Self-Assembly of the First Copper(II) Infinite 2D Network with Large Cavities Formed between the Two Adjacent Layers

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Introduction

In the past decade, considerable progress has been achieved in controlling the assembly and orientations of individual molecules in structures with specific network topologies and potentially interesting properties including molecular recognition, inclusion, etc.[1] Such progress makes possible the rational design and synthesis of supramolecules with one-, two-, or three-dimensional networks which contain channels or cavities of various sizes and shapes. Tridentate ligands have been proved to be one of the most important ligands in the design and construction of frameworks with honeycomb and cagelike topologies.[2−5] For example, 1,3,5-tris(4-pyridylmethyl)benzene gives an M_3L_2 type cage by assembly with $Pd(en)(NO_3)_2$ (en = ethylenediamine).[4a] While in the case of 1,3,5-tris(pyrazol-1-ylmethyl)-2,4,6-triethylbenzene, an M_6L_4 type cage was obtained by reaction of the ligand with $PdCl_2$.[5] Assembly of 2,4,6-tris(4-pyridyl)-1,3,5-triazine with $Pd(en)(NO_3)_2$ also produces an M_6L_4 cage.[4b] Most recently, Robson et al. reported an $M_{12}L_8$ type cage obtained by assembly of Cu(II) with a tris-bidentate ligand.[6] The results imply that the assembly of the framework strongly depends on the nature of the ligands as well as the metal ions.

To investigate the relationship between the topology of the assembly and the nature of the ligand and also to develop a new type of three-connecting ligand, we designed a tripodal ligand containing imidazolyl instead of the reported pyrazolyl and pyridyl groups: 1,3,5-tris(imidazol-1-ylmethyl)-2,4,6-trimethylbenzene (titmb). Such a ligand can adopt different conformations when it interacts with metal ions as shown in Chart 1. Complexes with specific topologies such as a two-dimensional (2D) network or cagelike structure can be expected to be obtained by reactions between the titmb ligand having the *cis,cis,cis* conformation and metal ions. Here we report the first example of an infinite 2D copper(II) network complex, $[Cu_3(titmb)_2(OCOCH_3)_6]_n(H_2O)_n$, with alternating "buckets" and upside down "buckets" which form large cavities through the interlayer $\pi-\pi$ and hydrogen-bonding interactions. These types of complexes were predicted to have specific properties, e.g. the inclusion of small molecules, as well as fascinating molecular structures.[3]

Experimental Section

Solvents were purified by standard methods prior to use. 1,3,5-Tris(bromomethyl)-2,4,6-trimethylbenzene was synthesized according to the reported procedures.[7]

Self-Assembly of $[Cu_3(titmb)_2(OCOCH_3)_6]\cdot H_2O$. The tripodal ligand 1,3,5-tris(imidazol-1-ylmethyl)-2,4,6-trimethylbenzene (titmb) was prepared by a procedure similar to that for 1-benzylindole using 1,3,5- tris(bromomethyl)-2,4,6-trimethylbenzene and imidazole under alkaline conditions.[8] Its copper(II) complex was synthesized by spontaneous assembly from the titmb ligand (0.1 mmol) and copper(II) acetate (0.05 mmol) in methanol solution (20 mL). Crystals of $[Cu_3(titmb)_2(OCOCH_3)_6]_n(H_2O)_n$ suitable for X-ray analysis were obtained by slow diffusion of diethyl ether into the methanol solution. Yield: 32%. Anal. Calcd for $C_{54}H_{66}N_{12}O_{12}Cu_3$ $[Cu_3(titmb)_2(OCOCH_3)_6]$: C, 51.23; H, 5.25; N, 13.27. Found: C, 51.20; H, 5.18; N, 13.33.

Crystallographic Analysis of $[Cu_3(titmb)_2(OCOCH_3)_6]\cdot H_2O$. A violet prismatic crystal of dimensions 0.22 × 0.22 × 0.24 mm was mounted in a glass capillary. All measurements were performed on a Rigaku AFC5R diffractometer with graphite-monochromated Mo Kα radiation, using an $\omega-2\theta$ scan mode. The data were collected at 296(2) K. The structure was solved by direct methods with SHELXS-86 and refined by full-matrix least-squares calculations on F^2 with SHELXL-93.[9,10] All non-hydrogen atoms were refined anisotropically, whereas the hydrogen atoms except for those of the water were generated geometrically. All calculations were performed on a PC-586 computer using the Siemens SHELXTL program package.[11,12] Crystal parameters and data collection and refinement details are listed in Table 1, and selected bond distances and angles are given in Table 2.

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Chart 1

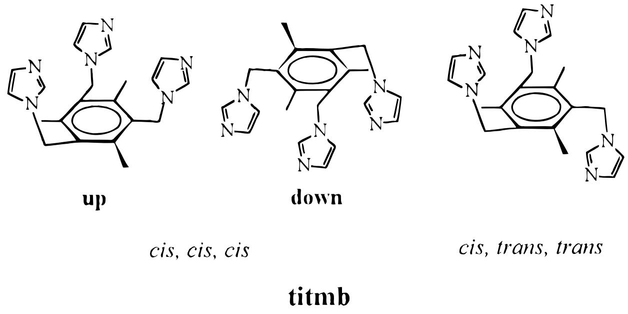

Table 1. Crystal Data and Structure Refinement Parameters for $[Cu_3(titmb)_2((OCOCH_3)_6]\cdot H_2O$

empirical formula	$C_{54}H_{68}Cu_3N_{12}O_{13}$	γ, deg	120.00
fw	1283.83	V, Å^3	4422.5(12)
space group	$R\bar{3}$ (No. 148)	Z	3
T, K	296(2)	ρ_{calcd}, g cm^{-3}	1.466
λ(Mo Kα), Å	0.710 73	μ mm^{-1}	1.146
a, Å	15.539(2)	R1[a]	0.0446
b, Å	15.539(2)	wR2[b]	0.1238
c, Å	21.149(4)		

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (0.0785P)^2 + 2.3469P]$; $P = (F_o^2 + 2F_c^2)/3$.

Table 2. Selected Bond Distances (Å) and Bond Angles (deg) for $[Cu_3(titmb)_2((OCOCH_3)_6]\cdot H_2O$

Cu1B−N1B	1.998(3)	Cu1B−N1C	1.998(3)
Cu1B−O1B	1.937(2)	Cu1B−O1C	1.937(2)
O1B−Cu1B−O1C	180.0	N1B−Cu1B−N1C	180.0
O1C−Cu1B−N1B	90.61(11)	O1B−Cu1B−N1B	89.39(11)
C1B−N1B−Cu1B	127.1(2)	C3B−N1B−Cu1B	128.0(3)
C8B−O1B−Cu1B	113.8(2)		

Physical Measurements. Elemental analyses were carried out on a Perkin-Elmer 240C elemental analyzer, at the Center of Materials Analysis, Nanjing University. Infrared (IR) spectra were recorded on a Nicolet FT-IR 170SX spectrophotometer using KBr disks. ESR spectra of the powder and the 50% (v/v) acetonitrile aqueous solution of the complex were measured on a Bruker ER200D-SRC spectrometer at room temperature and 110 K, respectively. Reflectance spectra for the solid state and electronic spectra for the complex in 50% acetonitrile aqueous solution were obtained on a Shimazu 240 spectrophotometer.

Results and Discussion

Assembly and Structure of $[Cu_3(titmb)_2(OCOCH_3)_6]\cdot H_2O$. The complex $[Cu_3(titmb)_2(OCOCH_3)_6]\cdot H_2O$ was obtained by treatment of $Cu(OCOCH_3)_2$ with the titmb ligand in methanol solution. The molecular structure of $[Cu_3(titmb)_2(OCOCH_3)_6]\cdot H_2O$ determined by single-crystal X-ray crystallography is shown in Figure 1a, along with its atom-labeling scheme. All the copper atoms have identical coordination environments with two imidazole nitrogen atoms from two different titmb ligands and two oxygen atoms from two acetate anions. The CuN_2O_2 chromophore is trans square planar for each copper site since the bond angles O1B−Cu1B−O1C and N1B−Cu1B−N1C are both 180° and O1B−Cu1B−N1B and O1C−Cu1B−N1B are 89.39(11) and 90.61(11)°, respectively (Table 2). On the other hand, each titmb ligand coordinated to three different copper atoms and the titmb ligands are in cis,cis,cis conformations with "up" and "down" orientations (Chart 1 and Figure 1a). The atoms of each benzene ring are almost coplanar since the deviations are less than 0.015 Å. However, the carbon atom of each methylene group (C4, C4A, C4B, etc.) is out of the benzene ring plane with a deviation of 0.22 Å in the opposite direction of the imidazole groups and the angle N2−C4−C5 is 115.2(3)° while the methyl carbons, e.g. C7, C7A, C7B, etc., are in the plane of benzene ring to which they attached (Figure 1a). As shown in Figure 1a, the two benzene ring planes of the two titmb ligands with "up" and "down" orientations and the plane containing copper atoms Cu1, Cu1A, Cu1B, Cu1C, and Cu1D are strictly parallel with each other. The distance between these two benzene rings is 10.00 Å, and the plane of copper atoms is at the middle of the two benzene ring planes; i.e., each copper atom is out of the benzene ring plane by distance of 5.00 Å.

The unit shown in Figure 1a can be repeated and joined by copper(II)−imidazole coordination bonds to generate an infinite two-dimensional network which spreads out along the *ab* plane (Figure 1b,c). In this network, all the titmb ligands are arranged in alternating "up" and "down" conformations which look like "buckets" and upside down "buckets", respectively. The benzene ring of each titmb ligand forms the bottom of a "bucket" and six imidazole groups, three of which are from one titmb ligand and three of which are from three different titmb ligands, three copper atoms, and three acetate anions which coordinate to the same titmb ligand from the wall of the "bucket" (Figure 1d).

The packing arrangement of the interlayers of the two-dimensional sheets is illustrated in Figure 2. The layers repeat in an - - -ABCABC- - - stacking sequence along the *c* axis. A view from the *b* axis and a schematic drawing with marked distances of the ABC stacking sequence are exhibited in Figure 2, parts a and b, respectively. The bucket of layer A and the upside down bucket of layer B assume a face-to-face orientation to form a large cavity which contains a disordered (two positions) water molecule with a distance of 7.65 Å between the oxygen atom of water and the benzene ring of the titmb ligand (the bottom of the cavity) as shown in Figure 2c. Up to now, no species with such a large cavity has been obtained by using flexible tripodal ligands such as 1,3,5-tris(4-pyridylmethyl)benzene and 1,3,5-tris(pyrazol-1-ylmethyl)benzene.[4a,5] The length of the cavity d_1 equals the distance (17.05 Å) between two benzene rings of the "up" titmb ligand of layer A and the "down" titmb ligand of layer B which orientate in a staggered conformation with an angle of 60° (Figure 2). The distance d_2 between the two benzene rings of the "up" titmb ligand of layer A and the "up" titmb ligand of layer B is 7.05 Å. The "down" titmb ligand of layer A and the "up" titmb ligand of layer C, which are in a back-to-back orientation, fill the Cu_6 hexagon hole of layer B (vide infra), and the distance d_3 of 4.10 Å between the two benzene rings of these two titmb ligands indicates that there are weak $\pi-\pi$ interactions between the two benzene rings of the two layers A and C (Figure 2a,b). Thus there are no open channels in the crystal of $[Cu_3(titmb)_2(OCOCH_3)_6]_n(H_2O)_n$. The copper atoms in adjacent layers are separated by 7.05 Å (d_4 in Figure 2b). In addition to the above $\pi-\pi$ interactions, one C−H- - -O=C hydrogen-bonding interaction formed between one of two methylene C−H groups of one layer and the O=C carbonyl of the acetate of the adjacent layer with a C- - -O distance of 3.31 Å (see Supporting Information, Figure 1S) also plays an important role in determining the interlayer packing arrangement.

In addition, six titmb ligands and six copper atoms in the same layer form a 72-membered macrocycle to generate large holes which are occupied by the bottom of the "bucket" of the adjacent layers as described above, and the six copper atoms form a planar hexagon. On the other hand, three copper atoms coordinated to the same titmb ligand form an equilateral triangle (Cu1A, Cu1B, and Cu1C in Figure 1b). Figure 1c shows the two-dimensional sheet where only the copper atoms are presented. This is a honeycomb-like network consisting of the

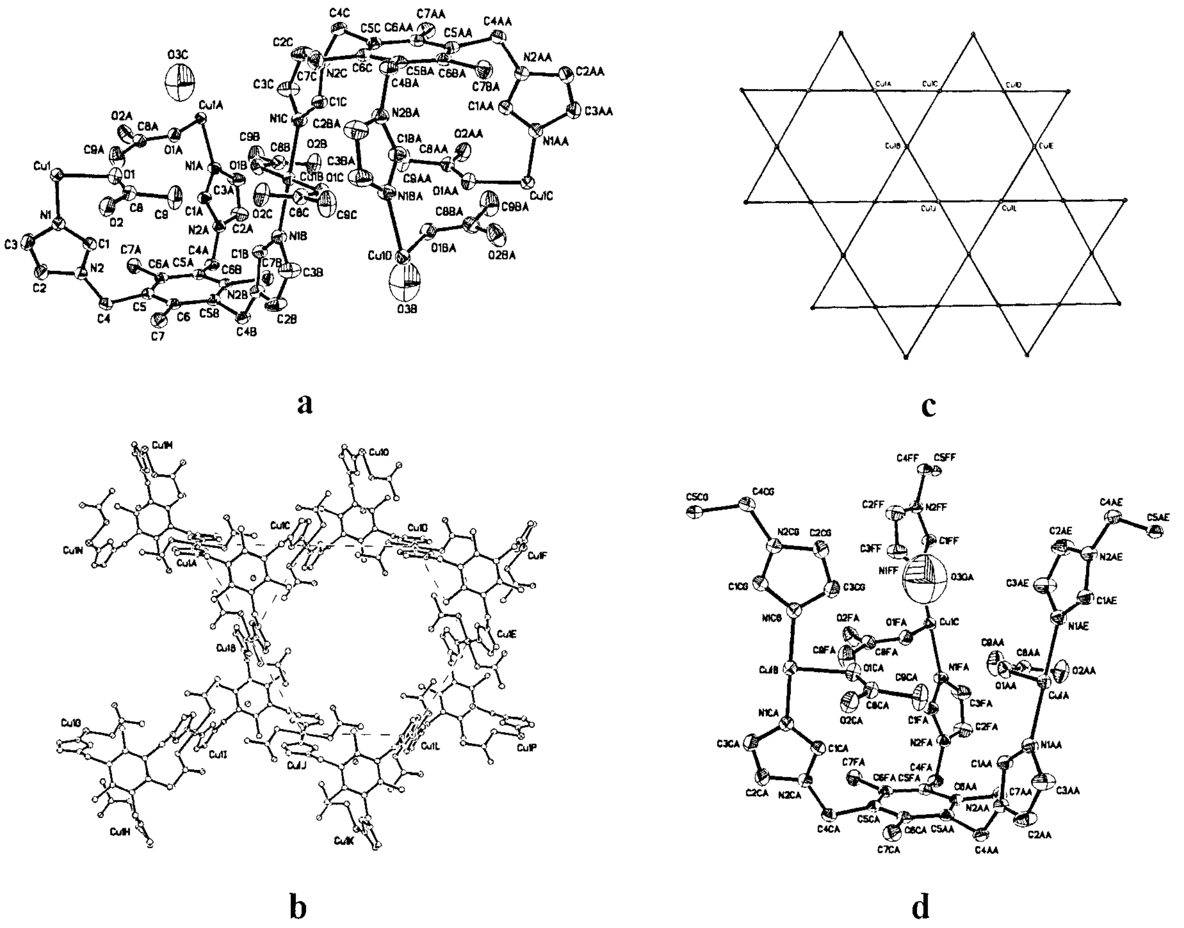

Figure 1. (a) Molecular structure of $[Cu_3(titmb)_2(OCOCH_3)_6]\cdot H_2O$. Thermal ellipsoids are drawn at 50% probability, and hydrogen atoms are omitted for clarity. (b) A 72-membered macrocycle with a Cu_6 hexagon and a Cu_3 triangle (dashed lines). The perspective view is in the *ab* plane. (c) The two-dimensional sheet consisting of the six-membered rings where only the copper(II) atoms are presented. (d) Side view of a "bucket".

Cu_6 hexagons and Cu_3 triangles while the honeycomb sheets reported as $[Ag(TCB)(CF_3SO_3)]$ (TCB = 1,3,5-tricyanobenzene) and $[Cu^I_2(pz)_3(SiF_6)]_n$ (pz = pyrazine) only contain hexagons.[3a,13] Furthermore, in the reported cases, the metal ions used in construction of honeycomb complexes are limited to monovalent ions such as copper(I) and silver(I).[2,3a,13] The distance between two adjacent copper atoms in the 2D network is 7.77 Å, and the angle formed by three adjacent copper atoms, e.g. Cu1B−Cu1C−Cu1D, is 120° within the Cu_6 hexagons. This means each Cu_6 motif is a perfect hexagon. The cavity of each Cu_6 honeycomb hexagon has a diameter of 15.54 Å. The size of this cavity is larger than those reported previously. $[Ag(TCB)(CF_3SO_3)]$ creates honeycomb cavities of 10.03 Å diamters, and $[Cu^I_2(pz)_3(SiF_6)]_n$ has honeycomb grids with bridged copper(I) cations 6.936 and 6.685 Å apart in a Cu_6 hexagon.[3a,13]

Properties. The structure of supramolecular networks of the titled complex suggests a porous structure which contains guest water molecules. It is important that such a porous structure should be stable even after removal of guest molecules in view of the development of molecular-based materials. TGA and DTA of the crystalline sample of $[Cu_3(titmb)_2(OCOCH_3)_6]_n(H_2O)_n$ showed the loss of guest water molecules at 181 °C. The X-ray powder pattern of the crystals after removing the water molecules showed that they remained identical to the original crystals. After removal of H_2O, we tried diffusion of new guest molecules into the crystals of $[Cu_3(titmb)_2(OCOCH_3)_6]_n$, and it was found that iodine (I_2) molecules could enter the porous $[Cu_3(titmb)_2(OCOCH_3)_6]_n$, which was confirmed by elemental analysis, but the X-ray powder pattern analysis indicates that the crystallinity is not preserved upon diffusion of I_2. This is because the I_2 molecule is too large to maintain the original porous structure.

The complex shows carboxyl antisymmetric (ν_{asym}) and symmetric (ν_{sym}) vibrations at 1592 and 1388 cm^{-1} in the infrared (IR) spectrum, respectively. The large separation between the ν_{asym} and ν_{sym} frequencies indicates the coordination of the acetate anion to the copper atom is monodentate.[14,15] The result is in agreement with the crystal structure. In the solid-state electronic reflectance spectra, a band maximum at 560 nm (17 860 cm^{-1}) and a lower energy shoulder at 660 nm (15 150 cm^{-1}) were observed.[16] A similar absorption maximum was also observed for the complex in solution. The electronic spectra of the titled complex in aqueous solution at room temperature shows a band maximum at 650 nm (15 380 cm^{-1}) which is due to the Cu(II) d−d transition. $[Cu^{II}(OCOH_3)_2(2\text{-}MeIm)_2]$ (2-MeIm = 2-methylimidazole) exhibits a d−d transition at 675 nm in methanol solution.[14]

The ESR spectra of $[Cu_3(titmb)_2(OCOCH_3)_6]_n(H_2O)_n$ recorded at 110 K and at room temperature (298 K) in aqueous solution

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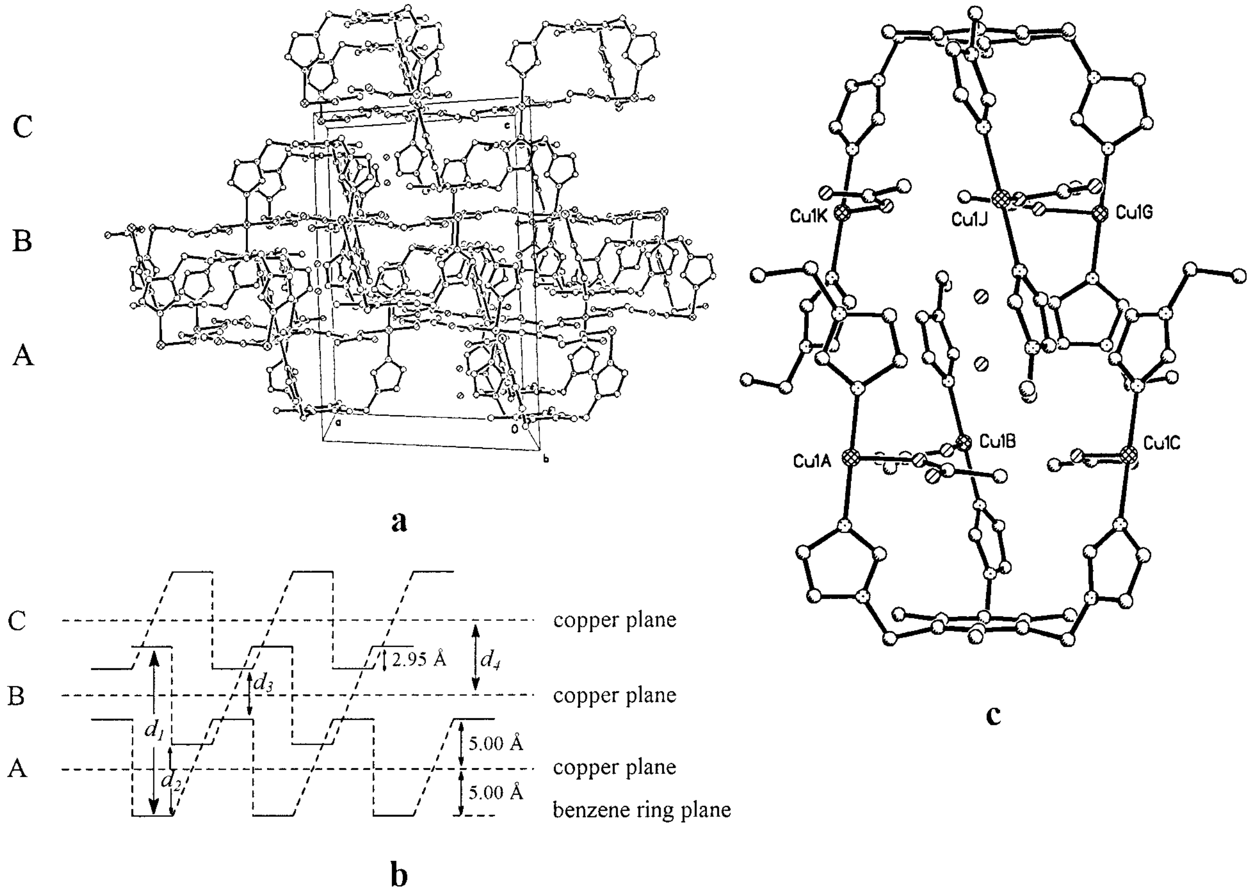

Figure 2. (a) Side view of the three layers in the *ac* plane, (b) schematic drawing of the ABC stacking sequence with distances marked, and, (c) normal and upside down "buckets" forming a large cavity containing a disordered water molecule in the packing arrangement of $[Cu_3(titmb)_2(OCOCH_3)_6]_n(H_2O)_n$.

show clear resolution of hyperfine structures with the following parameters: $g_{\text{iso}} = 2.155$, $A_{\text{iso}}(\text{Cu}) = 0.0078\ \text{cm}^{-1}$, $A_{\perp}(\text{N}) = 0.0014\ \text{cm}^{-1}$, $g_{||} = 2.260$, $A_{||}(\text{Cu}) = 0.0176\ \text{cm}^{-1}$, $g_{\perp} = 2.102$. The results confirm the square planar coordination of copper(II) by two nitrogen and two oxygen atoms for the CuN_2O_2 chromophore.[17]

The results described here demonstrate that the flexible tripodal titmb ligand is a new type of three-connecting ligand and will afford new types of framework complexes. The cis,cis, cis conformation of the titmb ligand, the weak $\pi-\pi$ interactions, and C−H- - -O═C hydrogen-bonding interactions are considered to play important roles in the self-assembly of $[Cu_3(titmb)_2(OCOCH_3)_6]\cdot H_2O$. Further studies of reactions between the titmb ligand and other metal ions are in progress in our laboratory.

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Supporting Information Available: A side view of the three layers of $[Cu_3(titmb)_2(OCOCH_3)_6]\cdot H_2O$ (Figure 1S) in the *ac* plane with C−H- - -O═C hydrogen bonding indicated by dashed lines and an X-ray crystallographic file in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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