C(37)—Os(2)—B(3)	119.6 (4)	C(31)—P(2)—Os(2)	110.7 (3)
P(1)—Os(2)—B(3)	91.2 (2)	C(25)—P(2)—Os(2)	120.6 (3)
P(2)—Os(2)—B(3)	96.5 (2)	C(19)—P(2)—Os(2)	113.4 (3)

Table 3. *A comparison of selected distances (Å) and angles (°) for* $[(CO)H(PPh_3)_2OsB_3H_8]$ *and* $[(CO)H(PPh_3)_2RuB_3H_8]$

	M = Os	*M* = Ru
B(1)—B(3)	1.75 (2)	1.738 (9)
B(1)—B(4)	1.783 (14)	1.802 (10)
B(3)—B(4)	1.827 (13)	1.808 (9)
M(2)—B(1)	2.441 (8)	2.439 (6)
M(2)—B(3)	2.437 (10)	2.484 (6)
P(1)—*M*(2)—P(2)	172.21 (7)	161.8 (1)
B(1)—B(4)—B(3)	58.0 (5)	57.6 (3)
B(1)—*M*(2)—B(3)	42.1 (3)	41.3 (2)
M(2)—B(1)—B(3)/B(1)—B(3)—B(4)	123.5	124.4

The structure was solved by the Patterson method. Full-matrix least-squares refinement was carried out by minimizing $\Sigma w(F_o^2 - F_c^2)^2$. The non-H atoms were refined anisotropically to convergence. All H atoms connected to B atoms were located from the difference Fourier synthesis and were included in the final refinement. The positional parameters of the hydride H(2) were refined. The phenyl H atoms were calculated using a riding model (*AFIX*43 in *SHELXL*93; Sheldrick, 1993*b*). All H atoms were assigned fixed isotropic displacement parameters of 0.08 Å^2. Attempts were made to resolve the disorder resulting in larger displacement ellipsoids for C(33)–C(36), but the disorder models could not be refined successfully.

Data reduction and structure solution were carried out using the *SHELXTL-Plus* (VMS) software package (Sheldrick, 1991). Least-squares refinement was achieved by using *SHELXL*93.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: SZ1031). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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trans(S)-(*S*-Methyl-D-penicillaminato)(D-penicillaminesulfinato)cobalt(III) Monohydrate

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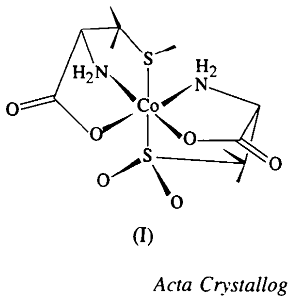
Abstract

The title complex {[3-methylthio-D-valinato(1−)]-[3-sulfino-D-valinato(2−)]cobalt(III) monohydrate, $[Co(C_5H_9NO_4S)(C_6H_{12}NO_2S)].H_2O$}, containing thioether and sulfinato moieties, has two different types of donor S atoms situated in *trans* positions to each other. The Co atom is octahedrally surrounded by the N, O and S atoms of each tridentate ligand. The complex molecule has been resolved spontaneously by crystallization. The absolute configuration of the coordinated S atom in the thioether ligand is *R*(S). The lengthening of the Co—S distances [2.376 (3) and 2.366 (3) Å] for the thioether ligand depends on the strong *trans* influence of the sulfinato group.

Comment

In the course of our investigations on the stereochemical and spectrochemical properties of Co^{III} complexes with sulfur-containing ligands, we have recently prepared the title complex, (I). It is difficult to prepare stably the *trans*(S) isomer of a Co^{III} complex with two thiolate and/or sulfinate groups because of the *trans* influence of these donor S atoms. Moreover, reports on the investigation of Co^{III} complexes containing two different types of donor S atoms are scarce. In order to elucidate the geometry adopted by (I), we have determined its structure crystallographically.



(I)

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There are two crystallographically independent molecules in the asymmetric unit, though their shapes and sizes are remarkably similar. Fig. 1 clearly shows that the neutral complex (I) adopts a six-coordinate structure and the coordination geometry around the Co atom is approximately octahedral. Both the *S*-methyl-D-penicillaminate (D-smp) and the D-penicillaminesulfinate (D-psi) coordinate facially to the Co atom as tridentate-*N*,*O*,*S* ligands. Of three possible geometric structures, *trans*(N), *trans*(O) and *trans*(S), (I) takes the *trans*(S) form. The absorption spectrum of (I) shows a characteristic sulfur-to-cobalt charge-transfer (SMCT) band at *ca* 29 × 10^3 cm^{-1}. Similar intense SMCT bands have been observed in the absorption spectra of *trans*(S)-$[Co(D\text{-}smp)_2]^+$ (Okamoto, Wakayama, Einaga, Yamada & Hidaka, 1983), *trans*(S)-$[Co(L\text{-}smc)_2]^+$ (L-smc = *S*-methyl-L-cysteinato) (Meester & Hodgson, 1976; Okamoto, Wakayama, Einaga, Yamada & Hidaka, 1983), and *trans*(S)-$[Co(aet)_2(en)]^+$ (aet = 2-aminoethanethiolato) (Yonemura, Okamoto, Ama, Kawaguchi & Yasui, 1993). The prochiral thioether group in the D-smp ligand can take the *R*(S) or *S*(S) configuration by coordination. Since two resonance peaks (δ = 2.22 and 2.34 p.p.m.) of the same intensity due to the *S*-methyl protons in the D-smp ligand were observed in the ^{1}H NMR spectrum, it is considered that both the *R*(S) and *S*(S) isomers are present in an aqueous solution. From a solution of (I), the spontaneously resolved single crystals were obtained and the absolute configuration of the chiral S atom in the D-smp ligand is estimated to be *R*(S).

The Co—S distances [2.376 (3) for Co1 and 2.366 (3) Å for Co2] for the thioether ligand are significantly longer than those [2.180 (3) for Co1 and 2.185 (2) Å for Co2] for the sulfinate (Table 2). The Co—S distances for the sulfinate ligand are similar to those in $[Co(aesi)(en)_2]^{2+}$ (aesi = 2-aminoethanesulfinato) [2.191 (2) Å] (Lange, Libson, Deutsch & Elder, 1976). In contrast, the Co—S distances for the thioether ligand are much longer (> 0.1 Å) than those in $[Co(mea)(en)_2]^{3+}$ (mea = *S*-methyl-2-aminoethanethiolato) [2.267 (10) Å] (Elder, Kennard, Payne & Deutsch, 1978) and $[Co(L\text{-}smc)_2]^+$ [2.270 (2) and 2.273 (2) Å], which contain the thioether-type S atoms. These indicate that the lengthening of the Co—S distances for the thioether ligand in the present complex depends on the strong *trans* influence of the sulfinato group.

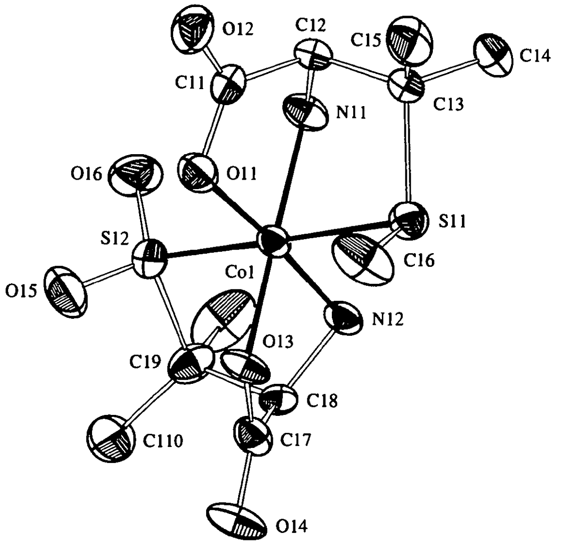

Fig. 1. Molecular structure of *trans*(S)-[Co(D-smp)(D-psi)] (50% probability displacement ellipsoids) with the atom-numbering scheme. H atoms are omitted for clarity.

Experimental

A suspension containing 7.65 g of Λ_{DDD}-*fac*-$Na_3[Co(D\text{-}pen\text{-}N,S)_3]$ (Okamoto, Yonemura, Konno & Hidaka, 1992) in 50 cm^3 of *N*,*N*-dimethylformamide (DMF) and 15.6 g of methyl iodide in 25 cm^3 of DMF was adjusted to pH *ca* 10 using a 0.3 mol dm^{-3} NaOH solution and stirred at room temperature for 15 h. After standing in a refrigerator for one day, excess methyl iodide in the diluted solution was extracted with chloroform. The aqueous phase was concentrated to a small volume and then was passed through columns (3 × 35 cm) of SP-Sephadex C-25 (Na^+ form) and QAE-Sephadex A-25 (Cl^- form) by eluting water. The orange band was eluted and the eluate was concentrated to a small volume. The solution was kept in a refrigerator overnight. Orange crystals appeared and were collected by filtration.

Crystal data

$[Co(C_5H_9NO_4S)(C_6H_{12}NO_2S)].H_2O$
M_r = 418.38
Monoclinic
$P2_1$
a = 11.653 (2) Å
b = 12.045 (1) Å
c = 12.594 (2) Å
β = 105.156 (8)°
V = 1706.2 (4) Å^3
Z = 4
D_x = 1.63 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 25 reflections
θ = 20–28°
μ = 1.27 mm^{-1}
T = 296 K
Prism
0.50 × 0.30 × 0.25 mm
Orange

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
5396 measured reflections
5186 independent reflections
4973 observed reflections [$F > 3\sigma(F)$]

θ_{max} = 30°
$h = 0 \rightarrow 16$
$k = 0 \rightarrow 16$
$l = -17 \rightarrow 17$
3 standard reflections frequency: 120 min intensity decay: 2.6%

Refinement

Refinement on F
R = 0.071
wR = 0.084

$(\Delta/\sigma)_{max}$ = 0.03
$\Delta\rho_{max}$ = 2.21 e Å^{-3}
$\Delta\rho_{min}$ = −0.37 e Å^{-3}

$S = 2.39$
4973 reflections
414 parameters
H-atom parameters not refined
$w = 4F_o^2/\sigma^2(F_o)$

Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)*

$$B_{eq} = (8\pi^2/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
Co1	0.6795 (1)	0.419	0.12506 (9)	1.78 (2)
S11	0.7665 (2)	0.4343 (2)	−0.0252 (2)	2.61 (4)
S12	0.6007 (2)	0.4065 (2)	0.2637 (2)	2.57 (4)
O11	0.8306 (6)	0.3764 (6)	0.2185 (5)	2.6 (1)
O12	1.0148 (6)	0.4419 (8)	0.2762 (6)	3.4 (2)
O13	0.6277 (6)	0.2690 (5)	0.0886 (6)	2.6 (1)
O14	0.4603 (7)	0.1713 (6)	0.0364 (7)	3.5 (2)
O15	0.6330 (8)	0.3042 (8)	0.3260 (7)	4.1 (2)
O16	0.6145 (8)	0.5078 (8)	0.3275 (7)	4.3 (2)
N11	0.7382 (7)	0.5694 (7)	0.1586 (7)	2.5 (2)
N12	0.5220 (7)	0.4519 (6)	0.0343 (6)	2.1 (1)
C11	0.9111 (9)	0.4527 (9)	0.2243 (7)	2.5 (2)
C12	0.8682 (8)	0.5582 (8)	0.1595 (8)	2.3 (2)
C13	0.8759 (9)	0.5431 (9)	0.0391 (8)	2.6 (2)
C14	0.834 (1)	0.648 (1)	−0.0277 (9)	3.5 (2)
C15	1.0035 (9)	0.513 (1)	0.0365 (9)	3.6 (2)
C16	0.848 (1)	0.302 (1)	−0.017 (1)	4.4 (2)
C17	0.5113 (9)	0.2594 (8)	0.0607 (8)	2.4 (2)
C18	0.4471 (7)	0.3677 (8)	0.0691 (6)	1.9 (1)
C19	0.4405 (8)	0.3912 (9)	0.1868 (8)	2.7 (2)
C110	0.382 (1)	0.298 (1)	0.237 (1)	4.5 (3)
C111	0.379 (1)	0.508 (1)	0.191 (1)	4.9 (3)
Co2	0.84196 (9)	0.8668 (1)	0.37470 (8)	1.38 (2)
S21	0.7117 (2)	0.8585 (2)	0.4905 (2)	1.94 (3)
S22	0.9694 (2)	0.8909 (2)	0.2766 (2)	1.72 (3)
O21	0.7185 (6)	0.8136 (6)	0.2546 (5)	2.3 (1)
O22	0.5304 (6)	0.8494 (8)	0.1706 (6)	3.4 (2)
O23	0.9033 (5)	0.7206 (5)	0.4116 (5)	2.0 (1)
O24	1.0691 (6)	0.6377 (6)	0.5066 (7)	3.2 (2)
O25	0.9655 (6)	0.8056 (7)	0.1931 (6)	3.0 (1)
O26	0.9686 (6)	1.0053 (6)	0.2377 (6)	2.5 (1)
N21	0.7663 (6)	1.0102 (6)	0.3288 (6)	1.9 (1)
N22	0.9738 (5)	0.9107 (6)	0.4974 (5)	1.6 (1)
C21	0.6252 (7)	0.8710 (9)	0.2350 (7)	2.2 (2)
C22	0.6372 (8)	0.9813 (9)	0.3024 (8)	2.3 (2)
C23	0.6045 (8)	0.9604 (9)	0.4116 (8)	2.4 (2)
C24	0.627 (1)	1.067 (1)	0.4821 (9)	3.7 (2)
C25	0.4741 (8)	0.925 (1)	0.392 (1)	4.2 (3)
C26	0.642 (1)	0.7232 (9)	0.462 (1)	4.1 (2)
C27	1.0126 (8)	0.7216 (8)	0.4712 (7)	2.1 (2)
C28	1.0699 (7)	0.8362 (7)	0.4870 (7)	1.8 (1)
C29	1.1118 (6)	0.8709 (8)	0.3875 (7)	1.9 (1)
C210	1.1889 (9)	0.7844 (9)	0.3505 (9)	2.9 (2)
C211	1.1775 (8)	0.9833 (8)	0.407 (1)	2.9 (2)
O1*W*	0.7320 (7)	0.0582 (7)	0.0899 (7)	3.6 (2)
O2*W*	0.100 (1)	0.221 (1)	0.292 (1)	8.3 (4)

Table 2. *Selected geometric parameters (Å, °)*

Co1—S11	2.376 (3)	Co2—S21	2.366 (3)
Co1—S12	2.180 (3)	Co2—S22	2.185 (2)
Co1—O11	1.913 (6)	Co2—O21	1.906 (6)
Co1—O13	1.918 (6)	Co2—O23	1.912 (6)
Co1—N11	1.948 (8)	Co2—N21	1.956 (7)
Co1—N12	1.934 (7)	Co2—N22	1.945 (6)
S11—Co1—S12	179.2 (1)	S21—Co2—S22	174.0 (1)
S11—Co1—N11	84.2 (3)	S21—Co2—N21	84.7 (3)
S12—Co1—O11	90.1 (2)	S22—Co2—O21	94.6 (2)
S12—Co1—N12	87.3 (3)	S22—Co2—N22	84.3 (2)
O11—Co1—N11	84.2 (3)	O21—Co2—N21	82.8 (3)
O11—Co1—N12	175.9 (3)	O21—Co2—N22	175.8 (3)
O13—Co1—N11	177.2 (4)	O23—Co2—N21	174.8 (3)
O13—Co1—N12	82.1 (3)	O23—Co2—N22	83.7 (3)

All non-H atoms were located by direct methods and difference Fourier synthesis. The structure was refined on F by full-matrix least-squares techniques. When the refinements were carried out by use of the set of the enantiomeric parameters of the R(S) configuration the residual values converged to $R = 0.073$ and $wR = 0.086$, respectively. This fact indicated that the R(S) configuration is probably the correct choice.

All calculations were performed using *MolEN* (Fair, 1990) on a VAX computer. Molecular graphics were obtained with *ORTEP*II (Johnson, 1976).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: PT1040). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Tetraaquabis(3,5-dinitrobenzoato-*O*)cobalt(II) Tetrahydrate

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Abstract

In the title compound, $[Co(C_7H_3N_2O_6)_2(H_2O)_4].4H_2O$, the coordination polyhedron around the Co atom is a slightly distorted octahedron involving one carboxy O atom from each 3,5-dinitrobenzoato ligand and the O atoms of four water molecules. The mean Co—O$_{water}$