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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*-pyruvidene-β-alaninato-*O*,*N*,*O*′)copper(II)†

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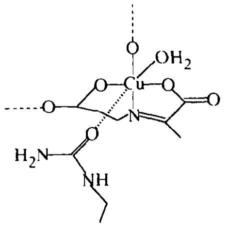
Abstract

In the title compound, $[Cu(C_6H_7NO_5)(C_3H_8N_2O)(H_2O)]_n$, the Cu^{II} ion is octahedrally coordinated by three donor atoms of the *N*-pyruvidene-β-alaninato 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*-salicylideneglycinato-*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*-pyruvidene-β-alaninato dianion as a tridentate Schiff base (TSB^{2-}) combined with a neutral ligand and, furthermore, presents a new pattern of chain building for this series of substances.



(I)

The Cu^{II} ion displays distorted octahedral coordination. In the equatorial plane, the Cu atom is coordinated by three donor atoms from the tridentate pyruvidene-β-alaninato dianion, *via* the ONO^{2-} group. The fourth ligand in this plane is the carboxylic $O4^i$ 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(pyruvidene-β-alaninato)copper(II) monohydrate [2.413 (6) Å; Ueki *et al.*, 1968], which was used to synthesize the title compound.

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

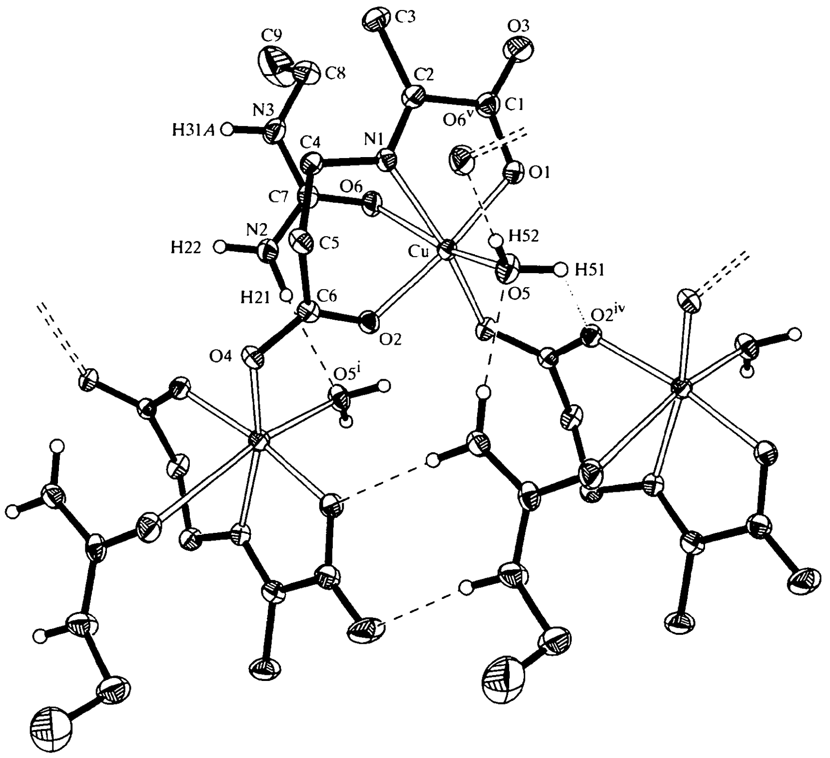

Fig. 1. View (Siemens, 1996*a*) of the title compound, showing the atom-numbering scheme together with part of the chain and part of the hydrogen-bonding system. Displacement ellipsoids are drawn at the 50% probability level. Non-bridging H atoms have been omitted for clarity. Symmetry codes are as given in Table 2.

Atom O6 of the *N*-ethylurea ligand is weakly coordinated to the Cu atom at a distance of 3.062 (2) Å, and the O5—Cu—O6 angle of 171.33 (5)° (Table 1) shows that the axial ligands are essentially linear at the Cu atom. One may conclude, on the basis of structural and spectroscopic results, that Cu^{II} is near the critical point of square-pyramidal/octahedral geometry but still in the octahedral region; an asymmetric elongated octahedron is a reasonable description.

Electron paramagnetic resonance (EPR) patterns of the title compound display the highest **g** tensor in this series of substances and this tensor is coupled, indicating a distorted antiferrodistortive ordering ($45 < 2\gamma < 90°$). There are two magnetically inequivalent orientations of copper. The tilting angle calculated from EPR spectra is 76°. The Cu···Cu distance between differently oriented polyhedra should be < 8.3 (1) Å (Warda, 1997). The present structure determination confirms the EPR results: the tilting angle amounts to 74.5 (2)° and the Cu···Cu distance is 4.8039 (7) Å.

A system of hydrogen bonding is present, involving the H atoms of *N*-ethylurea and of the coordinated water molecule. Intra-chain hydrogen bonds are formed by N2—H21···O5, N2—H22···O1, N3—H31···O3 and O5—H51···O2 (this last hydrogen bond displays a very narrow angle at hydrogen and may be part of a three-centre hydrogen bond). Inter-chain hydrogen bonds are also present, involving O5—H51···O4 and O5—H52···O6; more details are given in Table 2.

Experimental

Compound (I) was synthesized from diaqua(*N*-pyruvidene-β-alaninato)copper(II) monohydrate with *N*-ethylurea in ethanol at 323 K, according to the methods of Ueki *et al.* (1968) and Warda (1994). Well formed light-blue rectangular plates grew within a few weeks.

Crystal data

$[Cu(C_6H_7NO_5)(C_3H_8N_2O)(H_2O)]$
$M_r = 326.80$
Monoclinic
$P2_1/c$
$a = 15.0798 (16)$ Å
$b = 7.5653 (5)$ Å
$c = 12.6522 (14)$ Å
$\beta = 114.212 (11)°$
$V = 1316.4 (2)$ Å^3
$Z = 4$
$D_x = 1.649$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 5000 reflections
$\theta = 2.96–27.99°$
$\mu = 1.686$ mm^{-1}
$T = 173 (2)$ K
Rectangular plate
0.46 × 0.12 × 0.06 mm
Light blue

Data collection

Stoe IPDS diffractometer
Image plate scans
Absorption correction: integration (*XPREP*; Siemens, 1996*b*)
$T_{min} = 0.511$, $T_{max} = 0.906$
12 133 measured reflections
3116 independent reflections
2163 reflections with $I > 2\sigma(I)$
$R_{int} = 0.051$
$\theta_{max} = 28°$
$h = -18 \rightarrow 19$
$k = -9 \rightarrow 9$
$l = -16 \rightarrow 16$
Intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.029$
$wR(F^2) = 0.059$
$S = 0.903$
3116 reflections
188 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0271P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.393$ e Å^{-3}
$\Delta\rho_{min} = -0.390$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

Cu—O2	1.9346 (15)	Cu—N1	1.9905 (17)
Cu—O1	1.9544 (16)	Cu—O5	2.3103 (16)
Cu—O4^i	1.9816 (14)	Cu—O6	3.0621 (18)
O2—Cu—O1	171.99 (7)	O4^i—Cu—O5	104.82 (6)
O2—Cu—O4^i	85.07 (6)	N1—Cu—O5	93.61 (6)
O1—Cu—O4^i	96.26 (6)	O2—Cu—O6	93.64 (6)
O2—Cu—N1	93.66 (7)	O1—Cu—O6	78.72 (6)
O1—Cu—N1	82.57 (7)	O4^i—Cu—O6	83.17 (5)
O4^i—Cu—N1	161.52 (7)	N1—Cu—O6	78.51 (6)
O2—Cu—O5	90.43 (6)	O5—Cu—O6	171.33 (5)
O1—Cu—O5	96.83 (6)		

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

Table 2. *Hydrogen-bonding geometry (Å, °)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H21···O5^i	0.88 (2)	2.16 (2)	3.038 (3)	175 (3)
N2—H22···O1^{ii}	0.89 (2)	2.05 (2)	2.940 (3)	174 (3)
N3—H31···O3^{ii}	0.89 (1)	2.09 (2)	2.971 (3)	171 (2)
O5—H51···O4^{iii}	0.89 (1)	2.22 (2)	3.094 (2)	167 (2)
O5—H51···O2^{iv}	0.89 (1)	2.43 (2)	2.790 (2)	105 (2)
O5—H52···O6^v	0.89 (1)	1.86 (1)	2.739 (2)	166 (2)

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

All H atoms except the hydrogen-bond donors were included at calculated positions using *SHELXL*97 (Sheldrick, 1997) and refined using a riding model. The U_{iso} values for the H atoms on CH_2 or CH_3 were taken as $1.2U_{eq}$ and $1.5U_{eq}$ of the carrier atoms, respectively. The H atoms of C3 were refined as a rigid group. Atoms H21, H22, H31, H51 and H52 were found from difference Fourier syntheses and refined with $U_{iso} = 1.2U_{eq}$ of the carrier atoms; O—H and N—H distances were restrained to be equal with an s.u. of 0.01 Å. Analytical absorption correction based on face indexing was carried out with the following faces and distances (mm): (010) 0.2503, (0$\bar{1}$0) 0.2118, (001) 0.0192, (00$\bar{1}$) 0.0385, (20$\bar{1}$) 0.0008 and ($\bar{2}$01) 0.1155. The data completeness to $\theta = 28°$ amounts to 98.4%.

Data collection: *EXPOSE* (Stoe, 1997*b*). Cell refinement: *CELL* (Stoe, 1997*a*). Data reduction: *INTEGRATE* (Stoe, 1997*c*). Program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*97. Molecular graphics: *XP* (Siemens, 1996*a*). Software used to prepare material for publication: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1313). Services for accessing these data are described at the back of the journal.

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Micacocidin A

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Abstract

In the title compound, (4,5-dihydro-2-{2-hydroxy-1,1-dimethyl-2-[2,3,4′,5′-tetrahydro-3-methyl-2′-(2-oxido-6-pentylphenyl)-2,4′-bithiazolyl-4-yl-*N*,*N*′,*O*]ethyl-*O*}-4-methylthiazole-4-carboxylato-*N*,*O*)zinc(II), $[Zn(C_{27}H_{37}N_3O_4S_3)]$, the Zn atom is octahedrally coordinated by

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