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A Simultaneous Reduction, Substitution, and Self-Assembly Reaction under Hydrothermal Conditions Afforded the First Diiodopyridine Copper(I) Coordination Polymer

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A simultaneous reduction of copper(II) to copper(I) by pyridinecarboxylate and the substitution of carboxylato groups by iodo nucleophiles in a self-assembly process under hydrothermal conditions afforded a new iodine-inclusion coordination polymer $[CuI(C_5H_3NI_2)\cdot{}^1/_2I_2]$ **1**. The synthetic studies of the substitution process produced a new supramolecular compound $[IC_5H_3NCOOH]$ **2** and revealed that the catalytic properties of copper ions in redox and substitution reactions under hydrothermal conditions are attractive. Crystal data for $[CuI(C_5H_3NI_2)\cdot{}^1/_2I_2]$: triclinic, space group $P\bar{1}$; cell dimensions $a = 4.216(1)$ Å, $b = 11.254(2)$ Å, $c = 12.196(2)$ Å, $\alpha = 80.34(3)°$, $\beta = 88.44(3)°$, $\gamma = 83.10(3)$; $V = 566.2(2)$ Å^3, $Z = 2$. Crystal data for $[IC_5H_3NCOOH]$: monoclinic, space group $P2_1/c$; cell dimensions $a = 5.041(1)$ Å, $b = 17.313(2)$ Å, $c = 8.639(1)$ Å, $\beta = 95.042(2)°$; $V = 751.02(13)$ Å^3, $Z = 4$.

The design and synthesis of framework coordination polymers has attracted great attention in recent years.[1−5] The synthetic strategies used for preparing coordination polymeric structures are mostly conventional solution methodology in organic solvents or hydrothermal/solvothermal reactions under pressure. In most cases, reduction and oxidation reaction mechanisms were not invoked during the self-assembly of framework polymers. It is well accepted that Cu(II) ions can be reduced to Cu(I) by 4,4′-bipyridine or pyridine derivatives under hydrothermal conditions.[6] Oftentimes fascinating structures and reactions can be achieved from the reduction of copper valence states.[6,7] Hydrothermal processes are therefore considered necessary for these reductions. While both unpredictable structures and rational designs under hydrothermal conditions can be achieved (such as those demonstrated recently),[6,8] construction of coordination polymers via simultaneous substitution and reduction in a self-assembly process has never been observed. Here we present such a result, the first novel copper(I) diiodopyridine coordination polymer, $[CuI(C_5H_3NI_2)\cdot{}^1/_2I_2]$ **1**, produced via a simultaneous reduction of copper(II) to copper(I), and substitution of carboxylato groups by iodo nucleophiles in a self-assembly chemical process under hydrothermal conditions.

The reaction of $Cu(NO_3)_2\cdot 2.5H_2O$ with 3,5-pyridinedicarboxylic acid and iodine in a molar ratio of 1:1:1 under hydrothermal conditions at 140 °C for 3 days produced red crystals of **1** with 56% yield. The red plate crystals are characterized by elemental and single-crystal X-ray diffraction analysis.[9a] The structure of **1** consists of four distinct iodine atoms and one copper(I) atom. The copper atom displays a distorted tetrahedral (the angles vary from

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(9) (a) Crystal data for **1**: fw, 648.22; triclinic, space group $P\bar{1}$; cell dimensions $a = 4.216(1)$ Å, $b = 11.254(2)$ Å, $c = 12.196$ (2) Å, $\alpha = 80.34(3)°$, $\beta = 88.44(3)°$, $\gamma = 83.10(3)°$; $V = 566.2(2)$ Å^3, $Z = 2$, $\rho_{calc} = 3.802$ g cm^{-3}, $\mu = 12.779$ mm^{-1}, $T = 223(2)$ K. Reflections collected: 2953. Independent reflections: 1937 [R(int) = 0.0357]. Final R indices [$I > 2\sigma(I)$]: R1 = 0.0258, wR2 = 0.0647. Elemental anal. Calcd: C, 9.25; H, 0.46; N, 2.15. Found: C, 9.78; H, 0.5; N, 1.82. (b) Crystal data for **2**: fw, 249.00; monoclinic, space group, $P2_1/c$; cell dimensions $a = 5.041(1)$ Å, $b = 17.313(2)$ Å, $c = 8.639(1)$ Å, $\beta = 95.042(2)°$; $V = 751.02(13)$ Å^3, $Z = 4$, $\rho_{calc} = 2.202$ g cm^{-3}, $\mu = 4.200$ mm^{-1}, $T = 223(2)$ K. Reflections collected: 3487. Independent reflections: 1167 [R(int) = 0.0427]. Final R indices [$I > 4\sigma(I)$]: R1= 0.0401, wR2 = 0.1070.

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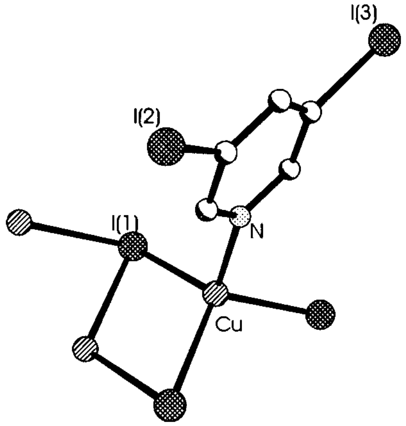

Figure 1. View of the copper coordination with atoms labeled.

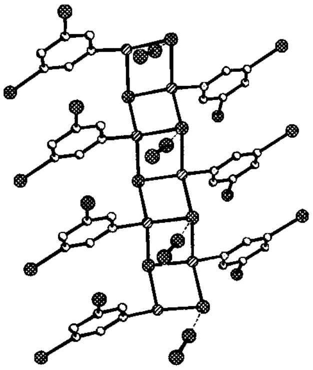

Figure 2. View of a zigzag ladder network with iodine molecular handle (the alternate iodine molecules are omitted for clarity).

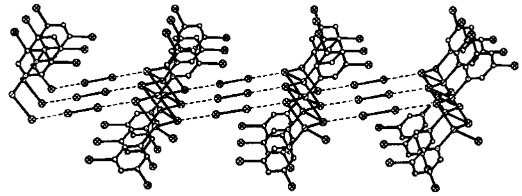

Figure 3. The ladder networks are connected by iodine molecules to form a 2-D layer.

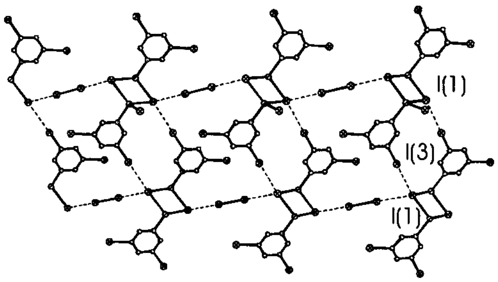

Figure 4. View of the I···I interaction layer.

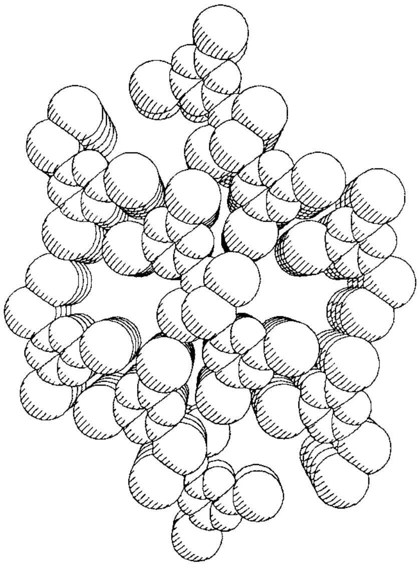

Figure 5. A space-filling view of the 3-D structure with open channels down to the *a* axis where the iodine molecules reside (iodine molecules are not shown for clarity).

104.92(4)° to 114.57(4)°) geometry coordinated by three I(1) atoms (Cu−I(1) ranges from 2.637(1) to 2.661(1) Å) and one nitrogen atom from 3,5-diiodopyridine (Figure 1). Each I(1) atom bridges to three copper atoms. The copper atom and I(1) atom bridging mode extends along the *a* axis to form a zigzag ladder network (Figure 2). The I(1) atom on the ladder connects to an iodine molecule (I(4)−I(4), 2.717(1) Å) by a strong long-range interaction (I(1)···I(4), 3.485 Å) that is shorter than those long-range interactions found in $(Hpy)_2I_3I_7$ (3.545 Å),[10] but longer than those recently reported by the Pennington group (3.367(1)−3.436(1) Å).[11] This extended ladder network with an iodine molecular handle on both sides propagates to form two-dimensional layers (Figure 3). The layers are then connected by mutually significant I···I contacts (Figure 4; I(1)···I(3), 3.697 Å), which is at the shorter end of the reported range (3.643(3)−3.824(3) Å).[12] The result of these long-range I···I interactions creates a 3-D network structure. The inclusion of iodine molecules (Figure 5) in this 3-D metal-organic network indicates that long-range interactions between inclusion molecules and network structures are important in constructing metal-organic polymers.

Note that the reaction chemistry is rather interesting. Under hydrothermal conditions, Cu^{2+} ions were likely reduced to Cu^+ by pyridinedicarboxylate (PDC), while the carboxylate groups on PDC were replaced by iodine nucleophiles:

$$2Cu^{2+} + 2C_5H_3N(COOH)_2 + 5I_2 \rightarrow 2[CuI(C_5H_3NI_2)\cdot{}^1/_2I_2] + 4CO_2 + 2I^- + 4H^+$$

To the best of our knowledge, the simultaneous self-assembly, substitution, and reduction reaction in constructing coordination polymers is unprecedented and unique. It is surprising that a search of the Cambridge Crystal Structural Data-Base revealed that 3,5-diiodopyridine compounds do not exist, although they would be reasonably expected.

Even though the mechanisms of redox reactions under hydrothermal conditions are still unknown,[6] the reactions absent copper ions in the present case were conducted under the same reaction conditions as for preparation of complex

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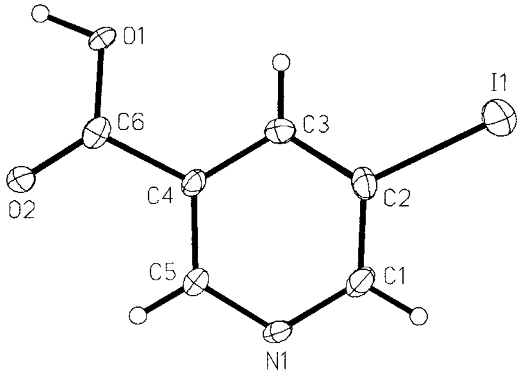

Figure 6. View of the molecule showing the atom-numbering scheme. Thermal ellipsoids are 40% equiprobability envelopes with hydrogen atoms as spheres of arbitrary diameter.

1. While the reaction of PDC with iodine in a molar ratio of 1:1 did not yield crystals of the expected product from 3-day reactions, a 7-day reaction under the same conditions resulted in uniform colorless crystals of a single iodine-substituted complex: IC_5H_3NCOOH **2**[9b] (Figure 6). The balanced reaction is

$$C_5H_3N(COOH)_2 + I_2 \rightarrow IC_5H_3NCOOH + CO_2 + HI$$

where iodine was reduced to iodide by pyridinecarboxylate. The complex **2** displays an extended one-dimensional chain structure linked by hydrogen bonds (O(1)−H···N(1), 2.649(7) Å). The chains are then connected by I(1)···O(2) (3.040 Å) donor−acceptor interactions to form 2-D layers (Figure 7). This result implies that copper ions are necessary for the simultaneous double substitution, as well as the formation of complex **1** under the given conditions.

Thermal analysis revealed that complex **1** started losing iodine at 190 °C and decomposed completely at 455 °C.

In summary, we have demonstrated an unprecedented coordination polymer synthesized via a simultaneous reduction of copper(II) to copper(I) by pyridinecarboxylate and the substitution of carboxylato groups by iodo nucleophiles in a self-assembly process under hydrothermal conditions. While redox mechanisms under hydrothermal conditions are attractive for future studies, the synthesis of the new complex **2** shows that the catalytic properties of copper ions in redox and substitution reactions under hydrothermal conditions are noteworthy.

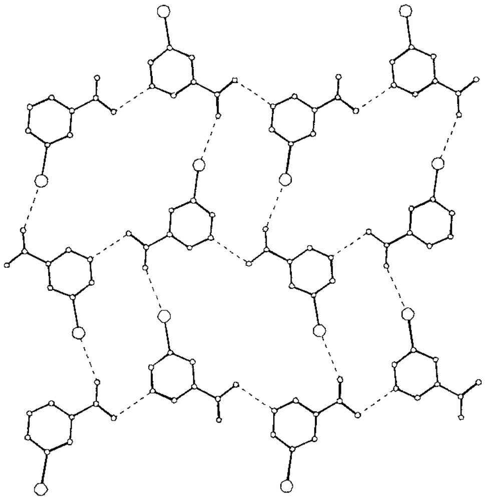

Figure 7. View of a section of one layer of the 2-D network, with hydrogen bonds and close contacts to iodine shown as dashed lines.

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Supporting Information Available: Crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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