

Diaquabis(3-methylpyridine-2-carboxamide- $\kappa^2N,O$ )copper(II) dinitrateHong Ruan,<sup>a</sup> Hong-Wei Chen<sup>b</sup> and Ri-Cheng Xuan<sup>c\*</sup><sup>a</sup>School of Medicine and Life Science, Zhejiang University City College, Hangzhou 310015, People's Republic of China, <sup>b</sup>College of Bioengineering, Changchun University of Technology, Changchun 130012, People's Republic of China, and <sup>c</sup>College of Pharmaceutical Sciences, Zhejiang University of Technology, Hangzhou 310014, People's Republic of China

Correspondence e-mail: xuanrc@hotmail.com

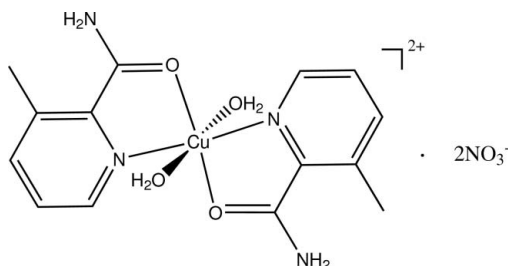
Received 15 May 2007; accepted 4 June 2007

Key indicators: single-crystal X-ray study;  $T = 293$  K; mean  $\sigma(C-C) = 0.003$  Å;  $R$  factor = 0.033;  $wR$  factor = 0.092; data-to-parameter ratio = 15.5.

The title compound,  $[Cu(C_7H_8N_2O)_2(H_2O)_2](NO_3)_2$ , was prepared by the reaction of 2-cyano-3-methylpyridine with  $Cu(NO_3)_2 \cdot 3H_2O$  in a methanol/water solution. In the crystal structure, the  $Cu^{II}$  ion is located on an inversion centre and is coordinated by two 3-methylpyridine-2-carboxamide ligands in the equatorial plane and two water molecules in the axial positions, forming an elongated octahedral coordination geometry. The  $Cu-O_{axial}$  bond distance of 2.4715 (18) Å is much longer than the  $Cu-O_{equatorial}$  bond distance of 1.9471 (17) Å, showing a Jahn–Teller distortion. The nitrate anions are linked with the  $Cu^{II}$  complex cation *via*  $O-H \cdots O$  hydrogen bonding.

## Related literature

For related structures, see: Pestov *et al.* (2005); Xuan *et al.* (2003).



## Experimental

## Crystal data

$[Cu(C_7H_8N_2O)_2(H_2O)_2](NO_3)_2$   
 $M_r = 495.9$   
 Monoclinic,  $P2_1/n$

$a = 6.656$  (4) Å  
 $b = 11.874$  (9) Å  
 $c = 12.472$  (6) Å

$\beta = 96.97$  (2)°  
 $V = 978.4$  (10) Å<sup>3</sup>  
 $Z = 2$   
 Mo  $K\alpha$  radiation

$\mu = 1.19$  mm<sup>-1</sup>  
 $T = 293$  (2) K  
 $0.20 \times 0.14 \times 0.10$  mm

## Data collection

Rigaku R-Axis RAPID  
 diffractometer  
 Absorption correction: multi-scan  
 (ABSCOR; Higashi, 1995)  
 $T_{min} = 0.840$ ,  $T_{max} = 0.885$

9362 measured reflections  
 2221 independent reflections  
 1853 reflections with  $I > 2\sigma(I)$   
 $R_{int} = 0.026$

## Refinement

$R[F^2 > 2\sigma(F^2)] = 0.033$   
 $wR(F^2) = 0.092$   
 $S = 1.09$   
 2221 reflections

143 parameters  
 H-atom parameters constrained  
 $\Delta\rho_{max} = 0.61$  e Å<sup>-3</sup>  
 $\Delta\rho_{min} = -0.26$  e Å<sup>-3</sup>

Table 1

Selected bond lengths (Å).

|        |             |        |           |
|--------|-------------|--------|-----------|
| Cu1—O1 | 1.9471 (17) | Cu1—N1 | 1.961 (2) |
| Cu1—O5 | 2.4715 (18) |        |           |

Table 2

Hydrogen-bond geometry (Å, °).

| $D-H \cdots A$          | $D-H$ | $H \cdots A$ | $D \cdots A$ | $D-H \cdots A$ |
|-------------------------|-------|--------------|--------------|----------------|
| $N2-H2A \cdots O2^i$    | 0.84  | 2.32         | 2.940 (4)    | 131            |
| $N2-H2B \cdots O5^i$    | 0.95  | 1.97         | 2.886 (3)    | 163            |
| $O5-H5A \cdots O2^{ii}$ | 0.82  | 2.14         | 2.949 (4)    | 169            |
| $O5-H5A \cdots O3^{ii}$ | 0.82  | 2.46         | 3.103 (4)    | 136            |
| $O5-H5B \cdots O4$      | 0.83  | 1.98         | 2.814 (4)    | 175            |

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

Data collection: *PROCESS-AUTO* (Rigaku, 1998); cell refinement: *PROCESS-AUTO*; data reduction: *CrystalStructure* (Rigaku/MS, 2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: XU2256).

## References

- Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.  
 Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.  
 Higashi, T. (1995). *ABSCOR*. Rigaku Corporation, Tokyo, Japan.  
 Pestov, A. V., Peresypkina, E. V., Virovets, A. V., Podbereskaya, N. V., Yatluk, Y. G. & Skorik, Y. A. (2005). *Acta Cryst.* **C61**, m510–m512.  
 Rigaku (1998). *PROCESS-AUTO*. Rigaku Corporation, Tokyo, Japan.  
 Rigaku/MS (2002). *CrystalStructure*. Version 3.00. Rigaku/MS, The Woodlands, Texas, USA.  
 Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.  
 Xuan, R.-C., Li, M.-C. & Wan, Y.-H. (2003). *Acta Cryst.* **C59**, m462–m464.

**supplementary materials**

*Acta Cryst.* (2007). E63, m1855 [ doi:10.1107/S1600536807027109 ]

## Diaquabis(3-methylpyridine-2-carboxamide- $\kappa^2N,O$ )copper(II) dinitrate

H. Ruan, H.-W. Chen and R.-C. Xuan

### Comment

The title compound is shown in Fig. 1. The pyridine ring, methyl and amide substituent groups are almost coplanar, and their bond lengths and angles are normal. The Cu<sup>II</sup> atom is coordinated by two N and two O atoms in the equatorial plane, and two O atoms at the apical positions of elongated octahedron (Table 1). The nitrate ion does not connect Cu<sup>II</sup> atom directly but links with the Cu<sup>II</sup> complex cation *via* O—H $\cdots$ O hydrogen bonding (Table 2).

Further analysis of the short contacts present in (I) shows that there are O5—H5B $\cdots$ O2, O5—H5B $\cdots$ O4, O5—H5A $\cdots$ O3<sup>ii</sup>, O5—H5A $\cdots$ O2<sup>ii</sup>, [symmetry code: (ii)- $x + 1/2, +y - 1/2, -z + 1/2 + 1$ ], N2—H2A $\cdots$ O2<sup>iii</sup>, and N2—H2B $\cdots$ O5<sup>iii</sup> [symmetry code: (iii)- $x + 1, -y + 1, -z + 1$ ] interactions. All these contacts can be regarded as hydrogen bonds, which hold the complex cations and nitrate anions together.

### Experimental

A methanol solution (5 ml) of 2-cyano-3-methylpyridine (0.2368 g, 0.20 mmol) was mixed with an aqueous solution (5 ml) of Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O (0.0491, 0.20 mmol) in a round-bottomed flask. The solution was refluxed for 10 min and then cooled to room temperature. Single crystals of the title compound were obtained after 5 d.

### Refinement

The H atoms bonded to N2 and O5 were found in a difference Fourier map and refined as riding in their as-found relative positions with  $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O}, \text{N})$ . Methyl H atoms were placed in calculated positions with C—H = 0.96 Å and torsion angle was refined to fit the electron density,  $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$ . Aromatic H atoms were placed in calculated positions with C—H = 0.93 Å and refined in riding mode with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ .

### Figures

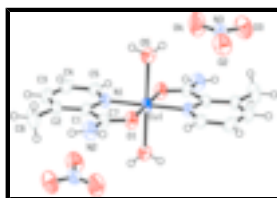


Fig. 1. A view of the molecular structure, showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

## Diaquabis(3-methylpyridine-2-carboxamide- $\kappa^2N,O$ )copper(II) dinitrate

### Crystal data

|  |   |
|--|---|
| $[\text{Cu}(\text{C}_7\text{H}_8\text{N}_2\text{O})_2(\text{H}_2\text{O})_2](\text{NO}_3)_2$ | $F_{000} = 510$                           |
| $M_r = 495.9$  | $D_x = 1.683 \text{ Mg m}^{-3}$           |
| Monoclinic, $P2_1/n$   | Mo $K\alpha$ radiation                    |
| Hall symbol: -P 2yn  | $\lambda = 0.71073 \text{ \AA}$           |
| $a = 6.656 (4) \text{ \AA}$  | Cell parameters from 7644 reflections     |
| $b = 11.874 (9) \text{ \AA}$   | $\theta = 3.2\text{--}27.0^\circ$         |
| $c = 12.472 (6) \text{ \AA}$   | $\mu = 1.19 \text{ mm}^{-1}$              |
| $\beta = 96.97 (2)^\circ$  | $T = 293 (2) \text{ K}$                   |
| $V = 978.4 (10) \text{ \AA}^3$   | Prism, blue                               |
| $Z = 2$  | $0.20 \times 0.14 \times 0.10 \text{ mm}$ |

### Data collection

|   |  |
|---|--|
| Rigaku R-Axis RAPID diffractometer                        | 2221 independent reflections           |
| Radiation source: fine-focus sealed tube                  | 1853 reflections with $I > 2\sigma(I)$ |
| Monochromator: graphite                                   | $R_{\text{int}} = 0.026$               |
| Detector resolution: $10.00 \text{ pixels mm}^{-1}$       | $\theta_{\text{max}} = 27.5^\circ$     |
| $T = 293(2) \text{ K}$                                    | $\theta_{\text{min}} = 3.3^\circ$      |
| $\omega$ scans  | $h = -8 \rightarrow 7$                 |
| Absorption correction: multi-scan (ABSCOR; Higashi, 1995) | $k = -15 \rightarrow 15$               |
| $T_{\text{min}} = 0.840$ , $T_{\text{max}} = 0.885$       | $l = -14 \rightarrow 16$               |
| 9362 measured reflections                                 |  |

### Refinement

|  |  |
|--|--|
| Refinement on $F^2$  | Secondary atom site location: difference Fourier map     |
| Least-squares matrix: full                                     | Hydrogen site location: inferred from neighbouring sites |
| $R[F^2 > 2\sigma(F^2)] = 0.033$                                | H-atom parameters constrained                            |
| $wR(F^2) = 0.092$  | $w = 1/[\sigma^2(F_o^2) + (0.0509P)^2 + 0.2656P]$        |
| $S = 1.09$   | where $P = (F_o^2 + 2F_c^2)/3$                           |
| 2221 reflections   | $(\Delta/\sigma)_{\text{max}} < 0.001$                   |
| 143 parameters   | $\Delta\rho_{\text{max}} = 0.61 \text{ e \AA}^{-3}$      |
| Primary atom site location: structure-invariant direct methods | $\Delta\rho_{\text{min}} = -0.25 \text{ e \AA}^{-3}$     |
|  | 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 ( $\text{\AA}^2$ )*

|     | <i>x</i>    | <i>y</i>     | <i>z</i>     | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|-----|-------------|--------------|--------------|----------------------------------|
| Cu1 | 0.0000      | 0.5000       | 0.5000       | 0.03437 (13)                     |
| N1  | -0.0100 (2) | 0.33946 (13) | 0.46298 (13) | 0.0350 (3)                       |
| N2  | 0.4421 (3)  | 0.38605 (17) | 0.34147 (17) | 0.0527 (5)                       |
| N3  | 0.1397 (3)  | 0.67879 (16) | 0.84496 (14) | 0.0448 (4)                       |
| O1  | 0.2432 (2)  | 0.49394 (11) | 0.42776 (14) | 0.0445 (4)                       |
| O2  | 0.2770 (3)  | 0.71509 (18) | 0.79573 (17) | 0.0717 (5)                       |
| H2A | 0.4694      | 0.3264       | 0.3106       | 0.108*                           |
| H2B | 0.5352      | 0.4471       | 0.3450       | 0.108*                           |
| O3  | 0.0465 (3)  | 0.74715 (19) | 0.89250 (18) | 0.0798 (6)                       |
| O4  | 0.0982 (5)  | 0.57935 (18) | 0.8442 (2)   | 0.1048 (9)                       |
| O5  | 0.2239 (2)  | 0.46062 (14) | 0.66877 (12) | 0.0495 (4)                       |
| H5A | 0.2408      | 0.3924       | 0.6774       | 0.074*                           |
| H5B | 0.1896      | 0.4927       | 0.7231       | 0.074*                           |
| C1  | 0.1385 (3)  | 0.30383 (16) | 0.40762 (14) | 0.0344 (4)                       |
| C2  | 0.1543 (3)  | 0.19255 (17) | 0.37466 (16) | 0.0415 (5)                       |
| C3  | 0.0070 (4)  | 0.11950 (18) | 0.40420 (19) | 0.0513 (6)                       |
| H3  | 0.0105      | 0.0442       | 0.3842       | 0.062*                           |
| C4  | -0.1453 (4) | 0.15636 (18) | 0.46297 (19) | 0.0499 (5)                       |
| H4  | -0.2427     | 0.1071       | 0.4830       | 0.060*                           |
| C5  | -0.1461 (3) | 0.26862 (17) | 0.49020 (16) | 0.0408 (4)                       |
| H5  | -0.2468     | 0.2952       | 0.5293       | 0.049*                           |
| C6  | 0.3131 (4)  | 0.1473 (2)   | 0.3118 (3)   | 0.0694 (8)                       |
| H6A | 0.2827      | 0.0704       | 0.2925       | 0.104*                           |
| H6B | 0.4426      | 0.1512       | 0.3549       | 0.104*                           |
| H6C | 0.3163      | 0.1913       | 0.2474       | 0.104*                           |
| C7  | 0.2820 (3)  | 0.40018 (17) | 0.39072 (15) | 0.0366 (4)                       |

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

|     | $U^{11}$   | $U^{22}$     | $U^{33}$   | $U^{12}$      | $U^{13}$     | $U^{23}$      |
|-----|------------|--------------|------------|---------------|--------------|---------------|
| Cu1 | 0.0337 (2) | 0.02471 (18) | 0.0487 (2) | -0.00089 (12) | 0.02154 (14) | -0.00463 (12) |
| N1  | 0.0358 (9) | 0.0301 (8)   | 0.0401 (8) | 0.0013 (6)    | 0.0092 (6)   | -0.0021 (6)   |

## supplementary materials

---

|    |             |             |             |              |              |              |
|----|-------------|-------------|-------------|--------------|--------------|--------------|
| N2 | 0.0418 (10) | 0.0568 (11) | 0.0642 (12) | 0.0062 (9)   | 0.0262 (9)   | -0.0048 (9)  |
| N3 | 0.0458 (10) | 0.0465 (11) | 0.0425 (9)  | 0.0032 (8)   | 0.0074 (8)   | -0.0063 (7)  |
| O1 | 0.0420 (8)  | 0.0365 (8)  | 0.0597 (9)  | -0.0018 (6)  | 0.0257 (7)   | -0.0037 (6)  |
| O2 | 0.0623 (11) | 0.0767 (13) | 0.0827 (13) | -0.0073 (10) | 0.0361 (10)  | -0.0132 (10) |
| O3 | 0.0647 (12) | 0.0893 (15) | 0.0897 (14) | 0.0180 (11)  | 0.0272 (10)  | -0.0272 (11) |
| O4 | 0.166 (3)   | 0.0532 (13) | 0.1063 (18) | -0.0334 (14) | 0.0600 (18)  | -0.0137 (11) |
| O5 | 0.0574 (10) | 0.0401 (8)  | 0.0512 (9)  | 0.0044 (7)   | 0.0076 (7)   | 0.0009 (7)   |
| C1 | 0.0331 (9)  | 0.0347 (10) | 0.0347 (9)  | 0.0086 (7)   | 0.0006 (7)   | -0.0046 (7)  |
| C2 | 0.0424 (11) | 0.0361 (11) | 0.0436 (10) | 0.0110 (8)   | -0.0048 (8)  | -0.0084 (8)  |
| C3 | 0.0623 (15) | 0.0307 (10) | 0.0570 (13) | 0.0035 (10)  | -0.0085 (11) | -0.0053 (9)  |
| C4 | 0.0535 (13) | 0.0361 (11) | 0.0573 (12) | -0.0113 (9)  | -0.0045 (10) | 0.0086 (9)   |
| C5 | 0.0435 (11) | 0.0367 (11) | 0.0427 (10) | -0.0017 (8)  | 0.0079 (8)   | 0.0028 (8)   |
| C6 | 0.0615 (16) | 0.0604 (17) | 0.0868 (19) | 0.0161 (13)  | 0.0112 (14)  | -0.0331 (14) |
| C7 | 0.0343 (10) | 0.0385 (10) | 0.0380 (9)  | 0.0075 (8)   | 0.0084 (8)   | -0.0016 (7)  |

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

|                                      |             |            |           |
|--------------------------------------|-------------|------------|-----------|
| Cu1—O1                               | 1.9471 (17) | O5—H5A     | 0.8237    |
| Cu1—O1 <sup>i</sup>                  | 1.9471 (17) | O5—H5B     | 0.8332    |
| Cu1—O5                               | 2.4715 (18) | C1—C2      | 1.392 (3) |
| Cu1—O5 <sup>i</sup>                  | 2.4715 (18) | C1—C7      | 1.521 (3) |
| Cu1—N1                               | 1.961 (2)   | C2—C3      | 1.392 (3) |
| Cu1—N1 <sup>i</sup>                  | 1.961 (2)   | C2—C6      | 1.490 (3) |
| N1—C5                                | 1.311 (3)   | C3—C4      | 1.392 (4) |
| N1—C1                                | 1.341 (2)   | C3—H3      | 0.9300    |
| N2—C7                                | 1.304 (3)   | C4—C5      | 1.376 (3) |
| N2—H2A                               | 0.8365      | C4—H4      | 0.9300    |
| N2—H2B                               | 0.9519      | C5—H5      | 0.9300    |
| N3—O4                                | 1.213 (3)   | C6—H6A     | 0.9600    |
| N3—O3                                | 1.218 (2)   | C6—H6B     | 0.9600    |
| N3—O2                                | 1.239 (2)   | C6—H6C     | 0.9600    |
| O1—C7                                | 1.244 (2)   |            |           |
| O1—Cu1—O1 <sup>i</sup>               | 180.0       | C1—C2—C6   | 125.6 (2) |
| O1—Cu1—N1                            | 82.04 (6)   | C3—C2—C6   | 118.8 (2) |
| O1 <sup>i</sup> —Cu1—N1              | 97.96 (6)   | C4—C3—C2   | 121.7 (2) |
| O1—Cu1—N1 <sup>i</sup>               | 97.96 (6)   | C4—C3—H3   | 119.2     |
| O1 <sup>i</sup> —Cu1—N1 <sup>i</sup> | 82.04 (6)   | C2—C3—H3   | 119.2     |
| N1—Cu1—N1 <sup>i</sup>               | 180.0       | C5—C4—C3   | 117.4 (2) |
| C5—N1—C1                             | 120.44 (18) | C5—C4—H4   | 121.3     |
| C5—N1—Cu1                            | 124.59 (14) | C3—C4—H4   | 121.3     |
| C1—N1—Cu1                            | 114.95 (13) | N1—C5—C4   | 122.3 (2) |
| C7—N2—H2A                            | 124.2       | N1—C5—H5   | 118.9     |
| C7—N2—H2B                            | 116.4       | C4—C5—H5   | 118.9     |
| H2A—N2—H2B                           | 119.3       | C2—C6—H6A  | 109.5     |
| O4—N3—O3                             | 121.6 (2)   | C2—C6—H6B  | 109.5     |
| O4—N3—O2                             | 121.1 (2)   | H6A—C6—H6B | 109.5     |
| O3—N3—O2                             | 117.3 (2)   | C2—C6—H6C  | 109.5     |

|            |             |            |             |
|------------|-------------|------------|-------------|
| C7—O1—Cu1  | 115.23 (13) | H6A—C6—H6C | 109.5       |
| H5A—O5—H5B | 112.9       | H6B—C6—H6C | 109.5       |
| N1—C1—C2   | 122.58 (19) | O1—C7—N2   | 120.5 (2)   |
| N1—C1—C7   | 110.39 (16) | O1—C7—C1   | 117.36 (17) |
| C2—C1—C7   | 127.01 (18) | N2—C7—C1   | 122.08 (18) |
| C1—C2—C3   | 115.63 (19) |            |             |

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

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

| <i>D</i> —H $\cdots$ <i>A</i>     | <i>D</i> —H | H $\cdots$ <i>A</i> | <i>D</i> $\cdots$ <i>A</i> | <i>D</i> —H $\cdots$ <i>A</i> |
|-----------------------------------|-------------|---------------------|----------------------------|-------------------------------|
| N2—H2A $\cdots$ O2 <sup>ii</sup>  | 0.84        | 2.32                | 2.940 (4)                  | 131                           |
| N2—H2B $\cdots$ O5 <sup>ii</sup>  | 0.95        | 1.97                | 2.886 (3)                  | 163                           |
| O5—H5A $\cdots$ O2 <sup>iii</sup> | 0.82        | 2.14                | 2.949 (4)                  | 169                           |
| O5—H5A $\cdots$ O3 <sup>iii</sup> | 0.82        | 2.46                | 3.103 (4)                  | 136                           |
| O5—H5B $\cdots$ O4                | 0.83        | 1.98                | 2.814 (4)                  | 175                           |

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

