

Quasi Self-Inclusion of a 1D Coordination Polymer within a 2D Hydrogen-Bonded Grid: A Chaperone Effect

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Keywords

coordination polymer; self-inclusion; hydrogen bonding; interpenetration; rhombohedral grid

Abstract

The one-dimensional (1D) coordination polymer $[\text{Ni}(\text{bdc})(\text{pico})_2(\text{H}_2\text{O})_2]$ (where: bdc = terephthalate, pico = 4-picoline) is hosted within a two-dimensional (2D) hydrogen-bonded grid $[\text{Ni}(\text{bdc})(\text{pico})_2(\text{H}_2\text{O})_2] \cdot (\text{pyz})$ (where pyz = pyrazine). Both coordination polymers are comprised of the same components and differ only by their hydrogen bonding patterns. The polymers of the 2D grids engage in O–H \cdots N hydrogen bonds to the included pyz. The grid **contains** rhombohedral cavities that **lie** along the crystallographic **ac-plane**. The grids self-assemble by C–H \cdots π interactions involving the

methyl group of pico and the aromatic ring of the bdc anion. The included polymer interacts with the 2D grids *via* O–H \cdots O hydrogen bonds involving coordinated water and the bdc anion.

1. Introduction

Coordination polymers continue to receive a great deal of attention in recent years for potential uses in catalysis, nonlinear optics, separation science, and molecular recognition, since their overall structure can be controlled at the molecular level.¹ The formation of these multi-dimensional frameworks is usually based upon coordination-driven self-assembly of metal-ions with rigid ditopic aromatic building blocks. These frameworks can exhibit the presence of cavities and pores that are modifiable not only in shape (*e.g.* square grid, octahedral, ladder, and diamondoid) but overall dimensionality.² Coordination polymers are also known to exhibit remarkable host-guest properties.³ In order to provide more space for guest encapsulation, counter-ions have been removed from the structure by utilizing ligands with charged functionalities (*e.g.* carboxylate groups) to coordinate and bridge the metal-ions. In addition to charge-balance purposes, the carboxylate groups can also be utilized as hydrogen bond acceptors to yield extended structures. Besides hosting neutral and charged species in cavities and pores, coordination polymers can also interpenetrate themselves to fill the voids embedded in the structures.⁴

The structure and inclusion chemistry of various coordination polymers based upon bridging anions has been a focus of us for some time. The research reported here is a continuation of the work that involved the formation of both an one-dimensional (1D) and two-dimensional (2D) coordination polymers based upon the terephthalate anion.⁵ Previously, we described the formation of a neutral coordination polymer [M(bdc)(pico)₂(H₂O)₂] \cdot 2(pico) (where M = Co(II) and Ni(II), bdc = terephthalate, pico = 4-picoline) that exhibited an ability to include an aromatic guest.^{5a} The guest inclusion was achieved by employing O–H \cdots N hydrogen bonds between coordinated water molecules and an included pico molecule.

Here, we report an unusual example of self-inclusion⁶ involving a coordination polymer.

$[\text{Ni}(\text{bdc})(\text{pico})_2(\text{H}_2\text{O})_2]$ is an example of a 1D coordination polymer with hydrogen-bond donors along the backbone that is capable to form an extended network due to these donor sites. In an attempt to construct a 2D coordination polymer by linking the 1D polymers of $[\text{Ni}(\text{bdc})(\text{pico})_2(\text{H}_2\text{O})_2]$ using the linear bridge pyrazine (pyz), the 1D chain co-crystallized with pyz to form the hydrogen-bonded 2D grid structure $[\text{Ni}(\text{bdc})(\text{pico})_2(\text{H}_2\text{O})_2] \cdot (\text{pyz})$. Remarkably, the 2D grid generates rhomboidal cavities that host independent 1D polymers of $[\text{Ni}(\text{bdc})(\text{pico})_2(\text{H}_2\text{O})_2]$ that thread through the grids. The coordination polymers that constitute the guest and the host are identical in composition, which makes the solid represent a form of self-inclusion that we term quasi self-inclusion. The pyz that co-crystallizes with the 1D polymer, in effect, acts as a supramolecular chaperone of the 1D polymer to facilitate the formation of the hydrogen-bonded rhombohedral grids.

2. Experimental

2.1 Materials

Anhydrous nickel(II) bromide, pyz, and pico were all purchased from Sigma-Aldrich Chemical and used as received. Sodium bdc was purchased from TCI American-Tokyo Chemical Industry via Fisher Scientific and required no purification.

2.2 Synthesis of $\{[\text{Ni}(\text{bdc})(\text{pico})_2(\text{H}_2\text{O})_2] \cdot (\text{pyz})\} \subset [\text{Ni}(\text{bdc})(\text{pico})_2(\text{H}_2\text{O})_2]$

An aqueous solution (5 mL) of anhydrous NiBr_2 (54.6 mg, 0.25 mmol) was combined with a solution (5 mL) of sodium bdc (52.4 mg, 0.25 mmol) and pyz (20.1 mg, 0.25 mmol) in water. After the addition of the solutions, one mL of pico was added to the test tube which dissolved a small amount of a precipitate that formed. Within one-week blue crystals of $\{[\text{Ni}(\text{bdc})(\text{pico})_2(\text{H}_2\text{O})_2] \cdot (\text{pyz})\} \subset [\text{Ni}(\text{bdc})(\text{pico})_2(\text{H}_2\text{O})_2]$ suitable for single crystal X-ray diffraction formed.

2.3 Single-crystal X-ray diffraction

A suitable single crystal was selected and mounted on a glass fiber and centered in the X-ray beam on the diffractometer. X-ray diffraction data was collected on a Siemens SMART system using MoK α radiation at a temperature of 173 K. A semi-empirical correction for the adsorption was applied using SADABS. The SHELXS and SHELXL were used for the solution and refinement of the crystal structure, respectively. A free variable refinement was used to determine the relative occupancies of the disordered pico molecule on the guest polymer. All non-hydrogen atoms were refined anisotropically and hydrogen atoms bound to carbon atoms were located in the difference Fourier map and were geometrically constrained using the appropriate AFIX commands. Selected X-ray diffraction and refinement data is found in Table 1.

Insert Table 1

Results and Discussion

Single crystal analysis revealed that $\{[\text{Ni}(\text{bdc})(\text{pico})_2(\text{H}_2\text{O})_2] \cdot (\text{pyz})\} \subset [\text{Ni}(\text{bdc})(\text{pico})_2(\text{H}_2\text{O})_2]$ crystallizes in the centrosymmetric monoclinic space group $C2/c$. The asymmetric unit contains two crystallographically unique 1D coordination polymers where in each case the Ni(II) atoms sit on an inversion center along with an included disordered pyz molecule (occupancies: 0.50:0.50). The bdc anion bridges the Ni(II) centers to form an infinite 1D polymeric structure (Figure 1a). These Ni(II) metal centers are coordinated to two *trans* μ -bdc anions, two *trans* water molecules, and two *trans* pico molecules being disordered over four equivalent sites (occupancies: 0.25:0.25:0.25:0.25) that give rise to a distorted octahedral coordination, which results in a charge neutral 1D polymer. Every coordinated water molecule interacts with the uncoordinated oxygen of the bdc anion via an O–H \cdots O hydrogen bonds [O \cdots O 2.678(7) and 2.605(7) Å]. Unlike the previous reported polymer based upon pico,^{5a} the presence of pyz in $[\text{Ni}(\text{bdc})(\text{pico})_2(\text{H}_2\text{O})_2] \cdot (\text{pyz})$ allows for the formation of a 2D grid owing to the hydrogen-bond accepting role with the coordinated water molecule [O \cdots N 2.87(2) and 2.94(2) Å]. As a consequence of the interaction, the 2D grid contains rhombohedral cavities with dimensions of 11.4 \times 11.9 Å along with corner angles of 101.5° and 78.5° that were calculated using the Ni(II) centers (Figure

1b). The hydrogen bonding results in the grid adopting a wave-like topology that runs along the crystallographic *c*-axis (Figure 1c).

Insert Figure 1

The 2D sheets are stacked and sustained by C–H $\cdots\pi$ interactions (3.4 Å) between the methyl groups of the coordinated pico molecule and the aromatic ring of the bridging bdc units of neighboring sheets (Figure 2a). The 3D structure of $\{[\text{Ni}(\text{bdc})(\text{pico})_2(\text{H}_2\text{O})_2]\cdot(\text{pyz})\}\subset[\text{Ni}(\text{bdc})(\text{pico})_2(\text{H}_2\text{O})_2]$ exhibits two sets of channels. Specifically, the first set propagates along the crystallographic *a*-axis (Figure 2b), whereas the second propagates through the structure parallel to the (110) and (001) crystallographic planes (Figure 2c).

Insert Figure 2

These channels of $[\text{Ni}(\text{bdc})(\text{pico})_2(\text{H}_2\text{O})_2]\cdot(\text{pyz})$ are occupied by a second crystallographically unique 1D coordination polymer $[\text{Ni}(\text{bdc})(\text{pico})_2(\text{H}_2\text{O})_2]$ as a guest. The guest is, therefore, identical in composition to the coordination polymer that makes up the hydrogen-bonded grid. Again, the Ni(II) centers exhibit a distorted octahedral coordination environment based on two *trans* μ -bdc anions, two *trans* water molecules, and two *trans* pico molecules. The coordinated pico ligand on the guest polymer is disordered over two positions (occupancies: 0.54:0.46). The difference in the two crystallographically unique 1D coordination polymers is related to the hydrogen-bonding pattern. The coordinated water molecule of the guest, in addition to forming an O–H \cdots O hydrogen bond to the uncoordinated oxygen atom of the bdc anion, interacts with the host via an O–H \cdots O hydrogen bonds [O \cdots N 2.78(1) Å] again to the uncoordinated oxygen atom of the bdc anion (Figure 3a). The guest 1D polymers within a hydrogen-bonded grid run parallel (Figure 3b). In contrast, the guests between nearest-neighboring grids are related by a two-fold rotation axis and run opposite (Figure 3c). Given that the 1D coordination polymer guest is identical to the 1D coordination polymer that makes up the host, we suggest the overall structure of $\{[\text{Ni}(\text{bdc})(\text{pico})_2(\text{H}_2\text{O})_2]\cdot(\text{pyz})\}\subset[\text{Ni}(\text{bdc})(\text{pico})_2(\text{H}_2\text{O})_2]$ to be regarded and termed as quasi self-inclusion. A common element of the self-inclusion in our study is the 1D coordination polymer.

An additional component, namely pyz, facilitates the formation of the host framework. Both the host and guest are compositionally identical, with the 1D polymers also being structurally identical. In facilitating the formation of the host, the additional component effectively serves as a ‘chaperone’. Thus, the pyz molecule is not only an edge of the hydrogen-bonded grid but acts as the chaperone within $[\text{Ni}(\text{bdc})(\text{pico})_2(\text{H}_2\text{O})_2] \cdot (\text{pyz})$ to allow self-inclusion to occur.

Insert Figure 3

Conclusion

We report here an example of a quasi self-inclusion involving a **rhombohedral** 2D hydrogen-bonded grid that is composed of a 1D coordination polymer. Cavities of the grid act to host a 1D coordination polymer identical in composition that makes up the grid. The host and guest coordination polymers only differ in their observed hydrogen bonding pattern. The ability to form extended solids based upon both coordinated and hydrogen bonds gives chemists and material scientists additional means of control over the geometry directly around the metal as well as throughout the structure. Currently, we are investigating networks that contain larger cavities and exploring their inclusion chemistry.

Disclosure Statement

No potential conflict of interest was reported by the authors.

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Table 1. X-ray diffraction and refinement data for $\{[\text{Ni}(\text{bdc})(\text{pico})_2(\text{H}_2\text{O})_2] \cdot (\text{pyz})\} \subset [\text{Ni}(\text{bdc})(\text{pico})_2(\text{H}_2\text{O})_2]$.

chemical formula	$\text{C}_{22}\text{H}_{24}\text{N}_3\text{NiO}_6$
molar mass / g mol^{-1}	485.15
crystal system	monoclinic
space group	$C2/c$
$a / \text{\AA}$	11.4158(9)
$b / \text{\AA}$	19.7456(15)
$c / \text{\AA}$	21.5427(18)
$\alpha / ^\circ$	90
$\beta / ^\circ$	102.692(2)
$\gamma / ^\circ$	90
$V / \text{\AA}^3$	4737.3(7)
Z	8
density / g cm^{-3}	1.360
$F(000)$	2024
$\mu(\text{CuK}\alpha) / \text{mm}^{-1}$	0.860
T / K	173(2)
index range	$-13 \rightarrow 13$ $-15 \rightarrow 23$ $-25 \rightarrow 23$
collected reflections	11480
unique reflections	4136
R_{int}	0.1265
reflections with $I > 2\sigma(I)$	2190
no. parameters	349
$R(F), F > 2\sigma(F)$	0.0961
$wR(F^2), F > 2\sigma(F)$	0.2262
$R(F)$, all data	0.1751
$wR(F^2)$, all data	0.2579
Δ_r (min., max.) e \AA^{-3}	-0.766, 1.208
CCDC deposition number	2039248

Figure Captions

Figure 1. X-ray crystal structures of $\{[\text{Ni}(\text{bdc})(\text{pico})_2(\text{H}_2\text{O})_2] \cdot (\text{pyz})\} \subset [\text{Ni}(\text{bdc})(\text{pico})_2(\text{H}_2\text{O})_2]$: (a) 1D coordination polymer of the host framework viewed along the crystallographic *a*-axes, (b) 2D rhombohedral grids containing pyz viewed along crystallographic *ac*-plane, and (c) wave-like pattern of the 2D grid viewed along the crystallographic *c*-axes. Hydrogen bonds are shown with yellow dashes. Hydrogen atoms and occupancy sites of the disordered pico and pyz molecules were omitted for clarity.

Figure 2. X-ray crystal structures of $\{[\text{Ni}(\text{bdc})(\text{pico})_2(\text{H}_2\text{O})_2] \cdot (\text{pyz})\} \subset [\text{Ni}(\text{bdc})(\text{pico})_2(\text{H}_2\text{O})_2]$ depicting the stacking of the grids sustained by C–H $\cdots\pi$ interactions and hydrogen bonds along: (a) crystallographic *c*-axis, (b) crystallographic *a*-axis, (c) (110) and (001) crystallographic planes. C–H $\cdots\pi$ interactions are shown with yellow dashes. Hydrogen atoms and occupancy sites of the disordered pico and pyz molecules were omitted for clarity.

Figure 3. X-ray crystal structures of $\{[\text{Ni}(\text{bdc})(\text{pico})_2(\text{H}_2\text{O})_2] \cdot (\text{pyz})\} \subset [\text{Ni}(\text{bdc})(\text{pico})_2(\text{H}_2\text{O})_2]$ depicting the different hydrogen-bonding between the 2D grid (green) and guest 1D coordination polymer (yellow): (a) a 2D rhombohedral grid, (b) parallel orientation of the guest 1D polymer within a grid, (c) opposite orientation of the 1D guest polymer between neighboring 2D grids. Hydrogen bonds are shown with yellow dashes. Hydrogen atoms and occupancy sites of the disordered pico and pyz molecules were omitted for clarity.