

Bis(benzohydrazide- κ^2O,N')bis(nitrato- κO)copper(II)

Elhadj Ibrahima Thiam,^a Aliou Hamady Barry,^a Alda Navaza,^b Pascal Retailleau,^c Mohamed Gaye^{a*} and Abdou Salam Sall^a

^aDépartement de Chimie, Faculté des Sciences et Techniques, Université Cheikh Anta Diop, Dakar, Sénégal, ^bANBioPhi FRE 3207 CNRS, Université de Paris 13, 74 Rue Marcel Cachin, 93017, Bobigny, France, and ^cICSN-CNRS, Laboratoire de Cristallogénie, 1 Avenue la Terrasse, 91198 Gif sur Yvette, France
Correspondence e-mail: mlgayeastou@yahoo.fr

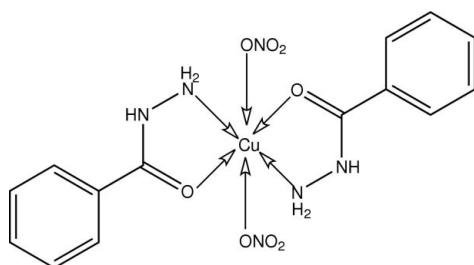
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Key indicators: single-crystal X-ray study; $T = 293$ K; mean $\sigma(C-C) = 0.006$ Å; R factor = 0.036; wR factor = 0.094; data-to-parameter ratio = 12.2.

In the title compound, $[Cu(NO_3)_2(C_7H_8N_2O)_2]$, the Cu^{II} atom is located on a centre of inversion, and is coordinated by two bidentate benzohydrazide ligands and two monodentate nitrate anions in an axially distorted octahedral geometry within an N_2O_4 donor set. The crystal structure is stabilized by $N-H\cdots O$ and weak $N-H\cdots N$ hydrogen bonds.

Related literature

For related structures, see: Sousa-Pedrares *et al.* (2008); Despaigne *et al.* (2009); Hernández-Gil *et al.* (2009).



Experimental

Crystal data

$[Cu(NO_3)_2(C_7H_8N_2O)_2]$
 $M_r = 459.86$
Monoclinic, $P2_1/c$

$a = 10.259$ (5) Å
 $b = 10.078$ (5) Å
 $c = 9.762$ (4) Å

$\beta = 106.85$ (1)°
 $V = 966.0$ (8) Å³
 $Z = 2$
Mo $K\alpha$ radiation

$\mu = 1.19$ mm⁻¹
 $T = 293$ K
 $0.10 \times 0.10 \times 0.10$ mm

Data collection

Nonius KappaCCD diffractometer
Absorption correction: none
3237 measured reflections

1768 independent reflections
1278 reflections with $I > 2\sigma(I)$
 $R_{int} = 0.029$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.036$
 $wR(F^2) = 0.094$
 $S = 1.05$
1768 reflections
145 parameters
3 restraints

H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{max} = 0.24$ e Å⁻³
 $\Delta\rho_{min} = -0.26$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

| $D-H\cdots A$ | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|-------------------------|------------|-------------|-------------|---------------|
| $N1-H1\cdots O4^i$ | 0.911 (17) | 1.94 (2) | 2.794 (4) | 156 (3) |
| $N1-H1\cdots N3^i$ | 0.911 (17) | 2.64 (2) | 3.371 (4) | 138 (2) |
| $N2-H2A\cdots O2^{ii}$ | 0.929 (18) | 2.03 (2) | 2.813 (3) | 141 (3) |
| $N2-H2A\cdots O3^i$ | 0.929 (18) | 2.60 (3) | 3.186 (3) | 122 (2) |
| $N2-H2B\cdots O2^{iii}$ | 0.912 (18) | 1.97 (2) | 2.834 (3) | 159 (3) |

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

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *DENZO/SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO/SCALEPACK*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *PLATON* (Spek, 2009); software used to prepare material for publication: *SHELXL97*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: TK2516).

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supplementary materials

Acta Cryst. (2009). E65, m1014 [doi:10.1107/S1600536809029936]

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Comment

The Cu^{II} cation in (I), Fig. 1, is located on a centre of inversion. The Cu^{II} ion is coordinated to two neutral hydrazone molecules functioning as chelating ligands through the amine-N and carbonyl-O atoms. The equatorial bond Cu–O and Cu–N lengths [1.940 (2) and 1.970 (3) Å, respectively] are similar to those observed in related compounds (Sousa-Pedrares et al., 2008; Despaigne et al., 2009). The remaining coordination positions are occupied by two nitrate-O atoms which are located in apical positions [O1–Cu–O3 = 82.49 (8) °; and Cu–O3 = 2.589 (2) Å]. The axially distorted N₂O₄ coordination geometry is consistent with a Jahn–Teller effect (Hernández-Gilet et al., 2009). In the crystal structure, intermolecular N—H...O and (weak) N—H...N hydrogen bonds interactions link the molecules into a 2-D array (Table 1).

Experimental

All purchased chemicals and solvents were reagent grade and used without further purification. To a mixture of benzohydrazide (0.2721 g, 2 mmol) and methanol (10 ml) was added dropwise a solution of copper nitrate trihydrate (0.2416 g, 1 mmol) in methanol (10 ml). The resulting green solution was stirred and refluxed for 2 h. The compound was filtered, and slow evaporation of the filtrate gave 0.2930 g (63.7 %) of (I). Analysis: calculated for C₁₄H₁₆CuN₄O₈: C 36.57, H 3.51, N 18.28 %; found: C 36.55, H 3.48, N 18.13. Crystals were obtained from slow evaporation of an ethanol solution of (I).

Refinement

The H atoms of the NH and NH₂ groups were located in the Fourier difference maps and refined with N—H = 0.96 (2) Å. The remaining H atoms were placed geometrically and refined in the riding model approximation with C—H = 0.93 Å, and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

Figures

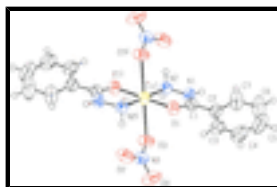


Fig. 1. The molecular structure of (I), showing 50% probability displacement ellipsoids and the atom-numbering scheme. Symmetry code: (i) $-x, -y, -z$

Bis(benzohydrazide- κ^2O,N')bis(nitrato- κO)copper(II)

Crystal data

[Cu(NO₃)₂(C₇H₈N₂O)₂]

$F_{000} = 470$

supplementary materials

$$M_r = 459.86$$

Monoclinic, $P2_1/c$

Hall symbol: -P 2ybc

$$a = 10.259 (5) \text{ \AA}$$

$$b = 10.078 (5) \text{ \AA}$$

$$c = 9.762 (4) \text{ \AA}$$

$$\beta = 106.85 (1)^\circ$$

$$V = 966.0 (8) \text{ \AA}^3$$

$$Z = 2$$

$$D_x = 1.581 \text{ Mg m}^{-3}$$

Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$

Cell parameters from 1847 reflections

$$\theta = 0.4\text{--}25.4^\circ$$

$$\mu = 1.19 \text{ mm}^{-1}$$

$$T = 293 \text{ K}$$

Prism, blue

$$0.10 \times 0.10 \times 0.10 \text{ mm}$$

Data collection

Nonius KappaCCD diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

$$T = 293 \text{ K}$$

π scans

Absorption correction: none

3237 measured reflections

1768 independent reflections

1278 reflections with $I > 2\sigma(I)$

$$R_{\text{int}} = 0.029$$

$$\theta_{\text{max}} = 25.4^\circ$$

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

$$h = -12 \rightarrow 12$$

$$k = -12 \rightarrow 11$$

$$l = -11 \rightarrow 11$$

Refinement

Refinement on F^2

Least-squares matrix: full

$$R[F^2 > 2\sigma(F^2)] = 0.036$$

$$wR(F^2) = 0.094$$

$$S = 1.05$$

1768 reflections

145 parameters

3 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

$$w = 1/[\sigma^2(F_o^2) + (0.0419P)^2 + 0.3254P]$$

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

$$(\Delta\sigma)_{\text{max}} = 0.003$$

$$\Delta\rho_{\text{max}} = 0.24 \text{ e \AA}^{-3}$$

$$\Delta\rho_{\text{min}} = -0.26 \text{ e \AA}^{-3}$$

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 | 0.0000 | 0.0000 | 0.0000 | 0.04486 (19) |
| O1 | -0.19749 (19) | 0.00452 (19) | -0.0567 (2) | 0.0488 (5) |
| O2 | -0.0400 (3) | -0.1377 (2) | -0.3265 (2) | 0.0779 (8) |
| O3 | -0.0372 (2) | 0.0668 (2) | -0.2647 (2) | 0.0604 (6) |
| O4 | -0.1549 (3) | 0.0048 (2) | -0.4748 (2) | 0.0777 (8) |
| N1 | -0.1582 (2) | 0.2195 (3) | -0.0063 (3) | 0.0490 (6) |
| H1 | -0.183 (3) | 0.3054 (19) | 0.001 (3) | 0.058 (9)* |
| N2 | -0.0173 (2) | 0.1913 (2) | 0.0322 (2) | 0.0431 (6) |
| H2A | 0.020 (3) | 0.212 (3) | 0.128 (2) | 0.065 (10)* |
| H2B | 0.023 (3) | 0.243 (3) | -0.020 (3) | 0.061 (10)* |
| N3 | -0.0780 (3) | -0.0207 (2) | -0.3550 (3) | 0.0492 (6) |
| C1 | -0.2427 (3) | 0.1197 (3) | -0.0488 (3) | 0.0466 (7) |
| C2 | -0.3914 (3) | 0.1439 (3) | -0.0875 (3) | 0.0544 (8) |
| C3 | -0.4773 (3) | 0.0501 (4) | -0.1710 (4) | 0.0732 (10) |
| H3 | -0.4410 | -0.0246 | -0.2024 | 0.088* |
| C4 | -0.6155 (4) | 0.0674 (6) | -0.2074 (4) | 0.0973 (14) |
| H4 | -0.6723 | 0.0049 | -0.2653 | 0.117* |
| C5 | -0.6709 (4) | 0.1739 (6) | -0.1605 (5) | 0.1008 (16) |
| H5 | -0.7649 | 0.1841 | -0.1857 | 0.121* |
| C6 | -0.5871 (5) | 0.2671 (5) | -0.0752 (6) | 0.1043 (16) |
| H6 | -0.6248 | 0.3400 | -0.0423 | 0.125* |
| C7 | -0.4457 (4) | 0.2523 (4) | -0.0379 (5) | 0.0804 (11) |
| H7 | -0.3890 | 0.3150 | 0.0198 | 0.096* |

Atomic displacement parameters (\AA^2)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|-----|-------------|-------------|-------------|--------------|--------------|--------------|
| Cu1 | 0.0462 (3) | 0.0307 (3) | 0.0588 (3) | -0.0001 (2) | 0.0170 (2) | -0.0012 (2) |
| O1 | 0.0476 (11) | 0.0350 (11) | 0.0640 (12) | -0.0019 (10) | 0.0166 (10) | -0.0027 (10) |
| O2 | 0.146 (2) | 0.0381 (13) | 0.0555 (13) | 0.0204 (14) | 0.0385 (14) | 0.0072 (10) |
| O3 | 0.0891 (17) | 0.0414 (12) | 0.0477 (12) | -0.0098 (12) | 0.0154 (12) | -0.0092 (10) |
| O4 | 0.104 (2) | 0.0504 (15) | 0.0546 (14) | -0.0168 (13) | -0.0155 (14) | 0.0068 (11) |
| N1 | 0.0501 (15) | 0.0358 (14) | 0.0573 (15) | 0.0064 (12) | 0.0097 (12) | -0.0033 (12) |
| N2 | 0.0495 (15) | 0.0348 (13) | 0.0426 (14) | -0.0011 (11) | 0.0095 (12) | -0.0008 (11) |
| N3 | 0.0673 (16) | 0.0380 (16) | 0.0437 (14) | -0.0045 (12) | 0.0182 (13) | 0.0015 (11) |
| C1 | 0.0523 (17) | 0.0462 (19) | 0.0420 (16) | 0.0038 (14) | 0.0147 (14) | 0.0047 (13) |
| C2 | 0.0501 (17) | 0.060 (2) | 0.0540 (18) | 0.0083 (16) | 0.0171 (15) | 0.0102 (16) |
| C3 | 0.054 (2) | 0.099 (3) | 0.062 (2) | 0.000 (2) | 0.0083 (17) | -0.004 (2) |
| C4 | 0.057 (2) | 0.150 (5) | 0.075 (3) | -0.007 (3) | 0.003 (2) | 0.005 (3) |
| C5 | 0.051 (2) | 0.136 (5) | 0.111 (4) | 0.017 (3) | 0.016 (2) | 0.051 (3) |
| C6 | 0.079 (3) | 0.097 (4) | 0.153 (4) | 0.040 (3) | 0.059 (3) | 0.039 (3) |
| C7 | 0.065 (2) | 0.068 (3) | 0.114 (3) | 0.014 (2) | 0.035 (2) | 0.011 (2) |

supplementary materials

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

| | | | |
|--------------------------------------|--------------|-------------|------------|
| Cu1—O1 ⁱ | 1.940 (2) | N2—H2B | 0.912 (18) |
| Cu1—O1 | 1.940 (2) | C1—C2 | 1.482 (4) |
| Cu1—N2 ⁱ | 1.970 (3) | C2—C7 | 1.377 (5) |
| Cu1—N2 | 1.970 (3) | C2—C3 | 1.385 (5) |
| Cu1—O3 | 2.589 (2) | C3—C4 | 1.369 (5) |
| O1—C1 | 1.261 (3) | C3—H3 | 0.9300 |
| O2—N3 | 1.249 (3) | C4—C5 | 1.355 (7) |
| O3—N3 | 1.231 (3) | C4—H4 | 0.9300 |
| O4—N3 | 1.233 (3) | C5—C6 | 1.378 (7) |
| N1—C1 | 1.314 (4) | C5—H5 | 0.9300 |
| N1—N2 | 1.413 (3) | C6—C7 | 1.397 (5) |
| N1—H1 | 0.911 (17) | C6—H6 | 0.9300 |
| N2—H2A | 0.929 (18) | C7—H7 | 0.9300 |
| O1 ⁱ —Cu1—O1 | 180.00 (3) | O4—N3—O2 | 118.7 (3) |
| O1 ⁱ —Cu1—N2 ⁱ | 83.53 (9) | O1—C1—N1 | 120.2 (3) |
| O1—Cu1—N2 ⁱ | 96.47 (9) | O1—C1—C2 | 120.4 (3) |
| O1 ⁱ —Cu1—N2 | 96.47 (9) | N1—C1—C2 | 119.4 (3) |
| O1—Cu1—N2 | 83.53 (9) | C7—C2—C3 | 119.7 (3) |
| N2 ⁱ —Cu1—N2 | 180.00 (14) | C7—C2—C1 | 122.2 (3) |
| O1 ⁱ —Cu1—O3 | 97.51 (8) | C3—C2—C1 | 118.0 (3) |
| O1—Cu1—O3 | 82.49 (8) | C4—C3—C2 | 120.0 (4) |
| N2 ⁱ —Cu1—O3 | 95.12 (8) | C4—C3—H3 | 120.0 |
| N2—Cu1—O3 | 84.88 (8) | C2—C3—H3 | 120.0 |
| C1—O1—Cu1 | 112.10 (18) | C5—C4—C3 | 121.2 (5) |
| N3—O3—Cu1 | 116.74 (17) | C5—C4—H4 | 119.4 |
| C1—N1—N2 | 117.4 (2) | C3—C4—H4 | 119.4 |
| C1—N1—H1 | 125.2 (19) | C4—C5—C6 | 119.7 (4) |
| N2—N1—H1 | 117.4 (19) | C4—C5—H5 | 120.2 |
| N1—N2—Cu1 | 106.71 (17) | C6—C5—H5 | 120.2 |
| N1—N2—H2A | 108.4 (19) | C5—C6—C7 | 120.2 (4) |
| Cu1—N2—H2A | 111 (2) | C5—C6—H6 | 119.9 |
| N1—N2—H2B | 109.6 (19) | C7—C6—H6 | 119.9 |
| Cu1—N2—H2B | 113 (2) | C2—C7—C6 | 119.2 (4) |
| H2A—N2—H2B | 108 (3) | C2—C7—H7 | 120.4 |
| O3—N3—O4 | 121.4 (3) | C6—C7—H7 | 120.4 |
| O3—N3—O2 | 119.8 (3) | | |
| N2 ⁱ —Cu1—O1—C1 | -179.41 (19) | N2—N1—C1—O1 | -1.4 (4) |
| N2—Cu1—O1—C1 | 0.59 (19) | N2—N1—C1—C2 | 178.8 (2) |
| O3—Cu1—O1—C1 | -85.07 (19) | O1—C1—C2—C7 | 157.9 (3) |
| O1 ⁱ —Cu1—O3—N3 | 105.7 (2) | N1—C1—C2—C7 | -22.2 (4) |
| O1—Cu1—O3—N3 | -74.3 (2) | O1—C1—C2—C3 | -19.0 (4) |
| N2 ⁱ —Cu1—O3—N3 | 21.6 (2) | N1—C1—C2—C3 | 160.8 (3) |
| N2—Cu1—O3—N3 | -158.4 (2) | C7—C2—C3—C4 | 1.9 (5) |

| | | | |
|----------------------------|--------------|-------------|------------|
| C1—N1—N2—Cu1 | 1.7 (3) | C1—C2—C3—C4 | 179.0 (3) |
| O1 ⁱ —Cu1—N2—N1 | 178.82 (16) | C2—C3—C4—C5 | -1.5 (6) |
| O1—Cu1—N2—N1 | -1.18 (16) | C3—C4—C5—C6 | 0.3 (7) |
| O3—Cu1—N2—N1 | 81.82 (16) | C4—C5—C6—C7 | 0.4 (7) |
| Cu1—O3—N3—O4 | 146.4 (2) | C3—C2—C7—C6 | -1.2 (5) |
| Cu1—O3—N3—O2 | -34.6 (3) | C1—C2—C7—C6 | -178.2 (3) |
| Cu1—O1—C1—N1 | 0.2 (3) | C5—C6—C7—C2 | 0.1 (6) |
| Cu1—O1—C1—C2 | -179.91 (19) | | |

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

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

| $D-H\cdots A$ | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|-----------------------------------|------------|-------------|-------------|---------------|
| N1—H1 \cdots O4 ⁱⁱ | 0.911 (17) | 1.94 (2) | 2.794 (4) | 156 (3) |
| N1—H1 \cdots N3 ⁱⁱ | 0.911 (17) | 2.64 (2) | 3.371 (4) | 138 (2) |
| N2—H2A \cdots O2 ⁱ | 0.929 (18) | 2.03 (2) | 2.813 (3) | 141 (3) |
| N2—H2A \cdots O3 ⁱⁱ | 0.929 (18) | 2.60 (3) | 3.186 (3) | 122 (2) |
| N2—H2B \cdots O2 ⁱⁱⁱ | 0.912 (18) | 1.97 (2) | 2.834 (3) | 159 (3) |

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

Fig. 1

