

catena-Poly[[[triaquacopper(II)]- μ -pyridine-2,3-dicarboxylato- $\kappa^3N,O^2:O^3$] monohydrate]

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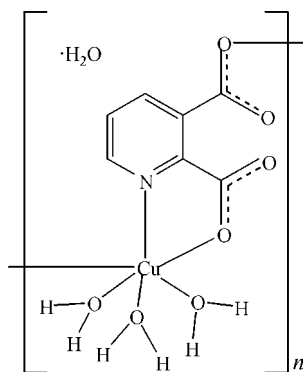
Received 15 June 2008; accepted 7 August 2008

Key indicators: single-crystal X-ray study; $T = 296$ K; mean $\sigma(C-C) = 0.007$ Å; R factor = 0.030; wR factor = 0.090; data-to-parameter ratio = 7.3.

In the title compound, $[[Cu(C_7H_3NO_4)(H_2O)_3] \cdot H_2O]_n$, the Cu^{II} ion is bonded to three water molecules, one N,O -bidentate pyridine-2,3-dicarboxylate dianion and one O -bonded symmetry-generated dianion, resulting in a distorted $CuNO_5$ octahedral geometry. The bridging ligand results in an infinite chain. A network of $O-H \cdots O$ hydrogen bonds helps to establish the crystal structure.

Related literature

For background, see: Serre *et al.* (2005).



Experimental

Crystal data

$[Cu(C_7H_3NO_4)(H_2O)_3] \cdot H_2O$
 $M_r = 300.71$
Monoclinic, C_c
 $a = 8.513$ (3) Å
 $b = 17.983$ (3) Å

$c = 7.493$ (3) Å
 $\beta = 114.486$ (10)°
 $V = 1043.9$ (6) Å³
 $Z = 4$
Mo $K\alpha$ radiation

$\mu = 2.13$ mm⁻¹
 $T = 296$ (2) K

$0.40 \times 0.28 \times 0.22$ mm

Data collection

Bruker APEXII CCD diffractometer
Absorption correction: multi-scan (SADABS; Bruker, 2004)
 $T_{min} = 0.484$, $T_{max} = 0.652$

2686 measured reflections
1322 independent reflections
1310 reflections with $I > 2\sigma(I)$
 $R_{int} = 0.028$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.030$
 $wR(F^2) = 0.089$
 $S = 1.00$
1322 reflections
180 parameters
14 restraints

H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{max} = 0.61$ e Å⁻³
 $\Delta\rho_{min} = -0.60$ e Å⁻³
Absolute structure: Flack (1983), 290 Friedel pairs
Flack parameter: 0.05 (3)

Table 1

Selected bond lengths (Å).

Cu1—O7	2.061 (3)	Cu1—O1	2.119 (4)
Cu1—O6	2.068 (3)	Cu1—O5	2.178 (5)
Cu1—O3	2.071 (3)	Cu1—N1	2.187 (4)

Table 2

Hydrogen-bond geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
O5—H3W \cdots O4 ⁱ	0.82 (9)	1.93 (8)	2.735 (6)	167 (8)
O5—H4W \cdots O6 ⁱⁱ	0.82 (2)	2.35 (8)	2.966 (5)	132 (10)
O6—H5W \cdots O5 ⁱⁱⁱ	0.82 (7)	2.29 (7)	2.966 (5)	140 (9)
O7—H7W \cdots O2 ^{iv}	0.83 (8)	1.90 (9)	2.720 (5)	169 (8)
O7—H8W \cdots O2 ⁱⁱ	0.83 (8)	2.03 (4)	2.825 (5)	162 (11)

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

Data collection: APEX2 (Bruker, 2004); cell refinement: SAINT-Plus (Bruker, 2004); data reduction: SAINT-Plus; 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.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HB2747).

References

- Bruker (2004). APEX2, SAINT-Plus and SADABS. Bruker AXS Inc., Madison, Wisconsin, USA.
Flack, H. D. (1983). *Acta Cryst.* **A39**, 876–881.
Serre, C., Marrot, J. & Ferey, G. (2005). *Inorg. Chem.* **44**, 654–658.
Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.

supplementary materials

Acta Cryst. (2008). E64, m1229 [doi:10.1107/S1600536808025439]

***catena*-Poly[[[triacuopper(II)]- μ -pyridine-2,3-dicarboxylato- $\kappa^3N,O^2:O^3$] monohydrate]**

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Comment

In recent years, carboxylic acids have been widely used as polydentate ligands, which can coordinate to transition or rare earth ions yielding complexes with interesting properties in biological systems (e.g. Serre *et al.*, 2005). Herein, we report the synthesis and structure of the title compound, (I).

As shown in Fig. 1, the Cu^{II} ion in (I) is hexacoordinated with five oxygen atoms and one nitrogen atom, exhibiting a slightly distorted octahedral geometry (Table 1). The pyridine-2,3-dicarboxylato ligand affords the pyridine N and one carboxylato oxygen atom in chelating coordination mode and a symmetry-generated ligand bonds from its carboxylate O-atom. The bridging ligand links neighboring copper(II) ions into a chain (Fig. 2). Extensive hydrogen bonding (Table 2) *via* hydrogen bonds between carboxylate oxygen atoms of pyridine-2,3-dicarboxylate and the uncoordinated water molecules or coordinated aqua ligands, giving rise to a three-dimensional network.

Experimental

A mixture of copper(II) chloride (0.5 mmol), pyridine-2,3-dicarboxylic acid (1 mmol), sodium hydroxide (1 mmol), H₂O (8 ml), and ethanol (8 ml) in a 25 ml Teflon-lined stainless steel autoclave was kept at 423 K for three days. Blue blocks of (I) were obtained after cooling to room temperature with a yield of 16%. Anal. calc. for C₇H₁₁CuNO₈: C 27.93, H 2.99, N 4.66%; found: C 27.89, H 2.92, N 4.63%.

Refinement

The O-bound H atoms were located in a difference map and their positions were freely refined with a fixed U_{iso} value. This has led to some extremely short intermolecular H...H contacts and the location of the water H atoms should be regarded as less certain. All the C-bound H atoms were placed in calculated positions with C—H = 0.93 Å and refined as riding with $U_{iso}(H) = 1.2U_{eq}(C)$.

Figures

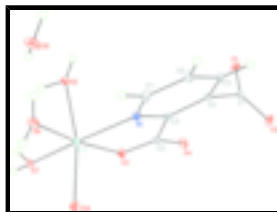


Fig. 1. The molecular structure of (I), drawn with 30% probability displacement ellipsoids for the non-hydrogen atoms. Atoms labeled with *i* are at the symmetry position ($x - 1/2, -y + 1/2, z - 1/2$).

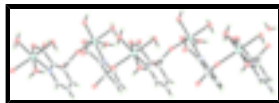


Fig. 2. Part of a polymeric chain in (I).

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Crystal data

[Cu(C₇H₃NO₄)(H₂O)₃] \cdot H₂O

$M_r = 300.71$

Monoclinic, *Cc*

Hall symbol: C -2yc

$a = 8.513 (3) \text{ \AA}$

$b = 17.983 (3) \text{ \AA}$

$c = 7.493 (3) \text{ \AA}$

$\beta = 114.486 (10)^\circ$

$V = 1043.9 (6) \text{ \AA}^3$

$Z = 4$

$F_{000} = 612$

$D_x = 1.913 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation

$\lambda = 0.71073 \text{ \AA}$

Cell parameters from 2692 reflections

$\theta = 2.9\text{--}28.1^\circ$

$\mu = 2.13 \text{ mm}^{-1}$

$T = 296 (2) \text{ K}$

Block, blue

$0.40 \times 0.28 \times 0.22 \text{ mm}$

Data collection

Bruker APEXII CCD
diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

$T = 296(2) \text{ K}$

ω scans

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

$T_{\min} = 0.484$, $T_{\max} = 0.652$

2686 measured reflections

1322 independent reflections

1310 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.028$

$\theta_{\text{max}} = 26.0^\circ$

$\theta_{\text{min}} = 2.9^\circ$

$h = -10 \rightarrow 10$

$k = -22 \rightarrow 22$

$l = -4 \rightarrow 9$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.030$

$wR(F^2) = 0.089$

$S = 1.00$

1322 reflections

180 parameters

14 restraints

Hydrogen site location: difmap and geom

H atoms treated by a mixture of
independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.079P)^2 + 0.0702P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\text{max}} < 0.001$

$\Delta\rho_{\text{max}} = 0.61 \text{ e \AA}^{-3}$

$\Delta\rho_{\text{min}} = -0.60 \text{ e \AA}^{-3}$

Extinction correction: SHELXL97 (Sheldrick, 2008),

$F_c^* = kF_c[1 + 0.001x F_c^2 \lambda^3 / \sin(2\theta)]^{-1/4}$

Extinction coefficient: 0.018 (2)

Primary atom site location: structure-invariant direct methods Absolute structure: Flack (1983), 290 Friedel pairs
 Secondary atom site location: difference Fourier map Flack parameter: 0.05 (3)

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)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Cu1	0.00453 (5)	0.118674 (19)	0.25189 (5)	0.0226 (2)
C1	-0.1893 (6)	0.1125 (2)	-0.2173 (8)	0.0257 (10)
C2	0.0162 (7)	0.2776 (2)	0.2417 (8)	0.0261 (9)
C3	0.1909 (5)	0.2542 (2)	0.2398 (6)	0.0220 (8)
C4	0.3188 (5)	0.3044 (2)	0.2468 (6)	0.0224 (8)
C5	0.4612 (5)	0.2816 (2)	0.2256 (6)	0.0222 (9)
H5	0.5443	0.3154	0.2266	0.027*
C6	0.4781 (6)	0.2094 (3)	0.2034 (7)	0.0325 (10)
H6	0.5747	0.1922	0.1878	0.039*
C7	0.3554 (7)	0.1592 (3)	0.2028 (8)	0.0350 (10)
H7	0.3719	0.1088	0.1890	0.042*
N1	0.2118 (5)	0.18178 (19)	0.2218 (6)	0.0262 (7)
O1	-0.1400 (5)	0.0911 (2)	-0.0470 (5)	0.0356 (8)
O2	-0.2392 (5)	0.07157 (19)	-0.3667 (5)	0.0363 (7)
O3	-0.0834 (4)	0.22671 (17)	0.2399 (6)	0.0323 (7)
O4	-0.0130 (6)	0.34452 (16)	0.2387 (9)	0.0401 (8)
O5	0.1420 (5)	0.12328 (17)	0.5699 (7)	0.0311 (9)
O6	0.1266 (5)	0.01799 (18)	0.2664 (7)	0.0427 (9)
O7	-0.2021 (4)	0.07356 (18)	0.2898 (5)	0.0309 (7)
O8	0.4601 (7)	-0.0181 (3)	0.4257 (10)	0.0777 (18)
H1W	0.553 (6)	-0.004 (6)	0.515 (11)	0.093*
H2W	0.377 (7)	-0.006 (6)	0.451 (14)	0.093*
H4W	0.105 (10)	0.080 (2)	0.551 (16)	0.093*
H5W	0.092 (12)	-0.008 (5)	0.167 (10)	0.093*
H6W	0.229 (5)	0.011 (5)	0.340 (12)	0.093*
H7W	-0.214 (15)	0.067 (5)	0.393 (9)	0.093*
H8W	-0.195 (16)	0.034 (3)	0.238 (13)	0.093*
H3W	0.248 (3)	0.126 (4)	0.620 (19)	0.093*

supplementary materials

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.0221 (3)	0.0153 (3)	0.0307 (3)	-0.0014 (2)	0.0111 (2)	0.0008 (2)
C1	0.024 (2)	0.021 (2)	0.033 (3)	0.0026 (14)	0.013 (2)	0.0011 (15)
C2	0.0229 (19)	0.0210 (17)	0.0315 (18)	0.0045 (18)	0.0084 (15)	-0.0004 (19)
C3	0.0223 (19)	0.0198 (18)	0.0229 (18)	0.0031 (15)	0.0083 (15)	0.0014 (14)
C4	0.0208 (18)	0.0218 (19)	0.0220 (17)	0.0000 (14)	0.0064 (15)	0.0016 (15)
C5	0.026 (2)	0.0141 (17)	0.032 (2)	0.0009 (13)	0.017 (2)	0.0013 (15)
C6	0.034 (3)	0.027 (2)	0.042 (3)	0.0042 (18)	0.022 (2)	0.0008 (16)
C7	0.045 (3)	0.0219 (18)	0.044 (2)	0.0067 (19)	0.025 (2)	0.0011 (18)
N1	0.0284 (18)	0.0215 (16)	0.0293 (17)	0.0018 (14)	0.0125 (15)	-0.0001 (14)
O1	0.0475 (19)	0.0275 (18)	0.0292 (16)	-0.0008 (15)	0.0133 (15)	0.0000 (14)
O2	0.055 (2)	0.0236 (14)	0.0343 (16)	-0.0049 (14)	0.0230 (16)	-0.0069 (13)
O3	0.0226 (17)	0.0253 (16)	0.0519 (19)	0.0004 (12)	0.0185 (14)	0.0011 (14)
O4	0.0274 (17)	0.0214 (15)	0.073 (2)	0.0041 (14)	0.0220 (17)	-0.0029 (19)
O5	0.0266 (16)	0.0281 (19)	0.033 (2)	-0.0011 (11)	0.0062 (16)	-0.0014 (12)
O6	0.0362 (17)	0.0247 (16)	0.056 (2)	0.0078 (15)	0.0077 (15)	-0.0088 (16)
O7	0.0313 (16)	0.0262 (15)	0.0355 (16)	-0.0074 (13)	0.0142 (14)	-0.0040 (14)
O8	0.035 (2)	0.054 (3)	0.108 (4)	0.0047 (18)	-0.006 (3)	-0.023 (3)

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

Cu1—O7	2.061 (3)	C4—C1 ⁱⁱ	1.525 (5)
Cu1—O6	2.068 (3)	C5—C6	1.325 (6)
Cu1—O3	2.071 (3)	C5—H5	0.9300
Cu1—O1	2.119 (4)	C6—C7	1.379 (7)
Cu1—O5	2.178 (5)	C6—H6	0.9300
Cu1—N1	2.187 (4)	C7—N1	1.350 (6)
C1—O1	1.228 (7)	C7—H7	0.9300
C1—O2	1.258 (6)	O5—H4W	0.82 (2)
C1—C4 ⁱ	1.525 (5)	O5—H3W	0.82 (9)
C2—O4	1.227 (5)	O6—H5W	0.82 (7)
C2—O3	1.244 (6)	O6—H6W	0.83 (7)
C2—C3	1.552 (6)	O7—H7W	0.83 (8)
C3—N1	1.328 (5)	O7—H8W	0.83 (8)
C3—C4	1.399 (6)	O8—H1W	0.84 (8)
C4—C5	1.349 (6)	O8—H2W	0.83 (8)
O7—Cu1—O6	95.00 (16)	C3—C4—C1 ⁱⁱ	123.2 (4)
O7—Cu1—O3	93.52 (13)	C6—C5—C4	117.5 (4)
O6—Cu1—O3	171.34 (14)	C6—C5—H5	121.2
O7—Cu1—O1	84.19 (14)	C4—C5—H5	121.2
O6—Cu1—O1	84.83 (16)	C5—C6—C7	121.3 (5)
O3—Cu1—O1	97.60 (15)	C5—C6—H6	119.3
O7—Cu1—O5	88.09 (15)	C7—C6—H6	119.3
O6—Cu1—O5	86.87 (16)	N1—C7—C6	121.4 (4)
O3—Cu1—O5	91.87 (14)	N1—C7—H7	119.3

O1—Cu1—O5	168.12 (14)	C6—C7—H7	119.3
O7—Cu1—N1	171.80 (13)	C3—N1—C7	118.0 (4)
O6—Cu1—N1	92.89 (17)	C3—N1—Cu1	110.5 (3)
O3—Cu1—N1	78.54 (13)	C7—N1—Cu1	131.3 (3)
O1—Cu1—N1	98.75 (15)	C1—O1—Cu1	145.4 (3)
O5—Cu1—N1	90.13 (15)	C2—O3—Cu1	117.2 (3)
O1—C1—O2	125.8 (4)	Cu1—O5—H4W	77 (8)
O1—C1—C4 ⁱ	118.0 (4)	Cu1—O5—H3W	119 (10)
O2—C1—C4 ⁱ	116.1 (4)	H4W—O5—H3W	114 (4)
O4—C2—O3	126.1 (5)	Cu1—O6—H5W	118 (7)
O4—C2—C3	117.0 (5)	Cu1—O6—H6W	122 (7)
O3—C2—C3	116.8 (4)	H5W—O6—H6W	114 (9)
N1—C3—C4	120.1 (4)	Cu1—O7—H7W	129 (8)
N1—C3—C2	115.9 (4)	Cu1—O7—H8W	92 (8)
C4—C3—C2	123.9 (4)	H7W—O7—H8W	112 (9)
C5—C4—C3	121.5 (4)	H1W—O8—H2W	111 (4)
C5—C4—C1 ⁱⁱ	115.3 (4)		

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

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O5—H3W \cdots O4 ⁱⁱ	0.82 (9)	1.93 (8)	2.735 (6)	167 (8)
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O6—H5W \cdots O5 ^{iv}	0.82 (7)	2.29 (7)	2.966 (5)	140 (9)
O7—H7W \cdots O2 ^v	0.83 (8)	1.90 (9)	2.720 (5)	169 (8)
O7—H8W \cdots O2 ⁱⁱⁱ	0.83 (8)	2.03 (4)	2.825 (5)	162 (11)

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

Fig. 1

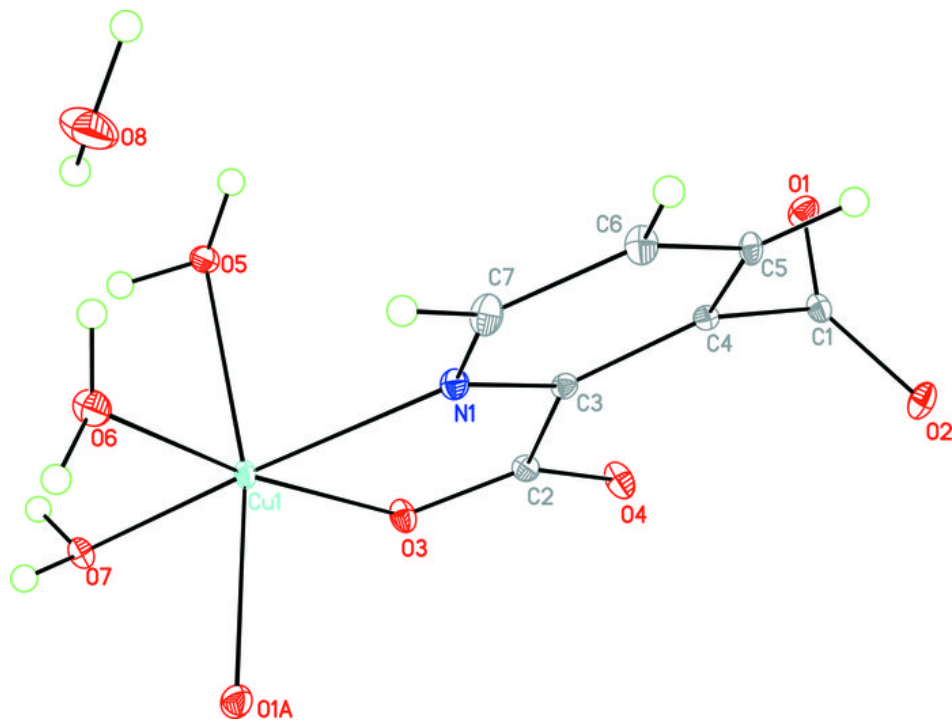


Fig. 2

