

(2-Aminoethanethiolato-*N,S*)bis-(ethylenediamine-*N,N'*)cobalt(III) dinitrate

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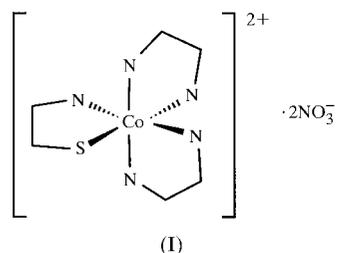
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In the title compound, $[\text{Co}(\text{C}_2\text{H}_6\text{NS})(\text{C}_2\text{H}_8\text{N}_2)_2](\text{NO}_3)_2$, the Co^{III} atom has a slightly distorted octahedral geometry, coordinated by one 2-aminoethanethiolate and two ethylenediamine ligands. The three five-membered chelate rings adopt a *gauche* conformation with the unfavoured (*lel*)₂(*ob*) form, which is ascribed to hydrogen bonds between the amine groups in the complex cation and the nitrate counter-anions [$\text{N}\cdots\text{O}$ 2.900 (3)–3.378 (3) Å].

Comment

It is recognized that mononuclear cobalt(III) complexes with 2-aminoethanethiolate (aet) can function as effective S-donating ligands toward a variety of metal ions to form S-bridged polynuclear complexes (Heeg *et al.*, 1980; Konno *et al.*, 1998, 1999). Our recent studies have shown that the structures of these polynuclear complexes can be made to vary by changes in the counter-anions (Tokuda *et al.*, 2000; Konno *et al.*, 2000). In order to elucidate this role of the counter-anions in the control of S-bridged polynuclear structures, it is desirable to investigate the crystal structures of mononuclear aet complexes by changing the counter-anions. Thus, we prepared single crystals of the title complex, $[\text{Co}(\text{aet})(\text{en})_2](\text{NO}_3)_2$ (I), and its structure is herein compared with the known structure of $[\text{Co}(\text{aet})(\text{en})_2](\text{SCN})_2$ (Elder *et al.*, 1973).



The X-ray structural analysis of (I) confirmed the presence of a divalent complex cation, $[\text{Co}(\text{aet})(\text{en})_2]^{2+}$, and two nitrate anions. The space group $P2_1/n$ indicates that the crystal

contains a racemic pair (Δ and Λ) of the chiral complex cation. In the cation of (I), the Co atom exhibits a slightly distorted octahedral geometry, coordinated by one S and five N atoms from one aet and two en ligands [*trans* N–Co–N 174.9 (1) and 176.9 (1)°, and *trans* N–Co–S 175.78 (7)°; Fig. 1]. The Co– $\text{N}_{\text{trans}(\text{S})}$ bond distance [Co–N5 2.022 (2) Å] is *ca* 0.05 Å longer than the four Co– $\text{N}_{\text{cis}(\text{S})}$ distances [1.958 (2)–1.976 (2) Å, average 1.967 (2) Å], which is associated with the *trans* influence of the thiolate S-donor atom (Elder *et al.*, 1973; Dickman *et al.*, 1980). A similar difference of 0.04 Å was observed for the *trans* influence in $[\text{Co}(\text{aet})(\text{en})_2](\text{SCN})_2$ (Elder *et al.*, 1973). However, the Co–S [2.2494 (8) Å] and Co– $\text{N}_{\text{trans}(\text{S})}$ distances in (I) are longer than those in $[\text{Co}(\text{aet})(\text{en})_2](\text{SCN})_2$ [Co–S 2.226 (2) Å, Co– $\text{N}_{\text{trans}(\text{S})}$ 2.001 (5) Å and average Co– $\text{N}_{\text{cis}(\text{S})}$ 1.960 (9) Å].

The aet and en chelate rings in (I) have a *gauche* confor-

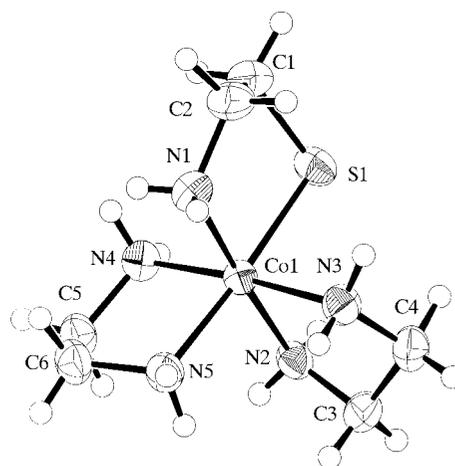


Figure 1

The ORTEP (Johnson, 1976) drawing of the cation of (I). Displacement ellipsoids are plotted at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

mation with the *lel*, *lel* and *ob* forms: λ , λ and δ for the Δ isomer, and δ , δ and λ for the Λ isomer. This is distinct from the (*lel*)₃ form found in $[\text{Co}(\text{aet})(\text{en})_2](\text{SCN})_2$ (Elder *et al.*, 1973). It has been postulated that the (*lel*)₃ form is the most stable for the isolated complex cation, but hydrogen bonds could lead to the formation of other, less favoured, forms (Hawkins, 1971). Thus, the (*lel*)₂(*ob*) form found in the cation of (I) can be ascribed to the hydrogen-bonding interactions with the nitrate anions (see below), taking into account the fact that only weak hydrogen bonds exist in $[\text{Co}(\text{aet})(\text{en})_2](\text{SCN})_2$ (Elder *et al.*, 1973).

All the amine H atoms of the aet and en ligands, except H5, are involved in hydrogen bonds with nitrate O atoms in the crystal [$\text{N}\cdots\text{O}$ 2.900 (3)–3.378 (3) Å]. Additionally, atoms H3 and H8 are hydrogen bonded to two O acceptors to form three-centre bonds (Table 2). All the nitrate O atoms participate in the hydrogen bonds, thus completing a three-dimensional hydrogen-bond network.

Experimental

The title complex was prepared by a method similar to that used for [Co(aet)(en)](ClO₄)₂ (Nosco & Deutsch, 1982). To a deaerated solution containing cobalt(II) nitrate hexahydrate (5.91 g, 20.3 mmol) in water (15 ml) was added a deaerated solution containing cystamine dihydrochloride (2.28 g, 10 mmol) and ethylenediamine (3.75 ml, 56 mmol) in water (30 ml). The mixture was stirred at room temperature for 30 min under a nitrogen atmosphere, followed by the addition of a saturated aqueous solution of NaNO₃ (70 ml). After the reaction, the mixture was allowed to stand in a refrigerator for 1 d. The resulting black crystals of (I) were collected by filtration and recrystallized from water by adding several drops of a saturated aqueous solution of NaNO₃ (yield 5.28 g, 82.1%).

Crystal data

[Co(C₂H₆NS)(C₂H₈N₂)₂](NO₃)₂
M_r = 379.28
 Monoclinic, *P*2₁/*n*
a = 9.509 (1) Å
b = 12.824 (1) Å
c = 12.635 (1) Å
 β = 99.780 (8)°
V = 1518.4 (3) Å³
Z = 4

D_x = 1.659 Mg m⁻³
 Mo *K*α radiation
 Cell parameters from 25 reflections
 θ = 14.5–15.0°
 μ = 1.306 mm⁻¹
T = 296 K
 Polyhedron, black
 0.35 × 0.25 × 0.18 mm

Data collection

Rigaku AFC-7S diffractometer
 $\omega/2\theta$ scans
 Absorption correction: ψ scan
 (North *et al.*, 1968)
 T_{\min} = 0.688, T_{\max} = 0.770
 3862 measured reflections
 3650 independent reflections
 2452 reflections with *I* > 2σ(*I*)

*R*_{int} = 0.017
 θ_{\max} = 27.5°
h = 0 → 12
k = 0 → 16
l = -16 → 16
 3 standard reflections
 every 150 reflections
 intensity decay: -0.56%

Refinement

Refinement on *F*
R = 0.031
wR = 0.041
S = 1.110
 2726 reflections
 266 parameters

H atoms treated by a mixture of independent and constrained refinement
 $w = 1/[\sigma^2(F_o) + 0.00038|F_o|^2]$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.30 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.29 \text{ e \AA}^{-3}$

Table 1

Selected geometric parameters (Å, °).

Co1—S1	2.2494 (8)	Co1—N3	1.976 (2)
Co1—N1	1.969 (3)	Co1—N4	1.963 (2)
Co1—N2	1.958 (2)	Co1—N5	2.022 (2)
S1—Co1—N1	87.85 (8)	N1—Co1—N5	90.1 (1)
S1—Co1—N2	89.97 (8)	N2—Co1—N3	85.2 (1)
S1—Co1—N3	90.57 (8)	N2—Co1—N4	90.3 (1)
S1—Co1—N4	91.90 (7)	N2—Co1—N5	92.2 (1)
S1—Co1—N5	175.78 (7)	N3—Co1—N4	174.9 (1)
N1—Co1—N2	176.9 (1)	N3—Co1—N5	93.2 (1)
N1—Co1—N3	92.6 (1)	N4—Co1—N5	84.5 (1)
N1—Co1—N4	92.0 (1)		
S1—C1—C2—N1	-52.7 (3)	N4—C5—C6—N5	-50.1 (3)
N2—C3—C4—N3	54.1 (3)		

Table 2

Hydrogen-bonding 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>
N1—H1...O23 ⁱⁱⁱ	0.84 (3)	2.21 (3)	3.000 (4)	156 (3)
N1—H2...O13	0.81 (3)	2.17 (3)	2.964 (3)	163 (3)
N2—H3...O11 ⁱ	0.81 (2)	2.15 (2)	2.900 (3)	154 (2)
N2—H3...O11 ⁱⁱ	0.81 (2)	2.65 (2)	3.130 (3)	119 (2)
N2—H4...O21 ⁱⁱ	0.89 (3)	2.25 (3)	3.089 (3)	157 (3)
N3—H6...O21	0.94 (3)	2.22 (3)	3.142 (3)	165 (3)
N4—H7...O22 ⁱⁱⁱ	0.91 (3)	2.08 (3)	2.914 (4)	152 (2)
N4—H8...O11 ⁱⁱ	0.87 (3)	2.42 (3)	3.088 (3)	134 (2)
N4—H8...O13 ⁱⁱ	0.87 (3)	2.33 (3)	3.189 (3)	172 (3)
N5—H9...O12 ⁱ	0.89 (3)	2.30 (3)	3.141 (3)	157 (2)
N5—H10...O13	0.90 (3)	2.61 (3)	3.378 (3)	143 (2)

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

H atoms bonded to C atoms were placed at calculated positions and refined with isotropic displacement parameters [*U*_{iso} = 1.2*U*_{eq} (C)] and a riding model. H atoms bonded to N atoms were refined freely.

Data collection: *MSC/AFD Diffractometer Control Software* (Molecular Structure Corporation, 1992); cell refinement: *MSC/AFD Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1995); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *TEXSAN*; software used to prepare material for publication: *TEXSAN*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1442). Services for accessing these data are described at the back of the journal.

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