A Novel Nanostructured Open-Channel Coordination Polymer with an Included Fused-Polyiodide Ring

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A novel three-dimensional nanostructured open-channel metal-organic framework polymer with inclusion of a polyiodide cluster has been synthesized via an oxidation reaction mechanism under hydrothermal conditions.

The synthesis of new metal-organic polymers via self-assembly processes is a topical and important subject.[1] The diversities of the structures and new topologies discovered in metal-organic polymers are due to the wide variety of metal centers and organic building blocks used. Metal centers play a key role in molecular recognition processes in extended materials and biological systems.[2] We and others have recently demonstrated that copper ions and carboxylate ligands form metal-organic frameworks in which the copper(II) atoms display either a mixed octahedral/square pyramidal geometry in a triple-layer two-dimensional (2-D) open-framework,[3a] a square pyramidal coordination 2-D net in an interpenetrating 2-D/3-D structure,[3b] a square planar motif,[3c] or a trigonal bipyramidal geometry in a mixed-bonding 3-D network;[3d] the copper oxidation states are +1,[2a] +2,[4a] mixed-valence,[4b,4c] and/or with Cu−Cu bonds.[2a,4b,4c] The interest in copper arises mainly from its attractive magnetic[4b] and photoluminescence properties,[2a] novel structural features[2b,3,4a,4b] and its biological relevance in the binuclear "Cu_A" site of cytochrome oxidases and related model compounds.[4c,5] The synthetic methods used for preparing metal-organic network structures are conventional solution methodology in organic solvents or hydrothermal/solvothermal reactions under pressure. In most cases, a reduction or oxidation reaction mechanism has not been invoked during the self-assembly of metal-organic polymers. It has been found that Cu^{II} ions can be reduced to Cu^{I} by pyridine[6a] or pyridylcarboxylate[6b] under hydrothermal conditions. Often, fascinating structures and reaction chemistry can be achieved from the reduction of copper valence states.[4b,6] Hydrothermal processes are therefore considered to be necessary conditions for these reductions. It may not be surprising that the synthesis utilizing oxidation reaction route under hydrothermal conditions is hardly explored.[7] Here we report a novel open-channel framework polymer with polyiodide guests synthesized via an oxidation reaction route under hydrothermal conditions: $\{[Cu_2(IN)_3]\cdot I_5^-\cdot 2/3I_2\cdot H_2O\}_\infty$ (IN: isonicotinato) **1**.

X-ray single crystal analysis[8] revealed that compound **1** consists of a 3-D open-channel metal-organic framework with large polyiodide rings formed from fused polyiodide clusters. The metal-organic framework is comprised of two independent Cu atoms and three isonicotinato ligands. The two independent copper atoms are bridged by the oxygen atoms of three bidentate isonicotinato ligands (Figure 1). Cu(1) has a square-pyramidal geometry made up of two pyridyl groups of two IN units and three oxygen atoms from three bridging carboxylate groups of the IN units. Cu(2) has a distorted square-planar geometry consisting of one pyridyl group of an IN ligand and three oxygen atoms from three bridging carboxylate groups of IN units. This mixed square-planar/square-pyramidal binuclear unit, $[Cu_2(IN)_3]$, propagates to form an unusual nanostructured open-channel metal-organic framework polymer (Figure 2). The $[Cu_2(IN)_3]_6$ fragment displays a spiral-galaxy shape open-channel structure along the (1 1 1) direction (Figure 2). The open channel has a diameter of about 1.15 nm, similar to that of carbon nanotubes (1.2 ± 0.1 nm).[9] The association of $[Cu_2(IN)_3]_6$ fragments leads to triangular and rhombohedral units (Figure 3). These open-channel units in the structure extend in three dimensions. This complex is very different from the binuclear copper-carboxylate networks reported previously[2b,4b,10] as it can accommodate large polyiodide clusters in the open channels. The polyiodide consists of an I_5^- unit that is constructed from an I^- and two I_2 units (Figure 4). The I_2 units [I(1)−I(2), 2.774(1) Å; I(4)−I(5), 2.790(1) Å] and I^- anion have distances [I(3)−I(4), 3.115(1) Å; I(3)−I(2), 3.187(1) Å] shorter than those found in known polyiodides {I^-−I: 3.357(2) Å,[11] and 3.3 Å[12]}. It is noteworthy that every six I_5^- units are fused together around an I_2 molecule [I(6)−I(7), 2.723(7)

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Å] with I(5)···I(6) interactions of 3.560(10) Å (Figure 4). This distance is similar to those long range I···I interactions reported in $(Hpy)_2I_3I_7$ [3.545(13) Å].[13] The iodine molecule in the center of the fused cluster is disordered about a $\bar{3}$ site with six orientations. The fused polyiodide clusters are then linked by another I_2 molecule [I(8)−I(8), 2.759(1) Å] via long range interactions [I(3)···I(8), 3.478(1) Å]. This type of linkage results in large polyiodide rings within the open channels of the metal-organic framework (Figure 5).

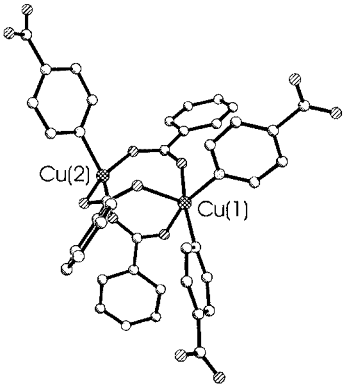

Figure 1. View of the coordination of the copper pair

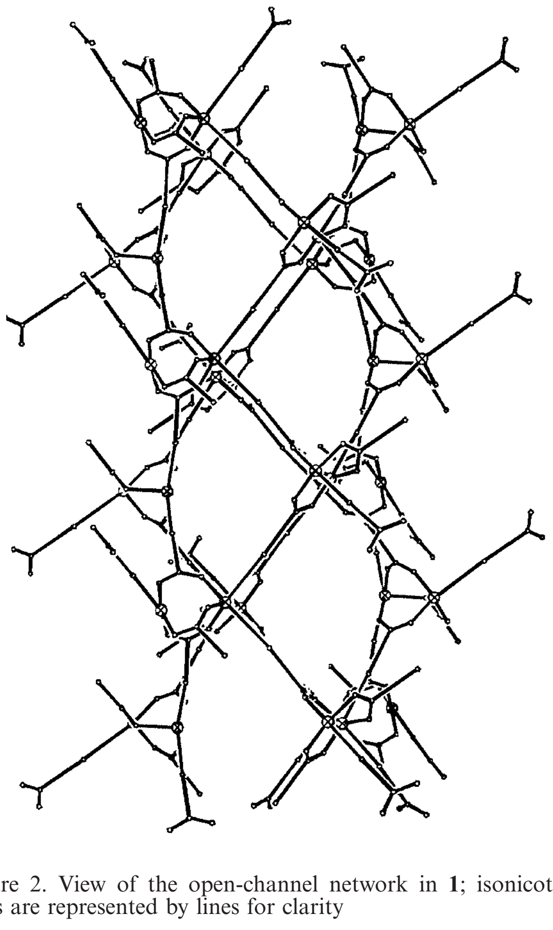

Figure 2. View of the open-channel network in **1**; isonicotinato units are represented by lines for clarity

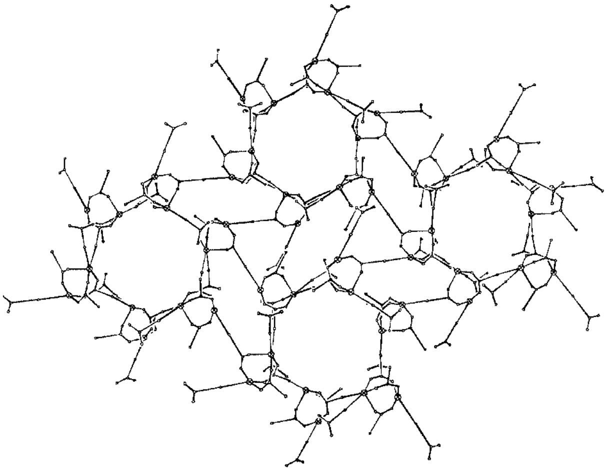

Figure 3. View of the different shape of the channels in the structure

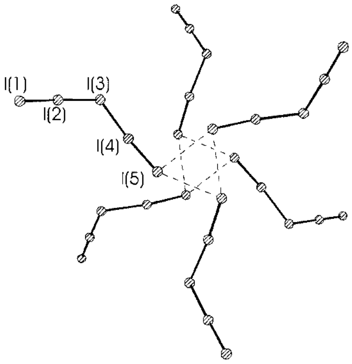

Figure 4. View of the I_5^- units in a fused polyiodide cluster; the iodine molecule with six orientations in the cluster center is not shown

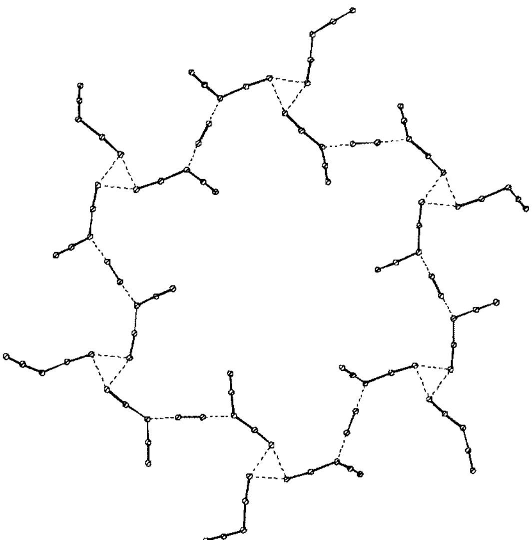

Figure 5. View of a polyiodide ring

The oxidation reaction route under hydrothermal conditions is different from that reported recently, where oxygen was used as an initiator.[7] The I_2 here acts as an oxidizer as well as an iodine source. The half-cell potential[14] of iodine in acidic aqueous solution is +0.615 V, and that of copper is +0.153 V, based on the following half-cell reactions:

$$I_2(aq) + 2\,e \rightleftarrows 2\,I^-$$

$$Cu^{2+} + e \rightleftarrows Cu^+$$

Cu^I may also undergo disproportionation (auto-oxidation reaction) based on the following potential diagram:

$$Cu^{2+} \xrightarrow{0.153\ V} Cu^+ \xrightarrow{0.521\ V} Cu$$

Once the reaction has been initiated, the formation of the $[Cu_2(IN)_3]^+$ unit and the formation of polyiodide shifts the equilibrium of the following reaction to the right-hand side:

$$IN + CuI + I_2 \rightarrow [(Cu_2(IN)_3](I_5^-)$$

Note that the nanostructured open-channel framework in **1** is formed from the inclusion of polyiodide species. This structure is unique and unprecedented. Polyiodide species have been attracting attention recently,[11-13] and metal-organic open-framework structures templated by iodine species should be even more attractive. The synthesis of this novel polyiodide inclusion open-channel framework polymer also demonstrates that novel compounds that may not be accessible using known methods can be synthesized by an oxidation reaction route.[7] The reaction conditions are mild enough to keep the building blocks intact during the oxidation and self-assembly process.

Experimental Section

Black lustrous crystals of **1** were obtained by reacting CuI, isonicotinic acid and iodine (1:2:1) in 6 mL of water under hydrothermal conditions at 140 °C for three days. Yield: 56%.

CCDC-168434 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

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[8] *Crystal data* for **1**: mol. wt. 1315.10; rhombohedral, space group, $R\bar{3}$; unit cell dimensions a = 20.934(1) Å, α = 115.808(1), V = 4734.3(3) Å^3, Z = 6, $D_{calcd.}$ = 2.768 gcm^{-3}, μ = 7.581 mm^{-1}, T = 223(2)K. Reflections collected: 21948; independent reflections: 4670 [R(int) = 0.0396]. Final R indices [$I > 4\sigma(I)$]: R_1 = 0.0251, wR_2 = 0.0590. The water molecule is disordered 50:50 over two different positions, and the I(6)–I(7) molecule is massively disordered about a $\bar{3}$ site.

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