Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

Bis[*N*-(2-hydroxyethyl)-β-alaninato]-copper(II)

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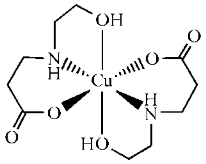
Received 21 July 2005
Accepted 19 October 2005
Online 11 November 2005

The Cu^{II} ion in the title complex, $[Cu(C_5H_{10}NO_3)_2]$ or [Cu(He-ala)$_2$] [He-ala = *N*-(2-hydroxyethyl)-β-alaninate], resides at the inversion centre of a square bipyramid comprised of two facially arranged tridentate He-ala ligands. Each He-ala ligand binds to a Cu^{II} ion by forming one six-membered β-alaninate chelate ring in a twist conformation and one five-membered ethanolamine ring in an envelope conformation, with Cu—N = 2.017 (2) Å, $Cu—O_{COO}$ = 1.968 (1) Å and $Cu—O_{OH}$ = 2.473 (2) Å. The [Cu(He-ala)$_2$] molecules are involved in a network of O—H$\cdots$O and N—H$\cdots$O hydrogen bonds, forming layers parallel to the $(10\overline{1})$ plane. The layers are connected into a three-dimensional structure by van der Waals interactions, so that the molecular centres form pseudo-face-centered close packing.

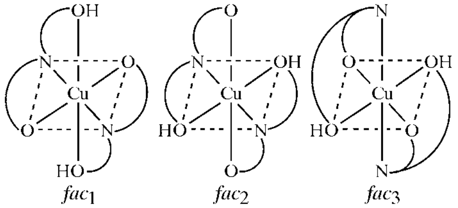
Comment

The title compound, [Cu(He-ala)$_2$] or (I), was synthesized as part of our systematic study of the coordination ability of dipodal ligands derived from β-alanine (Skorik *et al.*, 2002, 2003, 2004, 2005). The acid–base and complexation equilibria of *N*-(2-hydroxyethyl)-β-alanine with Cu^{II}, Ni^{II} and Co^{II} have been studied by means of pH–potentiometric titration in aqueous media. Evidence was found for the presence of the [*M*(He-ala)] and [*M*(He-ala)$_2$] complexes (Uhlig & Linke, 1964). In the case of Cu^{II} ions, the monoprotonated [CuH(He-ala)] complex can also be formed under strong acidic conditions. To the best of our knowledge, no complexes of He-ala have previously been structurally characterized. In order to determine the Cu^{II} coordination geometry and the chelating pattern, the present X-ray crystal structure determination has been carried out on the title complex and the results are presented here.

The molecular structure of the [Cu(He-ala)$_2$] complex and the atomic numbering scheme are shown in Fig. 1, while Table 1 lists selected bond lengths and angles. The structure of (I) consists of isolated [Cu(He-ala)$_2$] units, with the Cu^{II} ion located at the inversion centre in a square-bipyramidal geometry (4+2). The basal plane of the bipyramid is occupied by two N atoms of secondary amino groups and by two carboxylate O atoms, and the apices are occupied by two hydroxyl O atoms of two symmetrically arranged He-ala ligands. The axial Cu—O bonds are typically longer than the other in-plane bonds. The *trans* O—Cu—O or N—Cu—N angles are 180°, as required by symmetry. The *cis* angles involving the basal atom O2 differ only slightly from 90°, while the largest angular distortions of the octahedron occur for the N1—Cu1—O1 angles (Table 1).



(I)



Each singly deprotonated He-ala ligand binds to a Cu^{II} centre as an *O*,*N*,*O*′-tridentate ligand in a *fac* fashion by the formation of two chelate rings (one β-alaninate and one ethanolamine). There are three possible *fac* conformations for He-ala in a square-bipyramidal coordination, as shown in the scheme above.

The isolated complex turned out to be a *fac*$_1$ isomer (Fig. 1). The selective formation of this isomer can be rationalized by reasoning that the most thermodynamically preferable isomer

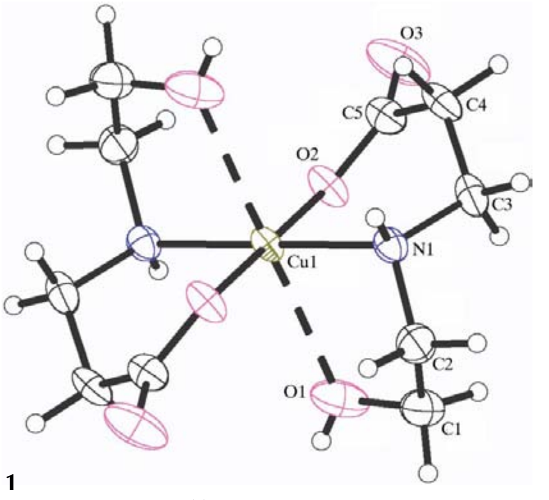


Figure 1
The molecular structure of (I). Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. The axial bonds to copper are shown as dashed lines.

DOI: 10.1107/S0108270105033780

has the stronger field ligands in equatorial positions and the weaker ligands at the apices of an axially elongated octahedron. Taking into account the spectrochemical series $RNH_2 > RCOO^- > ROH$ (Bersuker, 1996), the *fac*$_1$ conformation for He-ala appears to be the most thermodynamically stable. For the same reason, a *fac*$_1$ isomer is favourable for the glycine derivative of ethanolamine (Ananeva *et al.*, 1975; Ammar *et al.*, 2001).

The six-membered β-alaninate chelate ring adopts a twist conformation, with atoms C5 and N1 not involved in the distortion of the initial planar hexagon. The puckering parameters (Cremer & Pople, 1975) generated by *PLATON* (Spek, 2003) are Q = 0.7335 (19) Å, θ = 94.75 (15)° and φ = 29.83 (15)°. The sum of the internal angles [675.0 (4)°] has a positive deviation from the ideal value, *viz.* 648° = 120 + (109.5 × 4) + 90, and this exerts a stress, resulting in the flattening. The five-membered ethanolamine chelate ring adopts an envelope conformation, with atom C2 tilted by 0.646 (3) Å away from the Cu1/O1/C1/N1 plane; the puckering parameters are Q = 0.475 (2) Å and θ = 305.4 (2)°. The dihedral angle formed by the r.m.s. planes of the two chelate rings is 70.69 (9)°.

In the crystal structure of (I), the [Cu(He-ala)$_2$] molecules are involved in an extended two-dimensional system of hydrogen bonds, forming layers parallel to the $(10\overline{1})$ plane (Fig. 2*a*). Six intralayer molecules are hydrogen bonded to the reference molecule; two of them form two N—H···O contacts each, while the other four each form one O—H···O contact (Table 2). The whole molecular packing may be represented as a superposition of these layers. Its topology was characterized with coordination sequences (O'Keeffe, 1995) calculated using the *TOPOS4.0 Professional* program suite for crystallochemical analysis (Blatov *et al.*, 2000). The molecular centres of gravity form the coordination sequence 12, 42, 92; in other words, the first, second and third coordination sphere of any molecule contains 12, 42 and 92 molecules, respectively. This sequence corresponds topologically to three-layered face-centred cubic (fcc) packing (O'Keeffe, 1995) which is slightly distorted geometrically. The simplified three-layered packing motif in the structure is shown in Fig. 2(*b*), where the centres of the molecules are represented as balls. Three molecules of the upper and lower layers and six molecules of the middle layer are shown. Thus, the hydrogen-bonded layers are joined by van der Waals interactions to the distorted fcc packing that is typical for molecular compounds (Kitaigorodskii, 1973; Peresypkina & Blatov, 2000; Braun & Huttner, 2005).

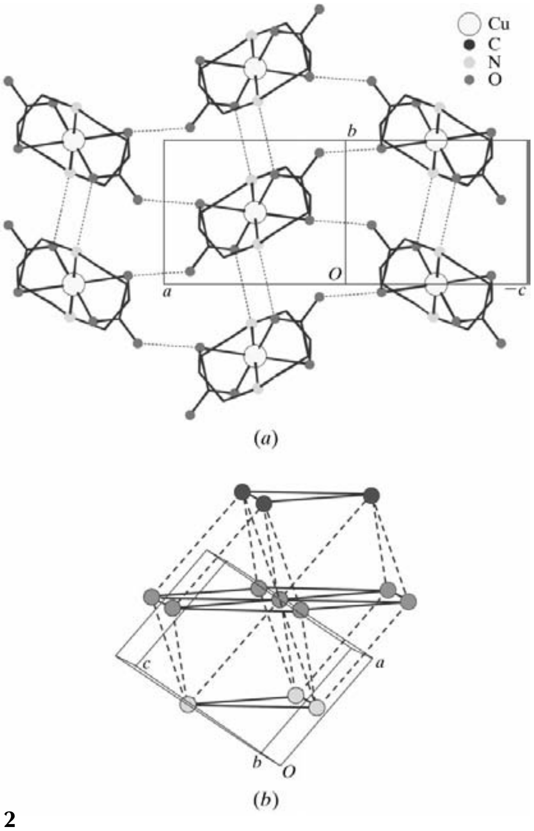


Figure 2
The crystal structure of (I), showing (*a*) the hexagonal layer parallel to the $(10\overline{1})$ plane (H atoms have been omitted for clarity) and (*b*) a fragment of the spatial arrangement of the centres of gravity of molecules of (I), illustrating the three-layered fcc packing motif. Upper, medium and lower levels are shown as dark-, medium- and light-grey balls, respectively. Solid and dashed lines show the intra- (hydrogen bonding) and interlayer (van der Waals) distances between the molecular centres.

Experimental

N-(2-Hydroxyethyl)-β-alanine was prepared using a modification of the literature procedure of Salov *et al.* (1985). A mixture containing acrylic acid (4.1 ml, 0.060 mol) and ethanolamine (10.8 ml, 0.18 mol) in water (56 ml) was heated under reflux for 8 h. The solvent and the excess ethanolamine were then evaporated on a water bath under vacuum. The resulting solid product was recrystallized from methanol [yield 2.28 g, 36%; m.p. 420 K (literature value 419–420 K; Salov *et al.*, 1985)]. Analysis found: C 44.92, H 8.62, N 10.43%; calculated for $C_5H_{11}NO_3$: C 45.10, H 8.33, N 10.52%. ^{1}H NMR (400 MHz, D_2O): δ 3.84 (t, J = 5.20 Hz, 2H), 3.26 (t, J = 6.69 Hz, 2H), 3.20 (t, J = 5.20 Hz, 2H), 2.58 (t, J = 6.69 Hz, 2H). For the preparation of the title complex, a mixture containing *N*-(2-hydroxyethyl)-β-alanine (4.7 g, 0.035 mol), $(CuOH)_2CO_3$ (9.0 g, 0.041 mol) and water (20 ml) was stirred at room temperature for 48 h. After filtration, the resulting solution was maintained at room temperature until evaporation resulted in the formation of blue–violet crystals of (I) suitable for X-ray diffraction analysis. Analysis found: C 36.53, H 6.38, N 8.55, Cu 19.14%; calculated for $C_{10}H_{20}CuN_2O_6$: C 36.64, H 6.15, N 8.55, Cu 19.38%.

Crystal data

$[Cu(C_5H_{10}NO_3)_2]$
M_r = 327.82
Monoclinic, $P2_1/n$
a = 9.5257 (6) Å
b = 5.6597 (3) Å
c = 12.4288 (7) Å
β = 96.779 (3)°
V = 665.38 (7) Å^3
Z = 2

D_x = 1.636 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 1481 reflections
θ = 2.6–28.1°
μ = 1.67 mm^{-1}
T = 295 (2) K
Block, blue–violet
0.35 × 0.33 × 0.23 mm

Data collection

Bruker X8 APEX CCD area-detector diffractometer
ω and φ scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.477, T_{max} = 0.682
3238 measured reflections

1553 independent reflections
1204 reflections with $I > 2\sigma(I)$
R_{int} = 0.019
θ_{max} = 28.2°
$h = -12 \rightarrow 7$
$k = -7 \rightarrow 6$
$l = -16 \rightarrow 16$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.027$
$wR(F^2) = 0.069$
$S = 1.03$
1553 reflections
91 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0293P)^2 + 0.3245P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.37$ e Å^{-3}
$\Delta\rho_{min} = -0.26$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cu1—N1	2.0172 (17)	Cu1—O2	1.9682 (14)
Cu1—O1	2.4733 (18)		
N1—Cu1—O1	76.42 (7)	O2—Cu1—O1	89.72 (6)
O2—Cu1—N1	92.30 (7)		

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O2^{i}	0.91	2.21	3.030 (2)	150
O1—H2···O3^{ii}	0.77 (2)	1.89 (2)	2.659 (2)	173 (3)

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

Atom H2 of the OH group was found in a difference electron-density map and refined with the O—H distance constrained to 0.82 (2) Å and with U_{iso}(H) = 1.2U_{eq}(O). All other H atoms were located geometrically and refined using a riding model, with C—H = 0.97 Å and N—H = 0.91 Å, and with U_{iso}(H) = 1.2U_{eq}(C,N). Intermolecular interactions and features of the crystal packing were investigated according to Peresypkina & Blatov (2000) using the *TOPOS4.0 Professional* program suite for crystallochemical analysis (Blatov *et al.*, 2000).

Data collection: *APEX2* (Bruker, 2005); cell refinement: *APEX2*; data reduction: *APEX2*; program(s) used to solve structure: *SHELXTL* (Bruker, 2005); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: local programs.

The authors thank Professor V. A. Blatov (Samara State University, Russia) for providing the *TOPOS* program set.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BG1015). Services for accessing these data are described at the back of the journal.

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