

**Bis[2-(hydroxymethyl)pyridine- $\kappa^2 N,O$ ]-dinitratocopper(II)****Feng He<sup>a\*</sup> and Di Liu<sup>b</sup>**

<sup>a</sup>School of Chemistry and Chemical Engineering, School of Pharmaceutical Science, Sun Yat-Sen University, Guangzhou 510275, People's Republic of China, and <sup>b</sup>School of Pharmaceutical Science, Sun Yat-Sen University, Guangzhou 510275, People's Republic of China

Correspondence e-mail: exstxr@zsu.edu.cn

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In the crystal structure of the title compound,  $[\text{Cu}(\text{NO}_3)_2 \cdot (\text{C}_6\text{H}_7\text{NO})_2]$ , the copper(II) ion resides at an inversion centre and it has a 4 + 2 elongated octahedral coordination environment. The equatorial positions are occupied by two OH groups and two N atoms from a pair of neutral 2-(hydroxymethyl)pyridine ligands, while the two axial positions are weakly ligated by two nitrate O atoms. Adjacent mononuclear copper(II) complexes are further joined together by O–H···O hydrogen bonds to form a linear chain along the *a* axis.

**Key indicators**

Single-crystal X-ray study

 $T = 293\text{ K}$ Mean  $\sigma(\text{C}-\text{C}) = 0.002\text{ \AA}$ 

Some non-H atoms missing

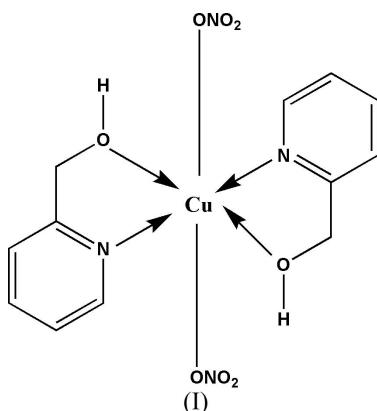
 $R$  factor = 0.025 $wR$  factor = 0.076

Data-to-parameter ratio = 14.4

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

**Comment**

Recently, we have synthesized and characterized a series of discrete dinuclear and polymeric heterometallic copper(II)–lanthanide(III) complexes. In particular, the ligand Htza (tetrazole-1-acetic acid) coordinates with Cu<sup>II</sup> and lanthanide(III) salts to form  $[\text{CuLn}(\text{tza})_4(\text{H}_2\text{O})_5\text{Cl}]$  complexes at pH = 3.5, but forms a multinuclear heterometallic complex at higher pH values (He *et al.*, 2005). We have utilized a related ligand, namely 2-(hydroxymethyl)pyridine, to see whether similar reactions occur or not. Moreover, the title compound, (I), can be used as a so-called ‘metallic ligand’ reagent to bind lanthanide metal ions for the subsequent preparation of heteronuclear complexes which may exhibit large ferromagnetic interactions (Costes, Dahan & Dupuis, 2000; Costes, Dahan, Dupuis & Laurent, 2000) or quadratic non-linear optical properties (Margeat *et al.*, 2004).

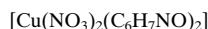


The copper(II) ion in (I) has an octahedral coordination environment (Fig. 1) and adjacent mononuclear copper(II) complexes are interlinked by O–H···O(nitro) hydrogen bonds to form a linear ribbon extending parallel to the *a* axis (Fig. 2).

## Experimental

$\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  (0.242 g, 1 mmol) in water (18 ml) was mixed with 2-(hydroxymethyl)pyridine (0.218 g, 2 mmol). The resulting blue solution was stirred for 5 min and then adjusted to pH 3 with 0.5 M of an aqueous sodium hydroxide solution. The solution was allowed to evaporate slowly at ambient temperature for 40 d. Blue polyhedral crystals were collected in 59% yield.

### Crystal data



$M_r = 405.82$

Monoclinic,  $P2_1/n$

$a = 7.4402$  (5) Å

$b = 12.4849$  (9) Å

$c = 8.4844$  (6) Å

$\beta = 104.5240$  (1)°

$V = 762.93$  (9) Å<sup>3</sup>

$Z = 4$

$D_x = 1.767$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation

Cell parameters from 3474 reflections

$\theta = 2.5\text{--}28.2^\circ$

$\mu = 1.49$  mm<sup>-1</sup>

$T = 293$  (2) K

Polyhedron, deep blue

0.39 × 0.36 × 0.23 mm

### Data collection

Bruker SMART APEX CCD diffractometer

$\varphi$  and  $\omega$  scans

Absorption correction: multi-scan (SADABS; Bruker, 2002)

$T_{\min} = 0.593$ ,  $T_{\max} = 0.726$

4602 measured reflections

1712 independent reflections

1593 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.013$

$\theta_{\text{max}} = 27.5^\circ$

$h = -8 \rightarrow 9$

$k = -15 \rightarrow 15$

$l = -10 \rightarrow 9$

### Refinement

Refinement on  $F^2$

$R[F^2 > 2\sigma(F^2)] = 0.025$

$wR(F^2) = 0.076$

$S = 1.05$

1712 reflections

119 parameters

H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0519P)^2$

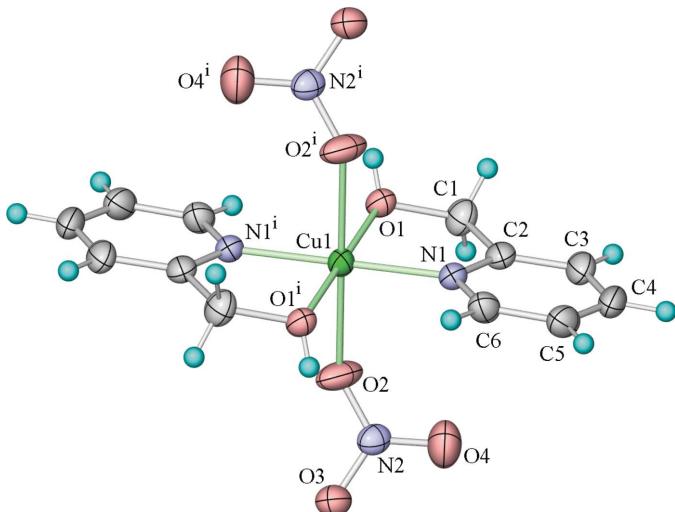
$+ 0.1296P]$

$\text{where } P = (F_o^2 + 2F_c^2)/3$

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

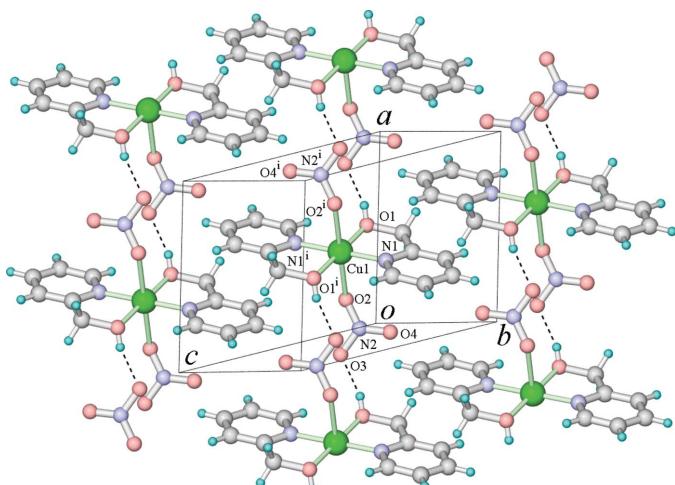
$\Delta\rho_{\text{max}} = 0.28$  e Å<sup>-3</sup>

$\Delta\rho_{\text{min}} = -0.31$  e Å<sup>-3</sup>



**Figure 1**

The molecular structure of the title compound. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry code: (i)  $1 - x, 1 - y, 1 - z$ .]



**Figure 2**

The crystal structure of the title compound. Dashed lines represent hydrogen bonds. [Symmetry code: (i)  $1 - x, 1 - y, 1 - z$ .]

*SHELXTL* (Sheldrick, 2000); software used to prepare material for publication: *SHELXL97*.

**Table 1**

Selected geometric parameters (Å, °).

Cu1—N1	1.952 (1)	Cu1—O1	1.971 (1)
N1—Cu1—N1 <sup>i</sup>	180	N1—Cu1—O1 <sup>i</sup>	97.37 (4)
N1—Cu1—O1	82.63 (4)	O1—Cu1—O1 <sup>i</sup>	180

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

**Table 2**

Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
O1—H1 <sup>i</sup> —O3 <sup>ii</sup>	0.84 (1)	1.75 (1)	2.5567 (16)	159 (2)

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

Data collection: *SMART* (Bruker, 2002); cell refinement: *SAINT* (Bruker, 2002); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics:

## References

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# supporting information

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#### Crystal data

[Cu(NO<sub>3</sub>)<sub>2</sub>(C<sub>6</sub>H<sub>7</sub>NO)<sub>2</sub>]

$M_r = 405.82$

Monoclinic,  $P2_1/n$

Hall symbol: -P 2yn

$a = 7.4402 (5)$  Å

$b = 12.4849 (9)$  Å

$c = 8.4844 (6)$  Å

$\beta = 104.5240 (1)^\circ$

$V = 762.93 (9)$  Å<sup>3</sup>

$Z = 4$

$F(000) = 414$

$D_x = 1.767$  Mg m<sup>-3</sup>

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

Cell parameters from 3474 reflections

$\theta = 2.5\text{--}28.2^\circ$

$\mu = 1.49$  mm<sup>-1</sup>

$T = 293$  K

Polyhedron, deep blue

0.39 × 0.36 × 0.23 mm

#### Data collection

Bruker SMART APEX CCD  
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

$\varphi$  and  $\omega$  scans

Absorption correction: multi-scan  
(SADABS; Bruker, 2002)

$T_{\min} = 0.593$ ,  $T_{\max} = 0.726$

4602 measured reflections

1712 independent reflections

1593 reflections with  $I > 2\sigma I$

$R_{\text{int}} = 0.013$

$\theta_{\max} = 27.5^\circ$ ,  $\theta_{\min} = 3.0^\circ$

$h = -8 \rightarrow 9$

$k = -15 \rightarrow 15$

$l = -10 \rightarrow 9$

#### Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.025$

$wR(F^2) = 0.076$

$S = 1.05$

1712 reflections

119 parameters

1 restraint

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

$w = 1/[\sigma^2(F_o^2) + (0.0519P)^2 + 0.1296P]$   
where  $P = (F_o^2 + 2F_c^2)/3$

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

$\Delta\rho_{\max} = 0.28$  e Å<sup>-3</sup>

$\Delta\rho_{\min} = -0.31$  e Å<sup>-3</sup>

#### 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 ( $\text{\AA}^2$ )*

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Cu1	0.5000	0.5000	0.5000	0.03274 (12)
O1	0.62504 (14)	0.62944 (8)	0.44707 (12)	0.0371 (2)
H1	0.7403 (14)	0.6233 (15)	0.461 (2)	0.043 (5)*
N1	0.39321 (19)	0.49814 (8)	0.26507 (18)	0.0326 (3)
C1	0.5426 (2)	0.67067 (12)	0.28890 (18)	0.0425 (3)
H1A	0.6392	0.6912	0.2364	0.051*
H1B	0.4704	0.7340	0.2981	0.051*
C2	0.41891 (19)	0.58785 (11)	0.18706 (17)	0.0348 (3)
C3	0.3378 (2)	0.60158 (13)	0.02223 (18)	0.0430 (3)
H3	0.3556	0.6647	-0.0300	0.052*
C4	0.2305 (2)	0.52029 (15)	-0.0629 (2)	0.0472 (4)
H4	0.1737	0.5283	-0.1731	0.057*
C5	0.2081 (2)	0.42644 (15)	0.01745 (18)	0.0479 (4)
H5	0.1376	0.3703	-0.0382	0.058*
C6	0.2921 (2)	0.41780 (13)	0.18074 (18)	0.0415 (3)
H6	0.2787	0.3546	0.2347	0.050*
N2	0.09078 (17)	0.63407 (10)	0.47588 (15)	0.0378 (3)
O2	0.25894 (16)	0.62575 (13)	0.54369 (19)	0.0627 (4)
O3	-0.02307 (16)	0.61935 (11)	0.56122 (15)	0.0517 (3)
O4	0.0353 (2)	0.65843 (14)	0.33405 (17)	0.0783 (4)

*Atomic displacement parameters ( $\text{\AA}^2$ )*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Cu1	0.02691 (16)	0.04410 (18)	0.02574 (16)	-0.00666 (8)	0.00382 (11)	0.00243 (8)
O1	0.0279 (5)	0.0465 (6)	0.0350 (5)	-0.0039 (4)	0.0044 (4)	0.0044 (4)
N1	0.0254 (6)	0.0434 (7)	0.0282 (7)	-0.0013 (4)	0.0051 (5)	0.0008 (4)
C1	0.0445 (8)	0.0394 (7)	0.0393 (8)	0.0025 (6)	0.0025 (6)	0.0071 (6)
C2	0.0276 (6)	0.0427 (7)	0.0336 (7)	0.0068 (5)	0.0069 (5)	0.0039 (5)
C3	0.0391 (7)	0.0543 (8)	0.0342 (7)	0.0113 (6)	0.0064 (6)	0.0093 (6)
C4	0.0346 (8)	0.0761 (11)	0.0281 (8)	0.0089 (7)	0.0025 (6)	0.0011 (7)
C5	0.0357 (8)	0.0706 (11)	0.0361 (8)	-0.0078 (7)	0.0065 (6)	-0.0089 (7)
C6	0.0354 (7)	0.0547 (8)	0.0343 (7)	-0.0101 (6)	0.0086 (6)	-0.0032 (6)
N2	0.0329 (6)	0.0404 (6)	0.0387 (6)	0.0008 (5)	0.0066 (5)	-0.0076 (5)
O2	0.0276 (6)	0.0863 (10)	0.0707 (9)	0.0050 (6)	0.0060 (6)	-0.0212 (7)
O3	0.0351 (6)	0.0752 (8)	0.0448 (7)	-0.0015 (5)	0.0102 (5)	-0.0024 (6)
O4	0.0759 (10)	0.1104 (12)	0.0439 (8)	-0.0091 (9)	0.0060 (7)	0.0129 (7)

Geometric parameters ( $\text{\AA}$ ,  $\text{^{\circ}}$ )

Cu1—N1	1.952 (1)	C2—C3	1.388 (2)
Cu1—N1 <sup>i</sup>	1.952 (1)	C3—C4	1.378 (2)
Cu1—O1	1.971 (1)	C3—H3	0.9300
Cu1—O1 <sup>i</sup>	1.971 (1)	C4—C5	1.386 (3)
O1—C1	1.4245 (1)	C4—H4	0.9300
O1—H1	0.840 (9)	C5—C6	1.374 (2)
N1—C2	1.338 (2)	C5—H5	0.9300
N1—C6	1.346 (2)	C6—H6	0.9300
C1—C2	1.505 (2)	N2—O4	1.209 (2)
C1—H1A	0.9700	N2—O2	1.243 (2)
C1—H1B	0.9700	N2—O3	1.258 (2)
N1—Cu1—N1 <sup>i</sup>	180.0	N1—C2—C3	121.44 (14)
N1—Cu1—O1	82.63 (4)	N1—C2—C1	115.70 (12)
N1 <sup>i</sup> —Cu1—O1 <sup>i</sup>	82.63 (4)	C3—C2—C1	122.85 (13)
N1—Cu1—O1 <sup>i</sup>	97.37 (4)	C4—C3—C2	119.03 (15)
N1 <sup>i</sup> —Cu1—O1	97.37 (4)	C4—C3—H3	120.5
O1—Cu1—O1 <sup>i</sup>	180.0	C2—C3—H3	120.5
C1—O1—Cu1	113.23 (8)	C3—C4—C5	119.34 (16)
C1—O1—H1	110.3 (13)	C3—C4—H4	120.3
Cu1—O1—H1	114.7 (13)	C5—C4—H4	120.3
C2—N1—C6	119.37 (14)	C6—C5—C4	118.81 (15)
C2—N1—Cu1	115.01 (10)	C6—C5—H5	120.6
C6—N1—Cu1	125.55 (10)	C4—C5—H5	120.6
O1—C1—C2	110.46 (11)	N1—C6—C5	121.97 (15)
O1—C1—H1A	109.6	N1—C6—H6	119.0
C2—C1—H1A	109.6	C5—C6—H6	119.0
O1—C1—H1B	109.6	O4—N2—O2	122.30 (15)
C2—C1—H1B	109.6	O4—N2—O3	119.89 (13)
H1A—C1—H1B	108.1	O2—N2—O3	117.77 (14)
N1—Cu1—O1—C1	16.04 (10)	C6—N1—C2—C1	-176.62 (14)
N1 <sup>i</sup> —Cu1—O1—C1	-163.96 (10)	Cu1—N1—C2—C1	6.33 (16)
O1 <sup>i</sup> —Cu1—O1—C1	50 (100)	O1—C1—C2—N1	6.74 (18)
N1 <sup>i</sup> —Cu1—N1—C2	174 (100)	O1—C1—C2—C3	-172.32 (13)
O1—Cu1—N1—C2	-12.35 (10)	N1—C2—C3—C4	-0.8 (2)
O1 <sup>i</sup> —Cu1—N1—C2	167.65 (10)	C1—C2—C3—C4	178.19 (15)
N1 <sup>i</sup> —Cu1—N1—C6	-2 (100)	C2—C3—C4—C5	-0.8 (2)
O1—Cu1—N1—C6	170.82 (13)	C3—C4—C5—C6	0.8 (2)
O1 <sup>i</sup> —Cu1—N1—C6	-9.18 (13)	C2—N1—C6—C5	-2.5 (2)
Cu1—O1—C1—C2	-16.42 (15)	Cu1—N1—C6—C5	174.24 (12)
C6—N1—C2—C3	2.5 (2)	C4—C5—C6—N1	0.8 (2)
Cu1—N1—C2—C3	-174.59 (11)		

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

*Hydrogen-bond geometry (Å, °)*

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1···O3 <sup>ii</sup>	0.84 (1)	1.75 (1)	2.5567 (16)	159 (2)

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