

(2,9-Dimethyl-1,10-phenanthroline- κ^2N,N')(pyridine-2,6-dicarboxylato- κ^3O^2,N,O^6)copper(II) trihydrate

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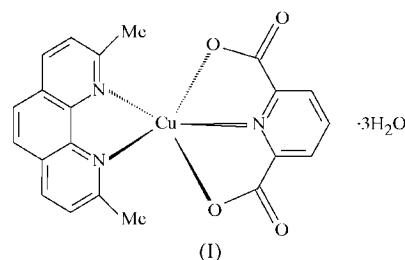
The copper(II) centre in the mononuclear title complex, $[\text{Cu}(\text{C}_7\text{H}_3\text{NO}_4)(\text{C}_{14}\text{H}_{12}\text{N}_2)] \cdot 3\text{H}_2\text{O}$, is surrounded by one bidentate 2,9-dimethyl-1,10-phenanthroline (dmphen) ligand and one tridentate pyridine-2,6-dicarboxylate ligand, and exhibits a distorted square-pyramidal geometry. The crystal packing involves both hydrogen-bonding and π - π interactions. The solvent water molecules link monomers to one another through hydrogen-bonding interactions, forming ladder-like chains in the *bc* plane. Face-to-face and slipped π - π interactions also occur between dmphen rings of neighboring molecules and are responsible for interchain packing.

Comment

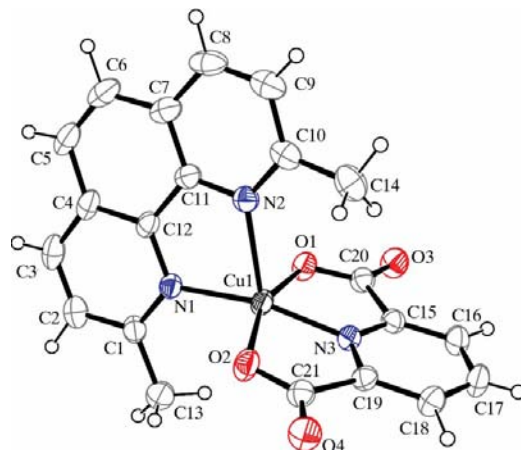
Pyridine-2,6-dicarboxylic acid (dipicolinic acid) is regarded as the key component for the high heat resistance of bacterial spores, owing to its ability to build stabilizing structures with divalent metals (Chung *et al.*, 1971). Metal complexes of this ligand have been studied extensively because of its ability to form stable chelates (Ducommun *et al.*, 1989) with different coordination modes, such as bidentate (Zhou & Kostic, 1988) or bridging (Sengupta *et al.*, 1983). Since rare-earth metals are known to have antitumor activity (Zhou *et al.*, 2001), a series of isomorphous dipicolinate complexes with these metals were synthesized and the structures reported (Chen *et al.*, 2002; Okabe *et al.*, 2002). To clarify further the coordination modes of chelates of dipicolinic acid with biologically important transition metal ions, we report here the synthesis and crystal structure of a mononuclear copper dipicolinate (dpc) compound with 2,9-dimethyl-1,10-phenanthroline (dmphen).

The structure of the title compound, (I) (Fig. 1), consists of a neutral $[\text{Cu}(\text{dpc})(\text{dmphen})]$ unit and three solvent water molecules. The dpc anion, with its two carboxylate groups in *ortho* positions with respect to the pyridine N atom, is potentially tridentate. The copper ion is bonded to the pyridine N atom [$\text{Cu1}-\text{N3} = 1.904(2) \text{ \AA}$], as well as to one O

atom of each carboxylate group [$\text{Cu1}-\text{O1} = 2.0343(18) \text{ \AA}$ and $\text{Cu1}-\text{O2} = 2.019(2) \text{ \AA}$]. The dmphen ligand chelates the copper center [$\text{Cu1}-\text{N1} = 1.987(2) \text{ \AA}$ and $\text{Cu1}-\text{N2} = 2.228(2) \text{ \AA}$]. These bond distances (Table 1) are comparable to those found in other copper-dipicolinate complexes (Okabe & Oya, 2000; Altin *et al.*, 2004; Chaigneau *et al.*, 2004). The degree of trigonality ($\tau = 0.1$) indicates that the Cu^{II} ion lies in a distorted square-pyramidal environment. [As defined by Addison *et al.* (1984), τ is 0 for a regular square-pyramidal (SQP) structure and increases to 1 for a trigonal-bipyramidal (TBP) structure.] The dmphen atom N2 occupies the axial position, while the base is formed by the two carboxylate O atoms, one pyridine N atom from the dpc anion and one N atom from the dmphen ligand. The Cu atom lies $0.1681(18) \text{ \AA}$ out of the basal plane, which is distorted from a square by the double chelate formed by dpc and which, furthermore, is not completely planar [the maximum atomic deviation is $0.0512(12) \text{ \AA}$].



The fact that the $\text{Cu1}-\text{N3}$ distance is significantly shorter than the two $\text{Cu}-\text{N}_{\text{dmphen}}$ distances indicates that atom N3 is the strongest donor site, since the two carboxylate groups in *ortho* positions enhance the basicity of this atom. The dpc chelate angles are $79.71(8)$ and $80.33(8)^\circ$, which are comparable to those found in other Cu -dipicolinate complexes (Okabe & Oya, 2000; Chaigneau *et al.*, 2004). The internal geometry of the dmphen ligand is similar to that established in previous studies (Kon *et al.*, 1987; Kovalevsky *et al.*, 2003). All atoms in the dpc anion are also nearly coplanar, with a maximum deviation of $0.0648(17) \text{ \AA}$ for atom O1. The

**Figure 1**

A view of the title compound, showing the atom-labeling scheme and 40% probability displacement ellipsoids. The water molecules have been omitted for clarity.

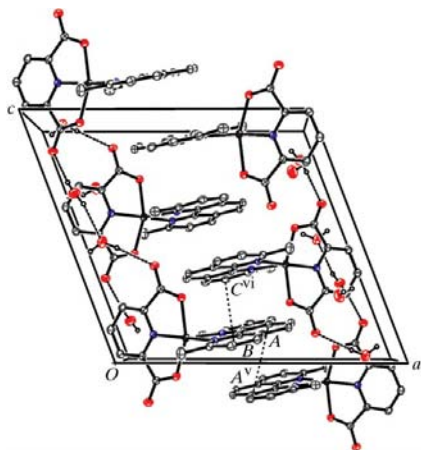


Figure 2
A partial view of the packing of (I), showing hydrogen-bond and π - π interactions as dashed lines. H atoms not involved in hydrogen bonding have been omitted. [Symmetry codes: (v) $1 - x, -y, -z$; (vi) $1 - x, -\frac{1}{2} + y, \frac{1}{2} - z$.]

dihedral angle between the dmphen and dpc planes is $80.29(4)^\circ$.

Both intermolecular hydrogen-bonding and π - π interactions combine to stabilize the extended structure (Fig. 2). The uncoordinated water molecules link molecules of the complex, acting as hydrogen-bond donors to the unligated carboxylate O atoms (Table 2). These interactions mediate the formation of ladder-like chains in the *bc* plane (Fig. 2). Adjacent chains are linked by π - π interactions, which are either face-to-face [$CgA \cdots CgA^v = 3.6307(15) \text{ \AA}$; CgA is the center of the C4-C7/C11/C12 ring; symmetry code: (v) $1 - x, -y, -z$] or slipped [$CgB \cdots CgC^{vi} = 3.7184(15) \text{ \AA}$; CgB is the center of the C1-C4/C12/N1 ring and CgC is the center of the C7-C10/N2/C11 ring; symmetry code: (vi) $1 - x, -\frac{1}{2} + y, \frac{1}{2} - z$]. Ring *A* is oriented in such a way that the perpendicular distance from *A* to A^v is 3.428 \AA , the closest interatomic distance being $C12 \cdots C7^v [3.451(4) \text{ \AA}]$. The perpendicular distance from ring *B* to ring C^{vi} is 3.281 \AA , the closest interatomic distance being $C12 \cdots C9^{vi} [3.392(4) \text{ \AA}]$; the dihedral angle between the planes of these rings is $14.99(6)^\circ$.

Experimental

To an ethanol/water solution (30 ml, *ca* 1:1 *v/v*) containing $CuCl_2 \cdot 4H_2O$ (1 mmol) and disodium dipicolinate (1 mmol), 2,9-dimethyl-1,10-phenanthroline (1 mmol) was added slowly with continuous stirring. The resulting solution was refluxed for 1 h and then filtered. The blue filtrate was allowed to stand for 21 d at room temperature, after which time blue crystals of (I) suitable for X-ray diffraction analysis were harvested.

Crystal data

$[Cu(C_7H_3NO_4)(C_{14}H_{12}N_2)] \cdot 3H_2O$	$D_x = 1.595 \text{ Mg m}^{-3}$
$M_r = 490.96$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 4580 reflections
$a = 14.6634(12) \text{ \AA}$	$\theta = 1.8\text{--}24.9^\circ$
$b = 10.8960(6) \text{ \AA}$	$\mu = 1.12 \text{ mm}^{-1}$
$c = 13.6985(11) \text{ \AA}$	$T = 297(2) \text{ K}$
$\beta = 110.866(6)^\circ$	Prism, blue
$V = 2045.1(3) \text{ \AA}^3$	$0.3 \times 0.2 \times 0.1 \text{ mm}$
$Z = 4$	

Data collection

Stoe IPDS-II diffractometer	3555 reflections with $I > 2\sigma(I)$
ω scans	$R_{int} = 0.092$
Absorption correction: integration (<i>X-RED32</i> ; Stoe & Cie, 2002)	$\theta_{max} = 27.9^\circ$
$T_{min} = 0.95, T_{max} = 0.98$	$h = -19 \rightarrow 19$
17419 measured reflections	$k = -14 \rightarrow 14$
4848 independent reflections	$l = -17 \rightarrow 17$

Refinement

Refinement on F^2	H atoms treated by a mixture of restrained and constrained refinement
$R[F^2 > 2\sigma(F^2)] = 0.042$	$wR(F^2) = 0.107$
$S = 0.99$	$w = 1/[\sigma^2(F_o^2) + (0.0533P)^2]$
4848 reflections	where $P = (F_o^2 + 2F_c^2)/3$
309 parameters	$(\Delta/\sigma)_{max} = 0.041$
	$\Delta\rho_{max} = 0.40 \text{ e \AA}^{-3}$
	$\Delta\rho_{min} = -0.74 \text{ e \AA}^{-3}$

Table 1

Selected geometric parameters ($\text{\AA}, ^\circ$).

Cu1—N2	2.228 (2)	Cu1—O1	2.0343 (18)
Cu1—N3	1.904 (2)	Cu1—O2	2.019 (2)
Cu1—N1	1.987 (2)		
N3—Cu1—N1	164.96 (8)	O2—Cu1—O1	158.89 (8)
N3—Cu1—O2	79.71 (8)	N3—Cu1—N2	115.70 (8)
N1—Cu1—O2	100.28 (8)	N1—Cu1—N2	79.06 (8)
N3—Cu1—O1	80.33 (8)	O2—Cu1—N2	103.75 (8)
N1—Cu1—O1	97.21 (8)	O1—Cu1—N2	91.08 (8)

Table 2

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>
O5—H5A \cdots O7	0.91 (3)	2.00 (3)	2.902 (4)	173 (5)
O5—H5B \cdots O4 ⁱ	0.88 (3)	2.08 (3)	2.945 (4)	169 (6)
O6—H6A \cdots O7 ⁱⁱ	0.79 (3)	2.06 (3)	2.841 (5)	168 (6)
O6—H6B \cdots O3	0.82 (3)	2.12 (3)	2.932 (4)	172 (6)
O7—H7A \cdots O6 ⁱⁱⁱ	0.78 (2)	2.19 (3)	2.927 (4)	158 (5)
O7—H7B \cdots O4 ^{iv}	0.83 (2)	2.07 (3)	2.894 (3)	172 (5)

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

H atoms attached to C atoms were placed at calculated positions (C—H = 0.93 and 0.96 \AA) and allowed to ride on their parent atoms [$U_{iso}(H) = 1.2U_{eq}(C)$ and $1.5U_{eq}(\text{methyl C})$]. Water H atoms were located in a difference map and refined with O—H and H \cdots H distances restrained to 0.85 (3) and 1.35 (3) \AA , respectively, and with $U_{iso}(H) = 1.5U_{eq}(O)$.

Data collection: *X-AREA* (Stoe & Cie, 2002); cell refinement: *X-AREA*; data reduction: *X-RED32* (Stoe & Cie, 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 for this paper are available from the IUCr electronic archives (Reference: FA1158). Services for accessing these data are described at the back of the journal.

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