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Key indicators

Single-crystal X-ray study
 T = 296 K
 Mean $\sigma(C-C)$ = 0.014 Å
 Disorder in main residue
 R factor = 0.052
 wR factor = 0.154
 Data-to-parameter ratio = 10.3

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

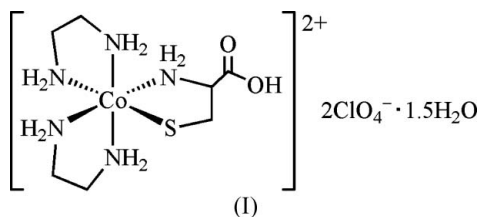
Λ_L -(L-Cysteinato- κ^2N,S)bis(ethylenediamine- κ^2N,N')cobalt(III) bis(perchlorate) sesquihydrate

In the crystal structure of the title compound, $[Co(C_3H_6NO_2S)(C_2H_8N_2)_2](ClO_4)_2 \cdot 1.5H_2O$, each Co^{III} atom is situated in a slightly distorted octahedral geometry, coordinated by one L-cysteinate and two ethylenediamine ligands. The compound has a non-coordinated COOH group, which adopts an equatorial orientation. The asymmetric unit contains two cations, four anions, and three water molecules.

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Comment

Freeman *et al.* (1978) prepared two isomers of the bis(ethylenediamine)cobalt(III) complex with L-cysteinate (L-cys), Δ_L - and Λ_L - $[Co(L-cys-N,S)(en)_2](ClO_4)$, which were converted to the protonated species, Δ_L - and Λ_L - $[Co(L-Hcys-N,S)(en)_2](ClO_4)_2$, respectively, by treatment with aqueous $HClO_4$. While the crystal structures of Δ_L - and Λ_L - $[Co(L-cys-N,S)(en)_2](ClO_4)$ were determined by X-ray crystallography, neither of Δ_L - and Λ_L - $[Co(L-Hcys-N,S)(en)_2](ClO_4)_2$ has been structurally characterized to date. During the course of our synthetic investigation of polynuclear complexes with Λ_L - $[Co(L-cys-N,S)(en)_2]^+$ units (Konno, 2004; Aridomi *et al.*, 2005), we obtained single crystals of Λ_L - $[Co(L-Hcys-N,S)(en)_2](ClO_4)_2 \cdot 1.5H_2O$, (I). We report here the crystal structure of (I), which is compared with the structure of Λ_L - $[Co(L-cys-N,S)(en)_2](ClO_4)$.



The asymmetric unit of (I) contains two crystallographically independent complex cations besides four ClO_4^- anions and three water molecules. The number of ClO_4^- anions implies that the complex cation of (I) is divalent. Each Co^{III} atom is coordinated by a bidentate-*N,S* L-Hcys and two bidentate-*N,N'* en ligands in a slightly distorted octahedral geometry (Fig. 1). The $Co-N_{trans(S)}$ bond distances [2.046 (8) and 2.019 (7) Å] are appreciably longer than the $Co-N_{cis(S)}$ distances [1.950 (8)–1.983 (8) Å], which is ascribed to the *trans* influence of the thiolate S donor (Elder *et al.*, 1973; Dickman *et al.*, 1980). The $Co-S$ distances in (I) [2.241 (3) and 2.241 (3) Å] are similar to those in Λ_L - $[Co(L-cys-N,S)(en)_2](ClO_4)$ [2.234 (1) Å] and $[Co(aet-N,S)(en)_2](NO_3)_2$ [aet = 2-aminoethanethiolate; 2.2494 (8) Å; Konno *et al.*, 2001]. The non-coordinated carboxyl group of the L-Hcys ligand in (I) is in a

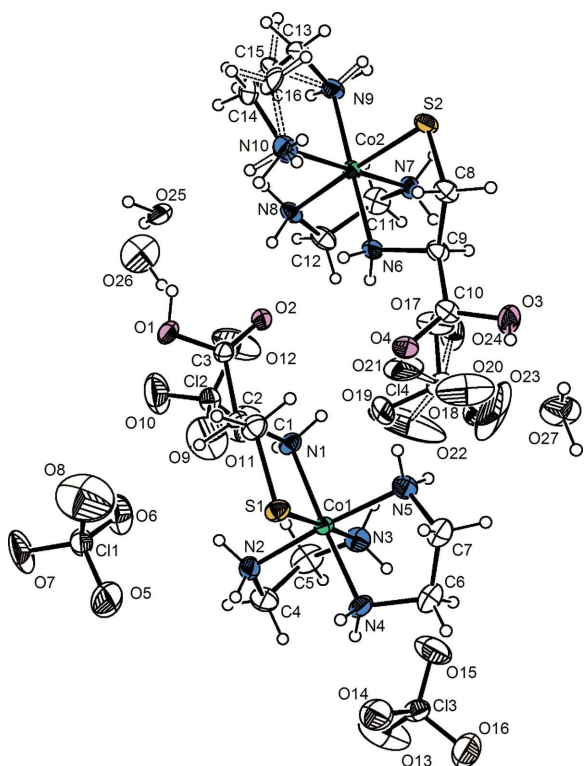


Figure 1
The molecular structure of (I), showing the atom-numbering scheme and 30% probability displacement ellipsoids. All disorder components are shown.

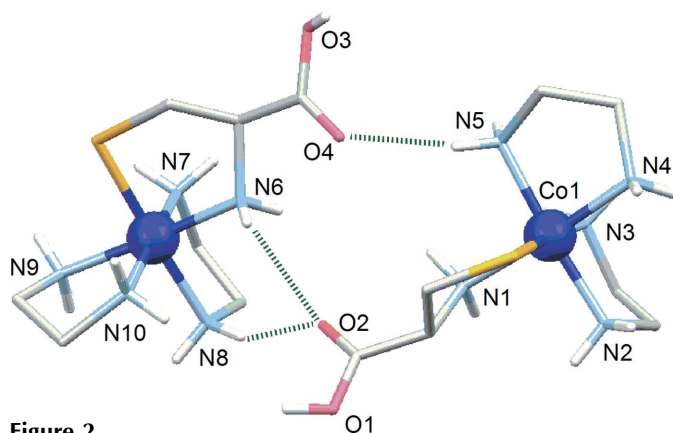


Figure 2
A view of the two independent complex cations of (I), showing N–H...O hydrogen bonds (dashed lines) between them. H atoms bonded to C atoms have been omitted for clarity.

protonated form, which is compatible with the asymmetric C–O bond distances (Table 1). The L-Hcys *N,S*-chelate ring in (I) has a λ conformation such that the COOH group adopts an equatorial orientation. This is in contrast to the structure of Λ_L -[Co(L-cys-*N,S*)(en)₂](ClO₄), in which the L-cys *N,S*-chelate ring has a δ conformation with the axially orientated COO[−] group (Freeman *et al.*, 1978). It is considered that the intramolecular hydrogen bonding between the COO[−] group and the adjacent en amine group in Λ_L -[Co(L-cys-*N,S*)(en)₂](ClO₄) is significantly weakened by the protonation, which allows the COOH group to adopt the preferable equatorial orientation in (I).

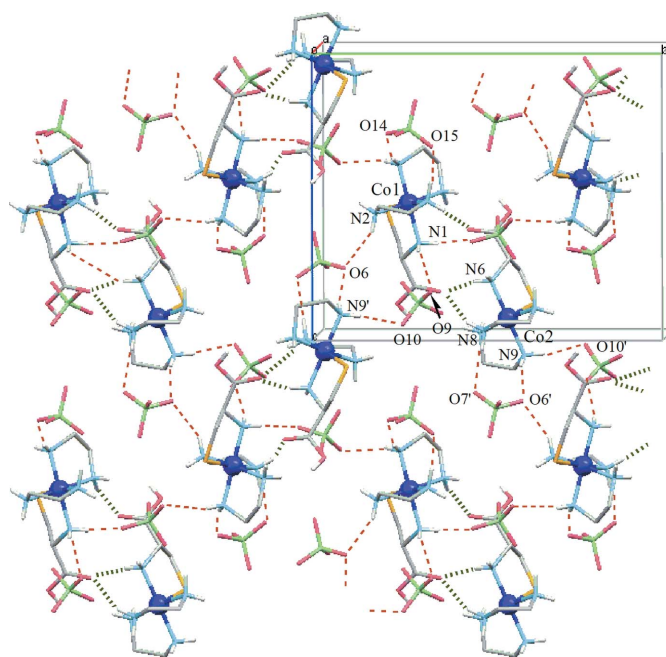


Figure 3
A view of the three-dimensional network through the N–H...OCIO₃ hydrogen bonds (dashed lines). H atoms bonded to C atoms, water molecules and the components of disordered ClO₄[−] anions (O21–O24) have been omitted for clarity.

It is interesting to note that en amine groups of a complex cation in (I) are hydrogen bonded with a COOH group of the neighboring cation to form a cyclic dimeric unit (Fig. 2 and Table 2). The dimer units are linked by ClO₄[−] anions through several hydrogen bonds, generating a three-dimensional network structure (Fig. 3 and Table 2).

Experimental

To a solution containing Λ_L -[Co(L-cys-*N,S*)(en)₂](ClO₄) (0.32 g, 0.80 mmol) in water (20 ml) were added KMnO₄ (0.03 g, 0.10 mmol) and 1 M aqueous H₂SO₄ (2.0 ml). The mixture was stirred at room temperature for 2 h. To the brown reaction solution was added Mn(ClO₄)₂·6H₂O (1.8 g, 5.0 mmol), and the resulting mixture was kept at room temperature for 3 d. The resulting dark-brown plate-shaped crystals of (I) were collected by filtration.

Crystal data

[Co(C ₃ H ₆ NO ₂ S)(C ₂ H ₈ N ₂) ₂]- (ClO ₄) ₂ ·1.5H ₂ O	$V = 1976.5 (13) \text{ \AA}^3$
$M_r = 525.22$	$Z = 4$
Monoclinic, $P2_1$	$D_x = 1.765 \text{ Mg m}^{-3}$
$a = 8.297 (5) \text{ \AA}$	Mo $K\alpha$ radiation
$b = 17.069 (3) \text{ \AA}$	$\mu = 1.31 \text{ mm}^{-1}$
$c = 13.957 (3) \text{ \AA}$	$T = 296 (2) \text{ K}$
$\beta = 90.82 (3)^\circ$	Plate, brown
	$0.40 \times 0.20 \times 0.05 \text{ mm}$

Data collection

Rigaku AFC-5R diffractometer	3031 reflections with $I > 2\sigma(I)$
ω - 2θ scans	$R_{\text{int}} = 0.039$
Absorption correction: ψ scan (North <i>et al.</i> , 1968)	$\theta_{\text{max}} = 30.0^\circ$
$T_{\text{min}} = 0.623$, $T_{\text{max}} = 0.938$	3 standard reflections
6307 measured reflections	every 150 reflections
5943 independent reflections	intensity decay: 5.0%

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.065P)^2 + 0.3906P]$
$R[F^2 > 2\sigma(F^2)] = 0.052$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.154$	$(\Delta/\sigma)_{\max} = 0.001$
$S = 1.02$	$\Delta\rho_{\max} = 0.53 \text{ e } \text{\AA}^{-3}$
5943 reflections	$\Delta\rho_{\min} = -0.81 \text{ e } \text{\AA}^{-3}$
577 parameters	Absolute structure: Flack (1983), no Friedel pairs
H atoms treated by a mixture of independent and constrained refinement	Flack parameter: -0.02 (3)

Table 1
Selected geometric parameters (\AA , $^\circ$).

Co1—S1	2.241 (3)	Co2—N7	1.977 (7)
Co1—N1	1.974 (7)	Co2—N8	2.019 (7)
Co1—N2	1.950 (8)	Co2—N9	1.980 (7)
Co1—N3	2.046 (8)	Co2—N10	1.972 (9)
Co1—N4	1.973 (7)	O1—C3	1.308 (10)
Co1—N5	1.983 (8)	O2—C3	1.220 (11)
Co2—S2	2.241 (3)	O3—C10	1.312 (11)
Co2—N6	1.979 (7)	O4—C10	1.201 (11)
S1—Co1—N3	176.3 (3)	S2—Co2—N8	177.1 (2)
N1—Co1—N4	174.9 (4)	N6—Co2—N9	175.2 (4)
N2—Co1—N5	175.5 (3)	N7—Co2—N10	174.5 (4)

Table 2
Hydrogen-bond geometry (\AA , $^\circ$).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N6—H13 \cdots O2	0.90	2.43	2.843 (10)	108
N8—H17 \cdots O2	0.90	2.10	2.947 (9)	157
N5—H12 \cdots O4	0.90	2.21	3.067 (11)	160
N1—H4 \cdots O9	0.90	2.21	3.030 (13)	151
N2—H6 \cdots O6	0.90	2.26	3.086 (13)	152
N3—H8 \cdots O15	0.90	2.23	3.061 (13)	154
N4—H10 \cdots O14	0.90	2.19	3.045 (12)	159
N8—H18 \cdots O7 ⁱ	0.90	2.20	3.084 (12)	167
N9—H20 \cdots O6 ⁱ	0.90	2.28	3.135 (13)	159
N9—H19 \cdots O10 ⁱ	0.90	2.20	3.059 (15)	160
N10—H25 \cdots O25	0.90	2.17	3.064 (12)	172
O1—H1 \cdots O25	0.89 (9)	1.77 (8)	2.630 (9)	162 (11)
O3—H2 \cdots O27	0.82 (11)	1.98 (10)	2.673 (10)	141 (12)
O25—H54 \cdots O26	0.85 (5)	1.87 (4)	2.696 (12)	165 (9)

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

H atoms bonded to C and N atoms were placed at calculated positions [$C-H = 0.97$ (methylene) and 0.98 (methine) \AA , and $N-$

$H = 0.90 \text{\AA}$] and refined as riding with $U_{\text{iso}}(H) = 1.2U_{\text{eq}}(C,N)$. H atoms of the carboxyl groups were located in a difference Fourier map and their positional parameters were refined with $U_{\text{iso}}(H) = 1.5U_{\text{eq}}(O)$ [$O-H = 0.82$ (11) and 0.89 (9) \AA]. H atoms of water molecules were also located in a difference Fourier map and were refined with restrained geometrical parameters [$O-H = 0.85$ (3) \AA , $H\cdots H = 1.38$ (4) \AA and $U_{\text{iso}}(H) = 1.5U_{\text{eq}}(O)$]. One en chelate ring is disordered over two positions (C13/C14 and C15/C16), which were refined with site occupancies of 0.66 (4) and 0.34 (4). One perchlorate anion is disordered over two positions (O17–O20 and O21–O24) and was refined with restrained geometrical parameters [$Cl-O = 1.40$ (1) \AA and $O-O = 2.29$ (1) \AA] and site occupancies of 0.5.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1992); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *CrystalStructure* (Rigaku/MS, 2004); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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