

Acta Crystallographica Section E

Structure Reports

Online

ISSN 1600-5368

Poly[*diaqua*(μ_3 -pyridine-3,5-dicarboxylato- $\kappa^3 N:O^3:O^5$)copper(II)]

Lin Du, Li-Nan Li and Qi-Hua Zhao*

School of Chemical Science and Technology, Key Laboratory of Medicinal Chemistry for Natural Resources, Ministry of Education, Yunnan University, Kunming 650091, People's Republic of China

Correspondence e-mail: qhzhao@ynu.edu.cn

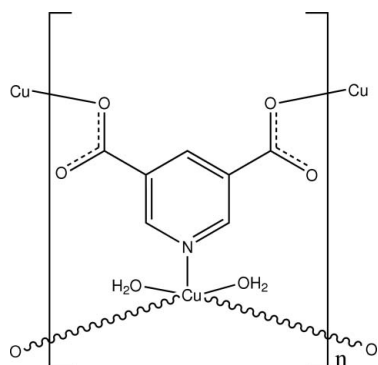
Received 25 March 2009; accepted 14 April 2009

Key indicators: single-crystal X-ray study; $T = 298$ K; mean $\sigma(C-C) = 0.005$ Å; R factor = 0.048; wR factor = 0.148; data-to-parameter ratio = 14.3.

The title complex, $[Cu(C_7H_3NO_4)(H_2O)_2]_n$, was prepared under hydrothermal reaction conditions. In the crystal structure, the Cu^{II} cation is located on a twofold rotation axis and is coordinated by two carboxylate O atoms and one N atom from three pyridine-3,5-dicarboxylate (PDA) anions and two water molecules with a distorted trigonal-bipyramidal geometry. The tridentate PDA anion is also located on the twofold rotation axis and bridges the Cu^{II} cations to form a two-dimensional polymeric layer. O—H...O hydrogen bonding between layers links the two-dimensional layers into a three-dimensional supramolecular framework.

Related literature

For background, see: Chang *et al.* (2005); Hou *et al.* (2004). For related structures, see: Plater *et al.* (1998); Whitfield *et al.* (2001).



Experimental

Crystal data

 $[Cu(C_7H_3NO_4)(H_2O)_2]$ $M_r = 264.68$

Monoclinic, $C2/c$
 $a = 10.1285$ (16) Å
 $b = 12.0669$ (19) Å
 $c = 7.2770$ (11) Å
 $\beta = 101.584$ (2)°
 $V = 871.3$ (2) Å³

$Z = 4$
 Mo $K\alpha$ radiation
 $\mu = 2.52$ mm⁻¹
 $T = 298$ K
 $0.23 \times 0.18 \times 0.07$ mm

Data collection

Bruker APEXII 1000 CCD area-detector diffractometer
 Absorption correction: multi-scan (SADABS; Sheldrick, 2004)
 $T_{min} = 0.588$, $T_{max} = 0.840$

2751 measured reflections
 1003 independent reflections
 892 reflections with $I > 2\sigma(I)$
 $R_{int} = 0.024$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.048$
 $wR(F^2) = 0.148$
 $S = 1.00$
 1003 reflections

70 parameters
 H-atom parameters constrained
 $\Delta\rho_{max} = 1.31$ e Å⁻³
 $\Delta\rho_{min} = -0.48$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

Cu1—O1W	1.964 (4)	Cu1—O1	2.236 (3)
Cu1—N1 ⁱ	2.149 (4)		

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

Table 2

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1W—H1WA...O1 ⁱⁱⁱ	0.85	2.53	3.377 (5)	178
O1W—H1WB...O2 ^{iv}	0.85	2.21	3.052 (5)	171

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

Data collection: APEX2 (Bruker, 2004); cell refinement: SAINT (Bruker, 2004); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: SHELXTL (Sheldrick, 2008); software used to prepare material for publication: SHELXTL.

The authors acknowledge the National Natural Science Foundation of China for financial support.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: XU2500).

References

- Bruker (2004). APEX2 and SAINT. Bruker AXS Inc., Madison, Wisconsin, USA.
 Chang, F., Wang, Z.-M., Sun, H.-L., Gao, S., Wen, G.-H. & Zhang, X.-X. (2005). *Dalton Trans.* pp. 2976–2978.
 Hou, H.-W., Xie, L.-X., Li, G., Ge, T.-Z., Fan, Y.-T. & Zhu, Y. (2004). *New J. Chem.* **28**, 191–199.
 Plater, M. J., Roberts, J. A. & Howie, R. A. (1998). *J. Chem. Res.* pp. 240–241.
 Sheldrick, G. M. (2004). SADABS. Bruker AXS Inc., Madison, Wisconsin, USA.
 Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
 Whitfield, T., Zheng, L.-M., Wang, X.-Q. & Jacobson, A. J. (2001). *Solid State Sci.* **3**, 829–835.

supplementary materials

Acta Cryst. (2009). E65, m556 [doi:10.1107/S1600536809013889]

Poly[*diaqua*(μ_3 -pyridine-3,5-dicarboxylato- $\kappa^3N:O^3:O^5$)copper(II)]

L. Du, L.-N. Li and Q.-H. Zhao

Comment

Over the past few years, much progress has been made toward the building of supramolecular structures with metal–organic compounds (Hou *et al.*, 2004). To get designed their intriguing frameworks and properties, an enormous amount of research is being focused in using versatile organic ligands and functional metal ions to construct the novel polymers (Chang *et al.*, 2005). The role of organic carboxylic acid ligand in synthesis such materials are of great interest. Here we report the hydrothermal synthesis and structure characterization of the title compound which is the isomorphism with Co^{II} complex reported in the previous literature (Whitfield *et al.*, 2001; Plater *et al.*, 1998).

The title compound crystallizes in space group *C2/c*. As illustrated in Fig. 1, in the asymmetric unit of it there is only one crystallographically distinct Cu^{II} ions which is coordinated by four O atoms and one N atom with the bond distance Cu—O 2.236 (3) and 2.236 (3) Å and Cu—N 2.149 (4) Å. The 3,5-PDA ligand acts as a tridentate ligand and bridges three equivalent Cu atoms with the Cu \cdots Cu 7.877 Å. The O2 atom of each carboxylate group is terminal and oriented to the Cu1 atom with the Cu1 \cdots O2 distance 2.655 Å which are slightly larger than the Co^{II} isomorphism (Co \cdots O_T 2.433 Å). A two-dimensional layer structure is thus constructed in the *ab* plane with openings along the *c* direction (Fig. 2). Hydrogen bonds are formed between coordinated water molecules and the carboxylate O atoms of adjacent layers (O1W \cdots O1 3.377 (5) Å, O1W \cdots O2 3.052 (5) Å) which furtherly connect the two-dimensional layers to a three-dimensional architecture. The shortest distance between Cu ions in the layers is 5.314 (2) Å.

Experimental

The compound was synthesized by heating a mixture of Cu(CH₃COO)₂ (0.25 mmol, 0.05 g), 3,5-pyridinedicarboxylic acid (0.25 mmol, 0.0418 g), CH₃OH (5 ml) and H₂O (5 ml) in a Teflon-lined autoclave (25 ml) at 150 °C for 3 d. Green crystals of the title compound appeared after cooling to room temperature.

Refinement

The water H atoms were placed in chemically sensible positions on the basis of hydrogen bonding, and were refined with distance restraint O—H = 0.85 Å. Other H atoms were placed in calculated positions and were refined in riding mode with C—H = 0.93 Å. $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C}, \text{O})$.

Figures

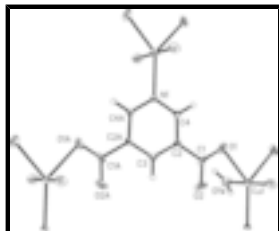


Fig. 1. The molecular structure of the title complex with displacement ellipsoids drawn at the 30% probability level [symmetry code: (A) $-x + 2, y, 1/2 - z$].

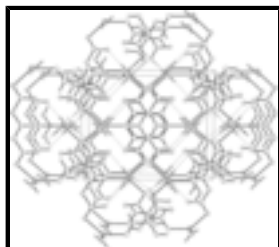


Fig. 2. The crystal packing diagram of the title compound, viewed along the c axis.

Poly[$\text{diaqua}(\mu_3\text{-pyridine-3,5-dicarboxylato-}\kappa^3\text{N:O}^3:\text{O}^5)\text{copper(II)}$]

Crystal data

$[\text{Cu}(\text{C}_7\text{H}_3\text{NO}_4)(\text{H}_2\text{O})_2]$

$M_r = 264.68$

Monoclinic, $C2/c$

Hall symbol: $-C 2yc$

$a = 10.1285$ (16) Å

$b = 12.0669$ (19) Å

$c = 7.2770$ (11) Å

$\beta = 101.584$ (2)°

$V = 871.3$ (2) Å³

$Z = 4$

$F_{000} = 532$

$D_x = 2.018$ Mg m⁻³

Mo $K\alpha$ radiation

$\lambda = 0.71073$ Å

Cell parameters from 2266 reflections

$\theta = 2.7\text{--}28.3^\circ$

$\mu = 2.52$ mm⁻¹

$T = 298$ K

Block, green

$0.23 \times 0.18 \times 0.07$ mm

Data collection

Bruker APEXII 1000 CCD area-detector diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

$T = 298$ K

φ and ω scans

Absorption correction: multi-scan (SADABS; Sheldrick, 2004)

$T_{\min} = 0.588$, $T_{\max} = 0.840$

2751 measured reflections

1003 independent reflections

892 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.024$

$\theta_{\text{max}} = 28.3^\circ$

$\theta_{\text{min}} = 2.7^\circ$

$h = -13 \rightarrow 12$

$k = -15 \rightarrow 12$

$l = -9 \rightarrow 9$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.048$	H-atom parameters constrained
$wR(F^2) = 0.148$	$w = 1/[\sigma^2(F_o^2) + (0.108P)^2 + 2.2514P]$
$S = 1.00$	where $P = (F_o^2 + 2F_c^2)/3$
1003 reflections	$(\Delta/\sigma)_{\max} < 0.001$
70 parameters	$\Delta\rho_{\max} = 1.31 \text{ e } \text{\AA}^{-3}$
Primary atom site location: structure-invariant direct methods	$\Delta\rho_{\min} = -0.48 \text{ e } \text{\AA}^{-3}$
	Extinction correction: none

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Cu1	0.5000	0.16047 (5)	0.2500	0.0252 (3)
O1W	0.4771 (4)	0.1611 (2)	-0.0245 (5)	0.0387 (8)
H1WA	0.5216	0.1161	-0.0782	0.046*
H1WB	0.4226	0.2065	-0.0896	0.046*
O1	0.6503 (3)	0.0232 (3)	0.2667 (5)	0.0387 (8)
O2	0.7647 (4)	0.1761 (3)	0.2777 (7)	0.0573 (12)
C1	0.7562 (4)	0.0748 (4)	0.2691 (6)	0.0289 (9)
C2	0.8837 (3)	0.0104 (3)	0.2610 (5)	0.0214 (7)
C3	1.0000	0.0672 (4)	0.2500	0.0227 (10)
H3A	1.0000	0.1443	0.2500	0.027*
C4	0.8885 (3)	-0.1037 (3)	0.2620 (5)	0.0227 (8)
H4A	0.8109	-0.1426	0.2713	0.027*
N1	1.0000	-0.1614 (3)	0.2500	0.0215 (9)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.0257 (4)	0.0176 (4)	0.0328 (4)	0.000	0.0073 (3)	0.000

supplementary materials

O1W	0.049 (2)	0.0299 (18)	0.0370 (17)	0.0036 (12)	0.0074 (15)	-0.0021 (12)
O1	0.0211 (15)	0.0452 (19)	0.0507 (19)	0.0075 (12)	0.0097 (13)	-0.0097 (15)
O2	0.040 (2)	0.0264 (19)	0.101 (4)	0.0149 (14)	0.005 (2)	-0.0080 (18)
C1	0.0189 (19)	0.029 (2)	0.036 (2)	0.0121 (15)	-0.0006 (15)	-0.0074 (16)
C2	0.0162 (16)	0.0185 (17)	0.0293 (17)	0.0049 (12)	0.0043 (14)	-0.0009 (14)
C3	0.022 (3)	0.013 (2)	0.032 (3)	0.000	0.001 (2)	0.000
C4	0.0135 (16)	0.0187 (18)	0.0352 (19)	-0.0015 (12)	0.0033 (14)	-0.0009 (14)
N1	0.017 (2)	0.013 (2)	0.035 (2)	0.000	0.0062 (18)	0.000

Geometric parameters (\AA , $^\circ$)

Cu1—O1W ⁱ	1.964 (4)	C1—C2	1.518 (5)
Cu1—O1W	1.964 (4)	C2—C4	1.378 (5)
Cu1—N1 ⁱⁱ	2.149 (4)	C2—C3	1.379 (4)
Cu1—O1 ⁱ	2.236 (3)	C3—C2 ⁱⁱⁱ	1.379 (4)
Cu1—O1	2.236 (3)	C3—H3A	0.9300
O1W—H1WA	0.8500	C4—N1	1.344 (4)
O1W—H1WB	0.8500	C4—H4A	0.9300
O1—C1	1.238 (5)	N1—C4 ⁱⁱⁱ	1.344 (4)
O2—C1	1.226 (5)	N1—Cu1 ^{iv}	2.149 (4)
O1W ⁱ —Cu1—O1W	179.54 (17)	O2—C1—C2	117.5 (4)
O1W ⁱ —Cu1—N1 ⁱⁱ	89.77 (8)	O1—C1—C2	118.9 (4)
O1W—Cu1—N1 ⁱⁱ	89.77 (8)	C4—C2—C3	117.8 (3)
O1W ⁱ —Cu1—O1 ⁱ	89.90 (13)	C4—C2—C1	122.8 (3)
O1W—Cu1—O1 ⁱ	90.44 (13)	C3—C2—C1	119.4 (4)
N1 ⁱⁱ —Cu1—O1 ⁱ	137.80 (9)	C2—C3—C2 ⁱⁱⁱ	120.4 (5)
O1W ⁱ —Cu1—O1	90.44 (13)	C2—C3—H3A	119.8
O1W—Cu1—O1	89.90 (13)	C2 ⁱⁱⁱ —C3—H3A	119.8
N1 ⁱⁱ —Cu1—O1	137.80 (9)	N1—C4—C2	123.2 (3)
O1 ⁱ —Cu1—O1	84.40 (18)	N1—C4—H4A	118.4
Cu1—O1W—H1WA	120.0	C2—C4—H4A	118.4
Cu1—O1W—H1WB	120.0	C4 ⁱⁱⁱ —N1—C4	117.6 (4)
H1WA—O1W—H1WB	120.0	C4 ⁱⁱⁱ —N1—Cu1 ^{iv}	121.2 (2)
C1—O1—Cu1	101.9 (3)	C4—N1—Cu1 ^{iv}	121.2 (2)
O2—C1—O1	123.7 (4)		

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

Hydrogen-bond geometry (\AA , $^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1W—H1WA \cdots O1 ^v	0.85	2.53	3.377 (5)	178
O1W—H1WB \cdots O2 ^{vi}	0.85	2.21	3.052 (5)	171

Symmetry codes: (v) $x, -y, z-1/2$; (vi) $x-1/2, -y+1/2, z-1/2$.

Fig. 2

