

Triaqua(2,6-pyridinedicarboxylato)copper(II) at 150 K

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Key indicators

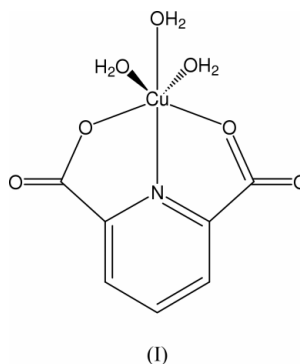
Single-crystal X-ray study
T = 150 K
Mean $\sigma(\text{C}-\text{C}) = 0.002 \text{ \AA}$
R factor = 0.021
wR factor = 0.061
Data-to-parameter ratio = 13.7For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.

The asymmetric unit of the title compound, $[\text{Cu}(\text{C}_7\text{H}_3\text{NO}_4)(\text{H}_2\text{O})_3]$, comprises a distorted tetragonally elongated octahedral copper(II) centre coordinated equatorially by a tridentate 2,6-pyridinedicarboxylate anion [$\text{Cu}-\text{N}$ 1.9093 (14), and $\text{Cu}-\text{O}$ 2.0368 (11) and 2.0397 (11) Å] and a strongly bound water molecule [$\text{Cu}-\text{O}$ 1.9047 (12) Å] and axially by two weakly bound water molecules [$\text{Cu}-\text{O}$ 2.3631 (12) and 2.4739 (12) Å]. The extended structure is based on a layered arrangement in which sheets of stacked molecular units are alternately linked by hydrogen-bonding and $\pi-\pi$ stacking interactions.

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Comment

Although the room-temperature structure of triaqua(2,6-pyridinedicarboxylato)copper(II), (I), has been discussed on four previous occasions (Chastain, 1965; Sarchet *et al.*, 1973; Sileo *et al.*, 1994, 1996), only limited details are available in the open literature. In this paper, we report in detail the results of a low-temperature (150 K) study of the compound.



The structure of (I) comprises $[\text{Cu}(\text{dipic})(\text{OH}_2)_3]$ ([dipic]²⁻ is the 2,6-pyridinedicarboxylate anion) molecular units, the tetragonally elongated octahedral geometry of which (Fig. 1 and Table 1) is typical of Jahn–Teller-distorted copper(II). The 2,6-pyridinedicarboxylate anion occupies three of the equatorial sites of the copper(II) centre [$\text{Cu}-\text{N}$ 1.9093 (14), and $\text{Cu}-\text{O}$ 2.0368 (11) and 2.0397 (11) Å] and the fourth site is occupied by a strongly bound water molecule [$\text{Cu}-\text{O}$ 1.9047 (12) Å]. Two weakly bound water molecules are located in the axial positions of the copper(II) centre [$\text{Cu}-\text{O}$ 2.3631 (12) and 2.4739 (12) Å].

The coordination of the anion in the title compound is similar not only to that previously described for both the monoclinic (Biagini-Cingi *et al.*, 1971; Sarchet *et al.*, 1973) and triclinic (Sileo *et al.*, 1994; Chastain, 1965) polymorphs of $[\text{Cu}(\text{dipic})(\text{OH}_2)_2]$, but also to that previously described for

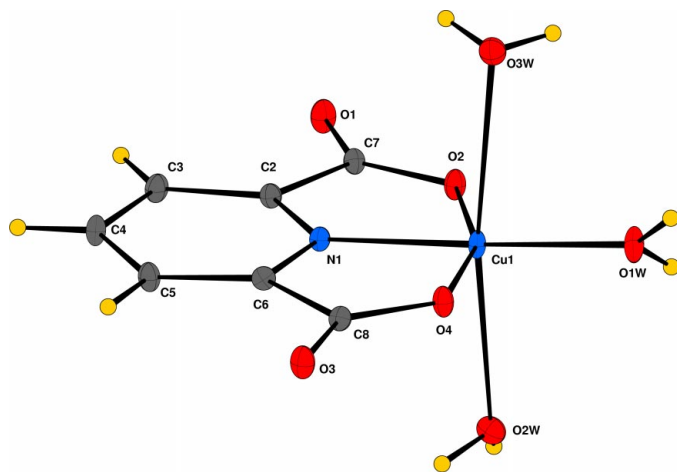


Figure 1
A view of the title compound showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

the coordinated anions in $[\text{Cu}(\text{dipic})(\text{H}_2\text{dipic})\cdot n\text{H}_2\text{O}]$ [$n = 1$ (Sileo *et al.*, 1996) or 3 (Sileo *et al.*, 1996; Biagini-Cingi *et al.*, 1972; Sarchet & Loiseleur, 1973)]. In $[\text{Cu}(\text{dipic})(\text{H}_2\text{dipic})\cdot n\text{H}_2\text{O}]$, acid molecules occupy the fourth equatorial position (pyridine N) and the two axial positions (carboxylate O) of the tetragonally elongated octahedral copper(II) coordination sphere. Pertinent interatomic distances are collated in Table 3.

The extended structure of the title phase is dependent on both hydrogen-bonding and π - π stacking interactions. $R_2^2(8)$ hydrogen-bonded motifs involving the protons on the equatorially located water molecule link molecular units to form a one-dimensional chain which lies in the (101) plane and runs perpendicular to the b axis (Fig. 2). The chains are linked by four $\text{O}-\text{H}\cdots\text{O}$ contacts involving each of the protons on the two axially located water molecules to form a two-dimensional sheet which lies parallel to the (010) plane (Fig. 3). The structural parameters for the $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds

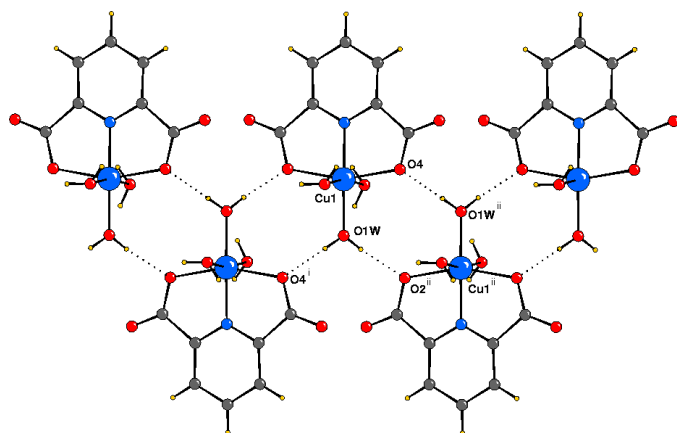


Figure 2
A projection of the title phase on to (101) showing the $R_2^2(8)$ hydrogen-bonding motifs which link the molecular units to form a one-dimensional chain. Atoms are identified as follows: Cu, large blue circles; C, black circles; N, blue circles; O, red circles; H, small yellow circles. Symmetry code: (i) $1/2+x, 1/2-y, -1/2+z$.

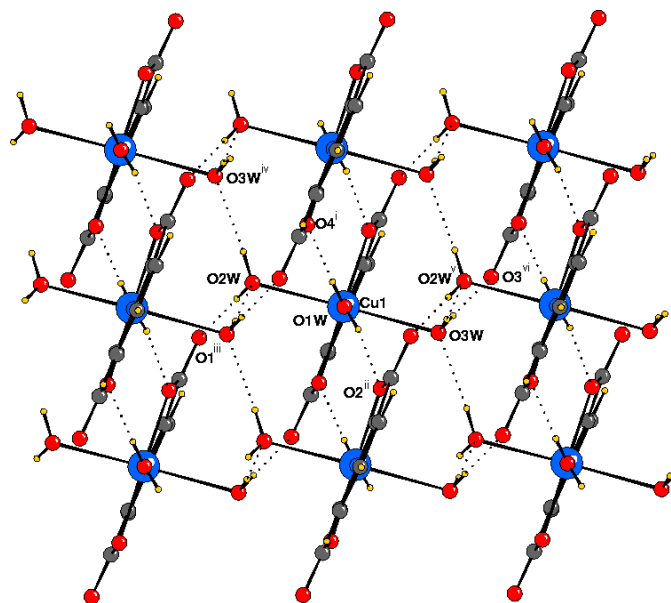


Figure 3
A projection of the title phase on to (010) showing the hydrogen-bonding interactions which link the chains into two-dimensional sheets. Atoms are identified as for Fig. 2. Symmetry codes: (i) $1/2+x, 1/2-y, -1/2+z$; (ii) $1/2+x, 1/2-y, 1/2+z$; (iii) $1+x, y, z$; (iv) $1/2+x, 1/2-y, -1/2+z$; (v) $-1+x, y, z$; (vi) $x, y, 1+z$.

(Table 2) suggest that those involved in chain construction [$\text{O1W}\cdots\text{O2}^{\text{ii}}$ 2.6596 (15) and $\text{O1W}\cdots\text{O4}^{\text{i}}$ 2.6627 (15) Å] are much stronger than those involved in sheet construction [$\text{O2W}\cdots\text{O1}^{\text{iii}}$ 2.8883 (16), $\text{O2W}\cdots\text{O3W}^{\text{iv}}$ 2.8367 (19), $\text{O3W}\cdots\text{O3}^{\text{vi}}$ 2.9056 (17) and $\text{O3W}\cdots\text{O2W}^{\text{v}}$ 2.9969 (19) Å]. The relative strengths of the hydrogen-bonded contacts can be related to the strength of the $\text{Cu}-\text{OH}_2$ coordinate interaction, the more strongly bound water molecules being more polarized and hence more acidic. The sheets are essentially bilayers with hydrophilic centres and hydrophobic faces. Interdigitation of adjacent bilayers (Fig. 4) generates π - π stacking

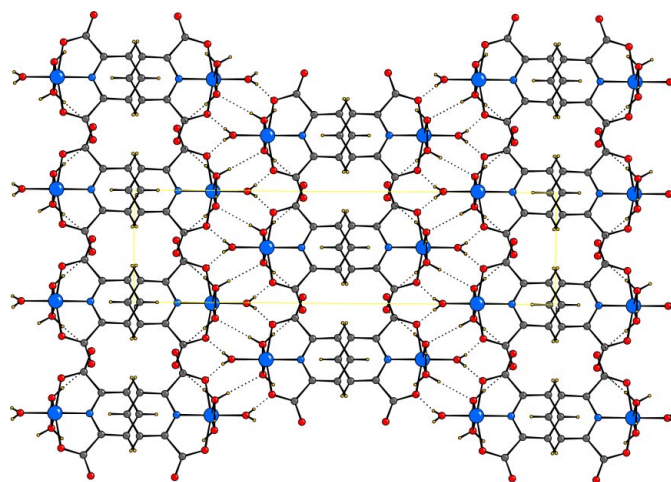


Figure 4
A projection of the title phase on to (001) showing the hydrogen-bonding and π - π stacking interactions which alternatively link sheets of stacked molecular units. Atoms are identified as for Fig. 2.

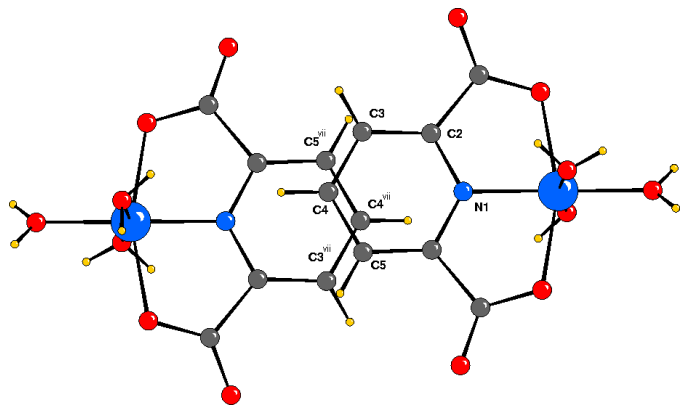


Figure 5

A detail of the projection of the title phase on to (001) showing the π - π stacking interactions. Atoms are identified as for Fig. 2. Symmetry code: (vii) $1-x, 1-y, 1-z$.

contacts (Fig. 5) which may be considered to be significant, as evidenced by the relatively short perpendicular separations [3.340 (10) and 3.335 (12) Å] and centroid-centroid distances [3.955 (10) and 4.065 (10) Å] between pyridine rings.

Experimental

Treatment of an aqueous solution (25 ml) of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (0.651 g, 0.38 mmol) with the disodium salt of 2,6-pyridinedicarboxylic acid (dipicolinic acid; 0.801 g, 0.38 mmol) previously prepared by neutralization of dipicolinic acid (0.668 g, 4.0 mmol) with Na_2CO_3 (0.424 g, 4.0 mmol) gave, in excellent (95%) yield, a microcrystalline sample of the title compound (1.018 g, 0.36 mmol) which was recrystallized under hydrothermal synthesis conditions at 453 K.

Crystal data

$[\text{Cu}(\text{C}_7\text{H}_3\text{NO}_4)(\text{H}_2\text{O})_3]$
 $M_r = 282.69$
 Monoclinic, $P2_1/n$
 $a = 6.4111$ (9) Å
 $b = 23.169$ (3) Å
 $c = 6.8348$ (9) Å
 $\beta = 106.377$ (2)°
 $V = 974.0$ (2) Å³
 $Z = 4$

$D_x = 1.928$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 4778 reflections
 $\theta = 2.7$ – 28.8°
 $\mu = 2.26$ mm⁻¹
 $T = 150$ (2) K
 Block, blue
 $0.45 \times 0.32 \times 0.28$ mm

Data collection

Bruker SMART 1000 CCD area-detector diffractometer
 ω scans

Absorption correction: multi-scan (SADABS; Bruker, 2001)
 $T_{\min} = 0.406$, $T_{\max} = 0.530$

6789 measured reflections

2308 independent reflections
 2075 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.022$
 $\theta_{\text{max}} = 28.8^\circ$
 $h = -8 \rightarrow 8$
 $k = -30 \rightarrow 27$
 $l = -8 \rightarrow 6$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.021$
 $wR(F^2) = 0.061$
 $S = 1.15$
 2248 reflections
 164 parameters
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.024P)^2 + 0.603P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 0.40$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.48$ e Å⁻³
 Extinction correction: SHELXL97
 Extinction coefficient: 0.0465 (15)

Table 1

Selected geometric parameters (Å, °).

Cu—N1	1.9093 (14)	Cu—O1W	1.9047 (12)
Cu—O2	2.0397 (11)	Cu—O2W	2.3631 (12)
Cu—O4	2.0368 (11)	Cu—O3W	2.4739 (12)
N1—Cu—O2	80.46 (4)	O4—Cu—O2W	87.47 (4)
N1—Cu—O4	80.34 (4)	O4—Cu—O3W	93.07 (4)
N1—Cu—O1W	177.86 (5)	O1W—Cu—O2W	86.52 (5)
N1—Cu—O2W	95.60 (4)	O1W—Cu—O3W	84.99 (4)
N1—Cu—O3W	92.88 (4)	O2W—Cu—O3W	171.47 (4)
O2—Cu—O4	160.79 (5)	C6—N1—Cu	118.61 (10)
O2—Cu—O1W	99.71 (5)	C2—N1—Cu	118.52 (10)
O2—Cu—O2W	94.66 (4)	C7—O2—Cu	114.65 (9)
O2—Cu—O3W	87.64 (4)	C8—O4—Cu	114.78 (9)
O4—Cu—O1W	99.47 (4)		

Table 2

Hydrogen-bonding geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
O1W—H1WA \cdots O4 ⁱ	0.813 (9)	1.850 (9)	2.6627 (15)	179 (2)
O1W—H1WB \cdots O2 ⁱⁱ	0.813 (9)	1.855 (10)	2.6596 (15)	170 (2)
O2W—H2WA \cdots O1 ⁱⁱⁱ	0.804 (9)	2.085 (10)	2.8883 (16)	176 (2)
O2W—H2WB \cdots O3W ^{iv}	0.815 (9)	2.023 (10)	2.8367 (19)	176 (2)
O3W—H3WA \cdots O2W ^v	0.817 (9)	2.181 (10)	2.9969 (19)	176 (2)
O3W—H3WB \cdots O3 ^{vi}	0.815 (9)	2.092 (9)	2.9056 (17)	176 (2)

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

Table 3

Co-ordination distances (Cu—N and Cu—O, Å) for the [dipic]²⁻ anion and the H₂dipic molecule in [Cu(dipic)(OH₂)_n] ($n = 2$ or 3) and [Cu(dipic)(H₂dipic)] $\cdot n\text{H}_2\text{O}$ ($n = 1$ or 3).

Compound	Cu—N	Cu—O	Cu—O
anionic [dipic] ²⁻			
[Cu(dipic)(OH ₂) ₂] ^a	1.9093 (14)	2.0368 (11)	2.0397 (11)
monoclinic [Cu(dipic)(OH ₂) ₂] ^b	1.898 (4)	2.037 (3)	2.050 (4)
triclinic [Cu(dipic)(OH ₂) ₂] ^b	1.901 (6)	2.005 (6)	2.018 (5)
[Cu(dipic)(H ₂ dipic)] $\cdot \text{H}_2\text{O}^c$	1.911 (4)	2.008 (3)	2.008 (3)
[Cu(dipic)(H ₂ dipic)] $\cdot 3\text{H}_2\text{O}^c$	1.907 (7)	2.027 (8)	2.063 (8)
[Cu(dipic)(H ₂ dipic)] $\cdot 3\text{H}_2\text{O}^c$	1.901 (7)	2.048 (7)	2.056 (7)
molecular H ₂ dipic			
[Cu(dipic)(H ₂ dipic)] $\cdot \text{H}_2\text{O}^c$	2.011 (4)	2.425 (3)	2.425 (3)
[Cu(dipic)(H ₂ dipic)] $\cdot 3\text{H}_2\text{O}^c$	2.003 (8)	2.310 (8)	2.465 (8)
[Cu(dipic)(H ₂ dipic)] $\cdot 3\text{H}_2\text{O}^c$	1.995 (8)	2.302 (8)	2.379 (8)

Notes: (a) this work; (b) Sarchet *et al.* (1973); (c) Sileo *et al.* (1996).

Water H atoms were located from ΔF syntheses and refined with the O—H and H \cdots H distances restrained to be 0.82 (1) and 1.33 (2) Å, respectively, and with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$. Aromatic H atoms, after location from ΔF syntheses, were placed geometrically and refined with a riding model for which the C—H distance was constrained to be 0.96 Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

Data collection: SMART (Bruker, 2001); cell refinement: SAINT (Bruker, 2000); data reduction: SAINT and SHELXTL (Bruker, 1997); program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: CAMERON (Watkin *et al.*, 1996); software used to prepare material for publication: SHELXL97 and PLATON (Spek, 2001).

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