

A novel mixed-valence copper complex, poly[[μ_2 -4,4'-bipyridine- μ_3 -pyridine-2,4,6-tricarboxylato-dicopper(I,II)] monohydrate]

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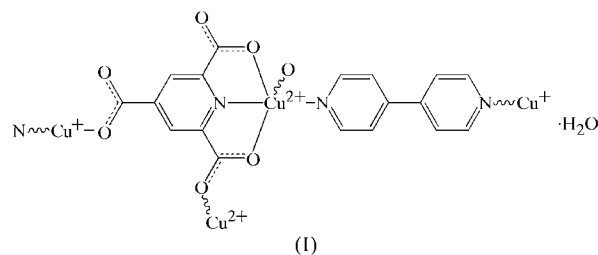
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In the title novel mixed-valence copper complex, $\{[\text{Cu}_2(\text{C}_8\text{H}_2\text{NO}_6)(\text{C}_{10}\text{H}_8\text{N}_2)] \cdot \text{H}_2\text{O}\}_n$, the Cu^{I} and Cu^{II} ions are linked by 4,4'-bipyridine (bpy) and pyridine-2,4,6-tricarboxylate (ptc) ligands into corrugated layers, which are assembled *via* interlayer C—H...O hydrogen bonds to give a three-dimensional supramolecular architecture.

Comment

In recent years, great interest has been focused on the rapidly expanding field of coordination polymers, due to their potential applications as catalysts and as materials with unique magnetic or optical properties (Eddaoudi *et al.*, 2002; Rouzo *et al.*, 1995; Li *et al.*, 1998). For the syntheses of two- or three-dimensional complexes, many rigid polydentate ligands, such as benzene-1,3,5-tricarboxylic acid (H_3tma) (Yaghi *et al.*, 1996), adamantane-1,3-dicarboxylic acid (Millange *et al.*,

2004), pyridine-2,6-dicarboxylic acid (H_2pdc) (Murtha & Walton, 1974), have been widely used. However, pyridine-2,4,6-tricarboxylic acid (H_3ptc) has rarely been explored to construct coordination polymers (Gao *et al.*, 2005; Ghosh *et al.*, 2004; Ghosh & Bharadwaj, 2005). The limited investigation to date shows that the structural dimensionality of ptc complexes depends on the coordination modes of the ptc ligand (Gao *et al.*, 2006). We report here the title novel mixed-valence copper complex, $[\text{Cu}^{\text{II}}\text{Cu}^{\text{I}}(\text{ptc})(\text{bpy}) \cdot \text{H}_2\text{O}]_n$, (I), which was obtained by hydrothermal reaction of bpy, H_3ptc and $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ at 423 K. Cu^{II} salts can be reduced to Cu^{I} or to mixed-valence compounds by 4,4'-bipyridine or 2,2'-bipyridine *via* hydrothermal reactions (Yang *et al.*, 1999).



Compound (I) is composed of solvent water molecules and two-dimensional corrugated polymeric layers, $[\text{Cu}^{\text{I}}\text{Cu}^{\text{II}}(\text{bpy})(\text{ptc})]_n$, where the cupric cations (Cu^{I}) are in a square-pyramidal N_2O_3 coordination environment defined by one bpy and two ptc anions, with one carboxylate atom at the apical position [O5^{i} ; symmetry code: (i) $\frac{1}{2} - x, \frac{1}{2} + y, \frac{3}{2} - z$] (Table 1), and the cuprous cations (Cu^{II}) are linearly coordinated by one N atom of one bpy ligand and one carboxylate O atom of one ptc anion. Within the polymeric layer, the cupric and cuprous cations (Cu^{I} and Cu^{II}) are alternately bridged by bpy and ptc ligands in the [001] direction and further interlinked through the apical carboxylate O5 atoms at the Cu^{I} atoms in the [010] direction. As illustrated in Fig. 2, the polymeric layers can be viewed topologically as rail-sharing ladders, which are oriented nearly perpendicular to one another [the dihedral angle between adjacent ladders is $86.02(2)^\circ$].

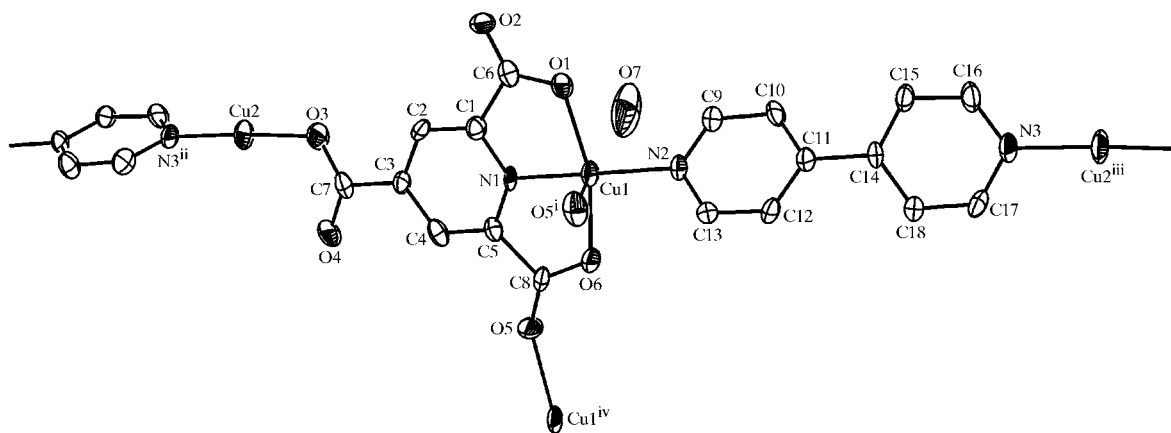


Figure 1

A view of the complex molecule of the title compound, showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 45% probability level. H atoms have been omitted for clarity. [Symmetry codes: (i) $\frac{1}{2} - x, \frac{1}{2} + y, \frac{3}{2} - z$; (ii) $x - \frac{3}{2}, \frac{3}{2} - y, z - \frac{1}{2}$; (iii) $\frac{3}{2} + x, \frac{3}{2} - y, \frac{1}{2} + z$; (iv) $\frac{1}{2} - x, y - \frac{1}{2}, \frac{3}{2} - z$.]

The bond lengths involving the cupric cations (Cu1) are comparable with those reported in the literature. The Cu—O and Cu—N distances are close to those observed in the compounds [Cu(phen)(BzCN)]₂·2BF₄ [phen is 1,10-phenanthroline; BzCN is the benzonitrile anion; Cu—N = 1.859 (9) and 1.877 (9) Å; Lopez & Keller, 1999] and [Cu₃(C₆H₂Me₃-2,4,6)(O₂CC₆H₅)₂] [Cu—O = 1.855 (5) Å; Aalten *et al.*, 1989], but a little shorter than those in [Cu₆(Iso)₆]₂·2H₂O [Iso is the isonicotinate anion; Cu—O = 2.1367 (14)–2.1919 (14) Å and Cu—N = 2.1389 (15)–2.1538 (15) Å; Liu & Yuan, 2005] [bond lengths and angles for (I) are listed in Table 1].

The ptc anions display nearly perfect coplanarity, with a maximum deviation from the best plane of 0.1837 (1) Å for atom O6. The coordination modes of the carboxylate groups are different. The 2-carboxylate atom O1 is bound to the cupric cation (Cu1) in an *anti* fashion, the 4-carboxylate atom O3 to the cuprous cation (Cu2) in a *syn* fashion, and the 6-carboxylate bidentately bridges two cupric cations in a *syn-anti* fashion. The bridging bpy ligands are twisted, with a dihedral angle of 39.6 (1)° between the component pyridyl rings.

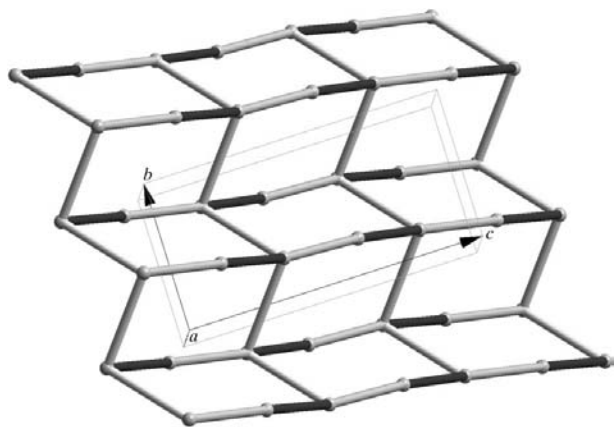


Figure 2
A topological view of the [Cu^{II}Cu^I(pte)(bpy)]_n layer. White bonds denote the bridging carboxylates, light-grey bonds the ptc ligands and dark-grey bonds the bpy ligands.

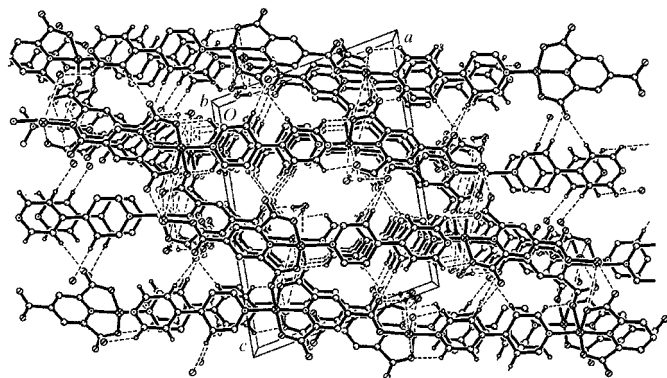


Figure 3
A perspective view of the crystal structure of (I), with hydrogen bonds shown as dashed lines. H atoms not involved in hydrogen bonds have been omitted for clarity.

The solvent water molecules form nearly linear hydrogen bonds to the coordinated (O1) and uncoordinated (O4) atoms of different ladders of one layer, with O···O distances in the range 2.786 (8)–3.284 (8) Å (Table 1). The polymeric layers are stacked along the [001] direction to meet the requirements of close packing, and weak classical interlayer C—H···O hydrogen bonding and a non-classical C17—H9···O1 hydrogen-bonding interaction (Steiner, 1996) make a significant contribution to the stabilization of the crystal structure.

Experimental

Cu(ClO₄)₂·6H₂O (0.3705 g, 1.00 mmol), bpy (0.1560 g, 1.00 mmol), H₃ptc (0.1402 g, 0.67 mmol) and H₂O (10 ml) were added to a 23 ml Teflon-lined autoclave retort and heated for 160 h at 443 K, then cooled to room temperature. Blue block-shaped crystals of (I) were collected, washed with methanol and dried in air [yield *ca* 2% based on the initial Cu(ClO₄)₂·6H₂O input].

Crystal data

[Cu ₂ (C ₈ H ₂ NO ₆)(C ₁₀ H ₈ N ₂)]·H ₂ O	Z = 4
<i>M_r</i> = 509.39	<i>D_x</i> = 1.939 Mg m ⁻³
Monoclinic, <i>P</i> 2 ₁ / <i>n</i>	Mo <i>K</i> α radiation
<i>a</i> = 12.823 (3) Å	<i>μ</i> = 2.49 mm ⁻¹
<i>b</i> = 8.2800 (17) Å	<i>T</i> = 298 (2) K
<i>c</i> = 16.776 (3) Å	Block, blue
<i>β</i> = 101.53 (3)°	0.10 × 0.08 × 0.06 mm
<i>V</i> = 1745.2 (6) Å ³	

Data collection

Siemens <i>P4</i> diffractometer	4011 independent reflections
<i>ω</i> scans	1439 reflections with <i>I</i> > 2σ(<i>I</i>)
Absorption correction: <i>ψ</i> scan	<i>R_{int}</i> = 0.065
(North <i>et al.</i> , 1968)	<i>θ_{max}</i> = 27.5°
<i>T_{min}</i> = 0.651, <i>T_{max}</i> = 0.758	3 standard reflections
(expected range = 0.740–0.861)	every 97 reflections
5160 measured reflections	intensity decay: none

Refinement

Refinement on <i>F</i> ²	<i>w</i> = 1/[σ ² (<i>F_o</i> ²) + (0.0277 <i>P</i>) ²]
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)] = 0.056	where <i>P</i> = (<i>F_o</i> ² + 2 <i>F_c</i> ²)/3
<i>wR</i> (<i>F</i> ²) = 0.116	(Δ/σ) _{max} = 0.005
<i>S</i> = 0.90	Δρ _{max} = 0.51 e Å ⁻³
4011 reflections	Δρ _{min} = -0.50 e Å ⁻³
272 parameters	Extinction correction: <i>SHELXL97</i>
H-atom parameters constrained	(Sheldrick, 1997)
	Extinction coefficient: 0.00052 (13)

Table 1

Selected geometric parameters (Å, °).

Cu1—N1	1.900 (4)	Cu1—O5 ⁱ	2.290 (5)
Cu1—N2	1.965 (5)	Cu2—O3	1.844 (4)
Cu1—O1	2.020 (4)	Cu2—N3 ⁱⁱ	1.876 (5)
Cu1—O6	2.022 (5)		
N1—Cu1—N2	170.3 (2)	N1—Cu1—O5 ⁱ	102.33 (19)
N1—Cu1—O1	80.8 (2)	N2—Cu1—O5 ⁱ	87.1 (2)
N2—Cu1—O1	100.9 (2)	O1—Cu1—O5 ⁱ	95.78 (18)
N1—Cu1—O6	80.1 (2)	O6—Cu1—O5 ⁱ	91.34 (18)
N2—Cu1—O6	97.3 (2)	O3—Cu2—N3 ⁱⁱ	177.5 (2)
O1—Cu1—O6	160.71 (17)		

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

H atoms attached to C atoms were positioned geometrically and refined using a riding model, with C—H = 0.93 and 0.97 Å, and *U*_{iso}(H) = 1.2*U*_{eq}(C). Water H atoms were found in a difference

Table 2
Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O7—H11 \cdots O1	0.85	2.44	3.284 (8)	176
O7—H12 \cdots O4 ⁱⁱⁱ	0.85	1.97	2.786 (8)	162
C10—H4 \cdots O4 ^{iv}	0.93	2.57	3.432 (8)	155
C15—H7 \cdots O2 ^v	0.93	2.39	3.310 (8)	168
C16—H8 \cdots O6 ^{vi}	0.93	2.47	3.238 (8)	140
C17—H9 \cdots O1 ^{vii}	0.93	2.58	3.257 (8)	130
C18—H10 \cdots O2 ^{viii}	0.93	2.40	3.327 (8)	174

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

Fourier synthesis and refined with the O—H bond distances fixed as initially found and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{O})$. The small crystal, a non-CCD instrument and room temperature resulted in a low ratio of observed to total reflections.

Data collection: *XSCANS* (Siemens, 1996); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1997); software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: AV3040). Services for accessing these data are described at the back of the journal.

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