

A unique eclipsed 2-D coordination polymer with removable iodine molecules in the open-channel structure†

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The first removable solid-state iodine inclusion eclipsed two-dimensional coordination polymer with an unusually stable open-channel structure has been synthesized and characterized by X-ray diffraction technique.

The design and synthesis of new open-framework coordination polymers have been the focus in current chemical and new materials research worldwide. Mimicking zeolites, new coordination polymers can be prepared to have open-frameworks *via* inclusion of removable solvents or exchangeable ions.¹ However, iodine, a volatile solid, has not been utilized for the synthesis of coordination polymers until recently.² The interest in iodine-containing coordination polymers research is three-fold. The first interest is the impact of donor–acceptor charge transfer interactions on the design of coordination polymers.^{2a,2b} The second interest is the metallic appearance of the resulting solids that may have potential for conducting framework polymers (single crystals or through intercalation).^{2c,2d} The third interest is the inclusion effects of solid-state iodine on new open-framework coordination polymers.^{2a,2d} Among the reported iodine-containing coordination polymers, although the inclusion of iodine in the open-framework structures has been observed in the cases of $[\text{Cu}(\text{C}_5\text{H}_3\text{NI}_2)_2] \cdot \frac{1}{2}\text{I}_2$ **1**,^{2a} and $\{[\text{Cu}_2(\text{IN})_3] \cdot \frac{1}{5}\text{I}_2 \cdot \text{H}_2\text{O}\}$ (IN: isonicotinato) **2** where **2** displays a remarkable nano-size open-framework structure,^{2d} removable solid-state iodine included open-framework polymers have never been reported prior to this study. Herein we present a new coordination polymer with removable iodine in an eclipsed two-dimensional (2-D) open-channel structure: $[\text{Cu}(\text{IN})_2] \cdot \text{I}_2$ **3**. After the iodine molecules were removed from the crystals of **3**, the color of the crystals changed dramatically from black-red to transparent blue. The transparent blue crystals has a formula of $[\text{Cu}(\text{IN})_2]$ **4** characterized by X-ray powder diffraction technique.

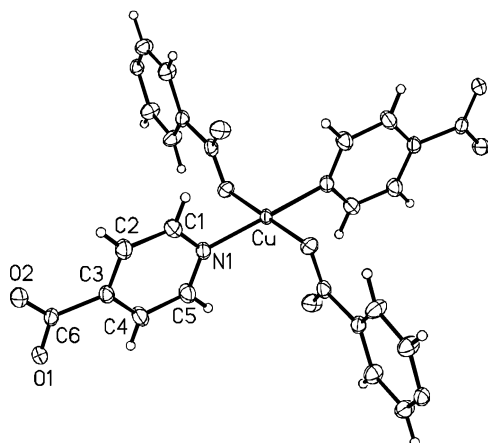


Fig. 1 View of the complete coordination about Cu showing the atom numbering scheme. Thermal ellipsoids are 50% equiprobability envelopes, with hydrogen atoms as spheres of arbitrary diameter.

† Electronic supplementary information (ESI) available: crystal data for $[\text{Cu}(\text{IN})_2] \cdot \text{I}_2$. See <http://www.rsc.org/suppdata/cc/b2/b210740f/>

Complex **3**, black-red crystals with a yield of 77%, is obtained by reacting $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$ with isonicotinic acid and iodine in the mole ratio of 1 : 2 : 1 mixed with 6 ml water under hydrothermal conditions at 140 °C for three days. The crystals were washed with water and acetone, and dried in air. X-ray single crystal analysis† revealed that the compound **3** consists of square planar copper centers (Angles around the copper atom: O(1)–Cu–O(1) 180.00, O(1)–Cu–N(1) 88.94(11), O(1)–Cu–N(1) 91.06(11), O(1)–Cu–N(1) 91.06(11), O(1)–Cu–N(1) 88.94(11), and N(1)–Cu–N(1) 180.00°) coordinated by two pyridyl groups of two IN units and two bidentate carboxylate groups of the isonicotinato-ligand mono-dentated using one of the oxygen atoms (Fig. 1). This square planar

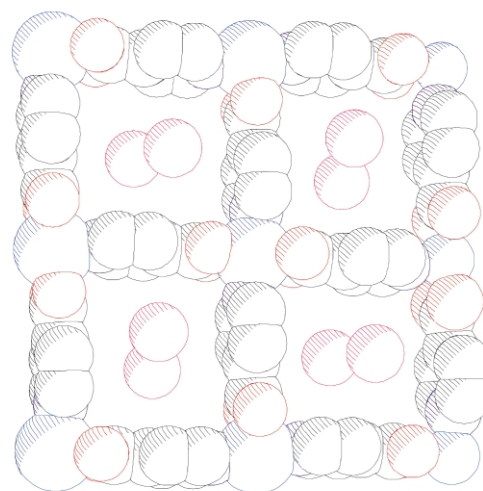


Fig. 2 A space-filling View down to [100] direction of a section of the 2-D layer including I_2 molecules.

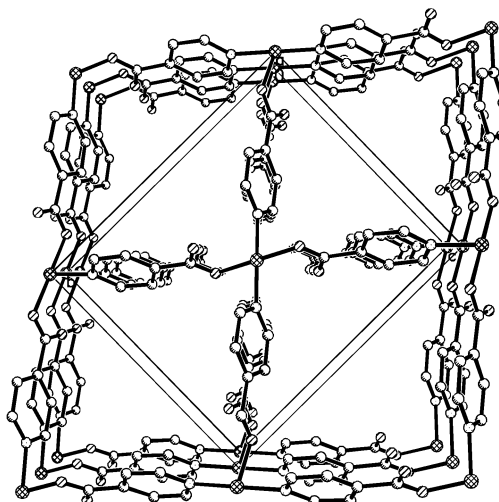


Fig. 3 View of the eclipsed 2-D open-channel multi-layers in **4** with unit cell outline down to [100] direction.

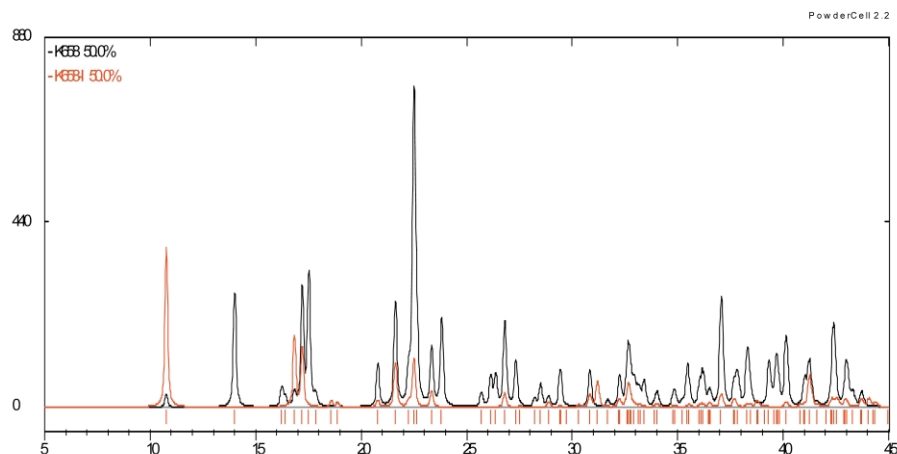


Fig. 4 Black color: simulation from as-synthesized single crystal structure of **3**; red color: simulation from iodine-removed single crystal structure of **3**.

copper unit connects adjacent copper atoms to form square-grids where iodine molecules reside. The inclusion square-grid propagates to form an unusual eclipsed 2-D open-channel coordination polymer (Figures 2 and 3). The copper–copper separations in the square-grid channel are $8.849 \times 8.771 \text{ \AA}$. The separation between the adjacent 2-D layers is about 3.629 \AA that indicates weak aryl–aryl interactions.³ Each iodine molecule has weak donor–acceptor electrostatic attractions to oxygen O(2) atoms in the neighboring layers (2.947 \AA).⁴ The distance between adjacent iodine molecules is 5.795 \AA along each open-channel. The complex **3** is clearly stabilized by both aryl–aryl and iodine–oxygen weak interactions.

Thermal analysis revealed that complex **3** started losing iodine at $190 \text{ }^\circ\text{C}$, and the framework started to decompose after $300 \text{ }^\circ\text{C}$. The decomposition process ended at about $410 \text{ }^\circ\text{C}$.

The iodine molecules in **3** were removed by evacuating the crystals at $195 \text{ }^\circ\text{C}$ for 4 hours. The black-red crystals became transparent blue crystals after the removal of iodine. The resulting blue crystals were then subjected to X-ray powder diffraction analysis against the simulation from the iodine-removed single crystal structure of **3**. The two X-ray patterns match well except for the appearance of a large peak at lower angle and confirm that these blue crystals have a composition of $[\text{Cu}(\text{IN})_2]$ **4**. This has been further confirmed by comparing the single crystal structure simulation of **3** with iodine-removed single crystal structure simulated powder pattern (Figure 4). The highest peak at the lower angle is clearly caused by the disappearance of iodine molecules from the structure.

Note that $[\text{Cu}(\text{IN})_2]$ **4**, the blue crystals resulting from the as-synthesized **3** after the removal of iodine, has an eclipsed two-dimensional structure with 1-D open-channel (Figure 3) that is now stabilized only by weak aryl–aryl interactions between the adjacent layers after the removal of iodine–oxygen interactions. Amazingly, this eclipsed 2-D layer structure is stable up to $300 \text{ }^\circ\text{C}$. Although many stable 3-D open-framework and staggered 2-D polymers have been characterized,^{1,5} the eclipsed 2-D open-channel layers with removable solid-state iodine has never been reported.

While the organic ligands used in this report are relatively small, both interpenetrating and open-channel structures have been obtained.^{2d,5b,5c} The large nano-size open-channel structures (1.15 nm in diameter) in the isonicotinato-ligand system have been observed from the incorporation of solid-state polyiodide.^{2d} It should be noted that one of the known stable open-channel structures formed from the isonicotinato-ligand,^{5c} similar to the structure in this report, displays a 3-D covalent-bonded framework with highly selective adsorption capability, whereas the reported compound in this paper has an unprecedented eclipsed 2-D layer structure.

The formation of the stable open-channel eclipsed 2-D layer structure with removable iodine molecules reveals interesting interactions that exist between the solid-state iodine and the

open-framework polymers. Further research to uncover the relationships between solid-state iodine (iodine molecule or polyiodide species) and open-framework polymers will be very attractive. Our investigations in this area are in progress.

In summary, we have demonstrated a unique eclipsed 2-D coordination polymer that is still stable after the removal of the iodine molecules from the open-channel of the eclipsed layers. The structures are characterized by X-ray diffraction technique.

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Notes and references

† Crystal data for **1**: FW, 561.54; monoclinic, space group, $P2_1/n$; cell dimensions $a = 5.795(1)$, $b = 12.646(1)$, $c = 10.816(1) \text{ \AA}$, $\beta = 91.253(1)$, $V = 792.4(1) \text{ \AA}^3$, $Z = 2$, $D_{\text{calc}} = 2.353 \text{ g cm}^{-3}$, $\mu = 5.288 \text{ mm}^{-1}$, $T = 223(2) \text{ K}$. Reflections collected: 4160; independent reflections: 1468 [$R(\text{int}) = 0.0266$]. Final R indices [$I > 4\sigma(I)$]: $R_1 = 0.0232$, $wR_2 = 0.0619$. CCDC 179063. See <http://www.rsc.org/suppdata/cc/b2/b210740f/> for crystallographic data in .cif or other electronic format.

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