

A New Inorganic–Organic Hybrid Copper Iodate with Potentially Large Void Volume

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A new one-dimensional hybrid copper iodate, $(2,2'\text{-bipy})_2\text{Cu}_2(\text{IO}_3)_3^+$, with potentially large void volume and a high amount of accessible volume, was synthesized by hydrothermal reactions and characterized by single crystal X-ray diffraction.

Inorganic–organic hybrid materials have shown interesting properties in the areas of catalysis, biology, electrical conductivity, magnetism, and photochemistry, resulting in a great deal of attention to their design and synthesis over the past few years.¹ A number of inorganic–organic hybrid crystal materials with one-dimensional (1D), two-dimensional (2D), and three-dimensional (3D) frameworks in the systems of M/O, M/P/O, M/As/O, M/S/O, M/Se/O, and M/Te/O (M = metal) were reported,^{1–7} but no study has been reported on the inorganic–organic hybrid systems of M/I/O so far. Only some simple metal iodates have been reported for years, including $\text{Co}(\text{IO}_3)_2$, $\text{Cu}(\text{IO}_3)_2$, $\text{M}(\text{IO}_3)_3 \cdot n\text{H}_2\text{O}$ (M = Ce–Lu), $\text{PuO}_2(\text{IO}_3)_2 \cdot \text{H}_2\text{O}$, $\text{UO}_2(\text{IO}_3)_2$, $\text{A}_2[(\text{UO}_2)_3(\text{IO}_3)_4\text{O}_2]$ (A = K, Rb, Tl), $\text{A}[(\text{UO}_2)_2(\text{IO}_3)_2\text{O}_2] \cdot \text{H}_2\text{O}$ (A = Sr, Ba, Pb), $\text{A}[\text{VO}_2(\text{IO}_3)_2]$ (A = K, Rb), $\text{A}[(\text{VO})_2(\text{IO}_3)_3\text{O}_2]$ (A = NH_4 , Rb, Cs), $\text{AMoO}_3 \cdot (\text{IO}_3)$ (A = K, Rb, Cs), and $\text{PuO}_2(\text{IO}_3)_2 \cdot \text{H}_2\text{O}$.⁸ Iodate anion, with nonbonded electron pairs, has a pyramidal geometry. This facilitates the formation of crystallographic noncen-

troscopic (NCS) structures when iodate anions are incorporated into crystalline materials. The crystalline materials with NCS structure are of considerable interest due to their potential nonlinear optical, pyroelectric, piezoelectric, and ferroelectric properties.⁹ In order to create new materials with NCS structure and to study the influence of organic molecules on the structure of inorganic compounds, we initiated an investigation of the hydrothermal synthesis of inorganic–organic hybrid materials in the systems of M/I/O. Here, we report the hydrothermal synthesis and X-ray crystal structure of a new inorganic–organic hybrid metal iodate, $(2,2'\text{-bipy})_2\text{Cu}_2(\text{IO}_3)_3 \cdot 1.5\text{Cl} \cdot 0.5\text{H}_3\text{O} \cdot 4\text{H}_2\text{O} \cdot x\text{I}_2$ ($x \approx 0.19$) (**1**).

The title compound was prepared from the reaction mixture of composition V_2O_5 , I_2O_5 , $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, 2,2'-bipy, HCl (38%), and NaHCO_3 in the presence of H_2O with molar ratio 1:2.5:1:1:10:7.5:500 under hydrothermal conditions at 120 °C for 7 days. While vanadium is not incorporated into the product, the vanadium(V) pentoxide plays an important role in the formation of the final product in the hydrothermal synthesis. However, only a small amount of powder product was synthesized when we mixed the reaction composition I_2O_5 , $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, 2,2'-bipy, HCl, NaHCO_3 , and H_2O with molar ratio 2.5:1:1:10:7.5:500 in the reaction without vanadium. In the synthesis, brown-green crystals of **1** and some green uncrystallized phases were mixed. Powder X-ray diffraction showed the green uncrystallized phase to be an unidentified medley. For FT-IR results,

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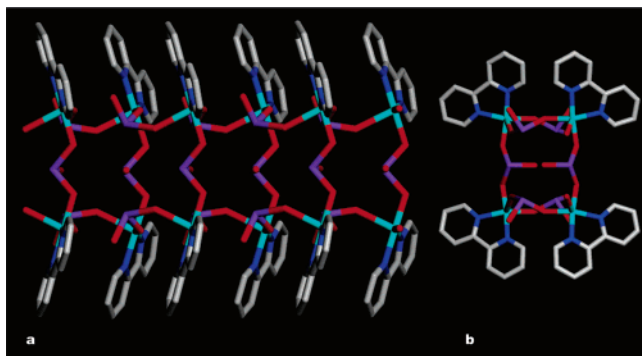


Figure 1. View of the one-dimensional chains in compound **1**. The following colors correspond to these atoms: iodine, purple; copper, light blue; oxygen, red; nitrogen, blue; carbon, gray.

see Supporting Information. The title compound is air-stable and characterized by single crystal X-ray diffraction.¹⁰

As shown in Figure 1, the title compound can be described as folded copper–iodine oxide ribbons decorated with 2,2'-bipy ligands extending sideways from four faces of the inorganic chain. The inorganic chain is constructed from the corner-sharing polyhedral connectivity of CuN_2O_3 square pyramids and IO_3 pyramids. The Cu(II) center exhibits CuN_2O_3 square pyramidal coordination geometry through bonding to two *cis* nitrogen donors of 2,2'-bipy ($\text{Cu}(1)–\text{N}(1)$ 2.010(6) Å, $\text{Cu}(1)–\text{N}(2)$ 1.988(7) Å), two oxygen donors of iodate ($\text{Cu}(1)–\text{O}(1)$ 1.986(6) Å, $\text{Cu}(1)–\text{O}(2)$ 1.980(5) Å) in the basal plane, and an oxygen of iodate ($\text{Cu}(1)–\text{O}(3)$ 2.344(6) Å) in the apical position. Each iodine site shows IO_3 pyramidal geometry, which has a terminal oxo group and shares two oxygen atoms with two CuN_2O_3 square pyramids. It is observed that the I–O bond lengths for oxygen atoms bound to CuN_2O_3 square pyramids are longer than those of the terminal oxo groups (the bridging oxygen atoms, $\text{I}(1)–\text{O}(1)$ 1.811(6) Å, $\text{I}(1)–\text{O}(3)$ 1.809(6) Å, $\text{I}(2)–\text{O}(2)$ 1.826(6) Å, and the terminal oxygen atoms, $\text{I}(1)–\text{O}(4)$ 1.780(6) Å, $\text{I}(2)–\text{O}(5)$ 1.789(8) Å). The bond valence sum calculations,¹¹ giving the oxidation states of the corresponding ions, indicate the occurrence of Cu^{2+} and I^{5+} . The adjacent inorganic chains are further connected through very strong $\pi–\pi$ interactions of the 2,2'-bipy. The close contact distance between adjacent 2,2'-bipy rings is about 3.31 Å. Therefore, the 1D chains of **1** are further extended into a 3D supramolecular array via the intercalation of the lateral aromatic groups. The chains pack as shown in Figure 2, giving rise to two different types of channels (channel A, channel B) among adjacent four chains along the *c*-axis. The channels A are occupied by chloride, and water guest molecules, and channels B are occupied by iodine guest

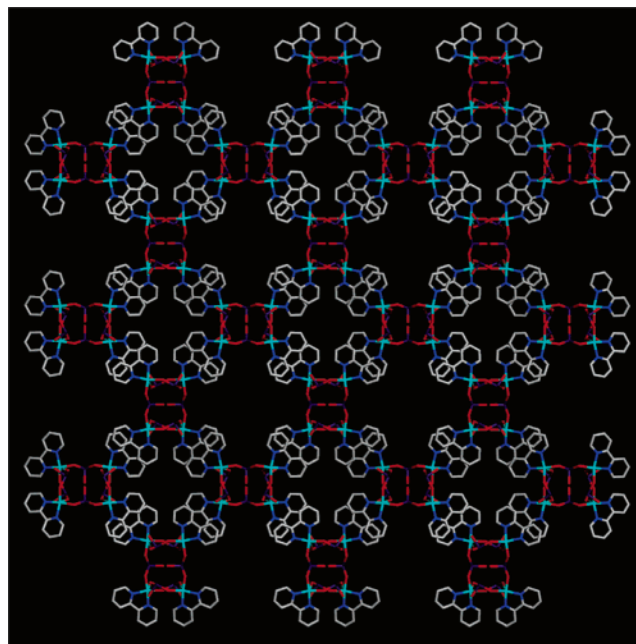


Figure 2. Structure of **1** showing the one-dimensional channels along the *c*-axis (guest molecules have been omitted for clarity). The purple, light blue, red, blue, and gray spheres represent iodine, copper, oxygen, nitrogen, and carbon atoms, respectively.

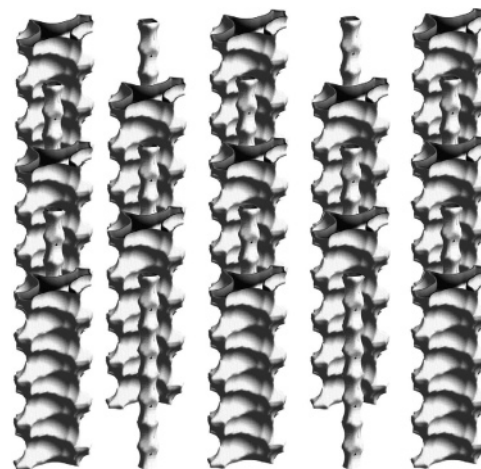


Figure 3. Profile of the channels with the *c*-axis vertical. The shaded area is the empty volume.

molecules. The chloride and iodine guest molecules are confirmed by XPS.¹² The approximate dimensions of the channels are $10.2 \times 10.2 \text{ \AA}^2$ (channels A) and $7.1 \times 7.1 \text{ \AA}^2$ (channels B), such that there is no restriction of the thermal vibration of the guest molecules in the channels. Therefore, a high degree of disorder of guest molecules is detected in compound **1**.

A remarkable feature of compound **1** is the presence of potentially large channels. The profile of the channels is shown in Figure 3. The amount of potential void volume and its accessibility (how easily guest molecules can be put into the structure from the outside) were calculated by the Free Volume module of the *Cerius2* package,¹³ which applies

(10) Crystal data for $\text{C}_{20}\text{H}_{25.50}\text{Cl}_{1.50}\text{Cu}_2\text{I}_{3.38}\text{N}_4\text{O}_{13.50}$ follow: $M = 1146.49$, tetragonal, space group $I4cm$, $a = 29.6755(4) \text{ \AA}$, $c = 6.98570(10) \text{ \AA}$, $V = 6151.85(15) \text{ \AA}^3$, $Z = 8$, $D_c = 2.476 \text{ g/cm}^3$, $\mu = 4.971 \text{ mm}^{-1}$, $R_1(I \geq 2\sigma(I)) = 0.0272$ and $wR_2 = 0.0771$. Data collection for **1** was performed on a Siemens SMART CCD diffractometer using graphite monochromated Mo K α radiation ($\lambda(\text{Mo K}\alpha) = 0.71073 \text{ \AA}$). The data were collected at 293 K. Data processing was accomplished with the SAINT processing program. The structures were solved with direct methods using the SHELXTL crystallographic software package and refined with full-matrix least-squares.

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(12) XPS data for **1**: the binding energy of Cl 2p is 198.4 eV for Cl^- , and the binding energy of I 3d_{5/2} is 621.8 eV for I^0 and 625.1 eV for IO_3^- .

(13) *Cerius2 v. 4.2*; Molecular Simulations Inc.: San Diego, CA, 1999.

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the Connolly method.¹⁴ With the *Cerius2* package, we first obtained the void volume and calculated the accessible volume by forcing a standard molecule (a radius of 1.4 Å) to enter the unit cell from the outside. The total and accessible void volumes of both types of channels are estimated to be about 44% and 18% of the volume of the unit cell, respectively. The surface enclosing the void volume is about 3073.14 Å²/unit cell. For large void volume and high amount of accessible volume, the structure is less thermodynamically stable. The thermogravimetry data also indicate that compound **1** is only stable to ca. 200 °C and not stable after the loss of guest molecules. Therefore, it is not possible to study the molecule adsorption features for the thermal property of compound **1**.

Interestingly, we did not obtain the same structure when we substituted copper for other metals, such as cobalt, nickel, and zinc, under the same hydrothermal conditions. This may be due to the nature of metals employed. Co(II), Ni(II), or Zn(II) atoms tend to produce four- or/and six-coordination with tetrahedral or/and octahedral geometry, while Cu(II)

atoms tend to produce [4 + 1] coordination with square pyramidal geometry owing to a strong Jahn–Teller effect.

In summary, we initiated a hydrothermal synthesis of inorganic–organic hybrid materials in the systems of M/I/O and synthesized a new inorganic–organic hybrid copper iodate. The compound has an infinite 1D structure, and the adjacent 1D chains are further connected through very strong π – π interactions into a 3D supramolecular array. The compound exhibits two different types of large channels with potentially large void volume and a high amount of accessible volume. We are currently studying other systems with iodate and searching for new inorganic–organic hybrid materials.

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Supporting Information Available: X-ray crystallographic files (CIF), additional figures, and other synthetic information for the title compound. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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