rightarrow \mathbf{1} + 2NaBr \qquad (1)$$

Crystals suitable for X-ray diffraction (yield 26.8%, single product) formed upon cooling in three days. Both single-crystal X-ray diffraction [6] and elemental analysis [7] confirmed the formation of **1**. Structure solution was accomplished with the aid of SHELXS-90 [8] and refinement was conducted using SHELXL96 [9]. Upon additional refinements, water hydrogen atoms were located and their isotropic thermal parameters refined.

A view depicting the metal ion coordination around **1** is shown in Figure 1. Each nickel center has two *cis* μ-pyrazine ligands along with four coordinated water molecules that gives rise to a distorted octahedral coordination environment. The network propagates in such a manner that produces a linear zigzag coordination polymer along the crystallographic *c*-axis. The metal–metal distance is 7.0 Å across each pyrazine. The height of the polymeric strand is 4.27 Å, which represents the distance between planes formed by the nickel centers. The closest intermolecular metal–metal distance is 7.41 Å between neighboring polymeric strands.

The lattice contains terephthalate anions that are required for charge balance. Each of the anions forms two unique O—H···O hydrogen bonds to four coordinated water molecules. As shown in Figure 2, two *cis* water molecules form a dual O—H···O hydrogen bond to the same carboxylate group. Both ends of the terephthalate along with all coordinated water molecules participate in this type of noncovalent bonding. These dual hydrogen bonds are the strongest found in the network, since they demonstrate the smallest O···O distance at 2.637 and 2.661 Å for O(1)···O(3) and O(2)···O(4), respectively. The second unique hydrogen bond in **1** are slightly longer in length with a O···O distance of 2.703 and 2.734 Å for O(1)···O(3) and

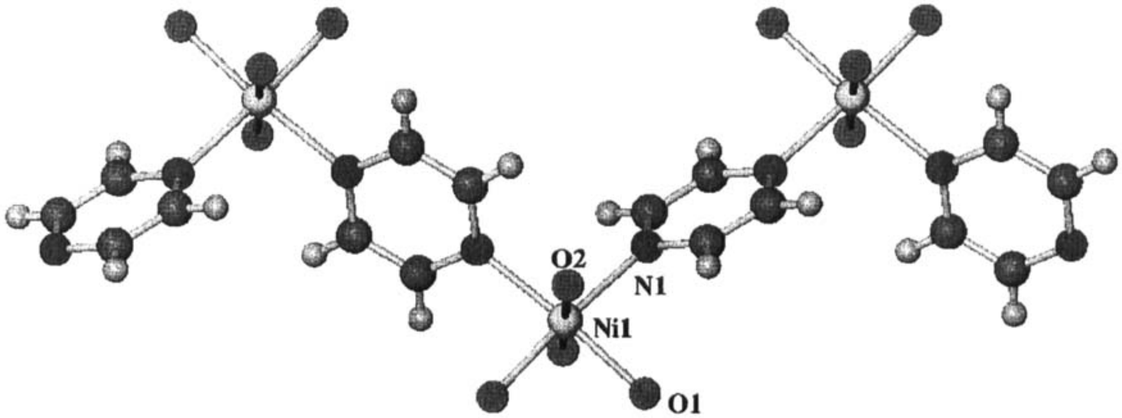

FIGURE 1 The coordination environment around the Ni(II) metal center along the polymeric strand. Selected interatomic distances (Å): Ni(1)–N(1) 2.113(3), Ni(1)–O(1) 2.017(3), Ni(1)–O(2) 2.042(3). All other bond distances are within expected range. The terephthalate anion has been omitted for clarity. (See Color Plate).

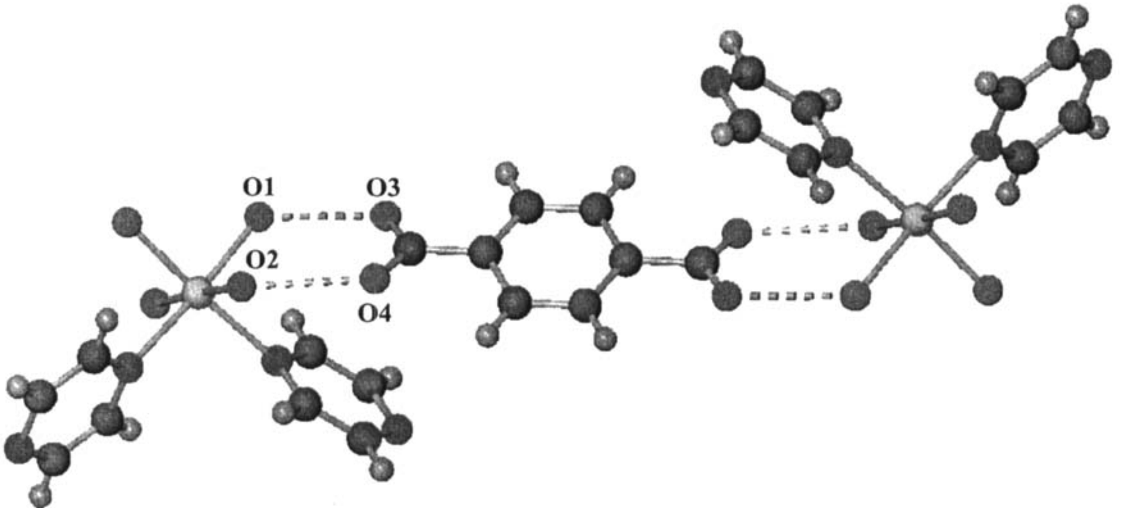

FIGURE 2 A view depicting the dual O—H···O hydrogen bonding between coordinated water molecules and the terephthalate anion. Hydrogen bond distances (Å): O(1)···O(3) 2.637, O(2)···O(4) 2.661. (See Color Plate).

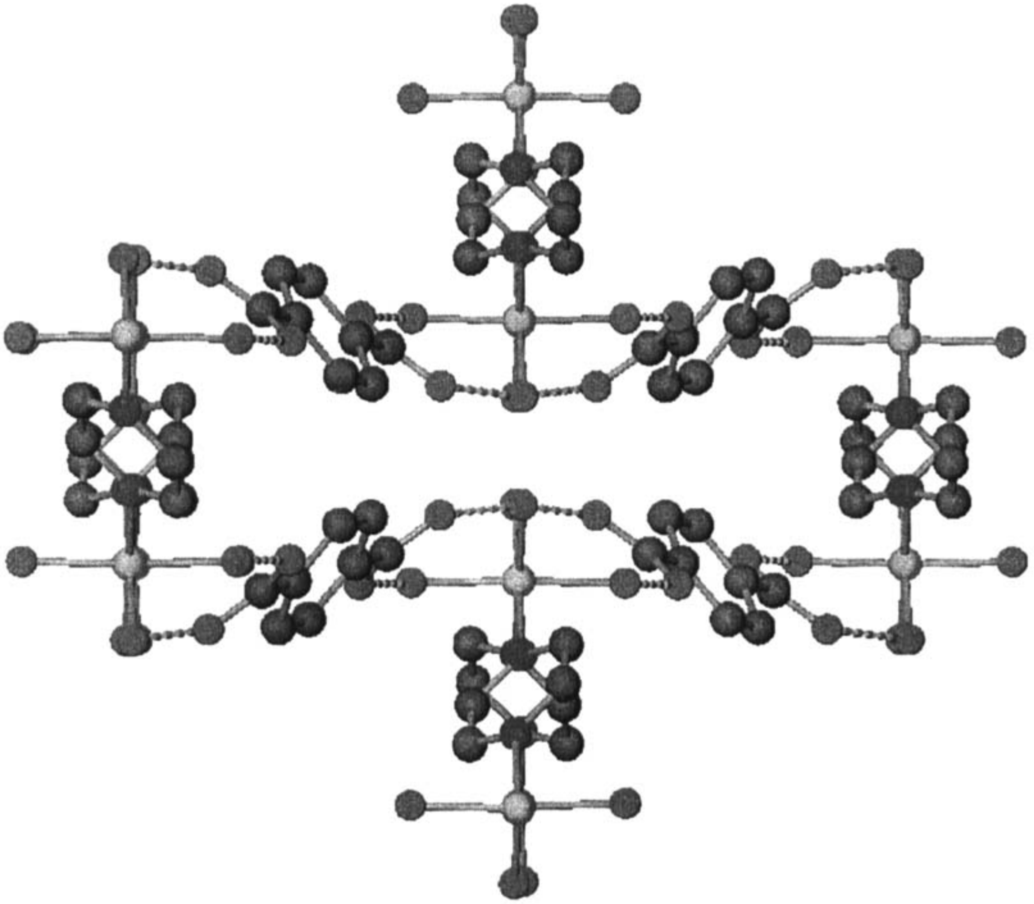

FIGURE 3 The linear nature of the polymeric strand viewed along the crystallographic *c*-axis. Shown are the terephthalate anions that facilitate noncovalent interactions in the form of both edge-to-face π-π interactions and O—H···O hydrogen bonds to the polymeric strands. (See Color Plate).

O(2) ⋯ O(4), respectively. The increased O ⋯ O length is observed, since only one hydrogen bond is formed to the included anion per strand. All hydrogen bonds observed in **1** are between coordinated water molecules to the terephthalate anion. As a result, there is no direct hydrogen bonding between water molecules. Each terephthalate accepts eight hydrogen bonds from six different polymeric strands, which is the exact number of hydrogen bonds formed by four water molecules.

In addition to O—H ⋯ O hydrogen bonds, there are edge-to-face π-π interactions between the bridging pyrazine and lattice terephthalate. To facilitate this interaction, the anion along with the pyrazine stacks appropriately in the solid state. Figure 3 demonstrates the edge-to-face π-π stacking and hydrogen bonding found between the polymeric strands to the included anion. The centroid ⋯ centroid distance between aromatic rings is 4.793 Å, which is well within the expected range [10]. The terephthalate π-π stacks with two distinct polymeric strands on each side of the arene ring. These noncovalent interactions help to give rise to this unique molecular architecture, since the system is based upon complementary components to form the extended network.

The results reported herein illustrate the synthesis and characterization of the first *cis*-coordination polymer based upon rigid aromatic bridging ligands. The network observed in **1** demonstrates a linear polymer that forms a zigzag coordination pattern running along the crystallographic *c*-axis. Along the polymeric backbone are a large number of hydrogen bond donors, which gives rise to interesting inclusion chemistry with the included terephthalate. Future work will be in the area of studying the inclusion chemistry of this system by the addition of other appropriate hydrogen bond acceptors to determine host/guest interactions. In addition, the formation of related polymers incorporating other transition metal-based assemblies will be investigated with the results to be reported in due course.

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[6] Crystal data for **1**: monoclinic, space group C2/c, $a=16.833(2)$, $b=9.173(1)$, $c=11.107(1)$, $\beta=119.373(2)$, $U=1715.0(3)$ Å^3, $D_c=1.55\,\mathrm{g/cm^3}$, Mo K$\alpha$ radiation ($\lambda=0.71070$ Å) for $Z=4$. Least-squares refinement based on 1646 reflections with $I_{\mathrm{net}}>2.0\sigma(I_{\mathrm{net}})$ (out of 4345 unique reflections) led to a final value of $R=0.052$. Aromatic hydrogen atoms were placed in their calculated positions with isotropic thermal parameters constrained to 1.2 times that of their parent atom. Intensity data were collected with the use of the Siemens SMART system at 173 K.

[7] Elemental Analysis for **1** [Ni(pyrazine)$_2$(H$_2$O)$_4$](terephthalate): Calculated C, 38.43; H, 4.31; N, 7.47. Found C, 38.27; H, 4.54; N, 6.99.

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