

atoms in the structure were located in the difference Fourier synthesis and refined isotropically. Program(s) used to solve structure: *SHELXL-Plus* (Sheldrick, 1989). Program(s) used to refine structure: *SHELXL92* (Sheldrick, 1992).

Table 1. Fractional atomic coordinates and equivalent isotropic thermal parameters (\AA^2)

$$U_{\text{eq}} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	x	y	z	U_{eq}
Fe	0.13360 (2)	-0.00692 (6)	0.86752 (4)	0.0371 (2)
O1	0.3867 (2)	0.0660 (5)	0.8688 (4)	0.093 (3)
O2	0.4887 (2)	-0.0475 (6)	0.8479 (4)	0.106 (2)
N	0.4281 (2)	-0.0527 (5)	0.8802 (4)	0.065 (2)
C1	0.1951 (2)	-0.1052 (4)	1.0257 (3)	0.041 (2)
C2	0.1238 (2)	-0.0668 (5)	1.0552 (3)	0.045 (2)
C3	0.0741 (2)	-0.1630 (5)	0.9729 (4)	0.050 (2)
C4	0.1134 (2)	-0.2619 (5)	0.8892 (4)	0.049 (2)
C5	0.1871 (2)	-0.2272 (4)	0.9213 (3)	0.043 (2)
C6	0.1954 (3)	0.1583 (8)	0.7769 (6)	0.087 (2)
C7	0.1479 (4)	0.2485 (6)	0.8439 (5)	0.082 (3)
C8	0.0773 (3)	0.2000 (7)	0.7932 (5)	0.085 (2)
C9	0.0858 (3)	0.0822 (7)	0.6937 (5)	0.080 (2)
C10	0.1567 (3)	0.0611 (7)	0.6873 (5)	0.077 (2)
C11	0.2588 (2)	-0.0186 (5)	1.0870 (3)	0.048 (2)
C12	0.3279 (2)	-0.0569 (5)	1.0825 (4)	0.051 (2)
C13	0.3555 (2)	-0.2141 (5)	1.0259 (3)	0.045 (2)
C14	0.4048 (2)	-0.2157 (5)	0.9339 (4)	0.049 (2)
C15	0.4316 (2)	-0.3644 (7)	0.8863 (5)	0.068 (2)
C16	0.4096 (3)	-0.5201 (7)	0.9296 (7)	0.084 (3)
C17	0.3623 (3)	-0.5249 (6)	1.0212 (7)	0.081 (3)
C18	0.3368 (2)	-0.3741 (6)	1.0702 (5)	0.061 (2)

Table 2. Geometric parameters (\AA , $^\circ$)

Fe—C7	2.026 (5)	C2—C3	1.408 (5)
Fe—C6	2.029 (5)	C3—C4	1.424 (5)
Fe—C2	2.029 (3)	C4—C5	1.411 (5)
Fe—C8	2.031 (4)	C6—C10	1.346 (8)
Fe—C5	2.034 (3)	C6—C7	1.379 (8)
Fe—C10	2.034 (4)	C7—C8	1.419 (8)
Fe—C4	2.039 (4)	C8—C9	1.403 (8)
Fe—C9	2.044 (4)	C9—C10	1.346 (7)
Fe—C3	2.045 (4)	C11—C12	1.334 (5)
Fe—C1	2.046 (3)	C12—C13	1.475 (5)
O1—N	1.203 (5)	C13—C18	1.388 (5)
O2—N	1.220 (5)	C13—C14	1.398 (5)
N—C14	1.472 (5)	C14—C15	1.375 (6)
C1—C2	1.433 (5)	C15—C16	1.372 (8)
C1—C5	1.436 (5)	C16—C17	1.368 (9)
C1—C11	1.455 (5)	C17—C18	1.386 (7)
O1—N—O2	123.8 (5)	C9—C10—C6	110.9 (5)
O1—N—C14	119.0 (4)	C12—C11—C1	129.3 (3)
O2—N—C14	117.2 (4)	C11—C12—C13	125.7 (4)
C2—C1—C5	106.1 (3)	C18—C13—C14	115.4 (4)
C2—C1—C11	123.3 (3)	C18—C13—C12	120.1 (4)
C5—C1—C11	130.4 (3)	C14—C13—C12	124.4 (3)
C3—C2—C1	109.2 (3)	C15—C14—C13	123.2 (4)
C2—C3—C4	107.8 (3)	C15—C14—N	117.1 (4)
C5—C4—C3	108.1 (3)	C13—C14—N	119.7 (3)
C4—C5—C1	108.8 (3)	C16—C15—C14	119.5 (5)
C10—C6—C7	107.8 (5)	C17—C16—C15	119.4 (5)
C6—C7—C8	107.7 (5)	C16—C17—C18	120.5 (5)
C9—C8—C7	105.7 (5)	C17—C18—C13	121.9 (5)
C10—C9—C8	108.0 (5)		

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55977 (15 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: VS1004]

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Structure of [(2*S*,4*R*)- γ -Hydroxynorvalinato][(2*R*,4*S*)- γ -hydroxynorvalinato]-copper(II)

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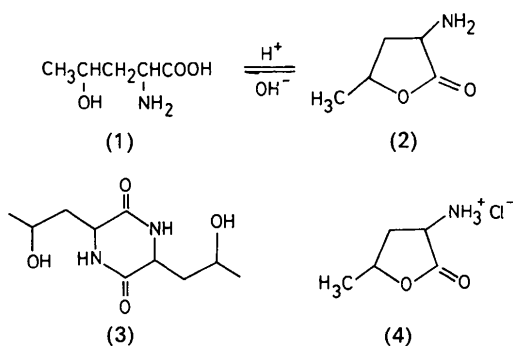
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Abstract

The molecule of the title compound, bis(2-amino-4-hydroxypentanoato-*N,O,O'*)copper(II), possesses crystallographic $\bar{1}$ symmetry. The Cu coordination geometry is distorted square bipyramidal. By virtue of the centre of symmetry, the metal atom and four of the six ligand donor atoms are in an equatorial plane and are rigorously coplanar. The structure consists of discrete molecules linked *via* O—H...O hydrogen bonds and van der Waals attractive forces.

Comment

The γ -hydroxy- α -amino acids are an important class of naturally occurring compounds (Wieland, Hasan & Pfaender, 1968; Narayanan, Iyengar, Ganju, Shomura, Tsuruoka, Inouye & Niida, 1980; Alcock, Crout, Gregorio, Lee, Pike & Samuel, 1989) and γ -hydroxynorvaline (1) is a typical representative of the class. The characteristic property of γ -hydroxynorvaline, as well as of the other γ -hydroxy- α -amino acids, is the pH-dependent equilibrium between the open form of the amino acid (1) and its intramolecular ester α -amino- γ -valerolactone (2) (Armstrong, 1949). Like other intramolecular esters of the γ -hydroxy- α -amino acids, the α -amino- γ -valerolactone is unstable. At room temperature, within a few days α -amino- γ -valerolactone transforms into a stable dimer 3,6-bis(2-hydroxypropyl)-2,5-piperazinedione (3) (Fischer & Leuchs, 1902). Unlike the unstable α -amino- γ -valerolactone, the N-protected α -amino- γ -valerolactones, such as α -amino- γ -valerolactone hydrochloride (4), are much more stable and can be stored for a long period without dimerization.



The title compound was synthesized and described by Fischer & Leuchs in 1902, and since that time the complex has not been described in the literature. As part of our ongoing preparative, spectroscopic, crystallographic and conformational study on stereochemistry of γ -hydroxy- α -amino acids and their transition-metal complexes, we prepared the complex of the same molecular formula and physical characteristics. We used the same procedure but with (\pm)-*cis*- α -amino- γ -valerolactone, *cis*-(2), instead of γ -hydroxynorvaline as the starting material. In the reaction with copper(II) oxide the lactone ring opened and both isomers, 2*S*,4*R* and 2*R*,4*S*, of (\pm)-*threo*- γ -hydroxynorvaline, *threo*-(1), coordinated to the Cu atom.

The crystal structure consists of discrete molecules linked mutually with both hydrogen bonds and van der Waals interactions. The packing of the molecules is dominated by the O—H...O hydrogen bond of length 2.697 (3) Å. The γ -hydroxynorvaline acts as a tridentate ligand. The coordination sphere around the Cu atom is distorted square bipyramidal. The N atom and carboxyl group O atom O1 are in *trans* positions to their

centrosymmetrically equivalent counterparts forming the equatorial plane [Cu—O1 1.982 (2), Cu—N 1.979 (2) Å], while the apex positions are occupied by the γ -hydroxy O atoms at a distances of 2.453 (2) Å. Heavily distorted square-bipyramidal copper coordination results from the O—Cu—O and O—Cu—N bond angles ranging from 79.77 (9) to 96.89 (9)°. The five-membered Cu, O1, C1, C2, N ring has the form of an open envelope with the C2 atom on the flap. The bond distances and bond angles within the γ -hydroxynorvaline ligand have expected values, as found in the copper complex with *N,N*-substituted valine (Kaitner, Kamenar, Paulić, Raos & Simeon, 1987). Certain similarities in the metal-atom coordination and molecular geometry can be found in crystal structures containing either two tridentate ligands coordinated to copper (Kramarenko, Polynova, Porai-Koshits,

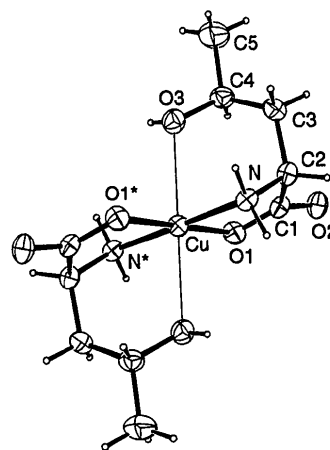


Fig. 1. An ORTEP perspective view of the molecule in general orientation showing the crystallographic numbering scheme. Thermal ellipsoids are drawn at the 35% probability level. H atoms are shown as spheres of arbitrary size. The asterisk refers to the symmetry code $-x, -y, -z + 1$.

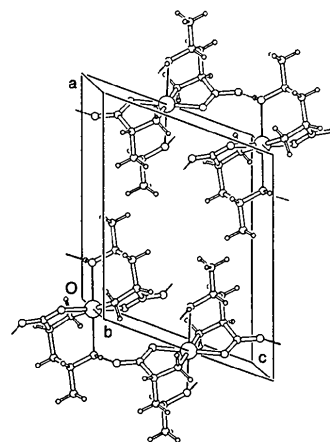


Fig. 2. A PLUTON unit-cell packing diagram. The hydrogen bonds, indicated by broken lines, link the molecules in the (*Ok*l) plane in such a way as to form puckered layers.

Chalyi & Mitrofanova, 1973; Riley, Pecoraro, Carrano & Raymond, 1983), or one hexadentate ligand coordinated to copper (Bulman, Jobanputra, Kuroda, McKinnon & Sadler, 1987; Sysoeva, Agre, Trunov, Dyatlova & Barkhanova, 1984), regardless of whether the equatorial O and N atoms are in *trans* or *cis* positions.

Experimental

Crystal data

[Cu(C₅H₁₀NO₃)₂]

M_r = 327.82

Monoclinic

*P*2₁/*c*

a = 12.353 (4) Å

b = 6.334 (1) Å

c = 10.044 (2) Å

β = 111.75 (2)°

V = 729.9 (3) Å³

Z = 2

D_x = 1.492 Mg m⁻³

Mo *K*α radiation

λ = 0.7093 Å

Cell parameters from 25 reflections

θ = 5–19°

μ = 1.5194 mm⁻¹

T = 293 K

Plate

0.24 × 0.24 × 0.12 mm

Pale blue

Data collection

Enraf-Nonius CAD-4 diffractometer

ω scans

Absorption correction: based on ψ scans

T_{min} = 0.8216, *T_{max}* = 0.9996

1592 measured reflections

1592 independent reflections

1480 observed reflections

[*I* ≥ 2σ(*I*)]

R_{int} = 0.013

θ_{max} = 54°

h = -15 → 14

k = 0 → 8

l = 0 → 12

3 standard reflections monitored every 250 reflections

intensity variation: <1%

Refinement

Refinement on *F*²

Final *R* = 0.032

wR = 0.046

S = 1.208

1100 reflections

[3σ(*I*) cut-off]

88 parameters

H-atom parameters not refined except for HO3

w = 1/[σ²(*F_o*) + 0.0008*F_o*²]

(Δ/σ)_{max} = 0.027

Δρ_{max} = 0.26 e Å⁻³

Δρ_{min} = -0.51 e Å⁻³

Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.3.1)

Table 1. Fractional atomic coordinates and equivalent isotropic thermal parameters (Å²)

$$U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U_{eq}</i> (Å ²)
Cu	0.0	0.0	0.5	0.0334 (3)
O1	-0.0506 (1)	-0.1057 (3)	0.3004 (2)	0.040 (1)
O2	-0.1742 (2)	-0.0328 (3)	0.0814 (2)	0.045 (1)
O3	-0.1973 (2)	-0.0602 (4)	0.4962 (3)	0.045 (1)
N	-0.0777 (2)	0.2624 (4)	0.4048 (3)	0.034 (1)
C1	-0.1282 (3)	0.0075 (5)	0.2111 (3)	0.036 (2)
C2	-0.1702 (3)	0.2004 (5)	0.2680 (3)	0.036 (2)
C3	-0.2848 (3)	0.1495 (5)	0.2871 (3)	0.042 (2)
C4	-0.2898 (3)	-0.0578 (5)	0.3589 (4)	0.044 (2)
C5	-0.4047 (4)	-0.0895 (10)	0.3745 (6)	0.085 (3)
HO3	-0.1908	-0.1849	0.5198	0.0500

Table 2. Geometric parameters (Å, °)

Cu—O1	1.982 (2)	N—C2	1.478 (4)
Cu—N	1.979 (2)	C1—C2	1.519 (4)
O1—C1	1.265 (4)	C2—C3	1.532 (4)
O2—C1	1.240 (4)	C3—C4	1.510 (5)
O3—C4	1.428 (4)	C4—C5	1.498 (5)
O3—HO3	0.820	O2 ⁱ —O3	2.697 (3)
O1—Cu—N	83.11 (9)	N—C2—C1	108.0 (2)
O1—Cu—N ⁱⁱ	96.89 (9)	N—C2—C3	111.9 (2)
Cu—O1—C1	113.4 (2)	C1—C2—C3	109.7 (2)
C4—O3—HO3	104.3 (2)	C2—C3—C4	116.5 (3)
Cu—N—C2	107.2 (2)	O3—C4—C3	108.1 (3)
O1—C1—O2	124.0 (3)	O3—C4—C5	110.4 (3)
O1—C1—C2	117.6 (3)	C3—C4—C5	112.0 (3)
O2—C1—C2	118.3 (3)		

Symmetry code: (i) *x*, -½ - *y*, *z* - ½; (ii) -*x*, -*y*, 1 - *z*.

The title compound was prepared by refluxing a mixture of aqueous solution of the (±)-*cis*-α-amino-γ-valerolactone and copper(II) oxide. The *cis* lactone (2) was obtained by removing the HCl with K₂CO₃ (Fischer & Leuchs, 1902) from (±)-*cis*-α-amino-γ-valerolactone hydrochloride, *cis*-(4) (A. Deljac & V. Vela, unpublished results). The sample suitable for X-ray investigation was obtained by recrystallization (vapour diffusion in a water/ethanol system) in the form of pale blue plates. The Cu-atom position was found by a manual Patterson solution. The positions of remaining non-H atoms were determined from subsequent difference Fourier syntheses. Full-matrix least-squares refinement was performed with anisotropic thermal parameters for all non-H atoms. H atoms were placed in geometrically expected positions (N—H 1.0, C—H 0.95 Å); their coordinates were kept fixed and included in the structure-factor calculations. The rotational orientation of the C5 methyl group was checked by the calculation of a contour Δ*F* plane through the corresponding H atoms. The O3 hydroxyl H atom was found in a difference Fourier synthesis calculated at *R* = 0.035. Isotropic thermal motion for each H atom was calculated as *U_{iso}* = 1.2 × *U_{eq}* of the associated N or C atom. Cell refinement and data collection used Enraf-Nonius CAD-4F software. Data reduction and semi-empirical ψ-scan absorption corrections used Enraf-Nonius CAD-4 SDP software (Frenz, 1978). Programs used to solve and refine the structure and prepare graphics and other material for publication were contained in the NRCVAX package (Gabe, Le Page, Charland, Lee & White, 1989), which includes ORTEPII (Johnson, 1976) and PLUTON (Spek, 1982).

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Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71066 (11 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: KA1023]

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Structure of [Di-*tert*-butyl(dimethoxy)-salen]cobalt(II)

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Abstract

In the monomeric title compound, {6,6'-di-*tert*-butyl-2,2'-[1,2-ethanediylbis(nitrilomethylidyne- κ N)]-4,4'-dimethoxy(diphenolato- κ O, O')}cobalt(III), the ligand is coordinated *via* two O and two N atoms and the Co atom exhibits an almost planar coordina-

tion sphere with a maximum deviation from planarity of 0.116 (3) Å.

Comment

It has been observed that the formal potential E^0 (Co^{II}/Co^{III}) of Co^{II}(salen) {H₂salen = 2,2'-[1,2-ethanediylbis(nitrilomethylidyne)]diphenol} in dimethylformamide (DMF) is shifted to a more positive value (–408 mV *vs* external F_c/F_c^+) when a *tert*-butyl group is substituted at the 3-position of the aromatic ring of the complex, although from the electronic effects of the *tert*-butyl substituent, a shift in the negative direction would be expected (Nishinaga, Tajima, Speiser, Eichhorn, Ohya-Nishiguchi & Ishizu, 1991). This leads to the assumption that the electronic effects of this bulky substituent are outweighed by steric effects. As a consequence, the planar structure of Co(salen) could become distorted and the coordination of an axial donor ligand (DMF) would be hindered. In order to study these effects we have undertaken X-ray investigations. The crystal structure determination shows only small deviations from planarity in the Co, O1, O2, N1, N2 core. The distances from the plane are –0.011 (2) (Co), 0.115 (2) (O1), –0.110 (2) (O2), –0.111 (3) (N1) and 0.116 (3) Å (N2). Therefore, the *tert*-butyl group should mainly exert a direct steric effect on the coordination of axial donor ligands, thus decreasing the ease of ionization of the Co atom.

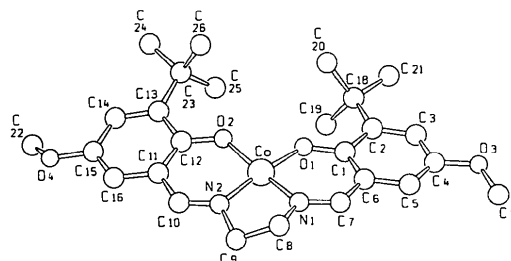


Fig. 1. Plot of the molecule showing the numbering scheme. H atoms have been omitted for clarity.

Experimental

Crystal data

[Co(C₂₆H₃₄N₂O₄)]
 $M_r = 497.50$
 Monoclinic
 $P2_1/n$
 $a = 11.182$ (1) Å
 $b = 17.816$ (1) Å
 $c = 12.137$ (1) Å
 $\beta = 97.437$ (1)°
 $V = 2397.8$ (2) Å³
 $Z = 4$

$D_x = 1.378$ Mg m⁻³
 Cu $K\alpha$ radiation
 $\lambda = 1.54056$ Å
 Cell parameters from 100 reflections
 $\theta = 18–29^\circ$
 $\mu = 61.464$ mm⁻¹
 $T = 223$ K
 Needle
 $0.4 \times 0.08 \times 0.08$ mm
 Red-brown