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Key indicators

Single-crystal X-ray study
T = 120 K
Mean $\sigma(\text{C}-\text{C}) = 0.002 \text{ \AA}$
R factor = 0.033
wR factor = 0.097
Data-to-parameter ratio = 20.4

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

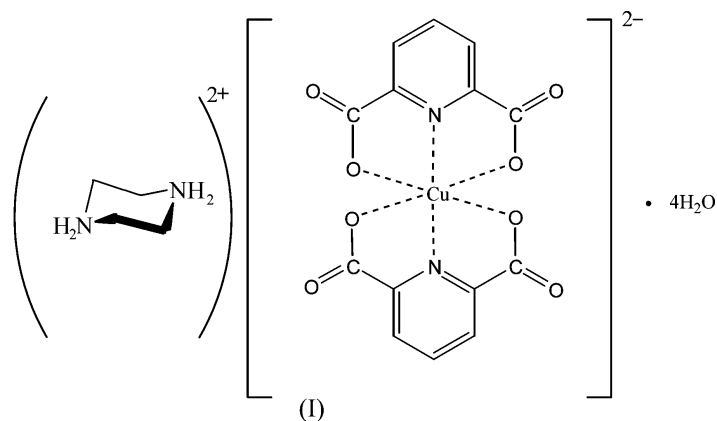
Piperazinediium bis(pyridine-2,6-dicarboxylato)-cuprate(II) tetrahydrate

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The reaction of copper(II) nitrate with the proton-transfer compound piperazinediium pyridine-2,6-dicarboxylate, or (pipzH₂)(pydc), in aqueous solution leads to the formation of the title compound, (C₄H₁₂N₂)[Cu(C₇H₃NO₄)₂] \cdot 4H₂O. The title compound is a six-coordinate complex with a distorted octahedral geometry around the central atom. In the crystal structure, a wide range of non-covalent interactions consisting of hydrogen bonding and π - π stacking connect the various components into a supramolecular structure.

Comment

There are several studies on proton transfer between a carboxylic acid and a heterocyclic amine. Continuing our research on proton-transfer systems, we have now found a route to combine a carboxylic acid with an amine and produce some almost water-soluble (about 5–8 g per 100 ml) self-associating ion-pair systems, which can react with metal ions and result in different complexes (Aghabozorg, Ghadermazi *et al.*, 2006; Soleimannejad *et al.*, 2005; Moghimi, Aghabozorg *et al.*, 2005; Moghimi *et al.*, 2002; Aghabozorg, Akbari & Ramezanipour, 2005; Moghimi *et al.*, 2003). The resulting compounds, with some remaining sites as electron donors, can coordinate to many metal ions (Aghabozorg, Nakhjavan *et al.*, 2006; Aghabozorg, Ghadermazi *et al.*, 2006; Sheshmani *et al.*, 2006; Moghimi, Sheshmani *et al.*, 2005; Moghimi, Sharif *et al.*, 2005; Aghabozorg, Moghimi *et al.*, 2005; Aghabozorg, Dalir Kheirollahi *et al.*, 2005; Moghimi, Alizadeh *et al.*, 2005; Ramezanipour *et al.*, 2005). We report here the crystal structure of the title compound, (I).



In the title compound, (I) (Fig. 1), the bond lengths and angles are within normal ranges (Allen *et al.*, 1987). The piperazine ring is not planar, having a total puckering ampli-

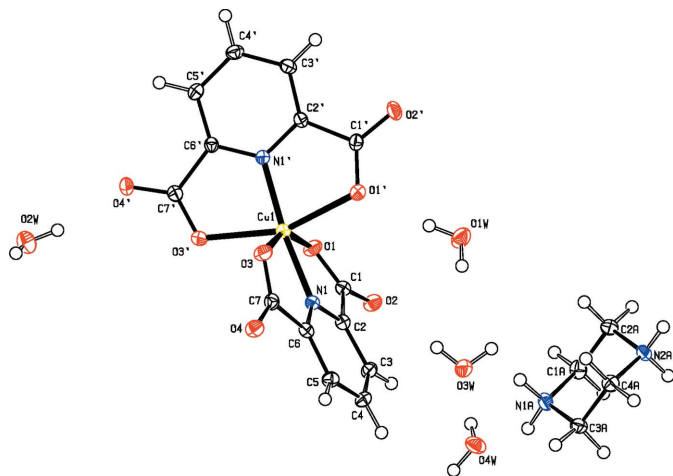


Figure 1
The structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

tude, Q_T , of 0.581 (3) Å and a chair conformation [$\varphi = 162.28$ (4)° and $\theta = 2.78$ (3)°] (Cremer & Pople, 1975). The Cu^{II} atom is six-coordinated by two pyridine-2,6-dicarboxylate, or (pydc)²⁻, groups, *i.e.* each (pydc)²⁻ is coordinated through one pyridine N atom and two carboxylate O atoms (Table 1). Atoms N1 and N1' of the two (pydc)²⁻ fragments occupy the axial positions, while atoms O1, O1', O3 and O3' form the equatorial plane.

The N1–Cu1–N1' angle deviates from linearity. Therefore, the coordination around Cu^{II} is distorted octahedral. There are four uncoordinated water molecules and one piperazinium ion as counter-ion, with some hydrogen bonds to water molecules and coordinated COO⁻ groups of (pydc)²⁻ fragments.

Intermolecular O–H...O, N–H...O and C–H...O hydrogen bonds (Table 2) seem to be effective in the stabilization of the crystal structure. Considerable π – π stacking interactions between two aromatic rings of (pydc)²⁻, with an average distances of 3.45 and 3.49 Å are observed (Fig. 2). Hydrogen bonds result in the formation of a supramolecular structure (Fig. 3). Dipole–dipole and van der Waals interactions are also effective in the packing.

Experimental

A mixture of an aqueous solution (30 ml) of the proton-transfer compound (pipzH₂)(pydc) (0.253 g, 1 mmol) and copper(II) nitrate (0.1163 g, 0.5 mmol) were stirred at room temperature, and the complexation reaction was complete after 30 min. Green crystals of (I) were obtained after four weeks at room temperature.

Crystal data

| | |
|--------------------------------------------------------------------------------------------------------------------------------------|-------------------------------------------|
| (C ₄ H ₁₂ N ₂)[Cu(C ₇ H ₃ NO ₄) ₂].4H ₂ O | $Z = 4$ |
| $M_r = 553.97$ | $D_x = 1.654 \text{ Mg m}^{-3}$ |
| Monoclinic, $P2_1/n$ | Mo $K\alpha$ radiation |
| $a = 7.9113$ (16) Å | $\mu = 1.06 \text{ mm}^{-1}$ |
| $b = 13.257$ (3) Å | $T = 120$ (2) K |
| $c = 21.208$ (4) Å | Cube, green |
| $\beta = 90.414$ (4)° | $0.20 \times 0.20 \times 0.20 \text{ mm}$ |
| $V = 2224.2$ (8) Å ³ | |

Data collection

Bruker SMART 1000 CCD area-detector diffractometer
 φ and ω scans
Absorption correction: multi-scan (SADABS; Sheldrick, 1998)
 $T_{\min} = 0.817$, $T_{\max} = 0.817$

19015 measured reflections
6436 independent reflections
5270 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.029$
 $\theta_{\text{max}} = 30.1^\circ$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.033$
 $wR(F^2) = 0.097$
 $S = 1.02$
6436 reflections
316 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0638P)^2 + 0.0065P]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 0.90 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.57 \text{ e \AA}^{-3}$

Table 1

Selected geometric parameters (Å, °).

| | | | |
|---------------|--------------|---------------|--------------|
| Cu1–N1' | 1.9143 (13) | O2–C1 | 1.2560 (17) |
| Cu1–N1 | 1.9433 (14) | O3–C7 | 1.2514 (19) |
| Cu1–O1' | 2.1240 (12) | O4–C7 | 1.2565 (18) |
| Cu1–O3' | 2.1368 (11) | O1'–C1' | 1.2694 (19) |
| Cu1–O1 | 2.2472 (12) | O2'–C1' | 1.2375 (17) |
| Cu1–O3 | 2.2674 (11) | O3'–C7' | 1.2768 (19) |
| O1–C1 | 1.2559 (18) | O4'–C7' | 1.2326 (17) |
| | | | |
| N1'–Cu1–N1 | 173.64 (5) | O1–Cu1–O3 | 154.11 (4) |
| N1'–Cu1–O1' | 79.65 (5) | O2–C1–O1 | 125.62 (14) |
| N1–Cu1–O1' | 94.22 (4) | O2–C1–C2 | 117.95 (13) |
| N1'–Cu1–O3' | 78.71 (5) | O1–C1–C2 | 116.42 (13) |
| N1–Cu1–O3' | 107.49 (4) | O3–C7–O4 | 126.07 (14) |
| O1'–Cu1–O3' | 158.19 (4) | O3–C7–C6 | 116.27 (13) |
| N1'–Cu1–O1 | 100.21 (4) | O4–C7–C6 | 117.66 (13) |
| N1–Cu1–O1 | 77.70 (4) | O2'–C1'–O1' | 126.71 (14) |
| O1'–Cu1–O1 | 87.96 (5) | O2'–C1'–C2' | 118.32 (14) |
| O3'–Cu1–O1 | 98.50 (5) | O1'–C1'–C2' | 114.95 (12) |
| N1'–Cu1–O3 | 105.64 (5) | O4'–C7'–O3' | 127.05 (14) |
| N1–Cu1–O3 | 76.73 (4) | O4'–C7'–C6' | 118.43 (14) |
| O1'–Cu1–O3 | 97.88 (5) | O3'–C7'–C6' | 114.52 (12) |
| O3'–Cu1–O3 | 85.39 (4) | | |
| | | | |
| O1'–Cu1–O1–C1 | 80.43 (10) | O1'–Cu1–O3–C7 | –103.12 (10) |
| O3'–Cu1–O1–C1 | –120.51 (10) | O3'–Cu1–O3–C7 | 98.58 (10) |

Table 2

Hydrogen-bond geometry (Å, °).

| $D-H\cdots A$ | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|-------------------------------|-------|-------------|-------------|---------------|
| N1A–H1AC...O4 ⁱ | 0.92 | 1.85 | 2.769 (2) | 176 |
| N1A–H1AD...O4W | 0.92 | 1.88 | 2.697 (2) | 146 |
| N2A–H2AC...O2 ⁱⁱ | 0.92 | 1.90 | 2.797 (2) | 164 |
| N2A–H2AD...O2 ⁱⁱⁱ | 0.92 | 1.88 | 2.776 (2) | 163 |
| O1W–H1WA...O1' | 0.85 | 1.97 | 2.821 (2) | 176 |
| O1W–H1WB...O4 ⁱ | 0.85 | 1.97 | 2.821 (2) | 174 |
| O2W–H2WA...O4' | 0.85 | 2.09 | 2.929 (2) | 169 |
| O2W–H2WB...O1W ^{iv} | 0.85 | 2.01 | 2.853 (2) | 175 |
| O3W–H3WA...O2 | 0.85 | 1.96 | 2.806 (2) | 177 |
| O3W–H3WB...O2 ⁱⁱ | 0.85 | 2.32 | 2.904 (2) | 126 |
| C3A–H3AB...O3 ⁱ | 0.99 | 2.56 | 3.175 (2) | 120 |
| C4A–H4AB...O1W ⁱⁱⁱ | 0.99 | 2.60 | 3.349 (2) | 133 |
| C1A–H1AA...O2W ^v | 0.99 | 2.57 | 3.454 (2) | 149 |
| C2A–H2AA...O4 ^{iv} | 0.99 | 2.36 | 3.161 (2) | 138 |
| C5'–H5'A...O1 ^{vi} | 0.95 | 2.55 | 3.415 (2) | 151 |
| C4A–H4AA...O3W ^{vii} | 0.99 | 2.48 | 3.264 (2) | 136 |

Symmetry codes: (i) $-x + 2, -y + 1, -z$; (ii) $-x + \frac{3}{2}, y + \frac{1}{2}, -z + \frac{1}{2}$; (iii) $-x + \frac{5}{2}, y + \frac{1}{2}, -z + \frac{3}{2}$; (iv) $x - \frac{1}{2}, -y + \frac{1}{2}, z - \frac{1}{2}$; (v) $x + \frac{1}{2}, -y + \frac{1}{2}, z + \frac{1}{2}$; (vi) $-x + 1, -y, -z$; (vii) $x + 1, y, z$.

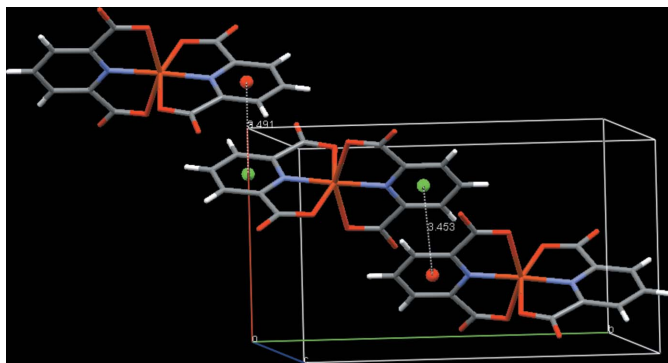


Figure 2
A view of the π - π stacking interactions between two aromatic rings of (I). The average distances between the planes are 3.45 and 3.49 Å.

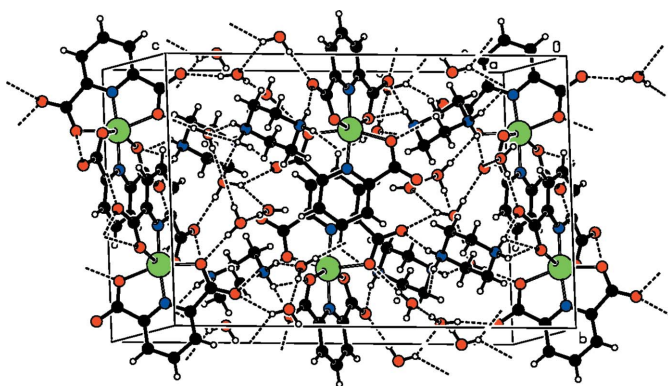


Figure 3
A packing diagram of (I). Hydrogen bonds are shown as dashed lines.

H atoms of water molecules were located in difference syntheses and refined as riding atoms, with $O-H = 0.85$ Å and $U_{iso}(H) = 1.5U_{eq}(O)$. The remaining H atoms were positioned geometrically, with $N-H = 0.92$ Å (for NH_2) and $C-H = 0.95$ and 0.99 Å for aromatic and methylene H atoms, respectively, and constrained to ride on their parent atoms, with $U_{iso}(H) = 1.2U_{eq}(C,N)$.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT-Plus* (Bruker, 1998); data reduction: *SAINT-Plus*; program(s) used to

solve structure: *SHELXTL* (Sheldrick, 1998); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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