ω–2θ scans
Absorption correction: none
3226 measured reflections
3035 independent reflections
2521 reflections with $I > \sigma(I)$

$h = 0 \rightarrow 11$
$k = -13 \rightarrow 14$
$l = -9 \rightarrow 8$
3 standard reflections
every 150 reflections
intensity decay: −1.4%

Refinement

Refinement on F^2
$R(F) = 0.063$
$wR(F^2) = 0.097$
$S = 1.500$
2521 reflections
181 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 4F_o^2/\sigma^2(F_o^2)$
$(\Delta/\sigma)_{max} = 0.010$
$\Delta\rho_{max} = 0.52$ e Å^{-3}
$\Delta\rho_{min} = -0.44$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

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

Co1—O2	2.037 (2)	C3—C4	1.352 (4)
Co1—O3	2.122 (2)	C4—C10	1.404 (4)
Co1—N1	2.226 (2)	C5—C6	1.361 (5)
O1—C1	1.246 (3)	C5—C10	1.412 (4)
O2—C1	1.264 (3)	C6—C7	1.401 (5)
O4—C12	1.411 (5)	C7—C8	1.370 (4)
N1—C2	1.326 (3)	C8—C9	1.405 (4)
N1—C9	1.372 (4)	C9—C10	1.421 (4)
C1—C2	1.509 (4)	C11—C12	1.430 (6)
C2—C3	1.409 (4)		
O2—Co1—O3	91.10 (8)	O1—C1—O2	124.3 (2)
O2—Co1—N1	77.23 (7)	O1—C1—C2	118.6 (2)
O3—Co1—N1	89.51 (8)	O2—C1—C2	117.1 (2)
Co1—O2—C1	118.9 (2)	N1—C2—C1	115.9 (2)
Co1—N1—C2	110.8 (2)	N1—C2—C3	123.6 (2)
Co1—N1—C9	131.0 (2)	C1—C2—C3	120.5 (2)
C2—N1—C9	118.2 (2)		

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O4—H16···O1^{i}	0.91 (5)	1.80 (5)	2.701 (4)	166 (4)
O3—H9···O1^{ii}	0.80 (4)	1.95 (4)	2.746 (3)	173 (4)
O3—H10···O5^{iii}	1.09 (4)	1.63 (4)	2.717 (3)	174 (3)
O5···O4^{iv}			2.757 (4)	
O5···O4^{v}			2.893 (4)	

Symmetry codes: (i) $-x, 1-y, 1-z$; (ii) $-x, 1-y, -z$; (iii) $x-1, y, z$; (iv) $1-x, -y, 1-z$; (v) $1+x, y, z$.

H atoms were placed in calculated positions and included in the structure-factor calculations, with the exception of those involved in hydrogen bonding, which were located in a difference Fourier map and were refined isotropically.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1985). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985) and *DIRDIF* (Beurskens, 1984). Program(s) used to refine structure: *TEXSAN*. Molecular graphics: *ORTEP*II (Johnson, 1976).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: DA1034). Services for accessing these data are described at the back of the journal.

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Bis[2-hydroxy-3-(1*H*-imidazol-4-yl)-propionato]cobalt(II)

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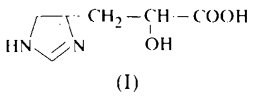
Abstract

In the title compound, $[Co(C_6H_7N_2O_3)_2]$, the Co^{II} ion has a slightly distorted octahedral coordination geometry. 2-Hydroxy-3-(1*H*-imidazol-4-yl)propanoic acid acts as a bidentate ligand. Two carboxylate O atoms and two hydroxyl O atoms are coordinated *cis* to each other and form the equatorial plane, and two imidazole N atoms are coordinated in axial positions. The molecules are held together by an intermolecular hydrogen-bonding network involving the carboxylate, imino and hydroxyl groups.

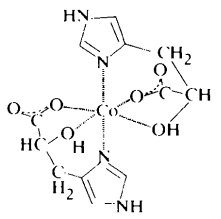
Comment

2-Hydroxy-3-(1*H*-imidazol-4-yl)propanoic acid, (I), also known as imidazolelactic acid, is one of the final well known products of L-histidine catabolism. Patients with liver cirrhosis or histidinemia have high urinary concentrations of (I) (Dubovsky & Dubovska, 1965; Murray *et al.*, 1993). It also has an inhibitory action

on cholinesterase and monoamine oxidase (Kurocochi *et al.*, 1956). Understanding the coordination ability and diversity of biologically important metal ions is helpful in clarifying their functions in biological systems. Therefore, we have begun to determine the structures of coordination compounds formed between biological substances and metal ions. In this study, the structural analysis of the Co^{II} complex of 2-hydroxy-3-(1*H*-imidazol-4-yl)propanoic acid, (II), was carried out.



(I)



(II)

The molecular structure of (II) is shown in Fig. 1. The Co^{II} ion is in a distorted octahedral environment, with the Co atom on a twofold axis. 2-Hydroxy-3-(1*H*-imidazol-4-yl)propanoic acid acts as a bidentate ligand and forms a distorted five-membered ring, which includes the Co atom and the 2-hydroxyl and carboxylate O atoms. These O atoms bind to cobalt in *cis* positions with respect to each other in the equatorial plane. The imidazole N atoms bind to cobalt in the axial positions. The constraints of the five-membered ring reduce the bite angle in the equatorial plane, forming a rectangular plane: O2—Co1—O3 75.37 (8)°. No significant distortion is observed among the six coordination bonds of the complex: Co1—O2 2.114 (2), Co1—O3 2.100 (2) and Co1—N3 2.103 (2) Å. The ionized propanoic acid side chain adopts a *gauche* conformation: C4—C6—C7—C8 −51.9 (3)°.

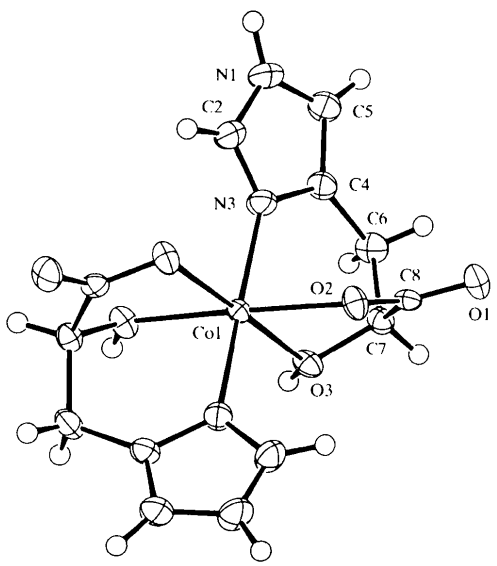


Fig. 1. *ORTEP*II (Johnson, 1976) drawing of the title compound, with the atomic numbering scheme. Ellipsoids for non-H atoms correspond to 50% probability.

Similar distorted octahedral coordination geometry is present in the crystal structure of di(histidino)zinc pentahydrate (Harding & Cole, 1963), in which an amino N atom binds to zinc, instead of the hydroxyl O atom of 2-hydroxy-3-(1*H*-imidazol-4-yl)propanoic acid. The bond lengths of the imidazole ring in (II) are similar to those in di(histidino)zinc pentahydrate (Harding & Cole, 1963) or histidine hydrochloride monohydrate (Donohue *et al.*, 1956). No stacking interactions between imidazole rings are observed in (II). The molecules of (II) are linked by intermolecular hydrogen bonds between carboxylate, imino and hydroxyl groups, as cited in Table 2.

Experimental

Pillar-shaped brown crystals of the title compound were obtained by the slow evaporation at room temperature of an aqueous solution (pH 10, aqueous ammonia) of 2-hydroxy-3-(1*H*-imidazol-4-yl)propanoic acid and cobalt(II) chloride hexahydrate (2:1 molar ratio).

Crystal data

$[Co(C_6H_7N_2O_3)_2]$
M_r = 369.2
Orthorhombic
$P2_12_12$
a = 10.735 (2) Å
b = 13.310 (2) Å
c = 5.205 (1) Å
V = 743.7 (2) Å^3
Z = 2
D_x = 1.649 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71069 Å
Cell parameters from 25 reflections
θ = 24.65–25.00°
μ = 1.185 mm^{-1}
T = 296 K
Pillar
0.4 × 0.4 × 0.3 mm
Brown

Data collection

Rigaku AFC-5*R* diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scan (North *et al.*, 1968)
T_{min} = 0.638, T_{max} = 0.701
1037 measured reflections
1037 independent reflections

1022 reflections with $I > 0$
θ_{max} = 27.5°
h = 0 → 13
k = 0 → 17
l = 0 → 6
3 standard reflections
every 150 reflections
intensity decay: none

Refinement

Refinement on F
R = 0.032
wR = 0.048
S = 1.25
1022 reflections
105 parameters
H atoms: see below
$w = 4F_o^2/\sigma^2(F_o^2)$

$(\Delta/\sigma)_{max}$ = 0.002
$\Delta\rho_{max}$ = 0.36 e Å^{-3}
$\Delta\rho_{min}$ = −0.84 e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

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

Co1—O2	2.114 (2)	N1—C5	1.365 (4)
Co1—O3	2.100 (2)	N3—C2	1.321 (3)
Co1—N3	2.103 (2)	N3—C4	1.390 (3)
O1—C8	1.223 (3)	C4—C5	1.361 (4)
O2—C8	1.280 (3)	C4—C6	1.500 (3)
O3—C7	1.434 (3)	C6—C7	1.530 (3)
N1—C2	1.342 (3)	C7—C8	1.533 (3)
O2—Co1—O3	75.37 (8)	N3—C4—C6	123.0 (2)
O2—Co1—N3	86.3 (1)	C5—C4—C6	128.8 (2)
O3—Co1—N3	87.6 (1)	N1—C5—C4	107.2 (2)
Co1—O2—C8	114.1 (2)	C4—C6—C7	113.9 (2)
Co1—O3—C7	109.0 (1)	O3—C7—C6	111.1 (2)
C2—N1—C5	107.4 (2)	O3—C7—C8	107.7 (2)
Co1—N3—C2	126.3 (2)	C6—C7—C8	111.3 (2)
Co1—N3—C4	126.8 (2)	O1—C8—O2	125.1 (2)
C2—N3—C4	106.0 (2)	O1—C8—C7	118.5 (2)
N1—C2—N3	111.3 (2)	O2—C8—C7	116.3 (2)
N3—C4—C5	108.2 (2)		

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O1^{i}	0.948	1.937	2.800 (3)	150.30
O3—H7···O2^{ii}	0.893	1.749	2.631 (3)	168.76

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

H atoms were generated by calculation, except for the hydroxyl H7 atom, which was located from a difference Fourier map and included in the structure-factor calculations at a fixed position.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1985). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985) and *DIRDIF* (Beurskens, 1984). Program(s) used to refine structure: *TEXSAN*. Molecular graphics: *ORTEP*II (Johnson, 1976).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: DA1037). Services for accessing these data are described at the back of the journal.

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Interactions of thiamine with anions: (Hthiamine)(thiamine) heptaiododimercurate dihydrate and its dimethanol monohydrate

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Abstract

In the title compounds, 3-[(4-amino-2-methyl-5-pyrimidinio)methyl]-5-(2-hydroxyethyl)-4-methylthiazolium(2+) 3-[(4-amino-2-methyl-5-pyrimidinyl)methyl]-5-(2-hydroxyethyl)-4-methylthiazolium(1+) heptaiododimercurate dihydrate, $(C_{12}H_{18}N_4OS)(C_{12}H_{17}N_4OS)[Hg_2I_7]\cdot 2H_2O$, (1), and its dimethanol monohydrate, $(C_{12}H_{18}N_4OS)(C_{12}H_{17}N_4OS)[Hg_2I_7]\cdot 2CH_3OH\cdot H_2O$, (2), a crystallographic centre of symmetry in (1) or a twofold axis in (2) is imposed between the protonated and deprotonated thiamine molecules, resulting in a statistically half-occupied proton attached at N1′ of the pyrimidine ring. The $Hg_2I_7^{3-}$ anion, residing on the centre of symmetry in (1) or on the twofold axis in (2), interacts with two thiamine molecules, each through a C2—H···I···pyrimidine-ring interaction. This bridging interaction is a characteristic of thiamine in the *F* conformation.

Comment

In the form of its pyrophosphate ester, thiamine {vitamin B_1; 3-[(4-amino-2-methyl-5-pyrimidinio)methyl]-5-(2-hydroxyethyl)-4-methylthiazolium} is a coenzyme for several enzyme systems (Krampitz, 1969). As a naturally occurring cationic host, thiamine interacts with different anion groups through characteristic hydrogen bonds and electrostatic contacts to form host–guest-like complexes (Aoki *et al.*, 1993). Thiamine compounds containing monovalent or divalent anions have been