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## Key indicators

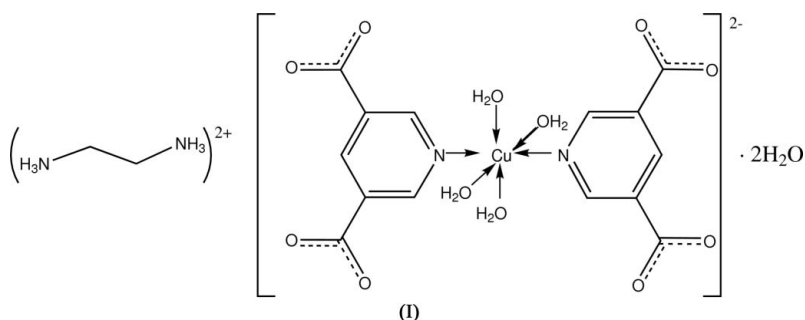
Single-crystal X-ray study  
 $T = 294\text{ K}$   
Mean  $\sigma(\text{C}-\text{C}) = 0.003\text{ \AA}$   
 $R$  factor = 0.029  
 $wR$  factor = 0.069  
Data-to-parameter ratio = 12.3For details of how these key indicators were  
automatically derived from the article, see  
<http://journals.iucr.org/e>.Ethylenediammonium tetraaquabis(pyridine-  
3,5-dicarboxylato- $\kappa N$ )cuprate(II) dihydrate

In the title compound,  $(\text{C}_2\text{H}_{10}\text{N}_2)[\text{Cu}(\text{C}_7\text{H}_3\text{NO}_4)_2(\text{H}_2\text{O})_4] \cdot 2\text{H}_2\text{O}$ , the  $\text{Cu}^{\text{II}}$  ion occupies a special position on an inversion center and has an elongated octahedral geometry with the pyridine-3,5-dicarboxylate ligands in *trans* positions. The ethylenediammonium cation is also in a special position on an inversion center located at the mid-point of the C—C bond. Multiple crystallographically independent hydrogen bonds form a three-dimensional network in the crystal structure.  $\pi$ – $\pi$  Interactions between aromatic rings of the pyridine-3,5-dicarboxylate ligand are observed. The electron-spin resonance (ESR) spectrum is in agreement with an elongated octahedral geometry.

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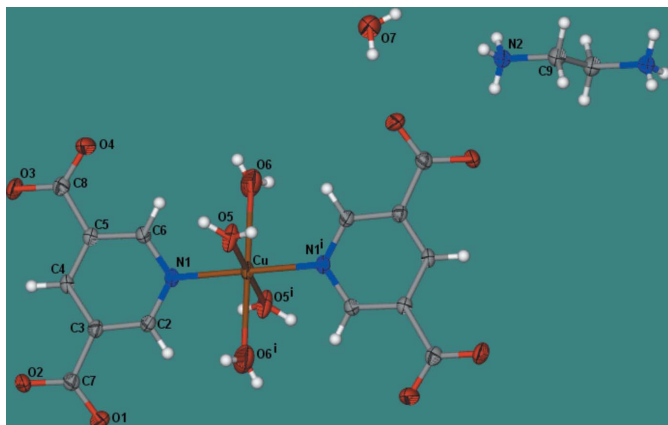
## Comment

Pyridine-3,5-dicarboxylic acid is an interesting ligand: it is highly symmetrical, potentially multidentate, can participate in hydrogen-bonding interactions with N and O H-atom acceptors and may also exhibit  $\pi$ – $\pi$  interactions. Mononuclear  $\text{Ni}^{\text{II}}$  (Xu *et al.*, 2002),  $\text{Co}^{\text{II}}$  (Min *et al.*, 2001) and  $\text{Pd}^{\text{II}}$  (Qin *et al.*, 2000; Qin *et al.*, 2002) complexes, as well as a tetranuclear  $\text{Cu}^{\text{II}}$  (Yao *et al.*, 2004), (Chaigneau *et al.*, 2004) and polymeric  $\text{Cd}^{\text{II}}$  (Xia, 2004),  $\text{Cu}^{\text{II}}$  (Lu & Schauss, 2001) and  $\text{Co}^{\text{II}}$  (Plater *et al.*, 1998) complexes have been published. In this paper, we report the structure of the title compound, (I), a monomeric anionic  $\text{Cu}^{\text{II}}$  compound with an organic hydrogen-bonding donor cation.

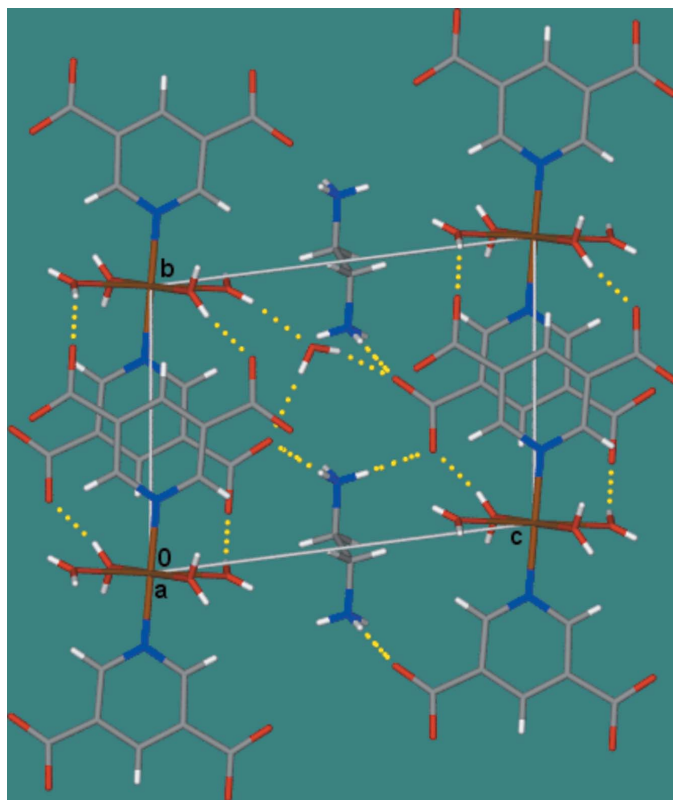


Compound (I) consists of centrosymmetric tetraaquabis(pyridine-3,5-dicarboxylato- $\kappa N$ )cuprate(II) anions, centrosymmetric ethylenediammonium dication and two water molecules (see Fig. 1). The  $\text{Cu}^{\text{II}}$  ions are hexacoordinated in an elongated octahedral geometry. Due to symmetry restrictions, the angles around the metal center are near to the expected  $90^\circ$  and  $180^\circ$  (see Table 1), but the distances differ due to Jahn–Teller distortion.

A complex structure of hydrogen bonds organizes the molecules in a three-dimensional hydrogen-bonded structure



**Figure 1**  
A view of (I). Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as circles of arbitrary radius [Symmetry code: (I)  $-x, 2 - y, 2 - z$ .]



**Figure 2**  
The hydrogen bonding (dashed lines) in (I).

(Fig. 2 and Table 2). The pyridine-3,5-dicarboxylate ligand is parallel to two other pyridine-3,5-dicarboxylate anions at  $(-x, 1 - y, 2 - z)$  and  $(1 - x, 1 - y, 2 - z)$  with centroid-centroid distances of 3.520 (1) and 3.750 (1) Å, respectively, indicating  $\pi$ - $\pi$  interactions between the rings.

A thermogravimetric study showed a weight loss of 15.8% at 416 K, corresponding to five water molecules (calculated 15.9%); the compound decomposes at 539 K. The solid-state electron paramagnetic resonance (EPR) spectra of (I) at 293 and 77 K are in agreement with an octahedral elongated geometry (Hathaway, 1987).

## Experimental

Ethylenediamine (0.4 mmol, 0.025 g) was added slowly to an aqueous solution (10 ml) of copper(II) perchlorate hexahydrate (0.4 mmol, 0.15 g). To this mixture, an aqueous solution (10 ml) of potassium pyridine-3,5-dicarboxylate, previously obtained from 3,5-pyridine-dicarboxylic acid (0.8 mmol, 0.14 g) and KOH (0.8 mmol, 0.0448 g), was added; a precipitate formed immediately. After filtration of the solution, the filtrate was left undisturbed, giving blue crystals of the product suitable for X-ray crystallography. The total yield corresponds to 83% based on copper. The reaction of copper nitrate hemipentahydrate with ethylenediamine and dipotassium pyridine-3,5-dicarboxylate gave the same product. Analysis found: C 34.30, H 5.23, N 9.74%; calculated for  $C_{16}H_{28}CuN_4O_{14}$ : C 34.08, H 5.00, N 9.93%. EPR data, at 293 K:  $g_z = 2.315$  (1),  $g_{x,y} = 2.074$  (1); at 77 K:  $g_z = 2.322$  (1),  $g_{x,y} = 2.073$  (1). EPR measurements for the solid were made at 293 and 77 K in quartz tubes in a Jeol JES-TE300 spectrometer (X band at 100 kHz field modulation).

### Crystal data

$(C_2H_{10}N_2)[Cu(C_7H_3NO_4)_2 \cdot (H_2O)_4] \cdot 2H_2O$   
 $M_r = 563.96$   
 Triclinic,  $P\bar{1}$   
 $a = 6.870$  (1) Å  
 $b = 8.476$  (1) Å  
 $c = 10.987$  (1) Å  
 $\alpha = 77.574$  (2)°  
 $\beta = 74.588$  (2)°

$\gamma = 67.865$  (1)°  
 $V = 566.55$  (12) Å<sup>3</sup>  
 $Z = 1$   
 $D_x = 1.653$  Mg m<sup>-3</sup>  
 Mo  $K\alpha$  radiation  
 $\mu = 1.04$  mm<sup>-1</sup>  
 $T = 294$  (2) K  
 Prism, blue  
 $0.20 \times 0.13 \times 0.04$  mm

### Data collection

Bruker SMART APEX CCD diffractometer  
 $\omega$  scans  
 Absorption correction: analytical (Sheldrick, 2000)  
 $T_{min} = 0.817$ ,  $T_{max} = 0.958$

4800 measured reflections  
 2073 independent reflections  
 1882 reflections with  $I > 2\sigma(I)$   
 $R_{int} = 0.029$   
 $\theta_{max} = 25.4^\circ$

### Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.029$   
 $wR(F^2) = 0.070$   
 $S = 1.05$   
 2073 reflections  
 169 parameters

H atoms treated by a mixture of independent and constrained refinement  
 $w = 1/[\sigma^2(F_o^2) + (0.0357P)^2]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{max} < 0.001$   
 $\Delta\rho_{max} = 0.37$  e Å<sup>-3</sup>  
 $\Delta\rho_{min} = -0.31$  e Å<sup>-3</sup>

**Table 1**

Selected geometric parameters (Å, °).

Cu—N1	2.0140 (15)	Cu—O6	2.5545 (16)
Cu—O5	1.9409 (14)		
O5—Cu—N1	90.02 (6)	O5—Cu—O6	89.80 (6)
N1—Cu—O6	89.10 (6)		
C2—C3—C7—O1	15.0 (3)	C6—C5—C8—O4	5.2 (3)

**Table 2**

Hydrogen-bond geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
O5—H5A $\cdots$ O3 <sup>i</sup>	0.85	1.79	2.6289 (19)	167
O5—H5B $\cdots$ O2 <sup>ii</sup>	0.85	1.78	2.6289 (19)	172
O6—H6A $\cdots$ O3 <sup>iii</sup>	0.85	2.05	2.890 (2)	167
O6—H6B $\cdots$ O7 <sup>iii</sup>	0.85	2.04	2.875 (2)	166

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O7–H7A $\cdots$ O1	0.85	2.14	2.947 (2)	159
O7–H7B $\cdots$ O4 <sup>iv</sup>	0.85	2.01	2.851 (2)	169
N2–H2A $\cdots$ O4 <sup>v</sup>	0.83 (2)	1.94 (2)	2.738 (2)	159 (2)
N2–H2B $\cdots$ O2 <sup>vi</sup>	0.84 (2)	1.92 (2)	2.757 (2)	176 (2)
N2–H2C $\cdots$ O1	0.84 (2)	1.96 (2)	2.780 (2)	168 (2)

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

All H atoms were located in a difference map. C-bound H atoms were placed in geometrically idealized positions [ $C-H = 0.93$  (CH),  $0.97$  (CH<sub>2</sub>) and  $0.96\text{Å}$  (CH<sub>3</sub>)], with  $U_{\text{iso}}(\text{H})$  values tied to those of the parent atoms [ $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}$  for  $Csp$ ,  $Csp^2$  and  $1.5U_{\text{eq}}$  for  $Csp^3$ ] and refined using a riding model. Water H atoms were constrained at idealized positions [ $O-H = 0.85\text{Å}$  and  $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$ ] and those bonded to N atoms were refined with a distance restraint [ $0.84$  (2) Å].

Data collection: *SMART* (Bruker, 1999); cell refinement: *SAINT-Plus* (Bruker, 1999); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2000); program(s) used to refine structure: *SHELXTL*; molecular graphics: *X-SEED* (Version 2.0; Barbour, 2001); software used to prepare material for publication: *SHELXTL* and *enCIFer* (Allen *et al.*, 2004).

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