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A Stable Sulfonato–Cobalt(III) Complex: Δ-[Co{OS(O)$_2$CH$_2$CH$_2$NH$_2$-*N*,*O*}(en)$_2$]-(ClO$_4$)$_2$

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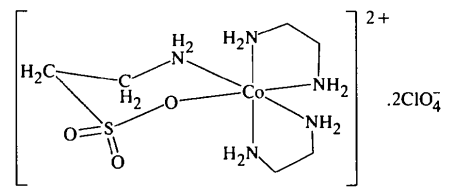
Abstract

A stable sulfonato complex, (2-aminoethanesulfonato-*N*,*O*)bis(ethylenediamine-*N*,*N*′)cobalt(III) perchlorate, [Co(C$_2$H$_6$NO$_3$S)(C$_2$H$_8$N$_2$)$_2$](ClO$_4$)$_2$, was prepared by oxidation of [Co{OS(O)CH$_2$CH$_2$NH$_2$-*N*,*O*}(en)$_2$]$^{2+}$ (en = NH$_2$CH$_2$CH$_2$NH$_2$) in acid media. This sulfonato complex was resolved by SP-Sephadex column chromatography and the absolute configuration of the slower eluted $(-)_{589}$-isomer was determined by X-ray analysis to be Δ.

Comment

Generally, monodentate sulfonato–cobalt(III) complexes are aquated easily and the coordinating ability of a monodentate sulfonate ligand is usually weak. For example, the half-life of aquation of [Co{OS(O)$_2$CH$_3$}-(NH$_3$)$_5$]$^{2+}$ is *ca* 58 min at 298 K (Jackson, Jurisson & O'Leary, 1993). In the present work, we considered that a cobalt(III) complex involving the 2-aminoethanesulfonate *N*,*O*-chelate may be stable enough to be isolated. Accordingly, we actually prepared the first stable sulfonato–cobalt(III) complex (Murata *et al.*, 1996). This sulfonato complex was resolved by SP-Sephadex column chromatography, and the slower eluted complex, $(-)_{589}$-[Co{OS(O)$_2$CH$_2$CH$_2$NH$_2$-*N*,*O*}(en)$_2$]$^{2+}$, was assigned the Δ configuration on the basis of the circular dichroism (CD) sign at *ca* 535 nm in the first spin-allowed *d–d* band region. We carried out the X-ray analysis of the title complex, (I), in order to confirm this assignment.



(I)

A perspective view of the complex cation obtained from the eluate containing the slower eluted isomer, $(-)_{589}$-Δ-[Co{OS(O)$_2$CH$_2$CH$_2$NH$_2$-*N*,*O*}(en)$_2$]$^{2+}$, is shown in Fig. 1. The coordination geometry around the Co atom is approximately octahedral. The sulfonate ligand coordinates to the Co atom with *N*,*O*-chelation. The S—O1 [1.482 (2) Å] bond length is longer than both S—O2 [1.446 (2) Å] and S—O3 [1.439 (2) Å]. The sulfonate O atom in the complex does not induce a significant *trans* influence. To our knowledge, this is the first example of a stable sulfonato–cobalt(III) complex.

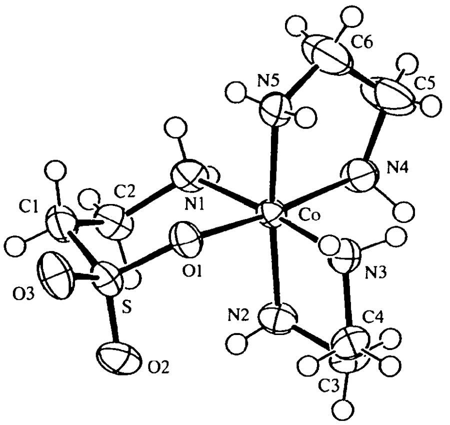


Fig. 1. An *ORTEP*II (Johnson, 1976) drawing for the complex cation, $(-)_{589}$-Δ-[Co{OS(O)$_2$CH$_2$CH$_2$NH$_2$}(en)$_2$]$^{2+}$, with displacement ellipsoids at the 50% probability level. H atoms are represented by circles (representing B = 1.0 Å^2).

Experimental

[Caution: perchlorate salts of metal complexes can be explosive and should be handled with care.] A mixture of 30% H$_2$O$_2$ (10 g, 88 mmol) and 60% HClO$_4$ (10 g) was added dropwise to a dimethyl sulfoxide solution (15 ml) of [Co{OS(O)CH$_2$CH$_2$NH$_2$-*N*,*O*}(en)$_2$](ClO$_4$)$_2$ (1 g, 2 mmol) (Mäcke, Houlding & Adamson, 1980) with stirring and at a temperature below 278 K. The color of the solution changed from red to orange–red during the addition. The mixture was stirred for 30 min and left overnight in a refrigerator. The solution was diluted with water (1000 ml), poured onto a column (φ 3 × 5 cm) of SP-Sephadex C-25, and the adsorbed complex was eluted with 0.3 *M* $NaClO_4$. The column showed a single orange–red band. The eluate containing the orange–red band was collected and evaporated to *ca* 5 ml under reduced pressure to yield an orange–red precipitate which was recrystallized from water. Analysis found: C 14.03, H 4.86, N 13.59, S 6.14%. Calculated for $C_6H_{24}CoCl_2N_5O_{12}S$ $\{[Co\{OS(O)_2CH_2CH_2NH_2\}(en)_2](ClO_4)_2.H_2O\}$: C 13.85, H 4.65, N 13.46, S 6.16%. This complex (0.1 g, 0.2 mmol) was charged on top of an SP-Sephadex C-25 column (φ 3 × 90 cm). Upon elution with 0.1 *M* $Na_2[Sb_2\{(+)\text{-tartrate}\}_2]$, two bands were developed. Each of the fractions was diluted with water, poured again onto a small column (φ 3 × 7 cm) of SP-Sephadex C-25, and the adsorbed complex was eluted with 0.3 *M* $NaClO_4$. The eluate was concentrated to dryness in a desiccator over P_4O_{10}. Single crystals were obtained by recrystallization from water by adding ethanol, and a crystal from the slower eluted isomer was used for X-ray structure determination. Analysis found for the faster eluted isomer: C 14.61, H 4.55, N 13.43, S 5.78%. Analysis found for the slower eluted isomer: C 14.31, H 4.62, N 13.19, S 6.99%. Calculated for $C_6H_{24}CoCl_2N_5O_{11}S$ $\{[Co\{OS(O)_2CH_2CH_2NH_2\}(en)_2](ClO_4)_2\}$: C 14.35, H 4.42, N 13.94, S 6.39%.

Crystal data

$[Co(C_2H_6NO_3S)(C_2H_8N_2)_2](ClO_4)_2$
$M_r = 502.17$
Monoclinic
$P2_1$
$a = 9.075\ (1)$ Å
$b = 11.282\ (2)$ Å
$c = 9.191\ (1)$ Å
$\beta = 108.37\ (1)°$
$V = 893.1\ (2)$ Å^3
$Z = 2$
$D_x = 1.867$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 10–11°$
$\mu = 1.441$ mm^{-1}
$T = 295$ K
Plate
0.50 × 0.50 × 0.05 mm
Orange–red

Data collection

Rigaku AFC-5*R* diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scan (*TEXSAN*; Molecular Structure Corporation, 1985)
$T_{min} = 0.549$, $T_{max} = 0.930$
4343 measured reflections
4098 independent reflections

3740 reflections with $I > 3\sigma(I)$
$R_{int} = 0.015$
$\theta_{max} = 27.5°$
$h = -11 \rightarrow 11$
$k = -14 \rightarrow 14$
$l = 0 \rightarrow 11$
3 standard reflections every 97 reflections intensity decay: none

Refinement

Refinement on *F*
$R = 0.029$
$wR = 0.028$
$S = 1.51$
3740 reflections
306 parameters
H atoms: see below
$w = 1/\sigma^2(F)$

$(\Delta/\sigma)_{max} = 0.10$
$\Delta\rho_{max} = 0.46$ e Å^{-3}
$\Delta\rho_{min} = -0.33$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

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

Co—O1	1.944 (2)	S—O1	1.482 (2)
Co—N1	1.978 (3)	S—O2	1.446 (2)
Co—N2	1.965 (2)	S—O3	1.439 (2)
Co—N3	1.952 (3)	S—C1	1.766 (4)
Co—N4	1.952 (3)	N1—C2	1.492 (4)
Co—N5	1.943 (2)	C1—C2	1.491 (5)
O1—Co—N1	91.1 (1)	O2—S—O3	114.1 (2)
Co—O1—S	128.5 (1)	O1—S—C1	104.6 (2)
Co—N1—C2	118.7 (2)	S—C1—C2	111.6 (3)
O1—S—O2	110.7 (1)	N1—C2—C1	112.5 (3)
O1—S—O3	110.6 (1)		

The absolute configuration was determined using the anomalous dispersion effect. When the Λ configuration was assumed, the refinement resulted in $R = 0.045$ and $wR = 0.048$, which were significantly larger than the values of $R = 0.029$ and $wR = 0.028$ for the Δ configuration. Furthermore, the inequality relationship was checked for 21 pairs of reflections with $\{|F_o(hkl)| - |F_o(h\bar{k}l)|\}$ larger than $10\sigma(F_o)$. The relationship was held without exception for the Δ configuration. Methylenic H atoms of one of the ethylenediamine groups (H91, H92, H101 and H102) were fixed at ideal positions, each with an isotropic displacement parameter of 1.2 times that of the parent C atom. All other H-atom parameters were refined.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1990). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1985). Program(s) used to solve structure: *MITHRIL* (Gilmore, 1984). Program(s) used to refine structure: *TEXSAN*. Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *TEXSAN*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: OA1028). Services for accessing these data are described at the back of the journal.

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