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Low-Dimensional Hybrid Copper Halides with Novel D6R Cu_6I_6 Cores

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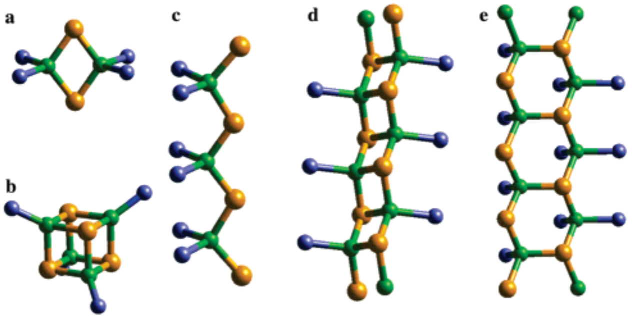
Two low-dimensional hybrid copper halides, (2,2′-bipy)Cu_3I_3 (**1**) and (2,2′-bipy)Cu_4I_4 (**2**) (2,2′-bipy = 2,2′-bipyridine), with novel D6R (double six-membered rings) Cu_6I_6 cores were synthesized by hydro(solvo)thermal reactions and characterized by single-crystal X-ray diffraction.

In recent years, aluminosilicate zeolites have been a major focus of research in inorganic chemistry because zeolites exhibit a wide range of structural topologies and practical properties involving ion exchange, separations, catalysis, and porosity.[1] This domain has expanded from aluminosilicates to many other inorganic functional materials.[2] Most of these materials are based on oxygen-containing materials, especially phosphates, but there are examples based on other chemistries, such as oxides, nitrides, sulfides, and halides. In recent years, considerable attention has been focused on the design and synthesis of inorganic functional materials with a hybrid approach.[3] Among the various families of inorganic functional materials, the family of metal halides is an important one. As a branch of the metal halides, copper halides occupy an important position. A variety of novel copper(I) halides exhibiting varying dimensionality have been synthesized. These include molecular to chainlike (1-D), layered, and three-dimensional extended systems.[4] To the best of our knowledge, the basic copper(I) halide (CuX) skeletons of these compounds generally exhibit several structural motifs (Chart 1): square (rhomboid) dimers, cubane tetramers, zigzag chains, double-stranded ladders, and hexagonal grid chains.[5] As an extension of our study of the synthesis of hybrid materials in M−P−O systems,[6] we have been focusing on using hydrothermal synthesis to discover new low-dimensional inorganic−organic hybrid copper halides and study the influence of the organic moieties on the dimensionality of the products. Our interest in low-dimensional materials is mainly due to the fact that low-dimensional solids often exhibit interesting anisotropic physical or chemical properties.[7] In this communication, we report the preparation and characterization of two low-

Chart 1. Basic Copper(I) Halide (CuX) Skeletons[a]



[a] Copper is represented by green spheres, halide by yellow spheres, and nitrogen by blue spheres.

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dimensional inorganic−organic hybrid copper halides, (2,2′-bipy)Cu_3I_3 **1** and (2,2′-bipy)Cu_4I_4 **2** (2,2′-bipy = 2,2′-bipyridine), with novel D6R Cu_6I_6 cores.

We first studied the reaction in Cu−I−2,2′-bipy systems, hoping to synthesize low-dimensional hybrid compounds, as 2,2′-bipyridine can serve as a protecting unit to passivate the metal centers for the formation of low-dimensional structure. **1** and **2** were synthesized from a reaction mixture containing $Cu(NO_3)_2 \cdot 2H_2O$, $NaClO_4$, H_5IO_6, 2,2′-bipy, and $NaHCO_3$ in the presence of $C_2H_6O_2$ (glycol) and H_2O with molar ratios of 2:4:3:1:8.6:65:300 and 2:4:3:1:6.4:65:300 under hydro(solvo)thermal conditions at 150 °C for 5 days. Differences in the reaction conditions show that pH (7.8 for **1** and 7.0 for **2**) is the main factor affecting the formation of **1** and **2**. The compounds were isolated in high yield as rod-shaped red and black-red crystals, respectively. The crystals were collected as a single phase, judged by powder X-ray diffraction measurement (see Supporting Information). The IR spectra of **1** and **2** are provided in the Supporting Information. It has been found, in the synthesis of the title compounds, that the hydro(solvo)thermal method is a promising technique for the preparation of inorganic−organic hybrid compounds with interesting properties such as a redox process of copper.

Single-crystal X-ray diffraction analysis[8] of **1** and **2** reveals the formation of 1-D ribbonlike structure. There are two types of Cu cations and two types of I anions (μ_3-I and μ_4-I) in compound **1**. The rule of charge balance indicated the valences of Cu to be +1. One type of Cu [Cu(1)], with distorted tetrahedral geometry, is coordinated to two I ions and two N atoms from one 2,2′-bipy molecule. The geometry of this type of Cu is quite distorted, with an I−Cu−I angle of 107.45(4)°, a N−Cu−N angle of 79.9(3)°, and N−Cu−I angles ranging from 107.2(2)° to 128.9(2)°. Another type of Cu [Cu(2) and Cu(3)], in the tetrahedral site, is coordinated to four I atoms. The Cu(1)−N distances, 2.043(7)−2.073(7) Å; the average Cu(1)−I distances, 2.5975(15) Å; the Cu(2)−I distance, in the range of 2.6125(12)−2.7061(16) Å; and the Cu(3)−I distance, in the range of 2.6429(16)−2.6605(14) Å, are comparable to those found in reported copper iodines.[4,5] The type of Cu coordinated with the 2,2′-bipy molecule shares corners via μ_3-I to form an extended 1-D zigzag chain, unit A. Another type shares corners via μ_4-I to form an extended 1-D complex chain, unit B. One unit B combines with two unit A's, finally forming the infinite 1-D ribbonlike polymer of **1** along the *c* axis (Figure 1a). In compound **1**, there are $\pi-\pi$ interactions between the adjacent 2,2′-bipy groups in a ribbonlike polymer, with a distance of 3.871 Å.

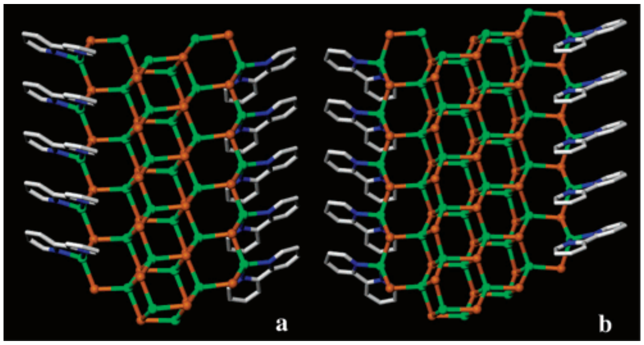

Figure 1. View of the structure of the 1-D ribbon in **1** and **2**.

The crystal structure of **2** can be considered to be an extension of the structure of **1**. There are also two types of Cu cations and two types of I anions (μ_3-I and μ_4-I) in compound **2**. The rule of charge balance indicated the valences of Cu to be +1. One type of Cu [Cu(1)], with distorted tetrahedral geometry, is coordinated to two I ions and two N atoms from one 2,2′-bipy molecule. Another type of Cu [Cu(2)−Cu(4)], in the tetrahedral site, is coordinated to four I atoms. The bond lengths and angles of Cu(1)−Cu(3) in compound **2** are very similar to those found in compound **1**. All of the Cu(4)−I bond distances [in the range of 2.6347(19)−2.6634(19) Å] and I−Cu(4)−I bond angles [in the range of 104.06(7)−113.26(7)°] are typical. The type of Cu coordinated with the 2,2′-bipy molecule shares corners via μ_3-I to form an extended 1-D zigzag chain, unit A. Another type shares corners via μ_4-I to form an extended 1-D complex chain, unit B. One unit B combines with two unit A's, finally forming the infinite 1-D ribbonlike polymer of **2** (Figure 1b). As for compound **1**, compound **2** also has $\pi-\pi$ interactions between the adjacent 2,2′-bipy groups in a ribbonlike polymer, with a distance of 3.808 Å. Two six-membered rings of a 2,2′-bipy molecule in compounds **1** and **2** are torsional; the torsion angles of the two six-membered rings in the two compounds being 17.8° and 11.0°, respectively.

A remarkable feature in compounds **1** and **2** is the presence of hexanuclear Cu_6I_6 cores (Chart 2a). Until now, only two compounds with hexanuclear Cu_6X_6 cores have been reported.[9] The hexanuclear Cu_6I_6 core is constructed by the combination of two boat-shaped trinuclear Cu_3I_3 cores via six I anions. The structure of the hexanuclear Cu_6I_6 cores is similar to that of the double six-membered rings (D6R, hexagonal prisms) found in zeolite.[10] The hexanuclear Cu_6I_6 cores in compound **1** are connected to each other by sharing Cu_2I_2 four-membered rings to form the main body of the 1-D ribbonlike structure (Chart 2b). The main body of the 1-D structure in compound **2** can be considered as being built of two face-sharing main bodies in compound **1** through

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(8) Crystal and structure refinement parameters: **1**, $M = 727.50$, orthorhombic, space group *Fdd*2, $a = 35.666(7)$, $b = 41.898(8)$, $c = 4.1881(8)$ Å, $V = 6259(2)$ Å^3, $Z = 16$, $D_c = 3.088$ g/cm^3, $\mu = 9.942$ mm^{-1}, R_1 [$I \geq 2\sigma(I)$] = 0.0329, and $wR_2 = 0.0714$; **2**, $M = 917.94$, monoclinic, space group $P2_1/c$, $a = 13.6242(7)$, $b = 4.1976(2)$, $c = 31.498(2)$ Å, $\beta = 99.722(4)°$, $V = 1775.48(18)$ Å^3, $Z = 4$, $D_c = 3.434$ g/cm^3, $\mu = 11.670$ mm^{-1}, R_1 [$I \geq 2\sigma(I)$] = 0.0455, and $wR_2 = 0.0940$. Data collection for **1** and **2** was performed on a Siemens SMART CCD diffractometer using graphite-monochromated Mo Kα radiation [λ(Mo Kα) = 0.71073 Å]. The data were collected at 293 K. Date 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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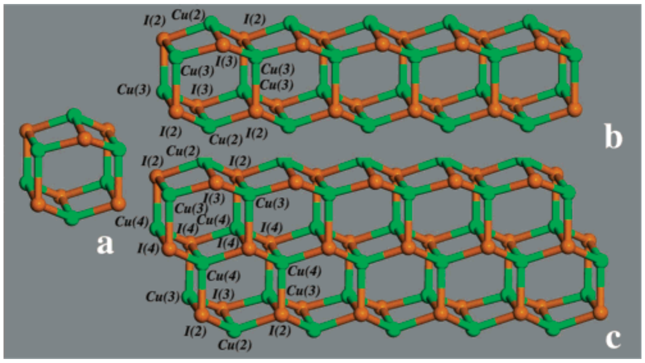
Chart 2. (a) Hexanuclear Cu_6I_6 Cores, (b) Main Body of the 1-D Structure in Compound **1**, (c) Main Body of 1-D Structure in Compound **2**[a]



[a] Copper is represented by green spheres, halide by yellow spheres.

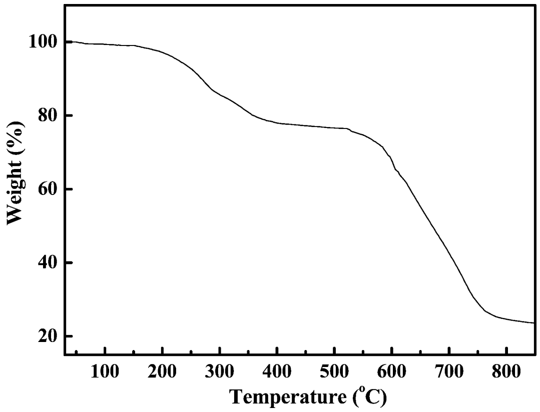


Figure 2. Thermogravimetric pattern for **1**.

the sharing of bridged double-stranded ladder chains (Chart 2c). To the best of our knowledge, compounds **1** and **2** are novel examples of 1-D infinite ribbonlike structures containing D6R Cu_6I_6 cores in copper halides.

Thermal analyses for **1** and **2** were performed in nitrogen gas from 30 to 850 °C. The weight loss (Figures 2 and 3) curves indicated that **1** was stable up to ca. 200 °C and **2** was stable up to ca. 230 °C. The TG curve for compound **1** showed that the initial weight loss in the temperature range 200−390 °C was due to the decomposition of 2,2′-bipy (weight loss: exptl 21.5%, calcd 21.44%). Over the range 390−770 °C, the weight loss should correspond to the sublimation of iodine (weight loss: exptl 52.1%, calcd 52.37%). The TG curve for compound **2** showed that 2,2′-bipy was decomposed in the temperature range 230−345 °C, with a weight loss of 16.9% (weight loss: calcd 17.01%), and exhibited a further weight loss of 54.9% in the range 345−810 °C, consistent with the sublimation of iodine (weight loss: calcd 55.30%).

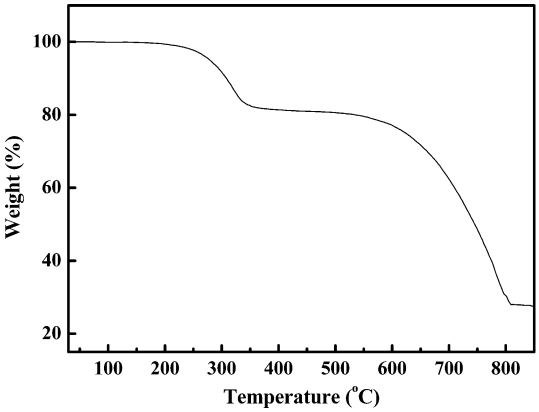


Figure 3. Thermogravimetric pattern for **2**.

In summary, we have reported the syntheses and crystal structures of two new low-dimensional inorganic−organic hybrid copper halides, (2,2′-bipy)Cu_3I_3 **1** and (2,2′-bipy)-Cu_4I_4 **2**. Compounds **1** and **2** are the first examples of 1-D infinite ribbonlike structures contained D6R Cu_6I_6 cores in copper halides. These results give us encouragement that we might be able to form new stable low-dimensional inorganic−organic hybrid copper halides. We are currently carrying out the substitution of 2,2′-bipy for other organic ligands in similar hydrothermal systems and are studying the rational synthesis of new inorganic−organic copper halides.

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Supporting Information Available: X-ray crystallographic files (CIF) and other data for **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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