

For both (1) and (2), H atoms were included in calculated positions (C—H = 0.96 Å) with isotropic displacement parameters set to 1.5*U*_{eq}(C) for methyl H atoms and 1.2*U*_{eq}(C) for all other H atoms. All non-H atoms were refined with anisotropic displacement parameters.

For both compounds, data collection: XSCANS (Fait, 1991); cell refinement: XSCANS; data reduction: XSCANS; program(s) used to solve structures: XS in SHELXTL/PC (Sheldrick, 1996); program(s) used to refine structures: XL in SHELXTL/PC; molecular graphics: XP in SHELXTL/PC; software used to prepare material for publication: XCIF in SHELXTL/PC.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1268). Services for accessing these data are described at the back of the journal.

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Aquatetrakis[(4-chlorobenzoato)(μ₃-2-dimethylaminoethanolato)copper(II)] hydrate

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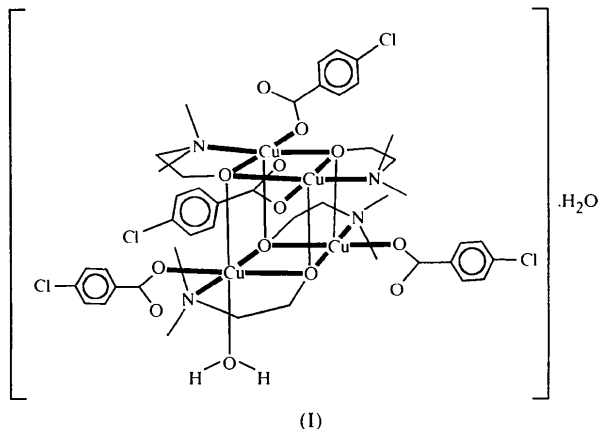
Abstract

A cubane-type core has been found in the tetrameric title complex, aqua-1κC-tetrakis(4-chlorobenzoato)-1κC,2κC,3κC,4κC-tetrakis[μ₃-(2-dimethylaminoethanolato)-κ³O:O:O]-tetrahedro-tetracopper(II) hydrate, [Cu₄-

(C₇H₄ClO₂)₄(C₄H₁₀NO)₄(H₂O)]·H₂O. The structure of the complex molecule is composed of two ethanolate O-bridged dimers, with Cu—O bond lengths in the range 1.919(5)–1.979(5) Å, and Cu···Cu distances of 2.855(2) and 2.890(2) Å. The dimers are bridged into the tetrameric unit by triply bridging ethanolate O atoms, with Cu—O distances in the range 2.417(5)–2.618(5) Å. Of the four Cu atoms, three are five-coordinated and one is six-coordinated.

Comment

Monomeric, dimeric, tetrameric, hexameric and nonameric complexes have been obtained from reactions between 2-dimethylaminoethanol and Cu^{II}-carboxylates (Turpeinen *et al.*, 1980, 1985, 1987, 1988, 1995; Turpeinen, Hämäläinen *et al.*, 1996; Turpeinen, Klinga *et al.*, 1996). The present structure, (I), is composed of two dimers, which are bridged into a tetrameric cubane-type unit by ethanolate O atoms, with Cu—O distances in the range 2.417(5)–2.618(5) Å. Within the



ethanolate O-bridged dimers, the Cu···Cu distances are 2.855(2) and 2.890(2) Å, and the Cu—O—Cu angles vary between 93.2(2) and 95.9(2)°. The Cu1, Cu2 and Cu3 atoms are five-coordinated in a square-pyramidal environment, while the Cu4 atom is six-coordinated. The two ethanolate O atoms, a carboxyl O atom and an amino N atom form the basal plane, with Cu—O bond lengths in the range 1.904(6)–1.982(5) Å and Cu—N distances in the range 2.007(8)–2.047(7) Å. The apical positions of the Cu1, Cu2 and Cu3 atoms are occupied by the ethanolate O atoms, with Cu—O distances in the range 2.417(5)–2.611(5) Å. The axial sites of the Cu4 atom are occupied by the ethanolate and water O atoms, with Cu—O distances of 2.618(5) and 2.671(12) Å, respectively. The structure is stabilized by hydrogen bonds between the water O and the non-coordinated carboxyl O atoms, with distances O1···O13 of 2.798(9) Å and O2···O43(−x+1, −y, −z+1) of 2.604(15) Å.

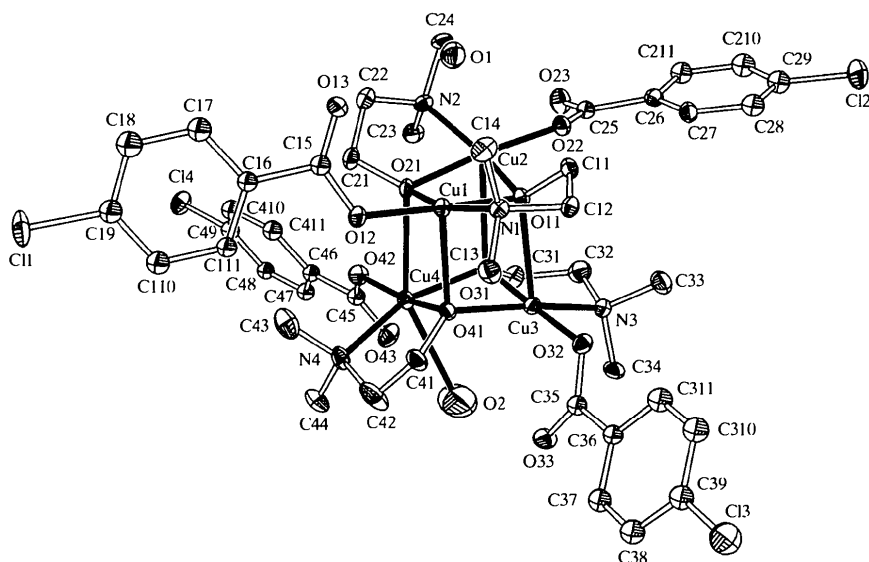


Fig. 1. The structure of the title compound showing 20% probability displacement ellipsoids. H atoms have been omitted for clarity.

Experimental

A dark-blue crystal of (I) was selected for the X-ray measurements and mounted on a glass fiber using the oil-drop method (Kottke & Stalke, 1993). Data were collected at 193 K.

Crystal data

[Cu₄(C₇H₄ClO₂)₄-
(C₄H₁₀NO)₄(H₂O)]·H₂O

M_r = 1264.92

Orthorhombic

Pccn

a = 27.447 (9) Å

b = 20.311 (6) Å

c = 18.718 (5) Å

V = 10435 (5) Å³

Z = 8

D_x = 1.610 Mg m⁻³

D_m not measured

Data collection

Rigaku AFC-7S diffractometer

ω-2θ scans

Absorption correction:

ψ scan (North *et al.*,
1968)

T_{min} = 0.604, *T_{max}* = 0.754

7277 measured reflections

7277 independent reflections

Mo *K*α radiation

λ = 0.71073 Å

Cell parameters from 25

reflections

θ = 3.5–7.0°

μ = 1.879 mm⁻¹

T = 193 (2) K

Irregular

0.30 × 0.25 × 0.15 mm

Dark blue

5042 reflections with

I > 2σ(*I*)

θ_{max} = 25°

h = -32 → 0

k = 0 → 23

l = 0 → 22

3 standard reflections

every 200 reflections

intensity decay: none

7277 reflections

501 parameters

H atoms not refined

$$w = 1/[\sigma^2(F_o^2) + (0.0397P)^2 + 47.8465P]$$

$$\text{where } P = (F_o^2 + 2F_c^2)/3$$

Scattering factors from

*International Tables for
Crystallography* (Vol. C)

Table 1. Selected geometric parameters (Å, °)

Cu1—O12	1.919 (5)	Cu3—O31	1.939 (5)
Cu1—O11	1.932 (5)	Cu3—O41	1.979 (5)
Cu1—O21	1.962 (5)	Cu3—N3	2.047 (7)
Cu1—N1	2.043 (7)	Cu3—O11	2.505 (3)
Cu1—O41	2.417 (5)	Cu3···Cu4	2.8549 (17)
Cu1···Cu2	2.8902 (16)	Cu4—O42	1.904 (6)
Cu1—O22	1.918 (5)	Cu4—O41	1.949 (5)
Cu2—O21	1.930 (5)	Cu4—O31	1.951 (5)
Cu2—O11	1.982 (5)	Cu4—N4	2.007 (8)
Cu2—N2	2.037 (7)	Cu4—O21	2.618 (5)
Cu2—O31	2.611 (5)	Cu4—O2	2.671 (12)
Cu3—O32	1.921 (5)		
O12—Cu1—O11	178.1 (2)	O32—Cu3—O31	177.7 (2)
O12—Cu1—O21	96.3 (2)	O32—Cu3—O41	97.5 (2)
O11—Cu1—O21	82.0 (2)	O31—Cu3—O41	82.4 (2)
O12—Cu1—N1	95.6 (3)	O32—Cu3—N3	94.7 (3)
O11—Cu1—N1	85.9 (2)	O31—Cu3—N3	85.9 (3)
O21—Cu1—N1	164.3 (2)	O41—Cu3—N3	163.9 (3)
O12—Cu1—O41	98.3 (2)	O42—Cu4—O41	166.6 (2)
O11—Cu1—O41	82.1 (2)	O42—Cu4—O31	100.6 (2)
O21—Cu1—O41	81.0 (2)	O41—Cu4—O31	82.8 (2)
N1—Cu1—O41	107.4 (2)	O42—Cu4—N4	94.3 (3)
O22—Cu2—O21	171.3 (2)	O41—Cu4—N4	85.6 (3)
O22—Cu2—O11	89.8 (2)	O31—Cu4—N4	160.6 (3)
O21—Cu2—O11	81.6 (2)	Cu1—O11—Cu2	95.2 (2)
O22—Cu2—N2	103.9 (3)	Cu2—O21—Cu1	95.9 (2)
O21—Cu2—N2	84.6 (3)	Cu3—O31—Cu4	94.4 (2)
O11—Cu2—N2	161.0 (2)	Cu4—O41—Cu3	93.2 (2)

Refinement

Refinement on *F*²

R[*F*² > 2σ(*F*²)] = 0.075

wR(*F*²) = 0.147

S = 1.031

(Δ/σ)_{max} = 0.009

Δρ_{max} = 0.723 e Å⁻³

Δρ_{min} = -0.490 e Å⁻³

Extinction correction: none

The intensity data were corrected for Lorentz and polarization effects, and for absorption. All non-H atoms were introduced in calculated positions.

Data collection: Rigaku AFC-7S software. Cell refinement: Rigaku AFC-7S software. Data reduction: *TEXSAN* (Molecular

Structure Corporation, 1993). Program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997). Molecular graphics: *SHELXTLIPC* (Sheldrick, 1994). Software used to prepare material for publication: *SHELXL97*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: OS1032). Services for accessing these data are described at the back of the journal.

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Polymeric aqua(*N*-ethylurea-*O*)(*N*-pyruv-*idene*- β -alaninato-*O,N,O'*)copper(II)†

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Abstract

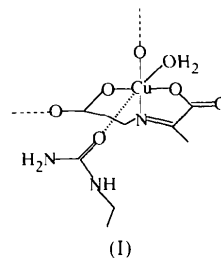
In the title compound, [Cu(C₆H₇NO₅)(C₃H₈N₂O)(H₂O)]_n, the Cu^{II} ion is octahedrally coordinated by three donor atoms of the *N*-pyruv-*idene*- β -alaninato

† Alternative name: *catena*-poly[[aqua(*N*-ethylurea-*O*)copper(II)]- μ -[*N*-(1-carboxyethylidene)- β -alaninato-*O*¹*N,O*:*O*¹]].

Schiff base dianion, and one carboxylic O atom of a symmetry-related molecule at a distance of 1.982 (1) Å in the central plane; the latter contact leads to the formation of polymeric chains. One axial position is occupied by a water O atom at an apical distance of 2.310 (2) Å. The distance between the Cu atom and the sixth donor, the O atom of the neutral *N*-ethylurea ligand, is 3.062 (2) Å. The chains are connected to each other by hydrogen bonding, forming a two-dimensional network along [010] and [100]. The Cu polyhedra have two magnetically inequivalent orientations.

Comment

The polymeric structures of (imidazole)- and (2-ethylimidazole)(*N*-salicylidene-glycinato-*N,O,O'*)copper(II) were recently reported (Warda, 1997). These two compounds polymerize *via* the carboxylic O atoms of symmetry-related molecules at the apical coordination site. The title compound, (I), is the first structure of Cu^{II} with the *N*-pyruv-*idene*- β -alaninato dianion as a tridentate Schiff base (TSB²⁻) combined with a neutral ligand and, furthermore, presents a new pattern of chain building for this series of substances.



The Cu^{II} ion displays distorted octahedral coordination. In the equatorial plane, the Cu atom is coordinated by three donor atoms from the tridentate pyruv-*idene*- β -alaninato dianion, *via* the ONO²⁻ group. The fourth ligand in this plane is the carboxylic O4ⁱ atom, from a symmetry-related neighbouring complex [symmetry code: (i) 1 - x, - $\frac{1}{2}$ + y, $\frac{1}{2}$ - z], thus leading to chains along [010] (Fig. 1). The Cu—N and Cu—O bond distances in the equatorial plane [Cu—N 1.991 (2); Cu—O(1,2,4) 1.954 (2), 1.935 (2) and 1.982 (1) Å, respectively] do not differ significantly from those in other members in this series (Warda, 1997, and references therein).

The Cu atom lies 0.224 (1) Å out of the equatorial plane, displaced towards the water O5 atom (PLATON; Spek, 1998), which occupies an axial coordination site at a distance of 2.310 (2) Å. This distance is shorter than the corresponding distance in diaqua(pyruv-*idene*- β -alaninato)copper(II) monohydrate [2.413 (6) Å; Ueki *et al.*, 1968], which was used to synthesize the title compound.