

catena-Poly[[copper(II)- μ -2-[bis(2-pyridylmethyl)amino]butyrato- $\kappa^4 N, N', N'', O: \kappa O'$] perchlorate]Ki-Young Choi,^{a*} Seung-Chul Choi,^a Jaejung Ko,^b
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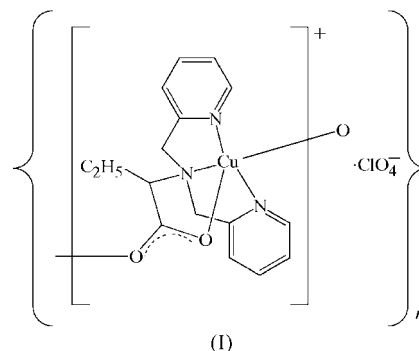
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The copper(II) ion in the *syn-anti* carboxylate-bridged one-dimensional zigzag chain title complex, $\{[\text{Cu}(\text{C}_{16}\text{H}_{18}\text{N}_3\text{O}_2)]\text{ClO}_4\}_n$, exhibits a distorted trigonal-bipyramidal environment. Two N atoms and one carboxylate O atom of the ligand form the basal plane, while the axial positions are filled by an N atom of the ligand and one O atom belonging to the carboxylate group of an adjacent molecule. The crystal packing is enhanced by C—H \cdots O(perchlorate) hydrogen bonds.

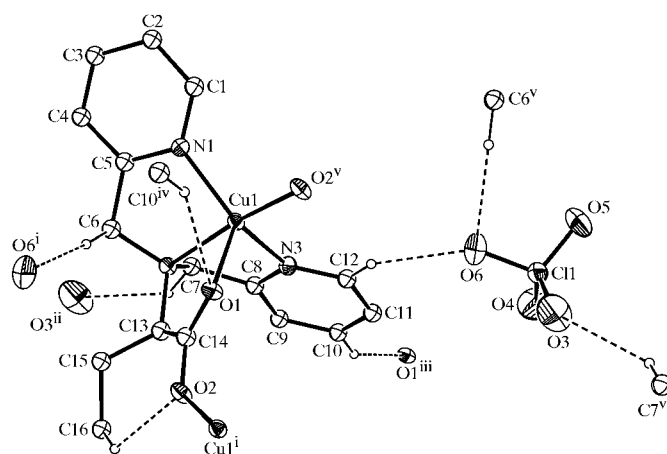
Comment

The inclusion of a carboxylate group in Schiff base polydentate ligands gives a wide variety of polynuclear complexes ranging from discrete entities to multidimensional chain complexes. It has been widely observed that such compounds can be influenced by the metal ion and the possible counterion effects (Choi, Jeon, Lee *et al.*, 2004; Colacio *et al.*, 1992; Doedens, 1976; Tanase *et al.*, 2005). For example, the self-assembly of copper(II) perchlorate with 2-[bis(2-pyridylmethyl)amino]ethanoic acid (Hpmea) leads to the carboxylate-bridged one-dimensional chain complex $\{[\text{Cu}(\mu\text{-pmea})]\text{ClO}_4 \cdot \text{H}_2\text{O}\}_n$, hereafter denoted (II), in which each copper(II) ion has a distorted square-pyramidal geometry with an N_3O basal plane and a carboxylate O atom in the axial position (Choi, Jeon, Lee *et al.*, 2004). However, 4-[bis(2-pyridylmethyl)amino]butyric acid (Hpmba) reacts with CuCl_2 to give the mononuclear compound $[\text{Cu}(\text{Hpmba})\text{Cl}_2] \cdot \text{H}_2\text{O}$, which exhibits a distorted square-pyramidal environment with an N_3Cl basal plane and a Cl atom in the axial position (Choi, Jeon, Ryu *et al.*, 2004). To investigate different molecular topologies, we have prepared and present the structure of the one-dimensional chain copper(II) title complex $\{[\text{Cu}(\mu\text{-paba})]\text{ClO}_4\}_n$ {Hpaba is 2-[bis(2-pyridylmethyl)amino]butyric acid}, (I).

Because the Hpaba ligand does not saturate the coordination position on the copper(II) ion, a self-assembly reaction



may occur through the deprotonated carboxylate group, leading to a carboxylate-bridged one-dimensional chain (Figs. 1 and 2) with an intramolecular Cu \cdots Cu distance of 5.241 (1) Å (Table 1). Each copper(II) ion involves a CuN_3O_2 chromophore. The Cu^{II} coordination geometry is distorted trigonal-bipyramidal with $\tau = 0.64$, where the structure index τ is defined as $(\beta - \alpha)/60$ (β and α are the largest coordination angles); τ has values of 1 and 0 for trigonal-bipyramidal (D_{3h}) and square-pyramidal (C_{4v}) geometries, respectively (Addison *et al.*, 1984). The three atoms in the trigonal plane are N1, N3 and O1 of the paba ligand, while the axial positions are filled by atom N2 and atom O2 of a symmetry-related carboxylate group. The average Cu—N and Cu—O distances are 2.025 (1) and 2.022 (1) Å, respectively, which are comparable to those found in (II) [2.013 (5) and 2.097 (7) Å], $\{[\text{Cu}(\mu\text{-pmpa})]\text{ClO}_4 \cdot 2\text{H}_2\text{O}\}_n$ {Hpmpa is 3-[bis(2-pyridylmethyl)amino]propionic acid; 1.995 (3) and 2.168 (3) Å; Choi, Jeon, Lee *et al.*, 2004] and $\{[\text{Cu}(\text{dpa})(\text{CH}_3\text{COO})]\text{ClO}_4 \cdot 0.5\text{THF}\}_n$ {dpa is *N,N*-bis(pyridine-2-ylmethyl)amine and THF is tetrahydrofuran;

**Figure 1**

The asymmetric unit of (I), including two polymeric linking atoms belonging to two different neighboring units. Displacement ellipsoids are drawn at the 20% probability level and H atoms have been omitted for clarity. All hydrogen-bond contacts are shown as dashed lines. [Symmetry codes: (i) $-x + \frac{3}{2}, y + \frac{1}{2}, -z + \frac{1}{2}$; (ii) $-x + \frac{3}{2}, y - \frac{1}{2}, -z + \frac{1}{2}$; (iii) $x + \frac{1}{2}, -y + \frac{3}{2}, z - \frac{1}{2}$; (iv) $x + \frac{1}{2}, -y + \frac{3}{2}, z + \frac{1}{2}$; (v) $x - \frac{1}{2}, -y + \frac{3}{2}, z - \frac{1}{2}$; (vi) $x - \frac{1}{2}, -y + \frac{3}{2}, z + \frac{1}{2}$.]

1.990 (2) and 2.169 (2) Å; Tanase *et al.*, 2005], hereafter denoted (III). The different molecular topology of (I) compared with *syn-anti* one-dimensional chain complex (II) ($\tau = 0.16$) may be attributed to steric hindrance through the substitution of the ethyl group at the 2-carbon position of the Hpmea ligand.

The Cu atom is displaced 0.270 (1) Å from the least-squares plane defined by the N₂O basal plane, towards carboxylate atom O2. The N1–Cu–N2 and N2–Cu–N3 bite angles of the five-membered chelate rings (Table 1) are similar to those expected for [[Cu(μ -papa)(H₂O)]ClO₄·2H₂O]_n [Hpapa is 3-(2-pyridylmethylamino)propionic acid; 81.5 (1)°; Colacio *et al.*, 2000], [[Cu(μ -pmao)(H₂O)]ClO₄·2H₂O]_n [Hpmao is 3-(2-pyridylmethylamino)butyric acid; 81.7 (1)°; Colacio *et al.*, 2000] and (III) [83.00 (14) and 82.20 (14)°]. The dihedral angle between the plane of the carboxylate group and the CuN₂O plane is 87.2 (2)°. The axial Cu1–N2 and Cu1–O2 linkages are not perfectly perpendicular to the CuN₂O plane, and the N2–Cu1–N, N2–Cu1–O1, O2–Cu1–N and O2–Cu1–O1 angles range from 80.7 (1) to 101.6 (1)°. The average Cu–N(secondary amine, basal plane) distance of 2.018 (1) Å is slightly shorter than that of Cu1–N2(tertiary amine, axial) [2.039 (2) Å]. The average N2–C [1.492 (2) Å] distance involving the tertiary amine is slightly longer than the average N1–C [1.339 (3) Å] and N3–C [1.343 (2) Å] distances involving the secondary amines. This may be due to the *sp*³-hybridization of the coordinated tertiary N atom. The IR spectrum of the complex shows the $\nu_{\text{as}}(\text{COO})$ stretching frequency at 1608 cm⁻¹ and $\nu_{\text{sym}}(\text{COO})$ at 1421 cm⁻¹. The difference, $\Delta\nu = 187 \text{ cm}^{-1}$, is characteristic of the *syn-anti* coordination mode of the bridging carboxylate group (Colacio *et al.*, 2000).

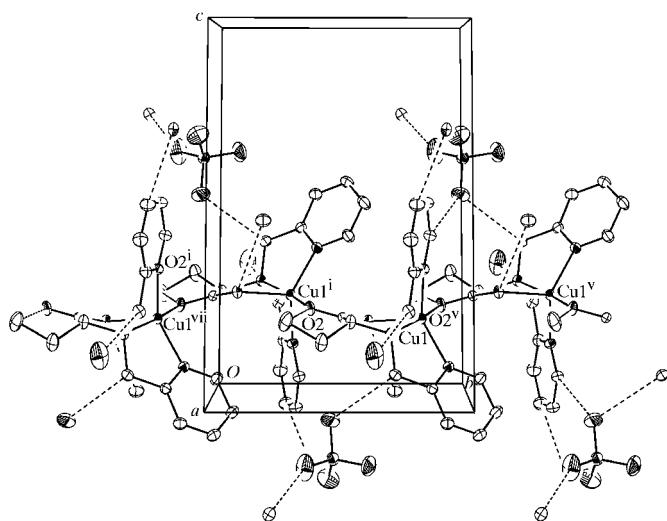


Figure 2 Part of the cell contents, showing a representative infinite carboxylate-bridged molecular chain parallel to the *b* axis. The large black spheres denote Cu atoms. Only the C12...O6 hydrogen bonds are shown for clarity. The symmetry codes are as in Fig. 1 [additional symmetry code: (vii) $x, y - 1, z$].

As illustrated in Fig. 1, the carboxylate polymer linking atoms O2 and C14 are generated by means of the 2₁ screw axes at $x = z = \frac{1}{4}$ parallel to the *b* axis, thus forming an infinite one-dimensional zigzag chain, as shown in Fig. 2. The perchlorate anion has typical geometry [Cl–O distance range 1.378 (3)–1.432 (3) Å, mean 1.405 (2) Å; O–Cl–O angle range 105.0 (2)–112.9 (2)°, mean 109.4 (1)°], similar to the perchlorate geometry reported by Hemmings *et al.* (1990). As shown in Fig. 1 and detailed in Table 2, atoms C6 and C7 in the cation are hydrogen bonded to atoms O6ⁱ and O3ⁱⁱ, respectively, of the perchlorate anions; pyridine atom C12 is also hydrogen bonded to perchlorate atom O6, so the latter atom is bifurcated. Additionally, atom C10 in the pyridine ring is hydrogen bonded to a carboxylate atom (O1ⁱⁱⁱ) of the polymer. The weak C16–H16B...O2ⁱ bond is noted for completeness. This intermolecular hydrogen-bond network further stabilizes the crystal structure of (I).

Experimental

An aqueous solution (20 ml) of Cu(ClO₄)₂·6H₂O (185 mg, 0.5 mmol) and 2-[bis(2-pyridylmethyl)amino]butyric acid (Hpaba; 129 mg, 0.5 mmol) was heated under reflux for 1 h and then cooled to room temperature. The solution was filtered and the filtrate left at room temperature until purple crystals formed. The product was filtered off and recrystallized from a hot water–methanol solution (1:1, 10 ml). Analysis found: C 42.85, H 4.14, N 9.46; calculated for C₁₆H₁₈Cl–CuN₃O₆: C 42.96, H 4.06, N 9.39%.

Crystal data

[Cu(C ₁₆ H ₁₈ N ₃ O ₂)]ClO ₄	Z = 4
<i>M_r</i> = 447.32	<i>D_x</i> = 1.603 Mg m ⁻³
Monoclinic, <i>P</i> 2 ₁ / <i>n</i>	Mo K α radiation
<i>a</i> = 14.0597 (11) Å	μ = 1.36 mm ⁻¹
<i>b</i> = 9.4711 (7) Å	<i>T</i> = 293 (2) K
<i>c</i> = 14.5223 (12) Å	Rectangular rod, purple
β = 106.626 (1)°	0.41 × 0.23 × 0.16 mm
<i>V</i> = 1853.0 (3) Å ³	

Data collection

Bruker SMART 1000 CCD diffractometer	18596 measured reflections
φ and ω scans	4627 independent reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	3844 reflections with <i>I</i> > 2 σ (<i>I</i>)
<i>T</i> _{min} = 0.643, <i>T</i> _{max} = 0.808	<i>R</i> _{int} = 0.022
	θ_{max} = 28.4°

Table 1 Selected geometric parameters (Å, °).

Cu–Cu ⁱ	5.241 (1)	N2–C6	1.479 (3)
Cu–O2 ⁱ	1.9234 (17)	N2–C7	1.491 (3)
Cu–N1	2.012 (2)	N2–C13	1.507 (3)
Cu–N3	2.023 (2)	N3–C12	1.341 (3)
Cu–N2	2.039 (2)	N3–C8	1.344 (3)
Cu–O1	2.1207 (16)	O1–C14	1.238 (3)
N1–C5	1.336 (3)	O2–C14	1.264 (3)
N1–C1	1.342 (4)		
O2 ⁱ –Cu–N1	101.56 (9)	O2 ⁱ –Cu–O1	88.41 (7)
O2 ⁱ –Cu–N3	100.73 (9)	N1–Cu–O1	117.75 (8)
N1–Cu–N3	130.90 (9)	N3–Cu–O1	106.02 (8)
O2 ⁱ –Cu–N2	169.12 (7)	N2–Cu–O1	80.71 (7)
N1–Cu–N2	83.71 (9)	O1–C14–O2 ⁱ	124.8 (2)
N3–Cu–N2	82.40 (9)		

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

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.038$
 $wR(F^2) = 0.110$
 $S = 1.02$
 4627 reflections
 244 parameters
 H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.0566P)^2 + 1.6027P]$$

where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.98 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.35 \text{ e } \text{\AA}^{-3}$

refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GA3027). Services for accessing these data are described at the back of the journal.

Table 2

Hydrogen-bond geometry (\AA , $^\circ$).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C6—H6A \cdots O6 ⁱⁱ	0.97	2.44	3.401 (5)	173
C7—H7B \cdots O3 ⁱⁱⁱ	0.97	2.46	3.258 (4)	140
C10—H10 \cdots O1 ^{iv}	0.93	2.50	3.323 (4)	148
C12—H12 \cdots O6	0.93	2.34	3.132 (4)	143
C16—H16B \cdots O2	0.96	2.41	3.021 (4)	122

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

All H atoms were positioned geometrically and constrained to ride on their carrier atoms, with $U_{\text{iso}}(\text{H})$ values equal to $1.5U_{\text{eq}}(\text{C16})$ for methyl H atoms and $1.2U_{\text{eq}}(\text{C})$ for the other H atoms. The highest peak and deepest hole in the final difference density map are 1.07 and 0.35 \AA , respectively, from atom C15.

Data collection: *SMART* (Bruker, 1999); cell refinement: *SAINT-Plus* (Bruker, 1999); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to

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