

Takashi Aridomi* and Takumi Konno

Department of Chemistry, Graduate School of Science, Osaka University, Toyonaka, Osaka 560-0043, Japan

Correspondence e-mail:
aridomi@ch.wani.osaka-u.ac.jp

Key indicators

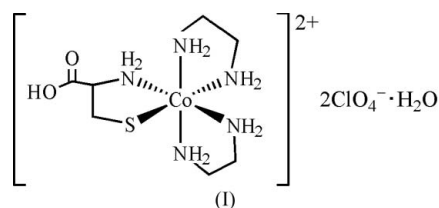
Single-crystal X-ray study
 $T = 296\text{ K}$
Mean $\sigma(\text{C}-\text{C}) = 0.004\text{ \AA}$
 R factor = 0.036
 wR factor = 0.099
Data-to-parameter ratio = 21.3For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>. Δ_L -(L-Cysteinato- κ^2N,S)bis(ethylenediamine- κ^2N,N')cobalt(III) bis(perchlorate) monohydrate

In the title compound, $[\text{Co}(\text{C}_3\text{H}_6\text{NO}_2\text{S})(\text{C}_2\text{H}_8\text{N}_2)_2](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$, the central Co^{III} atom is coordinated by one N,S -bidentate L-cysteine (L-H₂cys) and two N,N' -bidentate ethylenediamine (en) ligands in a slightly distorted octahedral geometry with a Δ configuration. The L-Hcys chelate ring adopts a λ conformation, while the two en chelate rings have a δ conformation.

Received 21 November 2006
Accepted 21 November 2006

Comment

Freeman *et al.* (1978) reported the synthesis and characterization of two diastereomers (Δ_L and Λ_L) of an L-cysteinato cobalt(III) complex, $[\text{Co}(\text{L-cys-}N,S)(\text{en})_2](\text{ClO}_4)$ (L-H₂cys is L-cysteine and en is ethylenediamine), together with those of its protonated form, $[\text{Co}(\text{L-Hcys-}N,S)(\text{en})_2](\text{ClO}_4)_2$. While they determined crystal structures of Δ_L - and Λ_L - $[\text{Co}(\text{L-cys-}N,S)(\text{en})_2](\text{ClO}_4)$ by X-ray crystallography, neither the Δ_L nor the Λ_L isomer of the protonated form has been structurally characterized. Recently, we obtained single crystals of the protonated Λ_L isomer in the course of the reactions of Λ_L - $[\text{Co}(\text{L-cys-}N,S)(\text{en})_2]^+$ with transition metal ions, and its structure was determined to be Λ_L - $[\text{Co}(\text{L-Hcys-}N,S)(\text{en})_2](\text{ClO}_4) \cdot 1.5\text{H}_2\text{O}$ by X-ray analysis (Aridomi *et al.*, 2006). In this study, we prepared single crystals of the protonated Δ_L isomer, Δ_L - $[\text{Co}(\text{L-Hcys-}N,S)(\text{en})_2](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$, (I), and its structure was established by X-ray crystallography.



X-ray analysis of (I) confirmed the presence of a divalent complex cation, $[\text{Co}(\text{L-Hcys-}N,S)(\text{en})_2]^{2+}$, two ClO_4^- anions and one water molecule (Fig. 1). The complex cation consists of a central Co^{III} atom, an N,S -bidentate L-Hcys ligand having a protonated COOH group, and two N,N' -bidentate en ligands. The Co^{III} atom in (I) is situated in a slightly distorted octahedral geometry with a Δ configuration, coordinated by an L-Hcys and two en ligands [*trans* $\text{N}-\text{Co}-\text{N} = 175.60$ (9) and 177.02 (9) $^\circ$, *trans* $\text{N}-\text{Co}-\text{S} = 176.78$ (7) $^\circ$; Table 1]. The average $\text{Co}-\text{N}$ distance in (I) is 1.984 (2) \AA , which is similar to that in Δ_L - $[\text{Co}(\text{L-cys-}N,S)(\text{en})_2](\text{ClO}_4)$ [1.978 (8) \AA]. On the other hand, the $\text{Co}-\text{S}$ distance in (I) [2.2376 (8) \AA] is slightly shorter than that in Λ_L - $[\text{Co}(\text{L-cys-}N,S)(\text{en})_2](\text{ClO}_4)$ [2.252 (3) \AA].

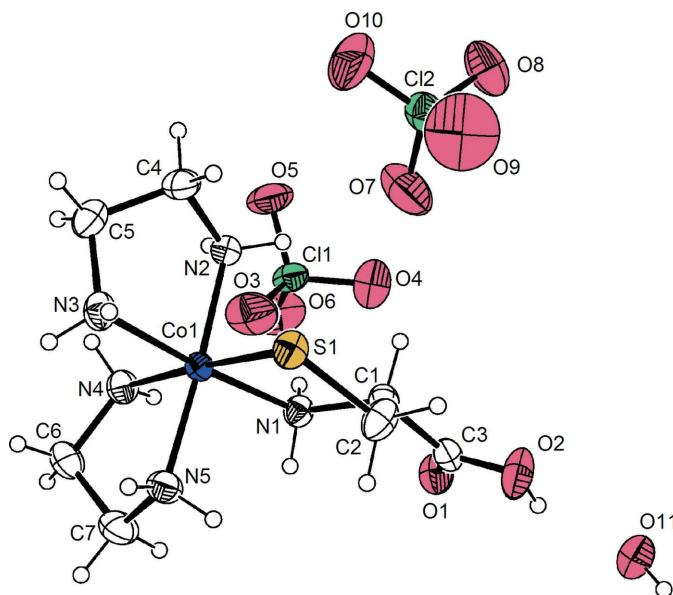


Figure 1
The molecular structure of (I), showing the atom-numbering scheme and 30% probability displacement ellipsoids.

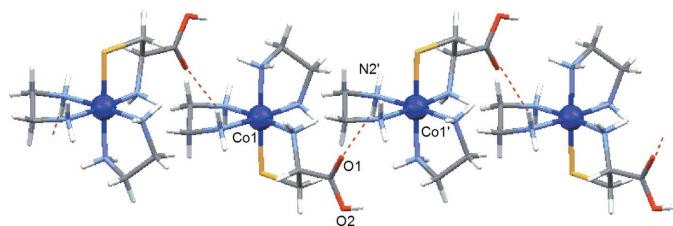


Figure 2
A view of the one-dimensional chain structure of (I), showing the atom-numbering scheme. Dashed lines indicate N–H...O hydrogen bonds. [Symmetry code: (') $x + \frac{1}{2}, -y + \frac{1}{2}, -z + 1$.]

In (I), the five-membered L-cys-*N,S* chelate ring adopts a *gauche* conformation with a preferred δ form such that the non-coordinated COOH group takes an equatorial orientation. This was also the case for the L-cys-*N,S* chelate ring in Δ_L -[Co(L-cys-*N,S*)(en)₂](ClO₄), which contains an equatorially oriented COO⁻ group. However, both the en chelate rings in (I) have a λ form, which is distinct from the λ and δ forms for the en chelate rings in Δ_L -[Co(L-cys-*N,S*)(en)₂](ClO₄).

As shown in Fig. 2, one of the five amine groups of the complex cation in (I) is hydrogen bonded with the COOH group of the neighboring complex cation, constructing a one-dimensional chain structure (Table 2). The other amine groups of the complex cation form hydrogen bonds with ClO₄⁻ counteranions (Table 2).

Experimental

To a solution containing Δ_L -[Co(L-Hcys-*N,S*)(en)₂](ClO₄)₂·H₂O (0.20 g, 0.39 mmol) in water (5 ml) was added CdCl₂ (0.09 g, 0.40 mmol). The mixture was stirred at room temperature for 1 h. To

the brown reaction solution was added *d,l*-tartaric acid (0.50 g), and the resulting solution was kept at room temperature for one week. The resulting dark-brown prism-shaped crystals of (I) were collected by filtration.

Crystal data

[Co(C₃H₆NO₂S)(C₂H₈N₂)₂]
(ClO₄)₂·H₂O
M_r = 516.21
Orthorhombic, *P*2₁2₁2₁
a = 11.987 (4) Å
b = 16.926 (6) Å
c = 9.209 (3) Å
V = 1868.5 (12) Å³

Z = 4
D_x = 1.835 Mg m⁻³
Mo *K*α radiation
 μ = 1.38 mm⁻¹
T = 296 (2) K
Prism, dark brown
0.60 × 0.40 × 0.32 mm

Data collection

Rigaku AFC-7R diffractometer
 ω -2 θ scans
Absorption correction: ψ scan
(North *et al.*, 1968)
*T*_{min} = 0.491, *T*_{max} = 0.666
6218 measured reflections
5431 independent reflections

5056 reflections with *I* > 2 σ (*I*)
*R*_{int} = 0.027
 θ _{max} = 30.0°
3 standard reflections
every 150 reflections
intensity decay: 1.0%

Refinement

Refinement on *F*²
 $R[F^2 > 2\sigma(F^2)] = 0.036$
 $wR(F^2) = 0.099$
S = 1.07
5431 reflections
255 parameters
H atoms treated by a mixture of
independent and constrained
refinement

$w = 1/[\sigma^2(F_o^2) + (0.0657P)^2 + 0.6912P]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.78 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.77 \text{ e } \text{Å}^{-3}$
Extinction correction: *SHELXL97*
Extinction coefficient: 0.0237 (14)
Absolute structure: Flack (1983), no
Friedel pairs
Flack parameter: -0.004 (12)

Table 1

Selected geometric parameters (Å, °).

Co1–S1	2.2376 (8)	Co1–N3	1.978 (2)
Co1–N1	1.991 (2)	Co1–N4	2.019 (2)
Co1–N2	1.954 (2)	Co1–N5	1.976 (2)
S1–Co1–N4	176.78 (7)	N1–Co1–N3	175.60 (9)
N2–Co1–N5	177.02 (9)		

Table 2

Hydrogen-bond geometry (Å, °).

<i>D</i> –H... <i>A</i>	<i>D</i> –H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> –H... <i>A</i>
N2–H5...O1 ⁱ	0.90	2.13	2.906 (3)	144
O2–H1...O11	0.809 (19)	1.89 (3)	2.603 (3)	147 (5)
N1–H3...O3	0.90	2.20	3.042 (4)	156
N1–H2...O5 ⁱⁱ	0.90	2.25	3.013 (3)	143
N2–H5...O3	0.90	2.43	3.095 (4)	131
N2–H4...O7	0.90	2.30	3.141 (4)	155
N3–H7...O8 ⁱⁱⁱ	0.90	2.67	3.307 (5)	128
N3–H6...O8 ^{iv}	0.90	2.61	3.379 (6)	144
N4–H9...O3	0.90	2.45	3.106 (3)	130
N5–H10...O5 ⁱⁱ	0.90	2.42	3.154 (4)	139
N5–H11...O6 ^v	0.90	2.32	3.106 (4)	147

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

H atoms bonded to C and N atoms were placed at calculated positions (C–H = 0.97 Å and N–H = 0.90 Å) and refined as riding with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C,N})$. The H atom of the carboxyl group was found in a difference Fourier map and refined with restrained geometrical parameters [O–H = 0.82 (2) Å and $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$]. H atoms of the water molecule were also found in a difference Fourier map and refined with restrained geometrical parameters [O–H = 0.85 (2) Å, H···H = 1.38 (2) Å and $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$].

Data collection: *WinAFC* (Rigaku/MSK, 2004); cell refinement: *WinAFC*; data reduction: *CrystalStructure* (Rigaku/MSK, 2004); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

TA expresses his special thanks for the center of excellence (21COE) program 'Creation of Integrated EcoChemistry of Osaka University'.

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