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1D Helical Polymeric Chain with a Pseudo-5_3 Screw Axis Formed by Cuprophilicity. Synthesis and Crystal Structure of Copper(I) Pivalate

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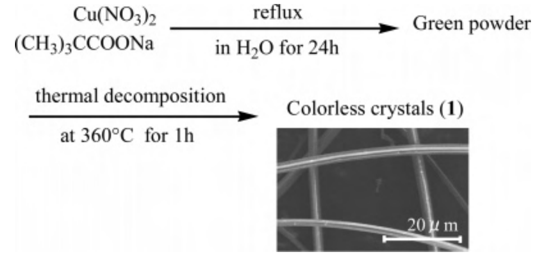
A coordination polymer, $[Cu_5(piv)_5]_n$ (piv = pivalate), was prepared by a thermal decomposition method. The unit cell of the crystal structure consisted of one right-handed helical chain and one left-handed helical chain, which were formed by an alternation of Cu^I ions and carboxylate (O–C–O) groups. This chain possessed a pseudo-5_3 screw axis; the second-order structure was suggested to be realized by a balance between the cuprophilicity and a steric effect of the *tert*-butyl groups.

The attractive interactions between closed-shell d^{10} metal ions have received considerable attention because they play an important role in the structural, optical, and electronic properties of polynuclei d^{10} metal complexes.[1−3] This behavior has been frequently observed in Au, with the term “aurophilicity” being used to describe Au^I-Au^I interactions that are theoretically attributed to correlation and relativistic effects.[4−7] The occurrence of analogous metallophilic effects has been found even in lighter Cu atoms, while most structurally characterized complexes featuring Cu^I-Cu^I interactions, namely, “cuprophilicity”, are associated with the other structure-controlling factors, such as ligand bridging, H bonding, electrostatic interaction, $\pi-\pi$ stacking, etc.[6−15] Here we report a novel topology of Cu^I self-assemblies formed by cuprophilicity; we describe the thermal-decomposition synthesis of $[Cu_5(piv)_5]_n$ (**1**; piv = pivalate) and its unusual crystal structure.

Scheme 1. Synthetic Route and SEM Image for **1**



The synthetic route for **1** is shown in Scheme 1. Sodium pivalate (30 mmol) was added to an 80-mL aqueous solution of $Cu(NO_3)_2{\cdot}3H_2O$ (8 mmol). During stirring for 1 h at 100 °C, a green powder precipitated gradually. This color suggested the existence of Cu^{II}. While the characterization of this material was unsuccessful, crystallization from 1-propanol gave a 16-nuclei Cu^{II} cluster **2**.[16] Thermal decomposition of the green powder material was performed in a glass tube at 360 °C under a stream of N_2 gas for 1 h, according to a method reported previously.[17] Air-sensitive

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(16) Sugiura, T.; Yoshikawa, H.; Awaga, K., unpublished data. The green rhombic crystals of a 16-nuclei Cu^{II} cluster **2**, $[Cu_{16}(\mu_4\text{-}O)_4(\mu_4\text{-}OH)_2(\mu_2\text{-}OH)_2(piv)_{12}(1\text{-}pro)_8]{\cdot}3(1\text{-propanol})$ (piv = pivalate, 1-pro = 1-propylate), were grown from 1-propanol in a few days with a yield of ca. 20%. Because this process is accompanied by ligation of 1-pro derived from 1-propanol, it is not a simple recrystallization. Figure S1 in the Supporting Information shows the crystal structure of **2**, in which all of the Cu ions are divalent. The IR spectrum of **2** is similar to that of the parent green powder. CCDC 255839 contains the supplementary crystallographic data for **2**. It can be obtained free of charge via www. ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, U.K. CB2 1EZ; fax (+44)1223-336-033 or e-mail deposit@ccdc.cam.ac.uk).

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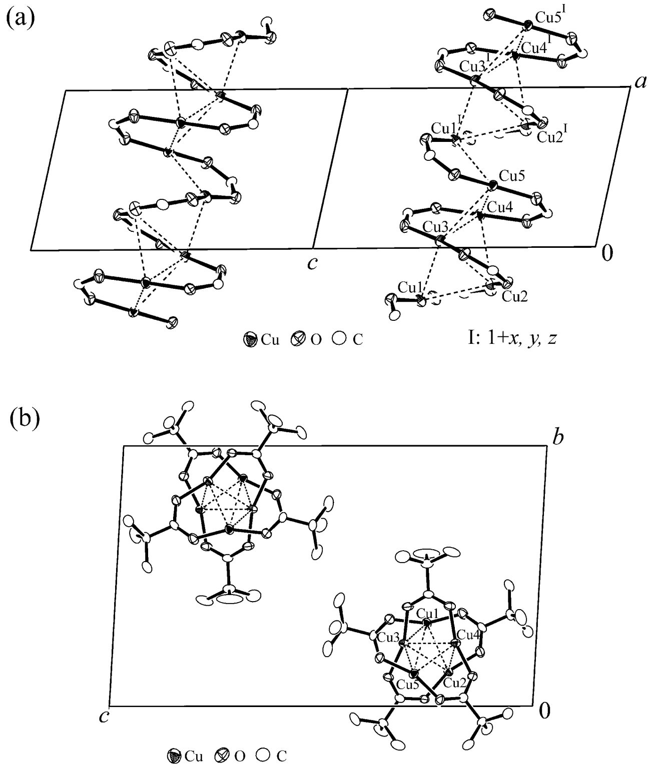

Figure 1. Projections of the unit cell of **1** along the [01$\bar{1}$] direction (a) and along the *a* axis (b). In the former, the *tert*-butyl groups are omitted for simplicity. Selected Cu^I-Cu^I distances [Å]: Cu1−Cu2 = 2.871(2), Cu1−Cu3 = 2.892(2), $Cu1^I-Cu5$ = 2.897(2), Cu2−Cu3 = 2.874(2), Cu2−Cu4 = 2.902(2), Cu3−Cu4 = 2.850(2), Cu3−Cu5 = 2.962(2), Cu4−Cu5 = 2.853(2). The symmetry code is as follows: I, 1 + *x*, *y*, *z*.

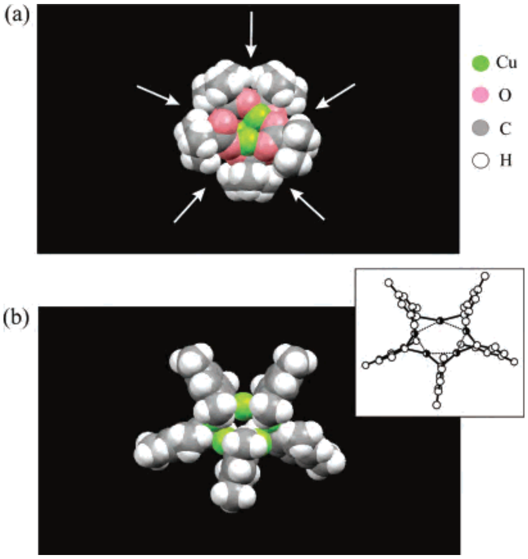

Figure 2. Comparison between the space-filling views of the structures of **1** (a) and **3** (b). The latter figure was produced using the data in ref 21 solely for the purposes of comparison.

colorless single crystals of **1** were sublimed onto the inner surface of the tube (yield: ca. 10%), together with decomposed metallic Cu. Scheme 1 includes a scanning electron microscopy (SEM) image for **1**, showing whiskers with a diameter of ca. 1 μm. This diameter varied from 0.1 to 10 μm, depending on the sublimation conditions, such as the decomposition temperature and the flow rate of N_2 gas. The X-ray photoemission spectroscopy (XPS) spectrum of **1** (Figure S2 in the Supporting Information) is very similar to that of a commercial Cu_2O, indicating that only Cu^I ions existed within it. This means that the thermal decomposition included the reduction of Cu^{II} into Cu^I, though it is hard to rationalize this reaction mechanism. Because the removal of the bridged O from the $Cu^{II}-O-Cu^{II}$ complexes at 500 K is known to be associated with the reduction of Cu^{II},[18] a similar process might happen in the present reaction.

X-ray crystallography of a crystal of **1** (0.3 × 0.01 × 0.01 mm) revealed that this material crystallized into triclinic space group $P\bar{1}$,[19] where an asymmetric unit consisted of five Cu^I ions and five piv ligands. Parts a and b of Figure 1 depict the projections of the unit cell along the direction of [01$\bar{1}$] and along the *a* axis, respectively; the *tert*-butyl groups are omitted from Figure 1a for simplicity. Interestingly, the crystal structure consisted of one right-handed cylindrical chain and one left-handed cylindrical chain along the *a* axis, which were formed by an alternation of Cu^I ions and carboxylate (O−C−O) groups. The first-order structure of these infinite chains is formed by the coordination bonding between them. The top view of the chain (Figure 1b) indicates a pentagon of Cu^I; there is a noncrystallographic 5-fold screw axis along the chain. Because the $C_5{}^1$ rotation corresponds to the 3/5 translation along the helical chain, this symmetry can be regarded as a pseudo-5_3 screw axis.

The broken lines in Figure 1 indicate Cu^I-Cu^I distances shorter than 3 Å due to cuprophilicity. It is notable that the neighboring Cu^I ions on the 1D chain are always connected by the cuprophilicity, while the cuprophilicity sometimes operates even between the second neighbors. It is clear that the cuprophilicity determines the conformation of the neighboring Cu^I ions and forms the second-order structure of this 1D coordination polymer. The cuprophilicity has sometimes been observed as a discrete interaction in Cu^I polymeric structures formed by other structure-controlling factors,[20] but, to our knowledge, the present structure is one example of a Cu^I polymeric structure in which the Cu^I ions are linked by the cuprophilicity.

Next, we will discuss the formation mechanism of the helical chains in **1**, in comparison with a pentagonal-shaped

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(19) Crystal data for **1**: $C_{25}H_{45}Cu_5O_{10}$, *M* = 823.31, triclinic, space group $P\bar{1}$ (No. 2), *a* = 6.353 (2) Å, *b* = 13.136(5) Å, *c* = 21.035(8) Å, α = 92.067(4)°, β = 95.692(6)°, γ = 101.207(7)°, *U* = 1711(1) Å^3, *Z* = 2, D_c = 1.598 g cm^{-3}, μ(Mo Kα) = 3.103 mm^{-1}, GOF = 1.130, and 361 variables. The final *R* factor was 0.0885 (wR2 = 0.2323 for all data) for 5568 reflections with $I_0 > 2\sigma(I_0)$. CCDC 608993 contains the supplementary crystallographic data for **1**. It can be obtained free of charge via www. ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, U.K. CB2 1EZ; fax (+44)1223-336-033 or e-mail deposit@ ccdc.cam.ac.uk).

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Cu^I cluster, $[Cu^I_5(2,4,6\text{-}Me_3C_6H_2)_5]$[21] (**3**; see the inset of Figure 2b). The pentagonal molecular structure of **3** has been shown to be formed by the cuprophilicity.[20] Parts a and b of Figure 2 show the space-filling views of **1** and **3**, respectively. The helical chain in **1** has a core−shell structure, in which the coordination chain formed by the cuprophilicity is surrounded by the organic *tert*-butyl groups. The space-filling view of **1** clearly indicates superpositions of the neighboring *tert*-butyl groups on the chain, as indicated by arrows. In contrast, the mesityl groups in **3** have no mutual overlap because of their propeller-like conformations. It is considered that the helical chain structure of **1** is realized by a balance between the Cu^I-Cu^I interactions and the steric effect between the *tert*-butyl groups.

It is worth noting the optical properties of **1**. We tried to record the luminescence of **1** using an optical parametric oscillator laser, but this material did not exhibit detectable emission in the solid state. Because most luminescent Cu^I complexes with cuprophilicity have pyridine or phosphine ligands,[22] the pivalate ligand in **1** would quench the emission. Another possibility is the infinite structure of **1**; all of the Cu^I ions are directly linked by the cuprophilicity in the chains. This may enhance the energy flow from the excited states to the thermal bath, i.e., the nonradiative decay.

In summary, the material **1** was synthesized by the thermal decomposition method. The crystal consisted of right- and left-handed cylindrical chains in which the second-order structure was formed by cuprophilicity. This structure was suggested to be realized by a balance between the cuprophilicity and the steric effect between the bulky ligands.

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Supporting Information Available: Crystallographic data (CIF) of $[Cu_5(piv)_5]_n$, crystal structure of a 16-nuclei cluster **2** (Figure S1), and XPS spectrum of **1** (Figure S2). This material is available free of charge via Internet at http://pubs.acs.org.

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