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Crystal and molecular structure of $[Cu_2(3,5\text{-dihydroxybenzoate})_4\ (\text{acetonitrile})_2] \cdot 8H_2O$

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The crystal and molecular structure of the title compound, $[Cu_2(3,5\text{-dihydroxybenzoate})_4 (\text{acetonitrile})_2] \cdot 8H_2O$ **1**, is reported. Crystal data for **1**: tetragonal, space group I 4/m, $a = 11.720(2)$ Å, $c = 15.304(3)$ Å, $V = 2102.4(6)$, and $D_c = 1.53$ g/cm^3, for $Z = 2$. The metal and organic components crystallize to form a Cu paddle-wheel complex, of idealized D_{4h} symmetry, that assembles in the solid-state, along with eight equivalents of water, to form a 3D hydrogen-bonded network held together by O—H···O hydrogens bonds. The metal complexes pack to form a 2D layered structure.

KEY WORDS: paddle-wheel complex; hydrogen-bonding; layered structure.

Introduction

Molecules that function as linear templates are emerging as tools for controlling reactivity in both solution and the solid-state.[1–3] In addition to providing an ability to construct molecular[1] and polymeric products,[2,3] in a similar way to classical covalent synthesis,[4] by design,[1a] such bifunctional molecules offer an ability to synthesize molecules and polymers not accessible using traditional approaches to synthesis.[5]

We are currently identifying molecules that function as linear hydrogen bond donor templates in the solid-state (e.g., 1,8-naphthalenedicarboxylic acid).[1a–c] In this context, during studies aimed at incorporating a metal atom into a linear template, we have isolated crystals of the title compound, $[Cu_2(3,5\text{-dihydroxybenzoate})_4(\text{acetonitrile})_2] \cdot 8H_2O$ **1**, which possesses molecular components that assemble to form a metal-carboxylate paddle-wheel complex.[6] Despite the number of structure studies concerning such paddle-wheel complexes,[7] we were surprised to discover paucity in structure data concerning metal-carboxylate complexes of the 3,5-dihydroxybenzoate ion, particularly considering the ability of the ion, and acid, to be utilized as potential building blocks in supramolecular chemistry.[8] In this paper, we report the crystal and molecular structure of **1**.

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Experimental

Synthesis

All reagents were purchased from Aldrich Chemical Co. and were used as received, unless otherwise stated.

$[Cu_2(3,5\text{-dihydroxybenzoate})_4(\text{acetonitrile})_2] \cdot 8H_2O$ **1**

A hot aqueous solution of one equivalent of $CuCl_2 \cdot 2H_2O$ was added to a hot aqueous

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Table 1. Crystal Data and Structure Refinement for **1**

CCDC deposit no.	CCDC-1003/6148
Empirical formula	$Cu_2C_{32}H_{42}N_2O_{24}$
Formula weight	965.78
Crystal size	0.35 × 0.35 × 0.40
Crystal system	Tetragonal
Space group	I 4/m
Temperature	−100° C
Unit cell dimensions	$a = 11.720(2)$ Å
	$c = 15.304(3)$ Å
Volume, Å^3	2102.4(6)
Z	2
ρ_{calc}, g cm^{-3}	1.53
μ, mm^{-1}	1.075
Final R index $[I > 2\sigma(I)]$	0.0343
$wR2$	0.1035

solution of two equivalents of the sodium salt of 3,5-dihydroxybenzoic acid. Upon cooling, blue needles of composition $[Cu_2(3,5\text{-dihydroxybenzoate})_4(H_2O)_2] \cdot 11H_2O$ were isolated by way of filtration, and washed with cold H_2O (yields: 75–85%). Single crystals of **1**, in the form of green plates, were obtained by recrystallization of a hot solution of the blue complex in acetonitrile.

X-ray crystallography

A single crystal of **1** was mounted on the end of a glass fiber and optically centered in the

Table 2. Final Positional Coordinates x, y, z and U_{eq} for **1**

	x	y	z	U_{eq}[a]
Cu(1)	0	0	−846(1)	15(1)
O(1)	−1509(2)	−665(3)	−709(2)	58(1)
O(2)	−5371(2)	−2228(2)	1545(2)	36(1)
O(3)	−2713(2)	949(2)	−2061(2)	50(1)
N(1)	0	0	−2230(4)	25(1)
C(1)	−1979(4)	−859(3)	0	19(1)
C(2)	−3153(4)	−1348(3)	0	18(1)
C(3)	−3692(3)	−1564(3)	793(2)	22(1)
C(4)	−4798(3)	−1981(3)	784(2)	26(1)
C(5)	−5360(4)	−2178(4)	0	28(1)
C(6)	0	0	−2965(5)	26(2)
C(7)	0	0	−3914(5)	42(2)

[a] U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 3. Interatomic Distances (Å) and Angles (deg) for **1**

Bond distances	
Cu(1)−O(1)a	1.944(3)
Cu(1)−O(1)b	1.944(3)
Cu(1)−O(1)	1.944(3)
Cu(1)−O(1)c	1.944(3)
Cu(1)−N(1)	2.117(6)
Cu(1)−Cu(1)d	2.5897(14)
O(1)−C(1)	1.237(3)
O(2)−C(4)	1.375(4)
N(1)−C(6)	1.125(9)
C(1)−O(1)e	1.237(3)
C(1)−C(2)	1.491(6)
C(2)−C(3)	1.391(4)
C(2)−C(3)e	1.391(4)
C(3)−C(4)	1.386(5)
C(4)−C(5)	1.388(4)
C(5)−C(4)e	1.388(4)
C(6)−C(7)	1.452(10)
Bond angles	
O(1)a−Cu(1)−O(1)b	89.33(2)
O(1)a−Cu(1)−O(1)	167.61(15)
O(1)b−Cu(1)−O(1)	89.33(2)
O(1)a−Cu(1)−O(1)c	89.33(2)
O(1)b−Cu(1)−O(1)c	167.61(15)
O(1)−Cu(1)−O(1)c	89.33(2)
O(1)a−Cu(1)−N(1)	96.20(7)
O(1)b−Cu(1)−N(1)	96.20(7)
O(1)−Cu(1)−N(1)	96.20(7)
O(1)c−Cu(1)−N(1)	96.20(7)
O(1)a−Cu(1)−Cu(1)d	83.80(7)
O(1)b−Cu(1)−Cu(1)d	83.80(7)
O(1)−Cu(1)−Cu(1)d	83.80(7)
O(1)c−Cu(1)−Cu(1)d	83.80(7)
N(1)−Cu(1)−Cu(1)d	180.0
C(1)−O(1)−Cu(1)	124.9(2)
C(6)−N(1)−Cu(1)	180.0
O(1)e−C(1)−O(1)	122.5(4)
O(1)e−C(1)−C(2)	118.7(2)
O(1)−C(1)−C(2)	118.7(2)
C(3)−C(2)−C(3)e	121.4(4)
C(3)−C(2)−C(1)	119.3(2)
C(3)e−C(2)−C(1)	119.3(2)
C(4)−C(3)−C(2)	118.7(3)
O(2)−C(4)−C(3)	121.6(3)
O(2)−C(4)−C(5)	117.7(3)
C(3)−C(4)−C(5)	120.7(3)
C(4)−C(5)−C(4)e	119.6(4)
N(1)−C(6)−C(7)	180.000(1)

Note. Symmetry transformations used to generate equivalent atoms: (a) $-x, -y, z$; (b) $-y, x, z$; (c) $y, -x, z$; (d) $-x, -y, -z$; (e) $x, y, -z$; (f) $-x-1, -y, -z$; (g) $-y-1/2, -x-1/2, z+1/2$.

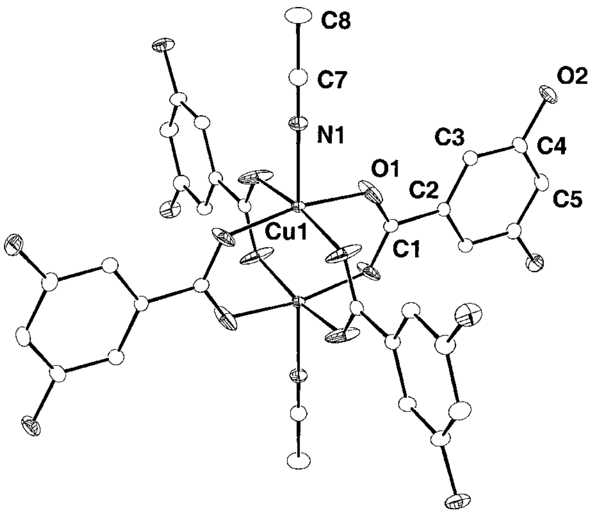

Fig. 1. ORTEP perspective of the Cu paddle-wheel complex.

X-ray beam of a Nonius Kappa system for data collection. Cell constants were calculated from reflections obtained from the data collection. The structure was solved using direct methods. After anistropic refinement of all nonhydrogen atoms, aromatic and methyl hydrogen atoms were placed in idealized positions and allowed to ride on the atom to which they are attached. Hydroxyl hydrogen atoms could not be located. A summary of data collection parameters is given in Table 1. Structure solution was accomplished with the aid of SHELXS-86[9] and refinement was conducted using SHELXL93[10] locally implemented on a Pentium-based IBM compatible computer. All crystallographic manipulations were performed with the aid of RES2INS.[11]

Results and discussion

Final positional coordinates and interatomic bond distances and angles are given in Tables 2 and 3, respectively.

An ORTEP perspective of the metal complex of **1** is shown in Fig. 1. In a similar way to $[Mo_2(3,5\text{-dihydroxybenzoate})_4] \cdot KCl$,[12] the metal and organic components of **1** have assembled to form a paddle-wheel complex, of idealized D_{4h} symmetry, where two Cu atoms are bridged by four bidentate carboxylate groups (Cu—O distance: 1.944(3) Å), the Cu—Cu separation (2.599(1) Å) being comparable to similar Cu-based systems.[6] In this arrangement, two molecules of acetonitrile occupy the axial positions of the complex (Cu—N distance: 2.117(6) Å), giving rise to an approximate square pyramidal coordination geometry around each metal center [X—M—X angles (deg): O(1)— Cu(1)— O(1)a 167.6(2), O(1)a—Cu(1)— O(1)b 89.33(2), O(1)—Cu(1)—O(1)b 89.33(2), O(1)—Cu(1)—N(1) 96.2(1)].

The paddle-wheel complex of **1** has crystallized with eight equivalents of water. As shown in Fig. 2, the complex assembles with the water molecules, by way of disordered O—H · · · O hydrogen bonds, to form a 3D hydrogen-bonded network wherein the metal complexes organize to form a layered structure within the crystallographic *ab*-plane. Adjacent layers lie stacked (stacking sequence: ABAB . . .) in an offset fashion (shortest interlayer Cu · · · Cu separation: 9.71 Å) (Fig. 2(a)). Depending upon the orientation of the guest, each water molecule acts as a bridge participating in two O—H · · · O hydrogen bonds either within or between the layers. In the former, the guest acts as a bridge between a hydroxyl group and a carboxylate moiety (Fig. 2(b)) while, in the latter, the guest serves to bridge a hydroxyl group and either a carboxylate group (Fig. 2(c)) or a hydroxyl group (Fig. 2(d)) of an adjacent layer [O · · · O separations (Å): O(1) · · · O(3) 3.139(4), O(3) · · · O(2)f 2.813(4), O(3) · · · O(2)g 2.636(4)].

Efforts are underway to determine an ability of the paddle-wheel complex to control reactivity by functioning as a linear template.

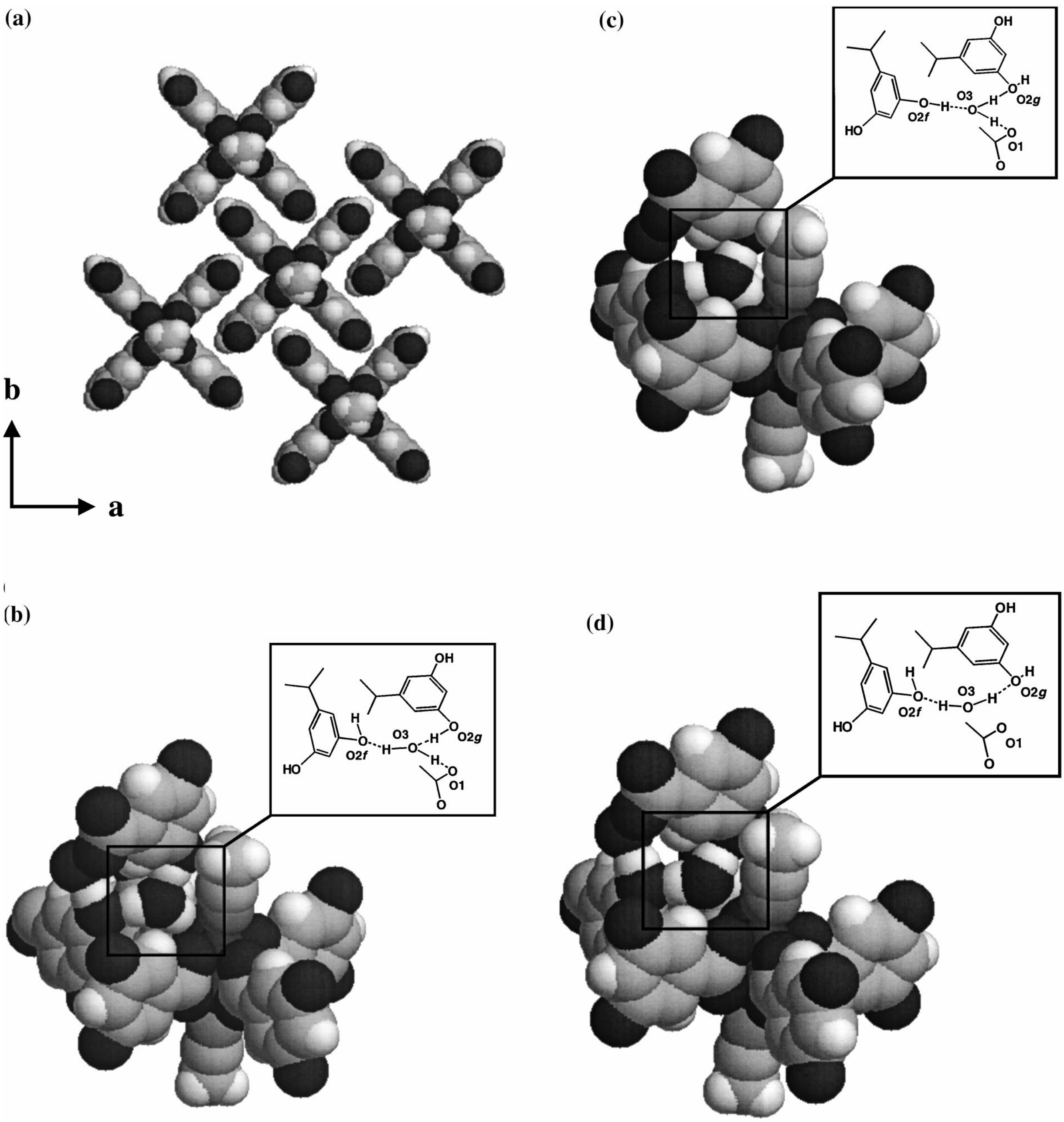

Fig. 2. Space-filling views depicting the included water molecules and the crystal structure of **1**. (a) Orientation of the paddle-wheel complexes within the crystallographic *ab*-plane and the water molecule as a hydrogen-bond bridge (b) within a layer and (c and d) between adjacent layers. Insets: schematic representations of the interaction between the water molecule and paddle-wheel complex. Selected interatomic distances (Å): O(1) · · · O(3) 3.139(4), O(3) · · · O(2)f 2.813(4), O(3) · · · O(2)g 2.636(4).

Acknowledgments

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