

Unique Three-dimensionally Expanded Nanoporous Structure Constructed with a Cu(I) and *cis,cis*-1,3,5-Triaminocyclohexane Having a 3-Fold Axial Symmetry

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Unique supramolecular crystal with a large macrocyclic channel structure has been prepared from the reaction of a $[\text{Cu}^{\text{I}}(\text{MeCN})_4]\text{SbF}_6$ and *cis,cis*-1,3,5-triaminocyclohexane with a three-fold axial symmetry, whose channel is constructed from a distorted pseudofive-fold axial symmetric ring with a pore size of $5 \times 12 \text{ \AA}^2$.

Design and synthesis of microporous materials such as the zeolites are of interest from the viewpoint of the molecular regulation at nanoscale level. The investigation of self-assembled coordination polymers consisted of metal ions and organic compounds has been proceeded extensively for a last decade.^{1,2} The advantage of the use of metal ions is that it is convenient to control a high dimensional structure by the geometric features characteristic of metal ions such as trigonal plane, tetragonal plane, and octahedron, although the counter ions accompanied by metal ions exert its effect for the structure framework, too.³ The high symmetry in the geometry often affords the microporous channel with a function such as gas adsorption and catalysis.⁴⁻⁸ These channels have almost hydrophobic environment because of the use of the ligands having aromatic ring such as pyridines and benzenes. Recently, Yaghi et al. have described that the topologies of structures with highly porous and robust metal-organic carboxylate frameworks can be predicted from the building units used. Here, we report the preparation of a new nanoporous material constructed from Cu(I) ion and *cis,cis*-1,3,5-triaminocyclohexane (TACH), where a Cu(I) ion prefers a trigonal planar structure and TACH ligand has a C_{3v} symmetry. The metal complex crystal that will be constructed from these building parts is anticipated of a higher symmetric structure such as a honeycomb structure, if the design concept of Yaghi et al. is also applicable for this system. However, the crystal obtained gave a curious three-dimensionally expanded nano porous structure with a large macrocyclic ring.

To an absolute methanol solution of $[\text{Cu}^{\text{I}}(\text{MeCN})_4]\text{SbF}_6$ was added the same solution of TACH under argon atmosphere,^{9,10} which was stirred for 10 min. The standing of the reaction solution for several days afforded $\{[\text{Cu}^{\text{I}}(\text{TACH})]\text{SbF}_6\}_n$ (**1**) as a colorless crystal suitable for X-ray diffraction measurement. The complex **1** is quite stable, although the Cu(I) complexes are generally air-sensitive. **1** crystallizes in the cubic system with space group $P2_13$, and the independent atoms in the unit cell are one-third parts of $[\text{Cu}^{\text{I}}(\text{TACH})]\text{SbF}_6$, in which Cu(I), the center of TACH molecule, and Sb atom of SbF_6^- anion are on a three-fold axis.¹¹ The geometry around the Cu(I) ion, as was expected from the higher symmetry in the crystal system, cubic, has a trigonal planar structure with coordination of three amine nitrogen atoms from three TACH molecules, in which the cyclohexane ring takes a chair form with a three-fold axis and the three amino groups orient

toward the equatorial direction because of its *cis,cis*-conformation. This is in contrast to the crystal structures that other TACH complexes with Ni(II) or Cu(II) ion are a capped type coordinated by axially-oriented amino groups of the ligand.^{12,13} The bond length of Cu–N is $2.023(4) \text{ \AA}$, which is similar to those of the copper(I) complexes with aliphatic amino ligands reported hitherto.¹⁴ The nearest Cu–Cu distance, which corresponds to one side length of a triangle formed by three Cu(I) atoms around one TACH molecule, is $7.4777(9) \text{ \AA}$. The expansion of three amino groups of TACH toward the equatorial direction contributes to formation of an infinite network structure through the linkage with the Cu(I) ions, as is described below.

The crystal structure contains two interesting structural features as follows. One is the formation of a three-dimensionally expanded nanopore having an infinite channel structure with a hole size of $5 \times 12 \text{ \AA}^2$.¹⁵ The counter anion SbF_6^- is weakly linked with the amino groups of the nanopore. Figure 1 represents the crystal structure viewed from the crystallographic *ab* plane, the same of which is also obtained from the *bc* and *ac* planes as is expected from the crystal system of cubic. The channel size is considerably larger in comparison with the Cu(I) ion-containing coordination polymers reported hitherto.^{16,17} Moreover, it is very interesting that this channel has a right-handed herical structure that is attributed to the crystallographically-occurring 2_1 -screw axis. It is likely that the channel is structurally robust because the sides of single strand are also connected by other TACH molecules.

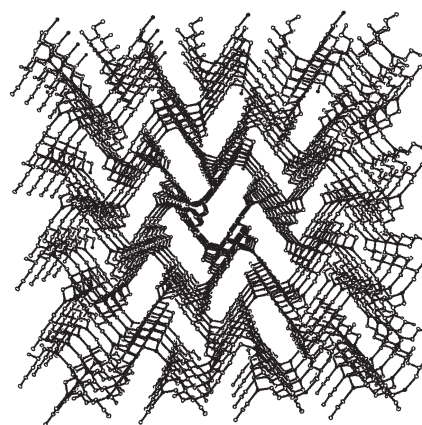


Figure 1. View of the infinite channel structure of **1** along the *c* axis, showing 30% probability thermal ellipsoids. The counter anions (SbF_6^- is weakly trapped with hydrogen bonding distances of $\text{F} \cdots \text{N} = 3.11 \text{ \AA}$) and hydrogen atoms except for amino groups are omitted for clarity.

The second remarkable structural feature is that the nanopore described above has a curious shape. The minimum unit of

nanopore of **1** forms a large macrocyclic ring constructed from five Cu(I) ions and five TACH molecules, as shown in Figure 2, whose large ring is not flat but wounded. The whole structure, as shown in Figure 1, has a streamlined shape. As described above, the used components, Cu(I) and TACH, were a building unit that leads to the formation of the compound with a three-fold axial symmetry. However, the nanopore revealed by the crystal structure analysis shows a distorted pseudofive-fold axial symmetry, which is quite unique. Because the crystallography teaches that the five-fold axis of rotation and five-fold axis of rotatory inversion are not present theoretically. Figure 3, which shows the view from the apex of the cubic cell, will give the solution for the question that the large macrocyclic ring with the distorted pseudofive-fold axial symmetry is prepared from the building units with a three-fold axial symmetry. The careful observation of this crystal structure exhibited that the center of TACH and Cu(I) ion lie on the same three-fold axis and both contribute to the formation of the large macrocycles. The three bonds expanded from the Cu(I) atom toward the planar triangular directions are connected to the three amino groups of the downward TACH molecule to form three macrocyclic rings, which are also used for the formation of another three rings expanded horizontally. The structure viewed from the three-fold

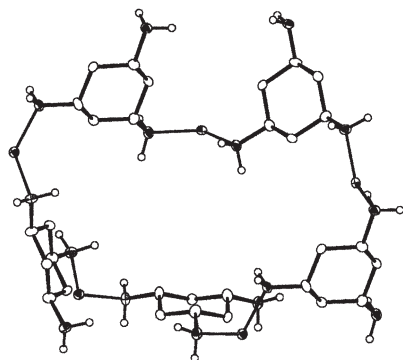


Figure 2. ORTEP view of the macrocyclic ring unit of **1** with a distorted pseudofive-fold axial symmetry, showing 30% probability thermal ellipsoids. The counter anions and hydrogen atoms except for amino groups are omitted for clarity.

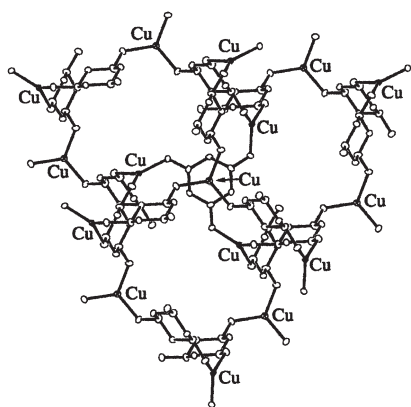


Figure 3. ORTEP view looking down from the apex of the cubic cell in **1**, showing 30% probability thermal ellipsoids. The counter anions and hydrogen atoms except for amino groups are omitted for clarity.

axis is a propeller-like one having six wings of macrocycles for the horizontal and vertical directions.

We succeeded in the preparation of an infinite right-handed single helical channel with a large nanopore. The macrocycle as a minimum unit of channel has a distorted pseudofive-fold axial symmetry, in which the large robust pore has been supported by other TACH molecules. These findings suggest that the use of lower symmetric building units leads to the formation of robust channel, one of most important factors in appearance of the functions.

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