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Key indicators

Single-crystal X-ray study
T = 233 K
Mean $\sigma(\text{C}-\text{C}) = 0.005 \text{ \AA}$
Disorder in main residue
R factor = 0.040
wR factor = 0.103
Data-to-parameter ratio = 17.8

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

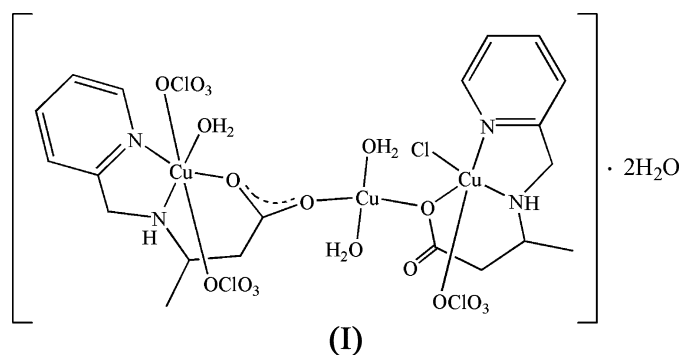
A trinuclear copper(II) complex: triaquachloro-triperchloratobis[μ_2 -3-(2-pyridylmethylamino)-butyrato]tricopper(II) dihydrate

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In the title compound, $[\text{Cu}_3(\text{C}_{10}\text{H}_{13}\text{N}_2\text{O}_2)_2\text{Cl}(\text{ClO}_4)_3(\text{H}_2\text{O})_3] \cdot 2\text{H}_2\text{O}$, the Cu atoms exhibit octahedral, square-pyramidal and square-planar coordination environments, and they are linked by carboxylate groups to form a trinuclear structure. The five water molecules participate in intra- and intermolecular hydrogen bonding.

Comment

The inclusion of a carboxylate group into Schiff base ligands gives a wide variety of polynuclear complexes, ranging from discrete entities to multidimensional chain complexes with carboxylate bridging groups. For example, self-assembly of copper(II) perchlorate with the tetradentate ligand bis(2-pyridylmethyl)amino-4-butyric acid (Hpmba) leads to the carboxylate-bridged one-dimensional chain complex $\{[\text{Cu}(\mu\text{-pmpa})](\text{ClO}_4) \cdot 2\text{H}_2\text{O}\}_n$, which reveals a distorted square-pyramidal environment with an N_3O basal plane and a water molecule in the apical position (Choi *et al.*, 2004). However, the reaction of CuCl_2 with 2-(imidazolomethyl)amino-3-propionic acid (Hiap) leads not to the carboxylate-bridged chain complex, but to the chloride-bridged dinuclear square-pyramidal structure $[\text{Cu}(\text{Hiap})(\mu\text{-Cl})_2]$, in which the bridged Cl^- anion prevents a self-assembly reaction through the carboxylate group (Colacio *et al.*, 2000). On the other hand, the reaction of CuCl_2 with 2-pyridylmethylamino-3-butyric acid (Hpaba) and excess NaClO_4 leads to the title trinuclear copper(II) complex, $[\text{Cu}_3(\text{paba})_2(\text{H}_2\text{O})_3\text{Cl}(\text{ClO}_4)_3] \cdot 2\text{H}_2\text{O}$, (I), and we present its crystal structure here.



In compound (I), the Cu atoms are linked by carboxylate groups to form a trinuclear structure. The coordination environment around atom Cu1 is an axially elongated octahedron, with one O and two N atoms of the ligand and one water molecule occupying the equatorial plane, and two O atoms from the perchlorate groups coordinating in the axial positions. Atom Cu3 is in a distorted square-pyramidal

environment, being coordinated by one O and two N atoms of the ligand, one Cl⁻ anion and one perchlorate group. Atom Cu2 exhibits a Cu2O₄ coordination geometry, being coordinated by two O atoms belonging to the bridging carboxylate group of an adjacent ligand and two water molecules. Atoms Cu1, Cu2 and Cu3 lie 0.011 (1), 0.178 (1) and 0.029 (1) Å, respectively, above the least-squares planes defined by their equatorial and basal planes.

The average Cu—OW distance of 1.951 (2) Å is in the normal range observed in related coordination complexes (Choi *et al.*, 2004). The axial Cu—O (perchlorate group) bond distances are in the range 2.488 (3)–2.591 (3) Å (Table 1). The Cu1—N1 and Cu3—N4 bond distances [1.981 (3) and 1.971 (3) Å, respectively] are comparable with the value found in {[Cu(μ-pmba)(H₂O)](ClO₄)·3H₂O}_n [1.978 (6) Å; Choi *et al.*, 2004]. The N—Cu—N bite angles of the five-membered chelate rings are 83.5 (1) and 82.9 (1)°, respectively. The dihedral angles (α) between the planes of the two carboxylate groups and the Cu2O₄ plane are 89.2 (2) and 82.6 (1)°. Interestingly, the average N2—C [1.484 (3) Å] and N3—C [1.466 (4) Å] distances involving the secondary N atom are approximately 0.13 Å longer than the average N1—C [1.344 (3) Å] and N4—C [1.342 (3) Å] distances involving the tertiary N atom. This result may be due to the sp³ hybridization by protonation of the secondary N atom.

The hydrogen-bond lengths and angles of the five water molecules are listed in Table 2 and their hydrogen bonds are indicated by dashed lines in Fig. 1. This hydrogen-bond network forms a stabilized structural arrangement.

Experimental

To a methanol solution (20 ml) of CuCl₂·2H₂O (85 mg, 0.5 mmol) was added 2-pyridylmethylamino-3-butyric acid (Hpaba) (97 mg, 0.5 mmol), and the mixture was heated at reflux for 2 h. Excess NaClO₄ was then added to the solution. The solution was filtered and left at room temperature until violet crystals of (I) formed. The product was filtered off and recrystallized from a hot H₂O—MeCN (1:1, 10 ml) mixture.

Crystal data

[Cu ₃ (C ₁₀ H ₁₃ N ₂ O ₂) ₂ Cl(ClO ₄) ₃ ·(H ₂ O) ₃ ·2H ₂ O]	Z = 2
<i>M_r</i> = 1000.95	<i>D_x</i> = 1.895 Mg m ⁻³
Triclinic, <i>P</i> 1̄	Mo <i>K</i> α radiation
<i>a</i> = 9.2569 (7) Å	Cell parameters from 6978 reflections
<i>b</i> = 12.6338 (9) Å	<i>θ</i> = 2.2–27.9°
<i>c</i> = 15.3446 (11) Å	<i>μ</i> = 2.20 mm ⁻¹
<i>α</i> = 82.383 (1)°	<i>T</i> = 233 (2) K
<i>β</i> = 82.779 (1)°	Rod, violet
<i>γ</i> = 82.824 (1)°	0.36 × 0.15 × 0.09 mm
<i>V</i> = 1753.9 (2) Å ³	

Data collection

Bruker SMART 1000 CCD area-detector diffractometer	8694 independent reflections
<i>φ</i> and <i>ω</i> scans	6333 reflections with <i>I</i> > 2σ(<i>I</i>)
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	<i>R_{int}</i> = 0.031
<i>T_{min}</i> = 0.504, <i>T_{max}</i> = 0.825	<i>θ_{max}</i> = 28.3°
23452 measured reflections	<i>h</i> = -12 → 12
	<i>k</i> = -16 → 16
	<i>l</i> = -20 → 20

Refinement

Refinement on *F*²
R [*F*² > 2σ(*F*²)] = 0.040
wR (*F*²) = 0.103
S = 1.02
 8694 reflections
 488 parameters
 H atoms treated by a mixture of independent and constrained refinement

w = 1/[σ²(*F_o*²) + (0.0429*P*)² + 2.5286*P*]
 where *P* = (*F_o*² + 2*F_c*²)/3
 (Δ/σ)_{max} = 0.001
 Δρ_{max} = 1.87 e Å⁻³
 Δρ_{min} = -0.55 e Å⁻³

Table 1

Selected geometric parameters (Å, °).

Cu1—O1	1.933 (2)	Cu1—Cu2	4.6097 (6)
Cu1—OW1	1.967 (2)	Cu2—Cu3	3.4332 (6)
Cu1—N1	1.981 (3)	Cu1—Cu3	6.7474 (6)
Cu1—N2	1.994 (3)	O1—C10	1.252 (4)
Cu1—O8	2.511 (3)	O2—C10	1.276 (4)
Cu1—O11	2.488 (3)	O3—C11	1.301 (4)
Cu2—OW3	1.935 (3)	O4—C11	1.227 (4)
Cu2—OW2	1.951 (3)	N1—C1	1.343 (4)
Cu2—O2	1.960 (2)	N1—C5	1.345 (4)
Cu2—O3	1.998 (2)	N2—C6	1.477 (4)
Cu3—O3	1.948 (2)	N2—C7	1.491 (4)
Cu3—N4	1.971 (3)	N3—C15	1.455 (5)
Cu3—N3	2.020 (3)	N3—C13	1.477 (5)
Cu3—Cl1	2.2747 (9)	N4—C20	1.341 (4)
Cu3—O13	2.591 (3)	N4—C16	1.343 (4)
O1—Cu1—OW1	85.55 (10)	O1—C10—O2	119.4 (3)
O1—Cu1—N1	178.40 (10)	O4—C11—O3	118.8 (3)
OW1—Cu1—N1	95.86 (11)	OW1—Cu1—O8	93.9 (1)
O1—Cu1—N2	95.08 (10)	O1—Cu1—O8	87.9 (1)
OW1—Cu1—N2	179.19 (11)	N1—Cu1—O8	92.8 (1)
N1—Cu1—N2	83.51 (11)	N2—Cu1—O8	86.6 (1)
OW3—Cu2—OW2	177.50 (11)	OW1—Cu1—O11	92.7 (1)
OW3—Cu2—O2	88.47 (11)	O1—Cu1—O11	91.7 (1)
OW3—Cu2—O3	88.85 (10)	N1—Cu1—O11	87.5 (1)
O2—Cu2—O3	156.69 (9)	N2—Cu1—O11	86.8 (1)
O3—Cu3—N4	173.02 (11)	OW3—Cu2—OW2	177.5 (1)
O3—Cu3—N3	93.07 (11)	O2—Cu2—OW2	91.4 (1)
N4—Cu3—N3	82.90 (12)	Cl1—Cu3—O13	95.8 (1)
O3—Cu3—Cl1	85.76 (7)	O3—Cu3—O13	91.5 (1)
N4—Cu3—Cl1	98.48 (9)	N3—Cu3—O13	82.1 (1)
N3—Cu3—Cl1	177.56 (9)	N4—Cu3—O13	93.6 (1)

Table 2

Hydrogen-bond geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
OW1—HW1A...OW5	0.83	1.83	2.665 (4)	176
OW1—HW1B...Cl1	0.84	2.41	3.234 (3)	170
OW2—HW2A...O4 ⁱ	0.82	1.87	2.657 (3)	159
OW2—HW2B...O7	0.98	1.92	2.894 (4)	169
OW3—HW3B...OW4	0.91	1.80	2.679 (4)	162
OW3—HW3A...O14	0.87	1.96	2.79 (2)	160
OW3—HW3A...O14 ⁱ	0.87	1.88	2.713 (15)	159
OW4—HW4A...O12	0.94	2.03	2.950 (4)	166
OW4—HW4B...O2 ⁱⁱ	0.97	1.83	2.791 (4)	168

Symmetry codes: (i) -*x* + 1, -*y* + 1, -*z*; (ii) -*x*, -*y* + 1, -*z*.

20 H atoms out of 26 attached to C and N atoms were placed in calculated positions, with C—H = 0.94 or 0.98 Å and N—H = 0.92 Å, and allowed to ride on their parent atoms, with *U*_{iso}(H) = 1.2*U*_{eq}(C,N), while the remaining six H atoms of the methyl groups C8 and C14 were treated as rotating rigid groups, with C—H = 0.97 Å and with *U*_{iso}(H) = 1.5*U*_{eq}(C). The ten H atoms of the water molecules OW1, OW2, OW3, OW4 and OW5 were located in a difference

Fourier map; they were fixed in position and their isotropic displacement parameters were refined.

The $U_{eq}(\text{max})/U_{eq}(\text{min})$ ratio of the atomic displacement parameters are abnormally large for the peripheral perchlorate groups, which may be due to librational and rotational disorder. In fact, perchlorate atom O14 is disordered over two positions with site-occupancy factors of 0.36 and 0.64. Similar disorder of a perchlorate O atom has been reported in bis[3,6-bis(6-methyl-2-pyridyl)pyridazine- κ^2N^2,N^2]chlorocopper(II) perchlorate (Choi *et al.*, 2001) and in hydrogen bonds in the framework of bis[2-[bis(2-aminoethyl)amino]ethanol]nickel(II) diperchlorate (Xia *et al.*, 2001). The largest difference density peak is 0.96 Å from atom Cl3.

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

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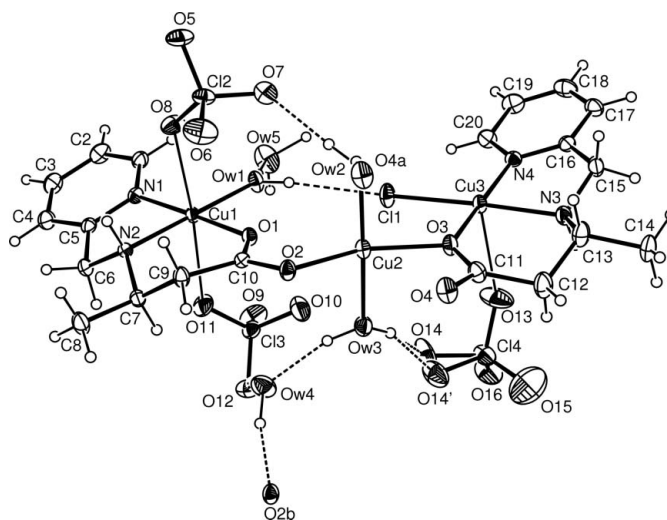


Figure 1

The molecular structure of (I), with displacement ellipsoids drawn at the 20% probability level. H atoms are shown as small spheres of arbitrary radii and hydrogen bonds are shown as dashed lines. [Symmetry codes: (a) $1 - x, 1 - y, -z$; (b) $-x, 1 - y, -z$.]

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