Acta Crystallographica Section E
Structure Reports
Online
ISSN 1600-5368

trans-Tetraaquabis(2,6-dimethylpyridinium-3,5-dicarboxylato)copper(II) tetrahydrate

Ai-E Shi, Bai-Yan Li, Guang-Feng Hou and Jin-Sheng Gao*

College of Chemistry and Materials Science, Heilongjiang University, Harbin 150080, People's Republic of China

Correspondence e-mail: hgf1000@163.com

Received 16 November 2006
Accepted 7 January 2007

In the title compound, $[Cu(C_9H_8NO_4)_2(H_2O)_4]\cdot 4H_2O$, the Cu atom lies on an inversion centre. It has a distorted octahedral coordination, formed by two O atoms of two monodentate monoanionic 2,6-dimethylpyridinium-3,5-dicarboxylate ligands and four water molecules. The extensive system of hydrogen bonding, which involves pyridinium NH groups and both coordinated and uncoordinated water molecules, links all residues into an infinite three-dimensional network.

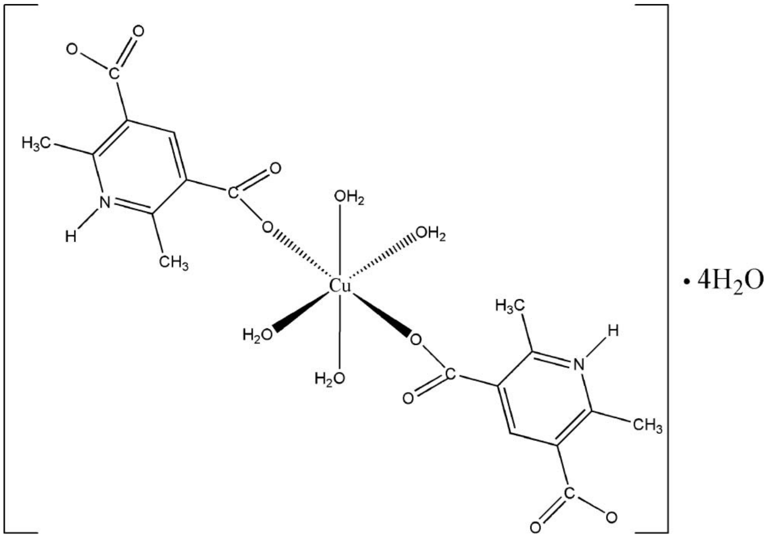
Key indicators

Single-crystal X-ray study
$T = 291$ K
Mean σ(C–C) = 0.003 Å
R factor = 0.029
wR factor = 0.102
Data-to-parameter ratio = 16.0

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

Even though structures of pyridine-3,5-dicarboxylic acid complexes have been extensively studied (Wang *et al.*, 2005), structural data on derivatives of closely related 2,6-dimethylpyridine-3,5-dicarboxylate are, to the best of our knowledge, limited to the dichlorobis(2,6-dimethylpyridine-3,5-dicarboxylate)palladium(II) complex (Zeng *et al.*, 2000; Zeng *et al.*, 2002). Here, we report the structure of the title copper complex, (I), synthesized by the reaction of 2,6-dimethylpyridine-3,5-dicarboxylic acid and copper(II) dinitrate trihydrate in aqueous solution.



(I)

Complex (I) consists of molecules of *trans*-tetraaquabis(2,6-dimethylpyridinium-3,5-dicarboxylate)copper(II), which occupy a special position on an inversion centre, and uncoordinated water molecules (O7 and O8) in general positions (Fig. 1). The Cu1 atom has a distorted octahedral coordination formed by two pyridinium dicarboxylate ligands and four water molecules. In contrast with the above-mentioned palladium complex with N-coordinated ligands, in

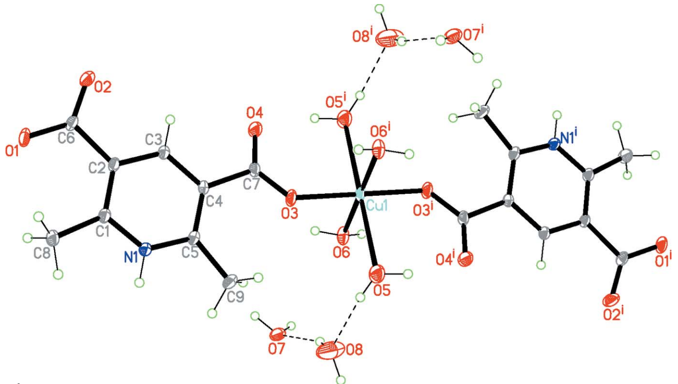


Figure 1
The molecular structure of the structure of the title complex, with the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are represented as spheres of arbitrary radius. Hydrogen bonds are shown as dashed lines. [Symmetry code: (i): $-x + 2$, $-y + 1$, $-z + 1$].

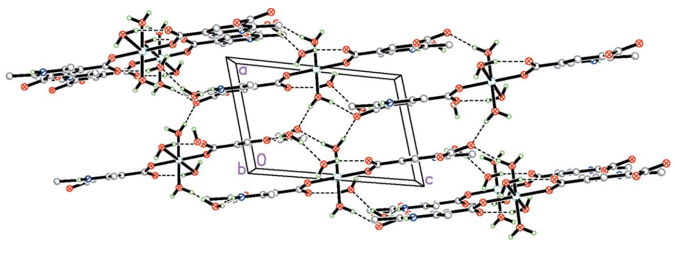


Figure 2
A packing diagram for the crystal structure of the title compound, viewed down the *b* axis and showing the three-dimensional hydrogen-bonding network. Hydrogen bonds are drawn as dashed lines. H atoms not involved in hydrogen bonds have been omitted for clarity.

(I) the pyridiniumcarboxylate ligands coordinate to the metal *via* their carboxylate O atoms. The Cu1 coordination environment has a pronounced tetragonal distortion, typical for Cu^{II} coordination geometry: the Cu1—O5 distance is significantly longer than the Cu1—O3 and Cu1—O6 bonds (Table 1).

There are nine symmetry-independent 'active' H atoms in the crystal structure; all of them participate in hydrogen bonds, which link the copper complex and water solvent molecules into an infinite three-dimensional network (Table 2, Fig. 2).

Experimental

2,6-Dimethylpyridine-3,5-dicarboxylic acid was prepared by basic hydrolysis of diethyl 2,6-dimethylpyridine-3,5-dicarboxylate, according to Checchi (1959). Diethyl 2,6-dimethylpyridine-3,5-dicarboxylate (25.1 g, 0.1 mol) and potassium hydroxide (13.44 g, 0.24 mol) were dissolved in a mixture of ethanol (150 ml) and water (150 ml), and the solution was then stirred for 3 h under reflux conditions. 2,6-Dimethylpyridine-3,5-dicarboxylic acid (10.5 g) formed as a white precipitate after adjusting the solution pH to 3 with 0.1 *M* HCl and evaporation of ethanol.

2,6-Dimethylpyridine-3,5-dicarboxylic acid (0.390 g, 2 mmol) and copper(II) dinitrate trihydrate (0.483 g, 2 mmol) were dissolved in water and the pH was adjusted to 6 with 0.01 *M* sodium hydroxide. Blue crystals of (I) suitable for X-ray diffraction work were separated from the filtered solution after several days.

Crystal data

$[Cu(C_9H_8NO_4)_2(H_2O)_4]\cdot 4H_2O$
$M_r = 596.01$
Triclinic, $P\overline{1}$
$a = 6.867$ (5) Å
$b = 9.203$ (6) Å
$c = 11.108$ (8) Å
$\alpha = 111.22$ (3)°
$\beta = 102.55$ (3)°
$\gamma = 96.83$ (3)°

$V = 623.6$ (8) Å^3
$Z = 1$
$D_x = 1.587$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 0.96$ mm^{-1}
$T = 291$ (2) K
Block, blue
0.36 × 0.33 × 0.24 mm

Data collection

Rigaku R-AXIS RAPID diffractometer
ω scans
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
$T_{min} = 0.728$, $T_{max} = 0.806$

6158 measured reflections
2823 independent reflections
2653 reflections with $I > 2\sigma(I)$
$R_{int} = 0.024$
$\theta_{max} = 27.5°$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.029$
$wR(F^2) = 0.102$
$S = 1.20$
2823 reflections
176 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0565P)^2 + 0.2023P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.38$ e Å^{-3}
$\Delta\rho_{min} = -0.41$ e Å^{-3}
Extinction correction: *SHELXL97* (Sheldrick, 1997*a*)
Extinction coefficient: 0.068 (7)

Table 1
Selected geometric parameters (Å, °).

Cu1—O3	1.9540 (19)	Cu1—O6	1.951 (2)
Cu1—O5	2.503 (2)		
O6^i—Cu1—O6	180	O6—Cu1—O5	86.42 (7)
O6—Cu1—O3	89.22 (7)	O3—Cu1—O5	87.26 (8)
O6—Cu1—O3^i	90.78 (7)	O6—Cu1—O5^i	93.58 (7)
O3—Cu1—O3^i	180	O3—Cu1—O5^i	92.74 (8)

Symmetry code: (i) $-x + 2, -y + 1, -z + 1$.

Table 2
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O8—H16···O4^{ii}	0.85	2.05	2.896 (3)	172
O8—H15···O7	0.85	2.11	2.935 (4)	162
O7—H14···O5^{iii}	0.85	1.92	2.735 (3)	161
O7—H13···O2^{iv}	0.85	1.85	2.695 (3)	178
O6—H12···O1^v	0.85	1.85	2.690 (3)	172
O6—H11···O1^{iv}	0.85	1.83	2.673 (3)	172
O5—H10···O8	0.85	1.92	2.765 (3)	174
O5—H9···O4^i	0.85	1.91	2.721 (3)	159
N1—H2···O7^{vi}	0.88 (3)	1.84 (3)	2.707 (3)	167 (2)

Symmetry codes: (i) $-x + 2, -y + 1, -z + 1$; (ii) $x, y + 1, z$; (iii) $x - 1, y, z$; (iv) $-x + 1, -y, -z$; (v) $x, y + 1, z + 1$; (vi) $-x + 1, -y + 1, -z$.

H atoms were located in a difference Fourier map, which confirmed the protonation of the pyridine atom N1. Atom H2 bound to atom N1 was subsequently refined isotropically, yielding a reasonable position [0.88 (3) Å from N1] and displacement parameter [U_{iso}(H) = 0.030 (6) Å^2]. The positions of the remaining H atoms were idealized, with C—H = 0.93 and 0.97 Å for aromatic and

m472 Shi *et al.* • $[Cu(C_9H_8NO_4)_2(H_2O)_4]\cdot 4H_2O$ *Acta Cryst.* (2007). E**63**, m471–m473

methyl H atoms, respectively, and with O—H = 0.85 Å; they were included in the refinement in a riding-model approximation, with $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(parent), or 1.5 $U_{\rm eq}$(parent) for methyl and water H atoms.

Data collection: *RAPID-AUTO* (Rigaku, 1998); cell refinement: *RAPID-AUTO*; data reduction: *CrystalStructure* (Rigaku/MSC, 2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997*a*); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997*a*); molecular graphics: *SHELXTL* (Sheldrick, 1997*b*); software used to prepare material for publication: *SHELXL97*.

The authors thank Heilongjiang University for supporting this study.

References

Checchi, S. (1959). *Gazz. Chim. Ital.* **89**, 2151–2162.

Higashi, T. (1995). *ABSCOR*. Rigaku Corporation, Tokyo, Japan.

Rigaku (1998). *RAPID-AUTO*. Rigaku Corporation, Tokyo, Japan.

Rigaku/MSC (2002). *CrystalStructure*. Rigaku/MSC Inc., The Woodlands, Texas, USA.

Sheldrick, G. M. (1997*a*). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.

Sheldrick, G. M. (1997*b*). *SHELXTL*. Version 5.10. Bruker AXS Inc., Madison, Wisconsin, USA.

Wang, P.-S., Moorefield, C. N., Panzer, M. & Newkome, G. R. (2005). *Chem. Commun.* pp. 4405–4407.

Zeng, Q.-Q., Jennings, M. C., Puddephatt, R. J. & Muir, K. W. (2000). *CrystEngComm*, **2**, 73–76.

Zeng, Q.-Q., Jennings, M. C., Puddephatt, R. J. & Muir, K. W. (2002). *Inorg. Chem.* **41**, 5174–5186.

Acta Cryst. (2007). E**63**, m471–m473 Shi *et al.* • $[Cu(C_9H_8NO_4)_2(H_2O)_4]\cdot 4H_2O$ **m473**