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Zeolite-like Copper Iodide Framework with New 6^6 Topology

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We have described an unprecedented three-dimensional zeolite-like copper iodide constructed from $Cu_4I_4(DABCO)_4$ (DABCO = 1,4-diazabicyclo[2.2.2]octane) supertetrahedron units. This compound forms a four-connected network with new 6^6 topology. Its structure reveals one-dimensional channels along the [001] direction, and the framework displays interesting self-penetration. The title compound shows photoluminescence at room temperature in the solid state.

Microporous materials that are based on aluminosilicate zeolites have large-scale technological applications in ion exchange, separation, and catalysis.[1] For over half a century, many research activities have been focused on developing microporous materials with either novel chemical compositions or new framework topologies because the functionality of the materials is related to their compositional and topological features. During the last 20 years, this domain has expanded from aluminosilicates to many other functional materials. Most of these materials are based on oxygen-containing materials, especially phosphates, but there are also some examples based on non-oxygen materials, such as nitrides, sulfides, and halides.[2] In recent years, considerable attention has been focused on the relatively new field of metal−organic frameworks (MOFs).[3] To prepare zeolite-like functional materials with novel topological features, an important advance in this field is building the frameworks of microporous materials with organic ligands and inorganic tetrahedral building blocks.[4] The incorporation of organic ligands within an inorganic framework promises access to a wider range of applications because the porosity of the microporous materials greatly depends on the size and shape of the inorganic polynucleus building blocks.

In our previous investigation on the assembly of crystal materials, we had successfully synthesized some low-dimensional inorganic−organic hybrid copper halides.[5] As an extension of our research on crystal materials, we are focusing on the synthesis and investigation of zeolite-like copper iodide with microporous properties by using bidentate organic ligands and tetrahedral inorganic building blocks. Here, we report the synthesis, structure, and some preliminary studies on the physical and chemical properties of a zeolite-like microporous compound, $[Cu_4I_4(DABCO)_2]\cdot xC_2H_5OH$ ($x \approx 1.00$).

An effective and powerful strategy for making new highly porous materials is to expand the frameworks of some reported inorganic dense materials by replacing the original structure units with larger structure units.[6] To create new zeolite-like microporous materials with novel topological features, we have been focusing on expanding the zeolite topologies by construction of Cu_4X_4 (X = iodide) cubane building blocks and DABCO organic ligands. The Cu_4X_4 cubane unit, which shows a cubane-like geometry, is a normal building block in copper halides, and some interesting structures have been reported from Cu_4X_4 cubane units.[7] The Cu_4I_4 cubane unit is formed by four Cu atoms and four I atoms. Each I or Cu atom occupies a corner of the cube, with the same type of atom located at the position of the opposite corner of the same face. In a Cu_4I_4 cubane unit, each Cu^+ cation connects three neighboring halide anions and uses a coordination sphere pointing outward of the cube to bond an organic ligand. The tetrahedral connectivity of Cu_4I_4 cubane units is similar to that of tetrahedral atoms (T atoms), such as Al^{3+} or Si^{4+}, in aluminosilicate zeolites. The two coordinate N atoms of the DABCO bidentate organic ligand are oriented at an angle of about 180°, so the DABCO organic ligand was chosen as a linker to replace O^{2-} (X atom)

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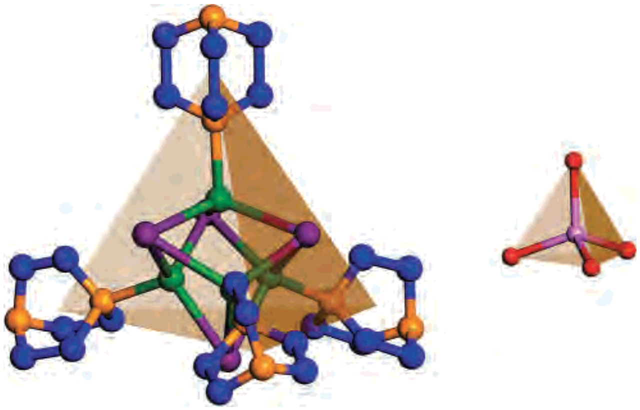

Figure 1. Secondary building block $Cu_4I_4(DABCO)_4$ (left) of the title compound and the tetrahedral unit SiO_4 of zeolites (right). Color code: C, blue; N, orange; Cu, green; I, purple; Si, pink; O, red.

in zeolites. If four DABCO organic ligands bond to a Cu_4I_4 cubane unit, we can regard the $Cu_4I_4(DABCO)_4$ unit (hereafter referred to as a supertetrahedron unit) as an artificial tetrahedral unit (Figure 1). The dimension of each edge of the supertetrahedron unit is about 8 Å, which is longer than that of TO_4 in zeolites (2.4 Å). With the $Cu_4I_4(DABCO)_4$ unit as an artificial tetrahedral unit, it is possible to construct structures with framework topology similar to that in zeolites.

The title compound was prepared from the reaction mixture of composition $CuCl_2{\cdot}2H_2O$ (1.20 mmol, 0.200 g), $HIO_4{\cdot}2H_2O$ (0.44 mmol, 0.100 g), $NaClO_4{\cdot}H_2O$ (1.42 mmol, 0.200 g), $NaHCO_3$(1.20 mmol, 0.100 g), and $C_6H_{12}N_2{\cdot}6H_2O$ (0.91 mmol, 0.200 g) in the presence of ethanol (5.0 mL) under solvothermal conditions. The mixture was stirred in ethanol (5.0 mL) at room temperature for ca. 3 h to give a precipitate, and then this heterogeneous mixture was placed in a 15 mL Teflon-lined steel autoclave and heated to 180 °C for 72 h. The resulting brown hexagonal blocks were obtained by filtration, washed with distilled water, and air-dried (yield: 60% based on $CuCl_2{\cdot}2H_2O$). The crystals were collected as a single phase and judged by powder X-ray diffraction measurement (see the Supporting Information). It has been found that the solvothermal method is a promising technique for the preparation of inorganic−organic hybrid compounds in a way that reduction of Cu^{2+} to Cu^+ has been carried out and Cu^+ has been introduced in the compound, which is not easy by any other technique.

As expected, single-crystal X-ray diffraction analysis of the title compound $[Cu_4I_4(DABCO)_2]{\cdot}xC_2H_6O$ reveals the formation of a three-dimensional (3D) zeolite-like microporous structure. The structure of this compound is constructed from $Cu_4I_4(DABCO)_4$ supertetrahedron units. In fact, the structure of the title compound can be considered as being built up by larger secondary building units (SBUs). In the structure of the title compound, six $Cu_4I_4(DABCO)_4$ supertetrahedron units alternately bond to each other, forming a planar six-membered-ring SBU in the *ab* plane (Figure 2). A 6-fold crystallographic axis passes through the center of the six-membered-ring SBU, and the center of the six-membered ring is located at (0, 0, 0). All six-membered-ring SBUs are in the crystallographic planes parallel to the *ab* plane, and the neighboring SBU layers are stacked in an ABAB sequence along the *c* axis. Each six-membered-ring SBU is connected to 12 adjacent six-membered-ring SBUs, 6 of which are in one neighboring plane and 6 other ones are in another neighboring plane, through 12 DABCO organic ligands of 6 $Cu_4I_4(DABCO)_4$ supertetrahedron units. In this way, all of these six-membered-ring SBUs bond to each other to give rise to the 3D framework of this compound.

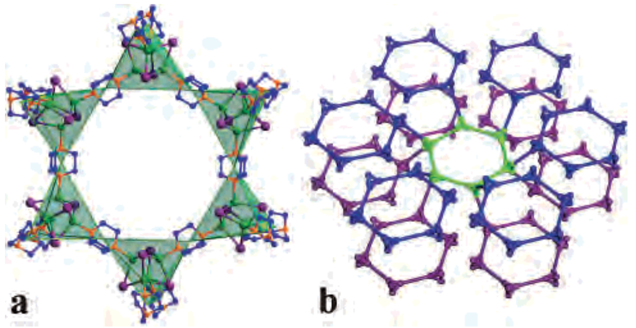

Figure 2. (a) Six-membered-ring SBU of the title compound. (b) Each six-membered ring connects 12 of the same SBUs.

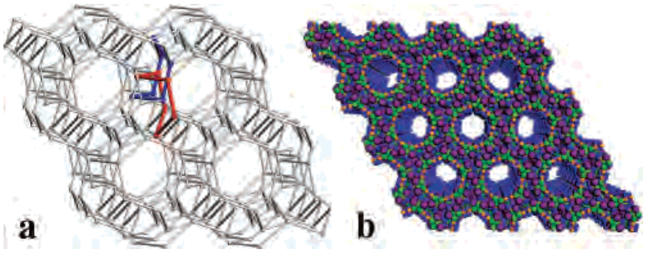

Figure 3. (a) Perspective view of the 3D (6, 6) net in structures along the *c* axis. Highlighted are the red ring and the blue ring interlocking each other. (b) Infinite 3D coordination framework of the title compound viewed along the [001] direction.

The structure analysis of the title compound shows that its structure reveals new topology. If the Cu_4I_4 cubane building block is assigned as a node and the DABCO organic ligand as a linker, the framework of the title compound displays a 3D four-connected net with 6^6 topology (Figure 3a). Traditionally, the frameworks constructed from four-connected tetrahedral nodes display diamond or diamond-related nets,[8] where all shortest circuits passing through one node are displayed as six-membered circuits with chair form. It is interesting that the framework of the title compound did not display diamond or diamond-related nets. In the title compound, there are five six-membered circuits with boat form and one planar six-membered form, the later being an unusual configuration.

An interesting and peculiar structural feature of the title compound is the presence of self-penetration. In this type of configuration, the shortest circuits are penetrated by rods of the same framework (the rods are shown in blue in Figure 3a). In the structure of the title compound, the other four six-membered circuits with boat form penetrate each six-membered circuit with boat form. In general, the topologies of nets of aluminosilicate zeolites and related metal phosphates do not show penetration, while the topologies of nets

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[8] Batten, S. R.; Robson, R. *Angew. Chem., Int. Ed.* **1998**, *37*, 1460.

of MOFs easily show interpenetration. Interpenetrating structures, which occupy positions of special importance in the area of entangled systems, are the subject of intensive current research. A vast range of intricate and fascinating structures with interpenetration features have been constructed and discussed comprehensively in some reviews.[8,9] These interpenetrating framework structures are constructed by two or more independent infinite networks, which interpenetrate each other. However, examples of self-penetration were relatively rare until recently, and the study of self-penetrating networks is still in its infancy.[10] The presence of self-penetration in the title compound has never been observed in the 6^6 nets, which may be attributed to the special configuration of the shortest circuits in the title compound.

A view down the [001] direction of the hexagonal cell of the title compound reveals three different types of one-dimensional (1D) channels. Three types of parallel channels form hexagonal, honeycomb arrays, which are similar to those of zeolite AFI[11] (Figure 3b). Ethanol guest molecules occupy the largest channels, and the presence of ethanol molecules has been confirmed by thermogravimetry. The transannular H···H distance of H atoms of two oppositely placed $-CH_2-$ groups of the DABCO ligands pointing toward the centers of the largest channels is 13.0 Å, which gives a major channel diameter of about 10.6 Å when the van der Waals radius of H (1.20 Å)[12] is taken into account. We used the Materials Visualizer module of the Materials Studio package to calculate the amount of void volume and its accessibility (whether guest molecules can be put into the structure from the outside). The calculation shows that the largest channels of the title compound are free for the guest molecules and the other two types of channels are not free. The total and accessible void volumes of the channels are estimated to be about 48.1% and 12.9%, respectively, of the volume of the unit cell. The van der Waals surface and accessible surface enclosing the void volumes are about 4956.74 and 593.84 Å^2/unit cell, respectively.

The title compound shows photoluminescence at room temperature in the solid state. The spectrum displays a single excitation peak with a maximum at 390 nm, leading to a broad yellow emission at 585 nm (Figure 4). The emission observed in the title compound cannot be assigned to MLCT (metal-to-ligand charge transfer) or LMCT (ligand-to-metal charge transfer) in nature and can be attributed to a triplet "cluster-centered" (^{3}CC*) excited state, which involves both the Cu_4 and I_4 tetrahedral units and has mixed iodide-to-metal charge transfer (^{3}XMCT*) and "metal cluster-centered" (^{3}MCC*; d^{10} Cu → d^9s^1 Cu) characters. The existence of a "metal cluster-centered" excited state is supported by a Cu···Cu nonbonding interaction of 2.650 Å for the title compound. The photoluminescence properties of the compound and the mechanism are similar to that of $Cu_4I_4L_4$ (L = ligand) cluster complexes, which have been investigated by the Ford group.[13]

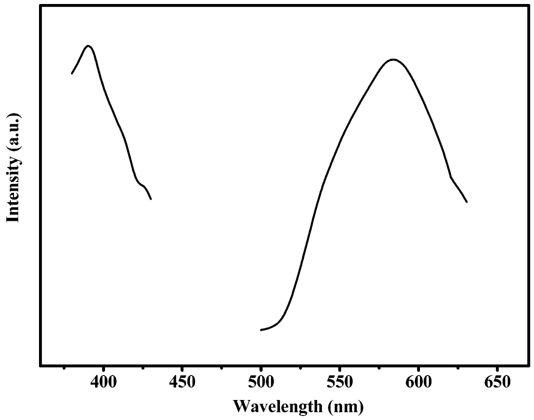

Figure 4. Emission and excitation spectra of the title compound: (left) excitation spectrum (k_{max} = 390 nm); (right) emission spectrum (k_{max} = 585 nm).

Thermal analysis performed under an air stream from 35 to 800 °C shows that the title compound is stable up to ca. 220 °C. The initial weight loss of the compound in the temperature range 90−155 °C is due to the removal of ethanol guest molecules (weight loss: 3.50%). Over the range 220−455 °C, the second and third steps of weight loss should correspond to the decomposition of DABCO ligands and the sublimation of iodine. Finally, the sample converts to CuO, which is stable in air.

In summary, we have described the novel features of an unprecedented 3D zeolite-like copper iodide constructed from $Cu_4I_4(DABCO)_4$ supertetrahedron units. This compound forms four-connected networks with novel 6^6 topology. Its structure reveals 1D channels along the [001] direction, and the framework displays interesting self-penetration. The title compound shows photoluminescence at room temperature in the solid state.

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Supporting Information Available: Crystal structure information (CIF) and more experimental details (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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