

Poly[[aquacopper(II)]- μ -adamantane-1,3-diacetato]

Denise J. Xu,^a Long Pan,^b Thomas J. Emge,^b Xiao-Ying Huang^b and Jing Li^{b*}

^aPrinceton High School, 151 Moore Street, Princeton, NJ 08542, USA, and

^bDepartment of Chemistry and Chemical Biology, Rutgers University, Piscataway, NJ 08854, USA

Correspondence e-mail: jingli@rutchem.rutgers.edu

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In the title compound, $[\text{Cu}(\text{C}_{14}\text{H}_{18}\text{O}_4)(\text{H}_2\text{O})]_n$, each Cu^{II} atom bonds to four O atoms of four adamantanediacetate (ada) ligands in equatorial positions and an O atom from a water molecule in the apical position. Two adjacent Cu^{II} atoms form a paddle-wheel unit with four ada ligands. The distance between the two Cu atoms is 2.5977 (3) Å. A crystallographic inversion center is located at the center of the Cu–Cu core. Each $\text{Cu}_2(\text{ada})_4$ paddle-wheel further bonds to four adjacent identical paddle-wheel units, generating a two-dimensional layered structure of $\text{Cu}(\text{ada})(\text{H}_2\text{O})$ with a 4^4 topology.

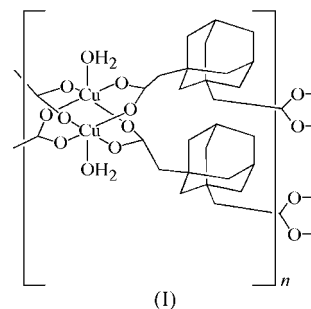
Comment

The need for renewable energy sources to replace fossil fuels (petroleum, coal and natural gas) has increased dramatically in recent years. Due to growing problems, such as the continuous decrease in fuel supply and the constant introduction of harmful air pollutants to the environment, alternative methods for powering automobiles have been sought extensively (Wigley *et al.*, 1996; Sailor *et al.*, 2000). Hydrogen, the most plentiful element in the universe, is a promising candidate of energy carriers. Not only would it be easily accessible, but its reaction with oxygen to create energy results in only water as a by-product (Turner, 1999). The foremost issue in using hydrogen as a source of power is its low volumetric density, which makes it difficult to store (Pan *et al.*, 2004). To date, none of the existing storage technologies meets the cost and performance targets set by the US Department of Energy.

Recent research has shown that highly porous crystalline metal coordination structures are promising for use as a new type of hydrogen storage material (Chun *et al.*, 2005; Dincă & Long, 2005; Kesanli *et al.*, 2004; Kubota *et al.*, 2005; Lee, Pan *et al.*, 2005; Lee, Li & Jagiello, 2005; Lee, Jang & Suh, 2005; Rowsell & Yaghi, 2005). While these substances exhibit similar sorption characteristics to carbon nanotubes, they also demonstrate stronger sorbate–sorber interactions and their

pores are perfectly ordered, allowing for effective access of hydrogen.

A number of approaches have been used to assemble three-dimensional porous structures. One successful strategy is to construct a secondary building unit (Kim *et al.*, 2001) of one- or two-dimensional structural motifs (Pan *et al.*, 2000). Assembly of targeted porous structures using these motifs can be achieved in a more controllable and predictable manner because of their well defined topology and rigid backbone. In addition, the pore characteristics and properties of porous structures depend largely on the metals and ligands that make up these structures. In an effort to design structures that contain pores of suitable dimensions and shape to maximize sorber–sorbate interactions, we have selectively worked with a number of organic ligands of different geometry, size and bonding nature. In this work, we describe a new Cu^{II} –ada (ada is adamantanediacetate) structure motif, the title compound, (I), which is highly suitable as a two-dimensional secondary building unit.



Compound (I) has a molecular formula of $[\text{Cu}(\text{ada})(\text{H}_2\text{O})]$. The asymmetric unit is shown in Fig. 1. The building block that acts as a node of the resultant two-dimensional net consists of a paddle-wheel-like $[\text{Cu}_2(\text{ada})_4]$ unit, with the two Cu atoms sharing four ada ligands through the four bridging carboxylate groups. There are no bonds between the Cu atoms but their interatomic distance [2.5977 (3) Å] is short enough for weak interactions. The Cu atoms are five-coordinated. In addition to the four equatorial bonds to the O atoms from the carboxyl groups, the Cu atom also bonds axially to the O atom of a terminal water molecule. The bond geometries for the ligand and the coordination sphere of Cu are as expected, based upon similar structures in the Cambridge Structural Database (Version 5.26 of 2005; Allen, 2002). One of the water H atoms points to a carboxylate O atom of the nearest neighboring paddle-wheel unit to form a hydrogen bond, while the second H atom does not. This is likely due to the relatively short Cu–OH₂ bond, which leads to O··H–O angles that are too small for a hydrogen bond, similar to a number of structures reported previously (Fujita *et al.*, 1993; Hamilton *et al.*, 2003; Strinna Erre *et al.*, 1985). Each $[\text{Cu}_2(\text{ada})_4]$ paddle-wheel unit interconnects with four adjacent identical units to form a two-dimensional layer of 4^4 net parallel to (10 $\bar{1}$), as shown in Fig. 2. The layers stack on top of each other to give rise to the overall structure, as illustrated in Fig. 3. Important bond distances and angles are listed in Table 1.

The topology of this two-dimensional $[\text{Cu}(\text{ada})(\text{H}_2\text{O})]$ structure motif is highly suitable for the formation of three-

dimensional porous structures, simply by replacing the water molecules with a proper nitrogen-containing bidentate ligand, such as pyrazine (pz) or 4,4'-bipyridine (bpy). We have successfully built a number of three-dimensional structures *via* this route (Pan, Liu, Kelly *et al.*, 2003; Pan, Liu, Lei *et al.*, 2003) and are currently applying the same strategy to construct Cu-ada-based porous three-dimensional networks.

The only known metal-organic framework structure that contains a similar adamantane dicarboxylic acid to (I) is [Eu₂(adc)₃] (where adc is adamantane-1,3-dicarboxylate) (Millange *et al.*, 2004). That compound forms a three-dimen-

sional network consisting of one-dimensional chains which are made of face-sharing polyhedra of nine-coordinated Eu and interconnected *via* *adc*. The ligand, metal coordination, topology and overall structure of [Eu₂(adc)₃] are very different from those of the title compound, [Cu(ada)(H₂O)].

Experimental

The synthesis of [Cu(ada)(H₂O)] was carried out under hydrothermal conditions. A mixture of Cu(NO₃)₂·3H₂O (6.2 mg, 0.0257 mmol), adamantane-1,3-diacetic acid (H₂ada) (6.5 mg, 0.0258 mmol) and distilled water (5 ml) was loaded into a Teflon-lined stainless steel acid digestion bomb and heated at 393 K for 5 d under autogenous pressure. After slow cooling to room temperature, turquoise-blue lath crystals of (I) about 1 mm in length were isolated and collected.

Crystal data

[Cu(C₁₄H₁₈O₄)(H₂O)]
M_r = 331.84
 Monoclinic, *P*2₁/*n*
a = 11.8324 (8) Å
b = 7.3549 (5) Å
c = 16.6078 (12) Å
 β = 102.070 (1)°
V = 1413.36 (17) Å³
Z = 4

D_x = 1.559 Mg m⁻³
 Mo K α radiation
 Cell parameters from 6206 reflections
 θ = 2.4–30.6°
 μ = 1.56 mm⁻¹
T = 100 (2) K
 Lath, blue
 0.22 × 0.18 × 0.16 mm

Data collection

Bruker SMART CCD area-detector diffractometer
 φ and ω scans
 Absorption correction: multi-scan (SADABS; Bruker, 2001)
T_{min} = 0.677, *T_{max}* = 0.779
 16213 measured reflections

4318 independent reflections
 4053 reflections with *I* > 2 σ (*I*)
R_{int} = 0.016
 θ_{max} = 30.6°
h = -16 → 16
k = -10 → 10
l = -23 → 23

Refinement

Refinement on *F*²
R[*F*² > 2 σ (*F*²)] = 0.021
wR(*F*²) = 0.059
S = 1.00
 4318 reflections
 207 parameters
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.033P)^2 + 0.67P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{max} = 0.002$
 $\Delta\rho_{max} = 0.50 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{min} = -0.22 \text{ e } \text{\AA}^{-3}$

Table 1

Selected geometric parameters (Å, °).

Cu—O2 ⁱ	1.9473 (8)	Cu—O4 ⁱⁱⁱ	1.9844 (8)
Cu—O3 ⁱⁱ	1.9614 (8)	Cu—O5	2.1644 (9)
Cu—O1	1.9667 (8)	Cu—Cu ⁱ	2.5977 (3)
O2 ⁱ —Cu—O3 ⁱⁱ	88.63 (3)	O1—Cu—O4 ⁱⁱⁱ	89.79 (3)
O2 ⁱ —Cu—O1	169.74 (3)	O2 ⁱ —Cu—O5	105.53 (4)
O3 ⁱⁱ —Cu—O1	91.09 (3)	O3 ⁱⁱ —Cu—O5	96.66 (3)
O2 ⁱ —Cu—O4 ⁱⁱⁱ	88.61 (3)	O1—Cu—O5	84.69 (4)
O3 ⁱⁱ —Cu—O4 ⁱⁱⁱ	169.29 (3)	O4 ⁱⁱⁱ —Cu—O5	94.06 (3)

Symmetry codes: (i) $-x + 1, -y, -z + 2$; (ii) $x + \frac{1}{2}, -y + \frac{1}{2}, z + \frac{1}{2}$; (iii) $-x + \frac{1}{2}, y - \frac{1}{2}, -z + \frac{1}{2}$.

Table 2

Hydrogen-bond geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O5—H1A...O4 ^{iv}	0.84 (2)	1.88 (2)	2.7131 (12)	172 (2)

Symmetry code: (iv) $x + \frac{1}{2}, -y - \frac{1}{2}, z + \frac{1}{2}$.

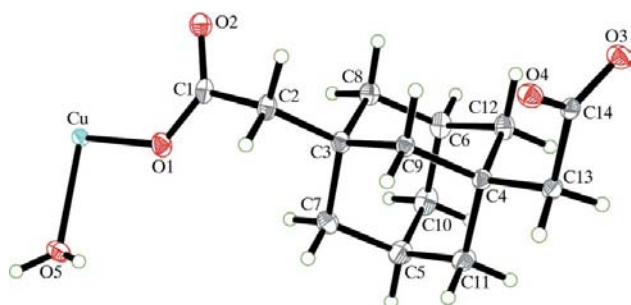


Figure 1

A drawing of the asymmetric unit in the structure of (I), showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 50% probability level.

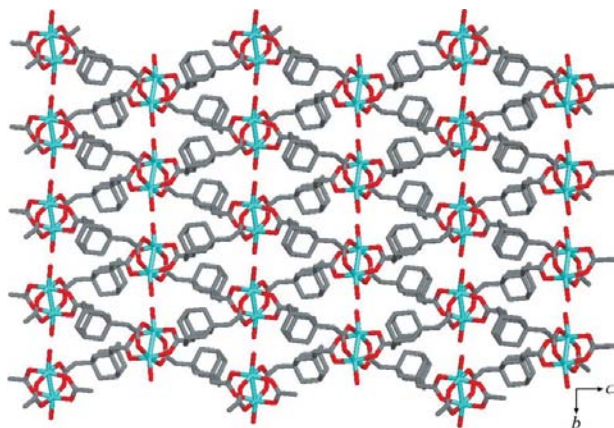


Figure 2

A view along the *a* axis, showing a single layer of [Cu(ada)(H₂O)].

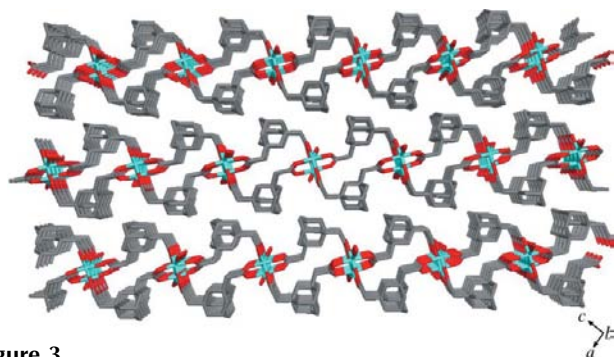


Figure 3

A view along the *b* axis, showing the stacking pattern of the two-dimensional layers in [Cu(ada)(H₂O)].

Direct phase determination yielded the positions of Cu and most of the non-H atoms. The remaining C and H atoms were located from the subsequent difference Fourier synthesis. For the two H atoms of the aqua ligand, their positions were positively detected in a difference map and refined. One of the two water H atoms is not involved in hydrogen bonding. The remaining H atoms were refined isotropically riding on their parent atoms with standard geometry, with C—H = 0.99–1.00 Å.

Data collection: *SMART* (Bruker, 2003); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 2003); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 2001); software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK3003). Services for accessing these data are described at the back of the journal.

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