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Controlling Aromatic Inclusion Within Nonaqueous Copper Iodide Coordination Polymers

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The formation and characterization of two novel coordination polymers based upon copper iodide and pyrazine have been observed that demonstrate varying aromatic inclusion. By changing the solvent from 1,2-dichlorobenzene to nitrobenzene, the ability to include the solvent as a guest molecule within the two-dimensional coordination polymer has been realized. In the nitrobenzene example, unlike the 1,2-dichlorobenzene example, honeycomb shaped cavities form along the polymeric chain that allows aromatic inclusion.

Keywords: coordination polymer, host-guest chemistry, and solvent templation

The synthesis of coordination polymers that have the ability to entrap aromatic guests has been investigated in recent years for their potential use in the area of separation science. Examples of aromatic inclusion can be found within both one-¹ and two-dimensional² polymeric frameworks. In one-dimensional coordination polymers, aromatic inclusion occurs via noncovalent interactions in the form of hydrogen bonds. In these examples the polymeric framework has hydrogen bond donors in the form of coordinated water molecules running along the polymeric chain. The included guest molecule is a nitrogen-based heterocycle that is able to accept a hydrogen bond. However, in the two-dimensional polymers, arene-arene interactions allow for the inclusion of aromatic guest molecules. To

afford desirable inclusion properties, it is advantageous for the framework to be electrostatically neutral to eliminate the need for counterions. Neutral networks can be achieved by using the anion to bridge the various metal centers within the structure.

In this contribution, we report the synthesis and characterization of two novel coordination polymers based upon copper iodide and pyrazine. Recently, there has been work in the area of copper halide chemistry to form infinite networks based upon organic bridging ligands.³ However, this work has provided no examples that have cavities large enough to entrap aromatic guests. We have now isolated the first example of aromatic inclusion within a copper iodide coordination polymer, where the included guest is nitrobenzene.

The formation of [CuI(pyrazine)]-nitrobenzene **1** and of [Cu₂I₂(pyrazine)] **2** was accomplished in one step via self-assembly. For **1**, CuI (19.0 mg, 0.10 mmol) was dissolved in 3 mL of acetonitrile, and then the container was placed in a larger vessel containing pyrazine (40.6 mg, 0.50 mmol) dissolved in 3 mL of nitrobenzene. The formation of **2** was achieved in a fashion similar to that used for **1**, except 1,2-dichlorobenzene was substituted for nitrobenzene. The formation of the final product results when vapors of the solvent

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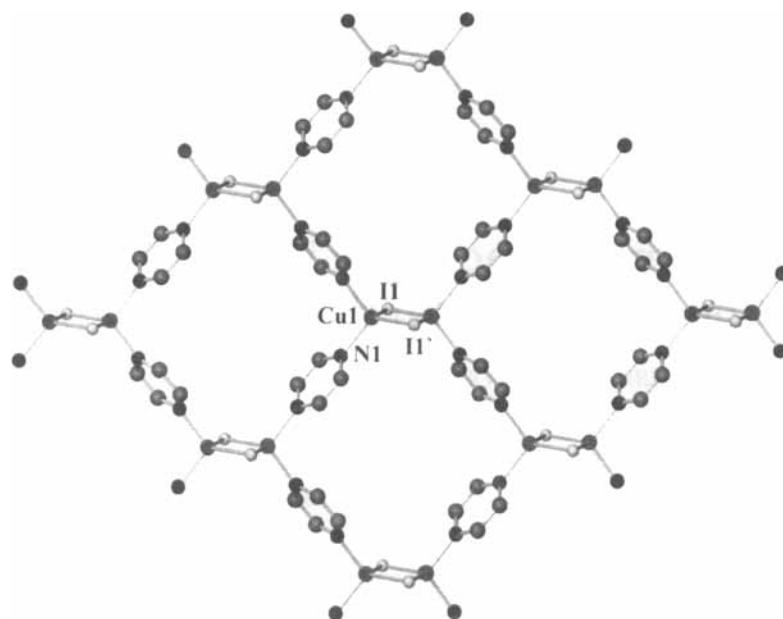


FIGURE 1 The coordination environment of the Cu(I) metal centers observed in **1**. Selected interatomic distances (Å): Cu(1)-I(1) 2.613(2), Cu(1)-I(1') 2.642(2), Cu(1)-N(1) 2.057(7). All other bond distances are within expected values. The nitrobenzene has been removed for clarity (See Color Plate I at the back of this issue)

and dissolved pyrazine diffuse into the inner vial that contains copper iodide. The vapor diffusion technique must be utilized, since the polymeric product is very insoluble, and no single crystals could be grown from direct addition of the components. Crystals for both **1** (yield, 24.4%, single product) and **2** (yield, 52.5%, single product) formed overnight, and were characterized using both X-ray diffraction⁴ and elemental analysis.⁵

A view depicting the metal ion coordination of **1** is shown in Figure 1. The copper metal center in **1** has two μ -iodide anions along with two bidentate μ -pyrazine ligands that form a slightly distorted tetrahedral coordination environment. As a result of this coordination pattern, honeycomb-like pores were found in the X-ray structure that has disordered nitrobenzene in the cavities. Figure 2 depicts a space-filling model of the framework with the included nitrobenzene. The nitrobenzene guest molecule interacts with

the polymeric framework through weak π - π interactions with the bridging pyrazine. The arene-arene distance was measured (centroid...centroid) to be 4.39 Å.⁶ The nitrobenzene molecule is disordered over two positions and was modeled in all X-ray calculations. Two unique metal-metal distances are found within **1**: 2.62 and 6.91 Å across the bridging iodide and across the bridging pyrazine, respectively. The interactions between the framework and the included nitrobenzene are weak and, therefore, the nitrobenzene is disordered within the structure.

The coordination around the copper metal center in **2** is depicted in Figure 3. Similar to **1**, **2** has a distorted tetrahedral coordination environment, but it is based on three triply bridged μ_3 -iodides with the last coordination site filled by a bridging μ -pyrazine. Due to this coordination pattern, no cavity was formed within the framework and aromatic inclusion can not be

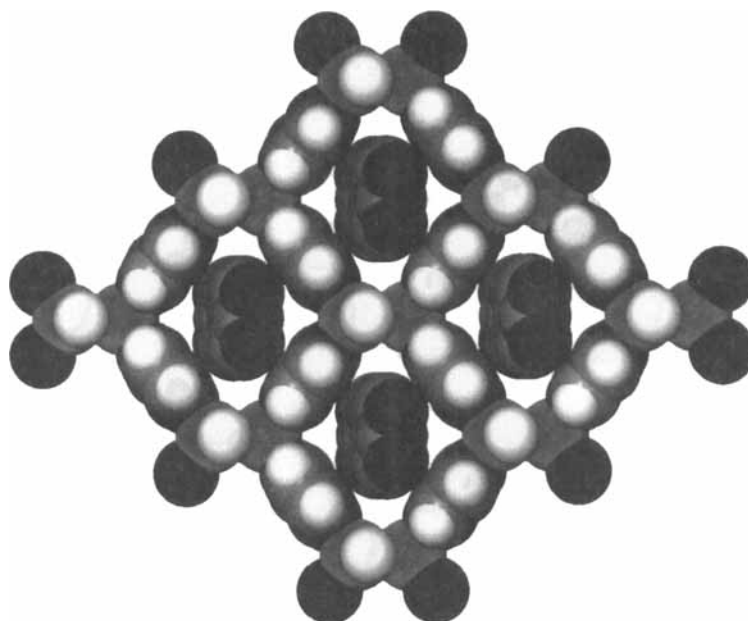


FIGURE 2 A space-filling model of **1**. Shown is how the include nitrobenzene interacts with the polymeric framework in the form of weak π - π interactions with the bridging pyrazine (See Color Plate II at the back of this issue)

achieved. Three unique metal-metal distances are found within **2**: 2.77, 2.79, and 6.92 Å, where the first two values are based upon the bridging iodides and the latter is from the bridging pyrazine. An infinite chain of copper iodide runs along the crystallographic *a*-axis, whereas a second dimension is produced by the bridging pyrazine. A framework similar to that found in **2** was reported by Li and coworkers who incorporated 4,4'-bipyridine, instead of pyrazine, to propagate the polymer.⁷ The copper iodide in **2** follows a similar bonding pattern, in which it forms a ladder-shaped coordination environment that is based upon triply-bridged anions.

The ability of the polymeric framework to include aromatic guests is based on the nature of the solvent. The only difference between **1** and **2** is the diffusion solvent used in the synthesis. Therefore, the formation of the two final polymeric products are based upon solvent effects. The two solvents are polar, but they have differ-

ent values for their van der Waals volume.⁸ The calculated volume of nitrobenzene is 64 cm³/mole and for 1,2-dichlorobenzene the volume is 72 cm³/mole. The increased volume of the 1,2-dichlorobenzene, along with it being a disubstituted aromatic, could explain the observed inclusion behavior.

These two coordination polymers demonstrate the importance of solvent templation in the formation of coordination polymers. In both examples, the solvent plays an important role in the formation of the final product, but only in **1** does the solvent appear within the crystal structure. Currently, we are investigating systems based upon *ortho*-, *meta*-, and *para*-xylenes to determine which, if any, can be included within copper iodide coordination polymers. In addition, we are studying size and substitution effects on the benzene ring to determine how that influences inclusion. The results of these studies will be reported in due course.

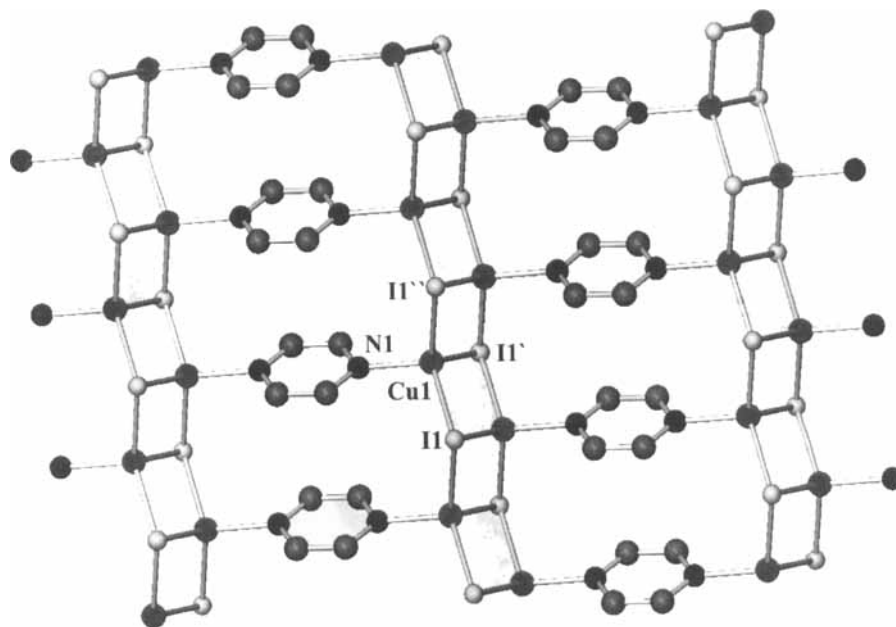


FIGURE 3 The coordination environment of the Cu(I) metal centers observed in **2**. Selected interatomic distances (Å): Cu(1)-I(1) 2.640(2), Cu(1)-I(1') 2.642(2), Cu(1)-I(1'') 2.660(2), Cu(1)-N(1) 2.057(7). All other bond distances are within expected values (See Color Plate III at the back of this issue)

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- Crystal data for **1**: Monoclinic, space group C2/m, $a = 13.492(4)$, $b = 10.779(4)$, $c = 8.091(3)$, $\beta = 125.172(5)^\circ$, $U = 961.9(5) \text{ \AA}^3$, $D_c = 2.718 \text{ g/cm}^3$, Mo-K α radiation ($\lambda = .71070 \text{ \AA}$) for $Z = 4$. Least-squares refinement based on 1124 reflections with $I_{\text{net}} > 2\sigma(I_{\text{net}})$ (out of 3023 unique reflections) gave a final value of $R = 0.070$. Crystal data for **2**: Triclinic, space group P-1, $a = 4.166(4)$, $b = 7.116(2)$, $c = 8.102(3)$, $\alpha = 109.513(5)^\circ$, $\beta = 125.172(5)^\circ$, $\gamma = 96.989$, $U = 217.3(2) \text{ \AA}^3$, $D_c = 3.522 \text{ g/cm}^3$, Mo-K α radiation ($\lambda = .71070 \text{ \AA}$) for $Z = 2$. Least-squares refinement based on 927 reflections with $I_{\text{net}} > 2\sigma(I_{\text{net}})$ (out of 1327 unique reflections) gave a final value of $R = 0.068$. Intensity data was collected with the use of the Siemens SMART system at 173 K. In spite of low temperature data collection the included nitrobenzene in **1** is disordered over two positions.
- Elemental Analysis for **1** [CuI(pyrazine)]-nitrobenzene: C, 28.48; H, 2.06; N, 11.36. Found: C, 30.51; H, 2.29; N, 10.67. Elemental Analysis for **2** [Cu₂I₂(pyrazine)]: C, 11.25; H, 0.80; N, 6.09. Found: C, 10.42; H, 0.87; N, 6.07.
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