Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

[*N*,*N*-Bis(carboxymethyl)-L-leucinato]-(1,2-ethanediamine)cobalt(III) monohydrate

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Key indicators

Single-crystal X-ray study
T = 173 K
Mean σ(C–C) = 0.002 Å
R factor = 0.025
wR factor = 0.052
Data-to-parameter ratio = 16.9

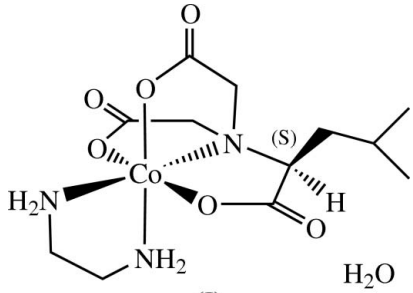
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Received 10 November 2005
Accepted 5 December 2005
Online 14 December 2005

The Co atom in the title compound, $[Co(C_{10}H_{14}NO_6)(C_2H_8N_2)]\cdot H_2O$, has an octahedral geometry with tetradentate *N*,*N*-bis(carboxymethyl)-L-leucine (L-bcmle) and bidentate ethylenediamine (en) ligands. The complexes and water molecules are linked *via* N—H···O and O—H···O hydrogen bonds, forming layers perpendicular to the *c* axis. Between these hydrophilic layers, hydrophobic bilayers are formed by the isobutyl groups of the L-bcmle ligands.

Comment

High efficiency and specificity of biological reactions are achieved by molecular recognition utilizing steric repulsion and weak non-covalent interactions, such as hydrogen bonding, electrostatic, hydrophobic and aromatic ring-stacking interactions (Rebek, 1990). In order to understand such non-covalent interactions of the molecular recognition sites of proteins, we have studied inorganic complexes containing amino acid derivatives as model compounds (Jitsukawa *et al.*, 1994; Kumita *et al.*, 2001). In this paper, we report the crystal structure of the title compound, $[Co^{II}(L\text{-bcmle})(en)]\cdot H_2O$, (I). The L-bcmle ligand was derived from the natural amino acid L-leucine (L-Leu).



(I)

For complex (I), there are three possible types of stereoisomers, depending on the position of the C^{α} site and the orientation of the isobutyl group of the L-Leu unit in L-bcmle. Our preparation method facilely gave the red single crystalline product, (I) (Fig. 1). ^{1}H NMR spectroscopic analysis also suggested that (I) was predominant in the synthetic solution through the procedure. The coordination mode of L-bcmle in (I) is the same as those observed in the crystal structures of analogous Co^{III} (Jitsukawa *et al.*, 1994; Kumita *et al.*, 1998, 2001) and Cr^{III} complexes (Borcarsly *et al.*, 1990). The CD spectrum of (I) in aqueous solution exhibited characteristically large positive and negative bands in the *d*–*d* region, which are induced by the coordination geometry and the absolute configuration at the asymmetric centres.

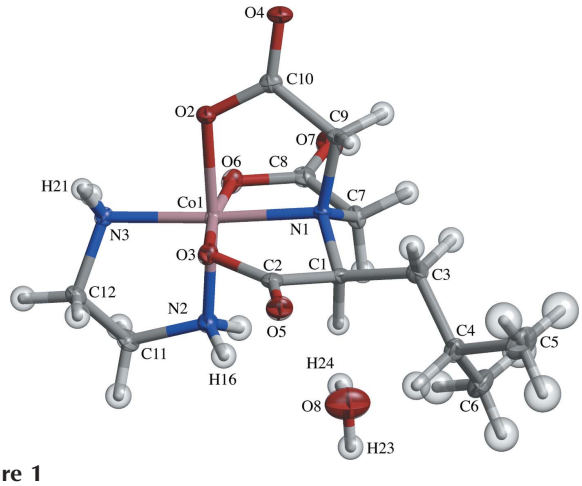


Figure 1
A view of the molecular structure of (I), showing the atomic labelling scheme. Displacement ellipsoids are drawn at the 50% probability level.

In (I), the Co^{III} centre has a distorted octahedral geometry (Table 1). The Co—O and Co—N bonds are slightly shorter than the generally reported values of Co—O(carboxylate) = 1.894–1.918 Å and Co—N(amine) = 1.938–1.977 Å (Orpen *et al.*, 1989), and are in the range of the reported values of Co—O(carboxylate) = 1.854 (9)–1.947 (3) Å and Co—N(amine) = 1.907 (4)–1.962 (3) Å for the corresponding Co^{III} complexes with nitrilotriacetic acid analogues (Jitsukawa *et al.*, 1994; Kumita *et al.*, 1998, 2001; Swaminathan *et al.*, 1989).

Intermolecular hydrogen bonds (Table 2) between the $[Co^{III}$(L-bcmle)(en)] and H_2O molecules form hydrophilic layers parallel to the (001) plane (Fig. 2). The isobutyl groups of the L-bcmle ligands are located outside the hydrophilic layers, and interdigitation of the alkyl chains forms a bilayer structure.

Experimental

The tripodal ligand *N*,*N*-bis(carboxymethyl)-L-leucine (H_3bcmle) was synthesized from L-leucine according to the literature method of Uehara *et al.* (1970). K_2[Co(bcmle)(CO_3)] was obtained from the reaction of K_3[Co(CO_3)$_3$] and H_3bcmle. To a 0.2 *M* aqueous solution (10 ml) of K_2[Co(bcmle)(CO_3)] was added an equimolar amount of ethylenediamine, neutralized with HCl, and the resulting mixture was stirred at 323 K for 12 h under conditions of pH 6–7 in the presence of active charcoal. After filtration, the reaction mixture was purified using a QAE Sephadex A-25 column (Cl^- form) in water, eluting a non-adsorbed red–violet solution of the product. Evaporation of the reddish-violet solution and recrystallization of the precipitated product in water gave the red crystals of (I) suitable for X-ray analysis (yield 4.2%).

Crystal data

$[Co(C_{10}H_{14}NO_6)(C_2H_8N_2)]\cdot H_2O$
M_r = 381.27
Orthorhombic, $P2_12_12_1$
a = 7.4740 (4) Å
b = 7.3532 (4) Å
c = 28.8604 (16) Å
V = 1586.10 (15) Å^3
Z = 4
D_x = 1.597 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 5217 reflections
θ = 3.1–27.5°
μ = 1.12 mm^{-1}
T = 173 (1) K
Prism, red
0.19 × 0.16 × 0.16 mm

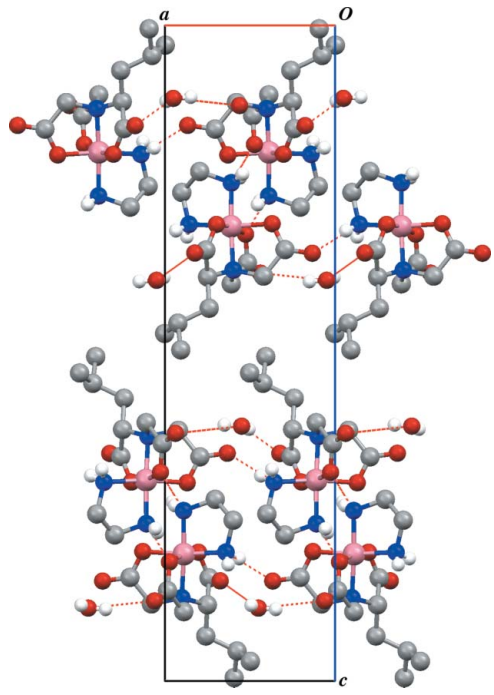


Figure 2
The molecular packing of (I), viewed along the *b* axis. H atoms bonded to C atoms have been omitted for clarity. Broken lines indicate the hydrogen bonding interactions.

Data collection

Rigaku Mercury CCD area-detector diffractometer
ω scans
Absorption correction: numerical (*ABSCOR*; Higashi, 1999)
T_{min} = 0.761, T_{max} = 0.799
12559 measured reflections
3626 independent reflections
3261 reflections with $F^2 > 2\sigma(F^2)$
R_{int} = 0.030
θ_{max} = 27.5°
$h = -9 \rightarrow 9$
$k = -9 \rightarrow 9$
$l = -37 \rightarrow 27$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.025
$wR(F^2)$ = 0.052
S = 1.02
3626 reflections
215 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0037P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.002
$\Delta\rho_{max}$ = 0.40 e Å^{-3}
$\Delta\rho_{min}$ = −0.27 e Å^{-3}
Absolute structure: Flack (1983), with 1510 Friedel pairs
Flack parameter: 0.001 (11)

Table 1
Selected geometric parameters (Å, °).

Co1—O2	1.8971 (12)	Co1—N1	1.9464 (14)
Co1—O3	1.8912 (12)	Co1—N2	1.9648 (15)
Co1—O6	1.8979 (12)	Co1—N3	1.9281 (14)
O2—Co1—O3	92.30 (5)	O3—Co1—N3	93.26 (6)
O2—Co1—O6	88.07 (5)	O6—Co1—N1	87.11 (5)
O2—Co1—N1	88.17 (5)	O6—Co1—N2	90.56 (6)
O2—Co1—N2	173.37 (6)	O6—Co1—N3	94.56 (5)
O2—Co1—N3	87.99 (5)	N1—Co1—N2	98.24 (6)
O3—Co1—O6	172.17 (5)	N1—Co1—N3	175.75 (6)
O3—Co1—N1	85.09 (6)	N2—Co1—N3	85.66 (6)
O3—Co1—N2	89.95 (5)		

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

D—H···A	D—H	H···A	D···A	D—H···A
O8—H23···O7^{i}	0.80 (2)	2.25 (2)	3.040 (2)	166
O8—H24···O5^{ii}	0.77 (2)	2.06 (2)	2.744 (2)	147
N2—H16···O4^{i}	0.92	2.03	2.922 (2)	162
N3—H21···O6^{iii}	0.92	2.02	2.8973 (19)	160

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

All H atoms were located in difference Fourier maps. The positions of the water H atoms were refined freely, with U_{iso}(H) = $1.2U_{eq}$(O). All other H atoms were constrained to ride on their parent atoms, with N—H = 0.92 Å and C—H = 0.98–1.00 Å, and with U_{iso}(H) = $1.2U_{eq}$(C,N). Each methyl group was allowed to rotate freely about the C—C bond. The absolute structure determination based on the Flack (1983) parameter is consistent with the known absolute configuration of L-leucine (Voet & Voet, 1990).

Data collection: *CrystalClear* (Rigaku, 1999); cell refinement: *CrystalClear*; data reduction: *CrystalStructure* (Rigaku/MSC, 2005); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *Raster3D* (Merritt & Bacon, 1997) and *MERCURY* (Bruno *et al.*, 2002); software used to prepare material for publication: *CrystalStructure*.

This work was supported partly by a Grant-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science, and Technology, Japan.

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