

***trans*-Bis(5-carboxy-2-methyl-1*H*-imidazole-4-carboxylato- κ^2N^3,O^4)copper(II)**

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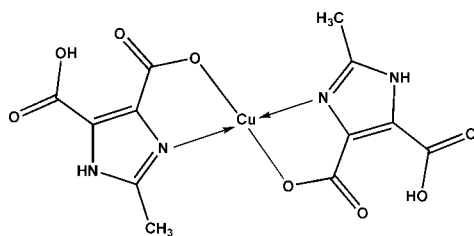
Received 25 April 2009; accepted 5 May 2009

Key indicators: single-crystal X-ray study; $T = 292$ K; mean $\sigma(C-C) = 0.003$ Å; R factor = 0.030; wR factor = 0.084; data-to-parameter ratio = 13.9.

In the title compound, $[Cu(C_6H_5N_2O_4)_2]$, the copper(II) atom lies on an inversion centre and is in an N_2O_2 four-coordinate environment with a nearly regular square-planar geometry. An extended network of intramolecular $O-H\cdots O$ and intermolecular $N-H\cdots O$ and $C-H\cdots O$ hydrogen bonds stabilizes the crystal structure.

Related literature

For the synthesis and crystal structure of metal complexes with *N*-heterocyclic carboxylic acids, see: Nie *et al.* (2007); Liang *et al.* (2002); Net *et al.* (1989); Zeng *et al.* (2008).

**Experimental***Crystal data*

$[Cu(C_6H_5N_2O_4)_2]$
 $M_r = 401.78$
Monoclinic, $P2_1/n$
 $a = 7.3780$ (17) Å

$b = 7.575$ (2) Å
 $c = 12.863$ (3) Å
 $\beta = 101.287$ (13)°
 $V = 705.0$ (3) Å³

$Z = 2$
Mo $K\alpha$ radiation
 $\mu = 1.61$ mm⁻¹

$T = 292$ K
 $0.30 \times 0.25 \times 0.20$ mm

Data collection

Rigaku SCXmini diffractometer
Absorption correction: multi-scan
(*CrystalClear*; Rigaku, 2005)
 $T_{min} = 0.638$, $T_{max} = 0.727$

5198 measured reflections
1609 independent reflections
1472 reflections with $I > 2\sigma(I)$
 $R_{int} = 0.019$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.030$
 $wR(F^2) = 0.084$
 $S = 1.07$
1609 reflections

116 parameters
H-atom parameters constrained
 $\Delta\rho_{max} = 0.28$ e Å⁻³
 $\Delta\rho_{min} = -0.66$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

| $D-H\cdots A$ | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|-------------------------|-------|-------------|-------------|---------------|
| $N2-H2A\cdots O2^i$ | 0.86 | 2.01 | 2.822 (2) | 157 |
| $C1-H1A\cdots O4^{ii}$ | 0.96 | 2.49 | 3.217 (2) | 132 |
| $C1-H1B\cdots O3^{iii}$ | 0.96 | 2.58 | 3.285 (3) | 130 |
| $C1-H1C\cdots O1^{iv}$ | 0.96 | 2.43 | 3.258 (3) | 144 |
| $O3-H3A\cdots O2$ | 0.91 | 1.67 | 2.576 (2) | 171 |

Symmetry codes: (i) $x + \frac{1}{2}, -y + \frac{1}{2}, z + \frac{1}{2}$; (ii) $-x + \frac{3}{2}, y + \frac{1}{2}, -z + \frac{1}{2}$; (iii) $x - \frac{1}{2}, -y + \frac{1}{2}, z + \frac{1}{2}$; (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/PC* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL/PC*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: RZ2318).

References

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supplementary materials

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trans-Bis(5-carboxy-2-methyl-1*H*-imidazole-4-carboxylato- κ^2N^3,O^4)copper(II)

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Comment

The study of metal complexes with *N*-heterocyclic carboxylic acids has been given considerable attention ((Nie *et al.*, 2007; Liang *et al.*, 2002; Net *et al.*, 1989; Zeng *et al.*, 2008). In this paper, we report on the synthesis and structure of the title compound, which was obtained by the hydrothermal reaction of CuCl₂ with 2-methyl-1*H*-imidazole-4,5-dicarboxylic acid.

Figure 1 shows the monomeric complex molecule along with the atom-labelling scheme. The copper(II) metal lies on an inversion centre and is in an N₂O₂ four-coordinate environment with a regular square-planar geometry. The Cu—O distance is 1.9633 (15) Å and the Cu—N distance is 1.9830 (14) Å. The five-membered chelating ring assumes an approximately planar conformation (maximum deviation -0.033 (1) Å for atom N1). The crystal structure is stabilized by an intramolecular O—H···O hydrogen bond, and by intermolecular N—H···O and C—H···O hydrogen interactions (Table 1), forming an extended three-dimensional network (Fig. 2).

Experimental

Blue single crystals of title compound were obtained by hydrothermal treatment of CuCl₂ (1 mmol), 2-methyl-1*H*-imidazole-4,5-dicarboxylic acid (1 mmol) and water (5 ml) over 2 days at 388 K. Yield: 61% (based on CuCl₂).

Refinement

The hydroxyl H atom was located from a difference Fourier map but not refined [$U_{\text{iso}}(\text{H})=1.5U_{\text{eq}}(\text{O})$]. All other H atoms were placed at calculated positions and refined as riding, with C—H = 0.96 Å, N—H = 0.86 Å, and with $U_{\text{iso}}(\text{H})=1.5U_{\text{eq}}(\text{C})$ and $U_{\text{iso}}(\text{H})=1.2U_{\text{eq}}(\text{N})$

Figures

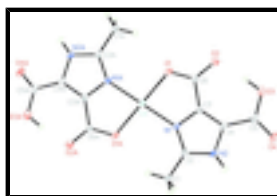


Fig. 1. The molecular structure of the title compound, showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. Atoms labelled with suffix A are generated by the symmetry operation $(-x, 1 - y, -z)$.

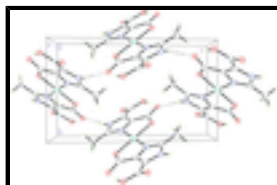


Fig. 2. Packing diagram of the title compound viewed along the *a* axis. Intermolecular hydrogen bonds are shown as dashed lines.

trans-Bis(5-carboxy-2-methyl-1H-imidazole-4-carboxylato- $\kappa^2\text{N}^3,\text{O}^4$)copper(II)

Crystal data

[Cu(C₆H₅N₂O₄)₂]

$M_r = 401.78$

Monoclinic, $P2_1/n$

Hall symbol: -P 2yn

$a = 7.3780$ (17) Å

$b = 7.575$ (2) Å

$c = 12.863$ (3) Å

$\beta = 101.287$ (13)°

$V = 705.0$ (3) Å³

$Z = 2$

$F_{000} = 406$

$D_x = 1.893$ Mg m⁻³

Mo $K\alpha$ radiation

$\lambda = 0.71073$ Å

Cell parameters from 2111 reflections

$\theta = 3.1$ – 27.5 °

$\mu = 1.61$ mm⁻¹

$T = 292$ K

Prism, blue

$0.30 \times 0.25 \times 0.20$ mm

Data collection

Rigaku SCXmini
diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

Detector resolution: 13.6612 pixels mm⁻¹

$T = 292$ K

ω scans

Absorption correction: multi-scan
(CrystalClear; Rigaku, 2005)

$T_{\min} = 0.638$, $T_{\max} = 0.727$

5198 measured reflections

1609 independent reflections

1472 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.019$

$\theta_{\max} = 27.5$ °

$\theta_{\min} = 3.1$ °

$h = -9 \rightarrow 9$

$k = -9 \rightarrow 8$

$l = -16 \rightarrow 16$

Refinement

Refinement on F^2

Least-squares matrix: full

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

$wR(F^2) = 0.084$

$S = 1.07$

1609 reflections

116 parameters

Primary atom site location: structure-invariant direct
methods

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring
sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0506P)^2 + 0.3299P]$

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

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

$\Delta\rho_{\max} = 0.28$ e Å⁻³

$\Delta\rho_{\min} = -0.66$ e Å⁻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)

| | <i>x</i> | <i>y</i> | <i>z</i> | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|-----|--------------|------------|---------------|----------------------------------|
| Cu1 | 0.0000 | 0.5000 | 0.0000 | 0.02591 (14) |
| C1 | 0.3363 (3) | 0.5580 (3) | 0.26068 (15) | 0.0322 (4) |
| H1A | 0.4201 | 0.6562 | 0.2725 | 0.048* |
| H1B | 0.3575 | 0.4828 | 0.3219 | 0.048* |
| H1C | 0.2114 | 0.6005 | 0.2482 | 0.048* |
| C2 | 0.3672 (2) | 0.4571 (3) | 0.16737 (14) | 0.0222 (4) |
| C3 | 0.3316 (2) | 0.3269 (2) | 0.01393 (13) | 0.0211 (3) |
| C4 | 0.5089 (2) | 0.2949 (2) | 0.06414 (13) | 0.0221 (4) |
| C5 | 0.6677 (3) | 0.2144 (3) | 0.02784 (15) | 0.0267 (4) |
| C6 | 0.2221 (2) | 0.2795 (3) | −0.09127 (14) | 0.0241 (4) |
| N1 | 0.24525 (19) | 0.4288 (2) | 0.07763 (11) | 0.0216 (3) |
| N2 | 0.5278 (2) | 0.3781 (2) | 0.16036 (11) | 0.0226 (3) |
| H2A | 0.6266 | 0.3796 | 0.2086 | 0.027* |
| O1 | 0.06229 (18) | 0.3460 (2) | −0.11265 (10) | 0.0328 (3) |
| O2 | 0.29058 (19) | 0.1816 (2) | −0.15194 (10) | 0.0325 (3) |
| O3 | 0.6306 (2) | 0.1289 (2) | −0.06309 (11) | 0.0362 (4) |
| H3A | 0.5102 | 0.1358 | −0.0972 | 0.054* |
| O4 | 0.8232 (2) | 0.2331 (2) | 0.07777 (12) | 0.0396 (4) |

Atomic displacement parameters (\AA^2)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|-----|--------------|-------------|--------------|--------------|---------------|---------------|
| Cu1 | 0.01512 (18) | 0.0374 (2) | 0.02196 (19) | 0.00490 (12) | −0.00433 (12) | −0.00595 (12) |
| C1 | 0.0263 (10) | 0.0449 (12) | 0.0231 (9) | 0.0015 (9) | −0.0008 (7) | −0.0072 (8) |
| C2 | 0.0190 (8) | 0.0268 (9) | 0.0190 (8) | −0.0015 (7) | −0.0004 (6) | 0.0029 (7) |
| C3 | 0.0172 (8) | 0.0242 (9) | 0.0205 (8) | −0.0010 (6) | 0.0000 (6) | 0.0001 (6) |
| C4 | 0.0189 (8) | 0.0240 (9) | 0.0217 (8) | 0.0008 (7) | −0.0001 (6) | 0.0029 (7) |
| C5 | 0.0210 (8) | 0.0291 (10) | 0.0294 (9) | 0.0036 (7) | 0.0034 (7) | 0.0054 (7) |
| C6 | 0.0201 (8) | 0.0304 (10) | 0.0196 (8) | −0.0010 (7) | −0.0013 (6) | −0.0023 (7) |
| N1 | 0.0165 (7) | 0.0275 (8) | 0.0190 (7) | 0.0003 (6) | −0.0013 (5) | −0.0017 (6) |
| N2 | 0.0172 (7) | 0.0294 (8) | 0.0184 (7) | 0.0003 (6) | −0.0038 (5) | 0.0025 (6) |
| O1 | 0.0206 (7) | 0.0470 (9) | 0.0263 (7) | 0.0062 (6) | −0.0065 (5) | −0.0103 (6) |

supplementary materials

| | | | | | | |
|----|------------|-------------|------------|------------|-------------|-------------|
| O2 | 0.0252 (7) | 0.0441 (8) | 0.0256 (7) | 0.0036 (6) | -0.0010 (5) | -0.0113 (6) |
| O3 | 0.0273 (7) | 0.0465 (9) | 0.0342 (8) | 0.0079 (6) | 0.0047 (6) | -0.0077 (6) |
| O4 | 0.0196 (7) | 0.0569 (10) | 0.0390 (8) | 0.0073 (7) | -0.0025 (6) | 0.0007 (7) |

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

| | | | |
|--------------------------------------|--------------|----------------------------|--------------|
| Cu1—N1 | 1.9633 (15) | C3—N1 | 1.370 (2) |
| Cu1—N1 ⁱ | 1.9633 (15) | C3—C6 | 1.478 (2) |
| Cu1—O1 | 1.9830 (14) | C4—N2 | 1.372 (2) |
| Cu1—O1 ⁱ | 1.9830 (14) | C4—C5 | 1.475 (3) |
| C1—C2 | 1.478 (3) | C5—O4 | 1.208 (2) |
| C1—H1A | 0.9600 | C5—O3 | 1.318 (2) |
| C1—H1B | 0.9600 | C6—O2 | 1.252 (2) |
| C1—H1C | 0.9600 | C6—O1 | 1.262 (2) |
| C2—N1 | 1.335 (2) | N2—H2A | 0.8600 |
| C2—N2 | 1.346 (2) | O3—H3A | 0.9117 |
| C3—C4 | 1.363 (2) | | |
| N1—Cu1—N1 ⁱ | 180.0 | C3—C4—N2 | 105.31 (15) |
| N1—Cu1—O1 | 83.56 (6) | C3—C4—C5 | 132.21 (17) |
| N1 ⁱ —Cu1—O1 | 96.44 (6) | N2—C4—C5 | 121.95 (16) |
| N1—Cu1—O1 ⁱ | 96.44 (6) | O4—C5—O3 | 122.69 (18) |
| N1 ⁱ —Cu1—O1 ⁱ | 83.56 (6) | O4—C5—C4 | 120.88 (18) |
| O1—Cu1—O1 ⁱ | 180.00 (5) | O3—C5—C4 | 116.37 (16) |
| C2—C1—H1A | 109.5 | O2—C6—O1 | 125.06 (16) |
| C2—C1—H1B | 109.5 | O2—C6—C3 | 119.96 (16) |
| H1A—C1—H1B | 109.5 | O1—C6—C3 | 114.98 (16) |
| C2—C1—H1C | 109.5 | C2—N1—C3 | 107.11 (14) |
| H1A—C1—H1C | 109.5 | C2—N1—Cu1 | 142.56 (13) |
| H1B—C1—H1C | 109.5 | C3—N1—Cu1 | 109.91 (11) |
| N1—C2—N2 | 108.89 (16) | C2—N2—C4 | 109.26 (14) |
| N1—C2—C1 | 126.93 (17) | C2—N2—H2A | 125.4 |
| N2—C2—C1 | 124.18 (16) | C4—N2—H2A | 125.4 |
| C4—C3—N1 | 109.42 (15) | C6—O1—Cu1 | 114.58 (11) |
| C4—C3—C6 | 133.84 (17) | C5—O3—H3A | 114.3 |
| N1—C3—C6 | 116.72 (15) | | |
| N1—C3—C4—N2 | 0.6 (2) | C4—C3—N1—C2 | -1.1 (2) |
| C6—C3—C4—N2 | 178.80 (19) | C6—C3—N1—C2 | -179.58 (16) |
| N1—C3—C4—C5 | -170.85 (19) | C4—C3—N1—Cu1 | 173.21 (12) |
| C6—C3—C4—C5 | 7.3 (4) | C6—C3—N1—Cu1 | -5.3 (2) |
| C3—C4—C5—O4 | 163.5 (2) | O1—Cu1—N1—C2 | 175.3 (2) |
| N2—C4—C5—O4 | -6.8 (3) | O1 ⁱ —Cu1—N1—C2 | -4.7 (2) |
| C3—C4—C5—O3 | -13.6 (3) | O1—Cu1—N1—C3 | 4.36 (12) |
| N2—C4—C5—O3 | 176.04 (17) | O1 ⁱ —Cu1—N1—C3 | -175.64 (12) |
| C4—C3—C6—O2 | 4.4 (3) | N1—C2—N2—C4 | -0.7 (2) |
| N1—C3—C6—O2 | -177.58 (17) | C1—C2—N2—C4 | 179.41 (18) |
| C4—C3—C6—O1 | -174.8 (2) | C3—C4—N2—C2 | 0.0 (2) |
| N1—C3—C6—O1 | 3.2 (3) | C5—C4—N2—C2 | 172.59 (17) |

| | | | |
|--------------|--------------|----------------------------|--------------|
| N2—C2—N1—C3 | 1.1 (2) | O2—C6—O1—Cu1 | -178.45 (16) |
| C1—C2—N1—C3 | -179.04 (19) | C3—C6—O1—Cu1 | 0.7 (2) |
| N2—C2—N1—Cu1 | -170.06 (15) | N1—Cu1—O1—C6 | -2.89 (14) |
| C1—C2—N1—Cu1 | 9.8 (4) | N1 ⁱ —Cu1—O1—C6 | 177.11 (14) |

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

Hydrogen-bond geometry (Å, °)

| <i>D—H...A</i> | <i>D—H</i> | <i>H...A</i> | <i>D...A</i> | <i>D—H...A</i> |
|----------------------------|------------|--------------|--------------|----------------|
| N2—H2A...O2 ⁱⁱ | 0.86 | 2.01 | 2.822 (2) | 157 |
| C1—H1A...O4 ⁱⁱⁱ | 0.96 | 2.49 | 3.217 (2) | 132 |
| C1—H1B...O3 ^{iv} | 0.96 | 2.58 | 3.285 (3) | 130 |
| C1—H1C...O1 ⁱ | 0.96 | 2.43 | 3.258 (3) | 144 |
| O3—H3A...O2 | 0.91 | 1.67 | 2.576 (2) | 171 |

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

Fig. 1

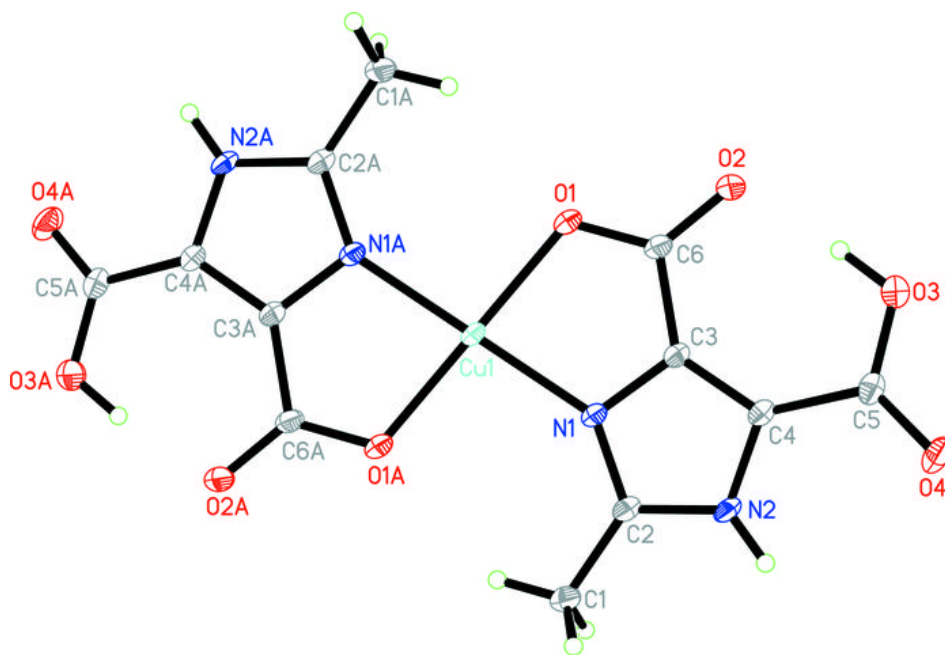


Fig. 2

