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Diaquabis(4-hydroxy-5-nitropyridine-2-carboxylato- κ^2N^1,O^2)copper(II)

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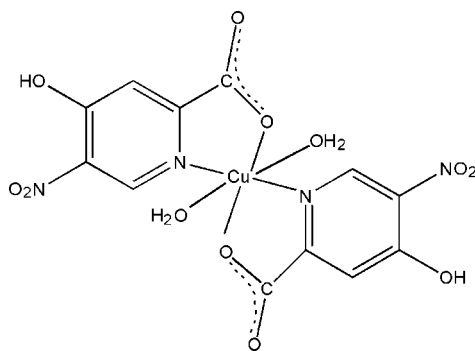
Received 28 November 2011; accepted 8 December 2011

Key indicators: single-crystal X-ray study; $T = 113$ K; mean $\sigma(C-C) = 0.003$ Å; R factor = 0.029; wR factor = 0.077; data-to-parameter ratio = 12.3.

In the title compound, $[Cu(C_6H_3N_2O_5)_2(H_2O)_2]$, the Cu^{II} ion, lying on an inversion center, is coordinated by two pyridine N atoms and two carboxylate O atoms from symmetry-related two 4-hydroxy-5-nitropyridine-2-carboxylate ligands, and two water molecules, forming a distorted octahedral geometry. In the crystal, $O-H \cdots O$ hydrogen bonds link the complex molecules. One of the H atoms of the water molecule is disordered over two sites of equal occupancy.

Related literature

For complexes based on the 4-hydroxypyridine-2,6-dicarboxylic acid ligand, see: Zhao *et al.* (2006, 2009, 2011). For a similar reaction to the formation of the ligand, see: Xu *et al.* (2011).



Experimental

Crystal data

 $[Cu(C_6H_3N_2O_5)_2(H_2O)_2]$ $M_r = 465.79$

Monoclinic, $P2_1/n$
 $a = 6.5327$ (7) Å
 $b = 9.7963$ (10) Å
 $c = 12.2562$ (12) Å
 $\beta = 102.86$ (2)°
 $V = 764.68$ (15) Å³

$Z = 2$
 Mo $K\alpha$ radiation
 $\mu = 1.52$ mm⁻¹
 $T = 113$ K
 $0.20 \times 0.18 \times 0.10$ mm

Data collection

Rigaku Saturn 724 CCD
 diffractometer
 Absorption correction: multi-scan
 (*CrystalClear*; Rigaku, 2005)
 $T_{min} = 0.752$, $T_{max} = 0.863$

9563 measured reflections
 1829 independent reflections
 1466 reflections with $I > 2\sigma(I)$
 $R_{int} = 0.053$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.029$
 $wR(F^2) = 0.077$
 $S = 1.04$
 1829 reflections
 149 parameters
 6 restraints

H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{max} = 0.39$ e Å⁻³
 $\Delta\rho_{min} = -0.49$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$O3-H3 \cdots O2^i$	0.79 (3)	1.79 (3)	2.544 (2)	160 (3)
$O6-H6A \cdots O2^{ii}$	0.84 (1)	2.28 (2)	3.014 (2)	146 (3)
$O6-H6B \cdots O6^{iii}$	0.85 (1)	2.00 (1)	2.836 (3)	170 (5)
$O6-H6C \cdots O3^{iv}$	0.85 (1)	2.49 (3)	3.109 (2)	130 (3)

Symmetry codes: (i) $-x + \frac{1}{2}, y + \frac{1}{2}, -z + \frac{3}{2}$; (ii) $-x + \frac{1}{2}, y - \frac{1}{2}, -z + \frac{3}{2}$; (iii) $-x + 1, -y + 1, -z + 1$; (iv) $x, y - 1, z$.

Data collection: *CrystalClear* (Rigaku, 2005); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; 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: HY2493).

References

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 Zhao, B., Gao, H.-L., Chen, X.-Y., Cheng, P., Shi, W., Liao, D.-Z., Yan, S.-P. & Jiang, Z.-H. (2006). *Chem. Eur. J.* **12**, 149–158.
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supporting information

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Diaquabis(4-hydroxy-5-nitropyridine-2-carboxylato- κ^2N^1,O^2)copper(II)

Fengjuan Shi, Jiguang Deng and Hongxing Dai

S1. Comment

Carboxylate ligands play an important role in constructing novel metal-organic frameworks (MOFs) in coordination chemistry. Especially, a large number of MOFs based on pyridyl dicarboxylic acid ligands containing N- and O-donors with multi-connecting ability have been constructed. 4-Hydroxyl-pyridine-2,6-dicarboxylic acid has been widely used in the construction of high-dimensional structures with large pores. It usually adopts diverse coordination binding modes such as chelating to one metal center, bridging bidentate in *syn-syn* or *syn-anti* configuration to two or three metal centers. A systematic study of 3d-4f, 4d-4f and 3d-4d-4f complexes based on 4-hydroxyl-pyridine-2,6-dicarboxylic acid ligand has been undertaken (Zhao *et al.*, 2006, 2009, 2011). However, to the best of our knowledge, no reports on the synthesis of the title compound have been seen in literature. In this paper, we report the synthesis and crystal structure of the title compound using a hydrothermal method with 4-hydroxyl-pyridine-2,6-dicarboxylic acid as ligand.

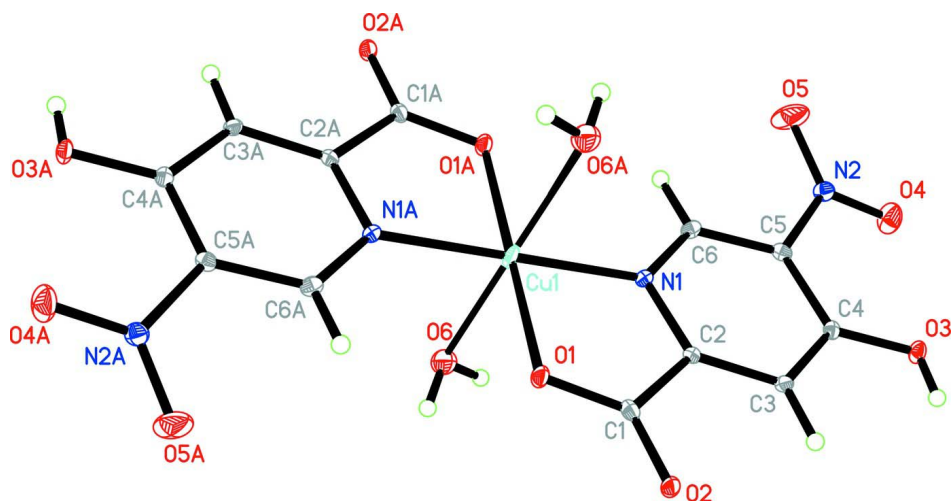
The title compound features a 3-nitro-4-hydroxyl-pyridine-6-carboxylate ligand, which was in situ generated by decarboxylation and nitration of 4-hydroxyl-pyridine-2,6-dicarboxylic acid under the hydrothermal conditions. A similar reaction has been reported (Xu *et al.*, 2011). Structure analysis shows that the Cu^{II} ion is centrosymmetrically coordinated by two N atoms [Cu—N = 1.9685 (16) Å] and two carboxylate O atoms [Cu—O = 1.9667 (15) Å] from two 3-nitro-4-hydroxyl-pyridine-6-carboxylate ligands and two water molecules [Cu—O = 2.479 (2) Å], forming a distorted octahedral geometry, as shown in Fig. 1. O—H \cdots O hydrogen bonds link the complex molecules (Table 1).

S2. Experimental

A mixture of 4-hydroxyl-pyridine-2,6-dicarboxylic acid (366 mg, 2.0 mmol), copper nitrate trihydrate (242 mg, 1.0 mmol), lanthanide nitrate hexahydrate (Ln = Eu, Sm, Pr, Tb) (1.0 mmol) and deionized water (10 ml) was placed in a 25 ml Teflon-lined steel autoclave, which was kept at 433 K for 3 days. The resulting blue prismatic crystals suitable for X-ray diffraction experiment were collected after washing with deionized water and diethyl ether (yield: 43% based on the mass of copper nitrate trihydrate).

S3. Refinement

H atoms bound to C atoms were positioned geometrically and refined as riding atoms, with C—H = 0.95 Å and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. H atoms bound to O atoms were located from a difference Fourier map and refined isotropically. One of H atoms of the water molecule is disordered over two sites with equal occupancy factors.

**Figure 1**

Molecular structure of the title compound. Displacement ellipsoids are drawn at the 30% probability level. One of the disordered H atom sites on water molecule is not shown. [Symmetry code: (A) $-x, 1-y, 1-z$.]

Diaquabis(4-hydroxy-5-nitropyridine-2-carboxylato- κ^2N^1,O^2)copper(II)

Crystal data

$[\text{Cu}(\text{C}_6\text{H}_3\text{N}_2\text{O}_5)_2(\text{H}_2\text{O})_2]$

$M_r = 465.79$

Monoclinic, $P2_1/n$

Hall symbol: $-P\ 2_1n$

$a = 6.5327$ (7) Å

$b = 9.7963$ (10) Å

$c = 12.2562$ (12) Å

$\beta = 102.86$ (2)°

$V = 764.68$ (15) Å³

$Z = 2$

$F(000) = 470$

$D_x = 2.023$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 3085 reflections

$\theta = 2.1$ – 27.9 °

$\mu = 1.52$ mm⁻¹

$T = 113$ K

Prism, colorless

$0.20 \times 0.18 \times 0.10$ mm

Data collection

Rigaku Saturn 724 CCD
diffractometer

Radiation source: rotating anode

Multilayer monochromator

Detector resolution: 14.22 pixels mm⁻¹

ω scans

Absorption correction: multi-scan

(*CrystalClear*; Rigaku, 2005)

$T_{\min} = 0.752$, $T_{\max} = 0.863$

9563 measured reflections

1829 independent reflections

1466 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.053$

$\theta_{\max} = 27.9$ °, $\theta_{\min} = 2.7$ °

$h = -8 \rightarrow 7$

$k = -12 \rightarrow 12$

$l = -15 \rightarrow 16$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.029$

$wR(F^2) = 0.077$

$S = 1.04$

1829 reflections

149 parameters

6 restraints

Primary atom site location: structure-invariant
direct methods

Secondary atom site location: difference Fourier
map

Hydrogen site location: inferred from
neighbouring sites

H atoms treated by a mixture of independent
and constrained refinement

$$w = 1/[\sigma^2(F_o^2) + (0.036P)^2]$$

where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$

$$\Delta\rho_{\max} = 0.39 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.49 \text{ e } \text{\AA}^{-3}$$

Special details

Experimental. Rigaku *CrystalClear*-SM Expert 2.0 r2

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>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
Cu1	0.0000	0.5000	0.5000	0.01573 (13)	
O1	0.0540 (2)	0.53885 (14)	0.66132 (12)	0.0145 (3)	
O2	0.1475 (2)	0.70789 (14)	0.78407 (11)	0.0150 (3)	
O3	0.3093 (2)	1.08681 (14)	0.52856 (13)	0.0144 (3)	
H3	0.331 (5)	1.107 (3)	0.592 (2)	0.058 (11)*	
O4	0.2830 (3)	1.07679 (17)	0.31323 (14)	0.0291 (4)	
O5	0.0819 (3)	0.9216 (2)	0.22215 (13)	0.0408 (5)	
O6	0.3578 (3)	0.40247 (18)	0.52615 (15)	0.0253 (4)	
H6A	0.371 (5)	0.381 (3)	0.5936 (10)	0.060 (11)*	
H6B	0.454 (7)	0.455 (5)	0.516 (3)	0.06 (2)*	0.50
H6C	0.348 (10)	0.332 (3)	0.484 (3)	0.09 (3)*	0.50
N1	0.1030 (3)	0.68775 (16)	0.49202 (13)	0.0113 (4)	
C1	0.1142 (3)	0.6591 (2)	0.68823 (16)	0.0121 (4)	
C2	0.1493 (3)	0.7498 (2)	0.59364 (16)	0.0108 (4)	
C3	0.2222 (3)	0.8799 (2)	0.61022 (16)	0.0109 (4)	
H3A	0.2576	0.9169	0.6837	0.013*	
C4	0.2450 (3)	0.9596 (2)	0.51800 (17)	0.0106 (4)	
C5	0.1881 (3)	0.8957 (2)	0.41301 (16)	0.0114 (4)	
C6	0.1219 (3)	0.7610 (2)	0.40323 (16)	0.0119 (4)	
H6	0.0891	0.7197	0.3313	0.014*	
N2	0.1874 (3)	0.97025 (17)	0.30795 (15)	0.0150 (4)	

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.0276 (2)	0.00876 (18)	0.0110 (2)	-0.00692 (15)	0.00460 (15)	-0.00212 (14)
O1	0.0212 (8)	0.0095 (7)	0.0123 (8)	-0.0040 (6)	0.0028 (6)	0.0002 (5)
O2	0.0251 (8)	0.0103 (7)	0.0088 (7)	-0.0004 (6)	0.0021 (6)	-0.0006 (6)
O3	0.0201 (8)	0.0090 (7)	0.0146 (8)	-0.0040 (6)	0.0052 (7)	-0.0001 (6)
O4	0.0442 (11)	0.0199 (9)	0.0253 (9)	-0.0091 (8)	0.0124 (8)	0.0029 (7)
O5	0.0523 (13)	0.0497 (12)	0.0151 (9)	-0.0240 (10)	-0.0036 (9)	0.0070 (8)

O6	0.0271 (10)	0.0238 (9)	0.0234 (10)	-0.0057 (8)	0.0019 (8)	0.0029 (8)
N1	0.0125 (9)	0.0104 (8)	0.0100 (8)	-0.0010 (7)	0.0004 (7)	-0.0013 (6)
C1	0.0107 (10)	0.0107 (10)	0.0149 (11)	0.0005 (8)	0.0027 (8)	0.0031 (8)
C2	0.0123 (10)	0.0102 (9)	0.0091 (10)	0.0006 (8)	0.0006 (8)	0.0012 (7)
C3	0.0109 (10)	0.0116 (10)	0.0093 (10)	0.0000 (8)	0.0007 (8)	-0.0011 (7)
C4	0.0077 (9)	0.0100 (9)	0.0145 (10)	0.0007 (7)	0.0030 (8)	-0.0003 (7)
C5	0.0104 (10)	0.0139 (10)	0.0105 (10)	-0.0004 (8)	0.0034 (8)	0.0030 (8)
C6	0.0117 (11)	0.0149 (10)	0.0099 (10)	-0.0002 (8)	0.0036 (8)	-0.0028 (8)
N2	0.0150 (9)	0.0165 (9)	0.0136 (9)	-0.0015 (7)	0.0033 (8)	0.0011 (7)

Geometric parameters (Å, °)

Cu1—N1	1.9685 (16)	O6—H6C	0.85 (1)
Cu1—O1	1.9667 (15)	N1—C6	1.332 (2)
Cu1—O6	2.479 (2)	N1—C2	1.358 (2)
O1—C1	1.263 (2)	C1—C2	1.518 (3)
O2—C1	1.242 (2)	C2—C3	1.360 (3)
O3—C4	1.312 (2)	C3—C4	1.409 (3)
O3—H3	0.79 (3)	C3—H3A	0.9500
O4—N2	1.211 (2)	C4—C5	1.405 (3)
O5—N2	1.219 (2)	C5—C6	1.385 (3)
O6—H6A	0.84 (1)	C5—N2	1.480 (2)
O6—H6B	0.85 (1)	C6—H6	0.9500
O1—Cu1—O1 ⁱ	180.0	O2—C1—C2	118.24 (17)
O1—Cu1—N1	83.24 (6)	O1—C1—C2	115.97 (17)
O1 ⁱ —Cu1—N1	96.76 (6)	N1—C2—C3	123.75 (18)
O1—Cu1—N1 ⁱ	96.76 (6)	N1—C2—C1	113.45 (17)
O1 ⁱ —Cu1—N1 ⁱ	83.24 (6)	C3—C2—C1	122.80 (18)
N1—Cu1—N1 ⁱ	180.0	C2—C3—C4	119.73 (18)
O1—Cu1—O6	89.52 (6)	C2—C3—H3A	120.1
O1—Cu1—O6 ⁱ	90.48 (6)	C4—C3—H3A	120.1
N1—Cu1—O6 ⁱ	87.50 (7)	O3—C4—C5	121.85 (18)
O6—Cu1—N1	92.50 (7)	O3—C4—C3	122.42 (18)
O6—Cu1—O6 ⁱ	180.00	C5—C4—C3	115.70 (18)
C1—O1—Cu1	114.76 (13)	C6—C5—C4	121.20 (18)
C4—O3—H3	109 (2)	C6—C5—N2	117.04 (17)
H6A—O6—H6B	112.7 (17)	C4—C5—N2	121.71 (17)
H6A—O6—H6C	111.5 (17)	N1—C6—C5	121.74 (18)
H6B—O6—H6C	111.2 (17)	N1—C6—H6	119.1
C6—N1—C2	117.79 (17)	C5—C6—H6	119.1
C6—N1—Cu1	129.69 (14)	O4—N2—O5	124.71 (18)
C2—N1—Cu1	112.42 (13)	O4—N2—C5	118.54 (17)
O2—C1—O1	125.79 (19)	O5—N2—C5	116.68 (17)
N1—Cu1—O1—C1	3.72 (14)	N1—C2—C3—C4	2.6 (3)
N1 ⁱ —Cu1—O1—C1	-176.28 (14)	C1—C2—C3—C4	-178.09 (18)
O1—Cu1—N1—C6	-178.60 (18)	C2—C3—C4—O3	178.19 (18)

O1 ⁱ —Cu1—N1—C6	1.40 (18)	C2—C3—C4—C5	0.1 (3)
O1—Cu1—N1—C2	-2.41 (13)	O3—C4—C5—C6	179.52 (18)
O1 ⁱ —Cu1—N1—C2	177.59 (13)	C3—C4—C5—C6	-2.4 (3)
Cu1—O1—C1—O2	176.32 (16)	O3—C4—C5—N2	-3.1 (3)
Cu1—O1—C1—C2	-4.1 (2)	C3—C4—C5—N2	175.00 (17)
C6—N1—C2—C3	-3.0 (3)	C2—N1—C6—C5	0.5 (3)
Cu1—N1—C2—C3	-179.66 (16)	Cu1—N1—C6—C5	176.56 (14)
C6—N1—C2—C1	177.69 (16)	C4—C5—C6—N1	2.1 (3)
Cu1—N1—C2—C1	1.0 (2)	N2—C5—C6—N1	-175.38 (17)
O2—C1—C2—N1	-178.33 (17)	C6—C5—N2—O4	-165.03 (19)
O1—C1—C2—N1	2.1 (3)	C4—C5—N2—O4	17.5 (3)
O2—C1—C2—C3	2.3 (3)	C6—C5—N2—O5	18.0 (3)
O1—C1—C2—C3	-177.27 (18)	C4—C5—N2—O5	-159.5 (2)

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

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
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O6—H6A \cdots O2 ⁱⁱⁱ	0.84 (1)	2.28 (2)	3.014 (2)	146 (3)
O6—H6B \cdots O6 ^{iv}	0.85 (1)	2.00 (1)	2.836 (3)	170 (5)
O6—H6C \cdots O3 ^v	0.85 (1)	2.49 (3)	3.109 (2)	130 (3)

Symmetry codes: (ii) $-x+1/2, y+1/2, -z+3/2$; (iii) $-x+1/2, y-1/2, -z+3/2$; (iv) $-x+1, -y+1, -z+1$; (v) $x, y-1, z$.