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Cobaltoceniumsulfonate

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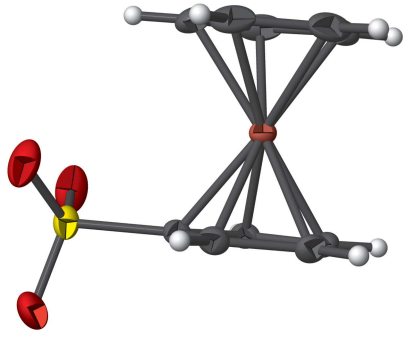
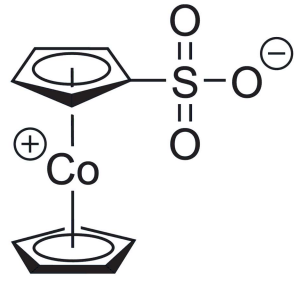
The title compound, $[Co(C_5H_5)(C_5H_4O_3S)]$, was synthesized by dediazoniation of cobaltoceniumdiazonium bis(hexafluoridophosphate) with CuCl and SO_2, crystallizing as yellow platelets. Structurally, a regular cobaltocenium sandwich moiety is observed containing coplanar cyclopentadienyl rings and displaying unexceptional carbon–cobalt [2.0230 (16)–2.0452 (14) Å] and carbon–carbon [1.410 (3)–1.431 (3) Å] bond distances. In this mesoionic molecule, the cationic cobaltoceniumyl part is connected to its anionic sulfonate part by a carbon–sulfur single bond of 1.7717 (15) Å.

3D view



Chemical scheme



Structure description

The title compound (Fig. 1) is the first and only sulfonic acid derivative in the compound class of cobaltocenium salts. As a result of the strongly electron-withdrawing cationic cobaltocenium moiety, the corresponding sulfonic acid is fully dissociated, thereby stabilizing the title compound as its zwitterionic cobaltoceniumsulfonate.

Structurally, a regular cobaltocenium sandwich moiety is observed containing coplanar cyclopentadienyl rings and displaying unexceptional carbon–cobalt [2.0230 (16)–2.0452 (14) Å] and carbon–carbon [1.410 (3)–1.431 (3) Å] bond distances. The structural properties of the sulfonate group are also unexceptional, showing a tetrahedral sulfonate functional group with sulfur–oxygen bond distances [1.4402 (12)–1.4499 (14) Å] and oxygen–sulfur–oxygen angles [113.04 (9)–114.09 (9)°] in line with expectations. In this mesoionic molecule, the cationic cobaltoceniumyl part is connected to its anionic sulfonate part by a carbon–sulfur single bond of 1.7717 (15) Å. The arrangement of molecular entities in the unit cell is shown in Fig. 2.

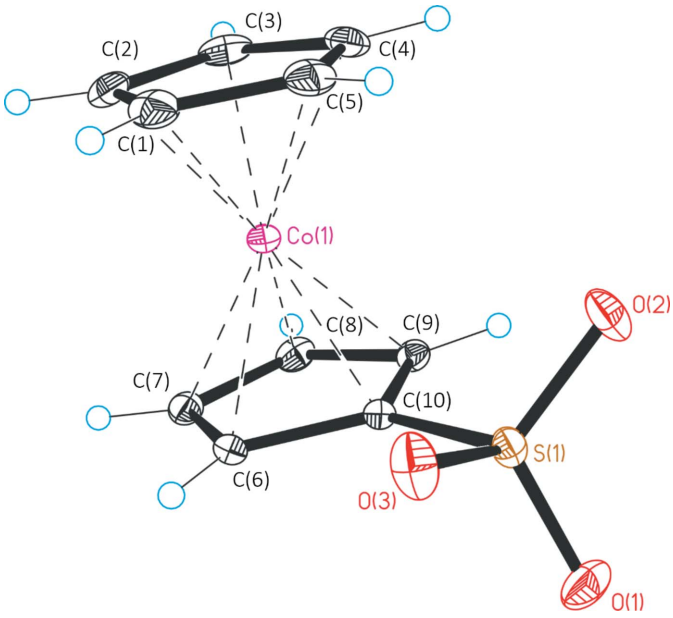


Figure 1
The structure of the title compound, with displacement ellipsoids drawn at the 50% probability level for non-H atoms.

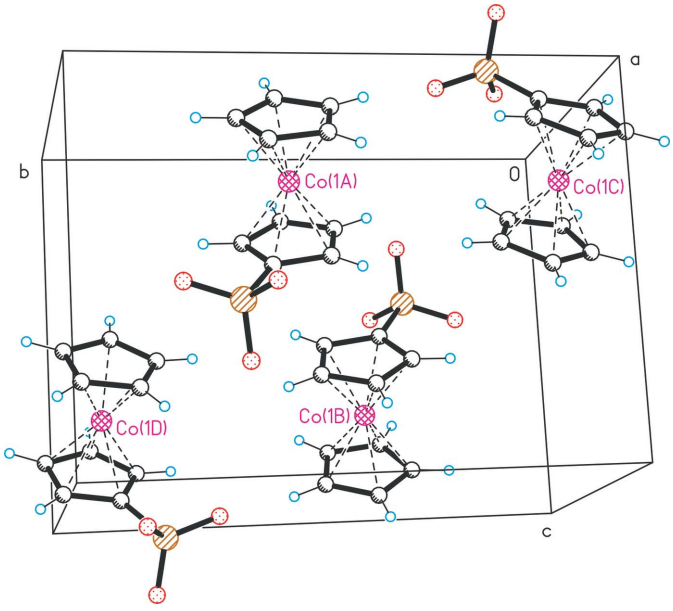


Figure 2
The arrangement of molecular entities of the zwitterionic title compound in the unit cell. [Symmetry codes: (A) x, y, z; (B) $1-x, 1-y, 1-z$; (C) $\frac{3}{2}-x, y-\frac{1}{2}, \frac{1}{2}-z$; (D) $x-\frac{1}{2}, \frac{3}{2}-y, \frac{1}{2}+z$.]

Synthesis and crystallization

Cobaltoceniumsulfonate was obtained by a Sandmeyer-type chlorosulfo-dediazoniation reaction of cobaltoceniumdiazonium bis(hexafluoridophosphate) (Vanicek *et al.*, 2016) with sulfur dioxide in the presence of cupric chloride in hydrochloric acid according to literature (Hoffman, 1981), followed by aqueous workup. From the resulting product mixture containing various cobaltocenium compounds according to ^{1}H and ^{13}C NMR analysis, single crystals of the title compound were obtained at room temperature from a mixture of acetonitrile and water.

Table 1
Experimental details.

Crystal data	
Chemical formula	$[Co(C_5H_5)(C_5H_4O_3S)]$
M_r	268.16
Crystal system, space group	Monoclinic, $P2_1/n$
Temperature (K)	193
a, b, c (Å)	7.6234 (4), 13.1489 (6), 9.6785 (5)
β (°)	94.206 (1)
V (Å^3)	967.55 (8)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	1.97
Crystal size (mm)	0.18 × 0.14 × 0.14
Data collection	
Diffractometer	Bruker D8 QUEST PHOTON 100
Absorption correction	Multi-scan (*SADABS*; Bruker, 2014)
T_{min}, T_{max}	0.676, 0.790
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	22746, 2116, 2032
R_{int}	0.025
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.639
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.020, 0.054, 1.08
No. of reflections	2116
No. of parameters	136
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.24, −0.43

Computer programs: *APEX2* and *SAINT* (Bruker, 2014), *SHELXT2014* (Sheldrick, 2015*a*), *SHELXL2014* (Sheldrick, 2015*b*), *ORTEP-3 for Windows* (Farrugia, 2012) and *Mercury* (Macrae *et al.*, 2008).

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1.

Funding information

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full crystallographic data

IUCrData (2017). **2**, x171703 [https://doi.org/10.1107/S2414314617017035]

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Crystal data

$[Co(C_5H_5)(C_5H_4O_3S)]$
M_r = 268.16
Monoclinic, $P2_1/n$
a = 7.6234 (4) Å
b = 13.1489 (6) Å
c = 9.6785 (5) Å
β = 94.206 (1)°
V = 967.55 (8) Å^3
Z = 4
$F(000)$ = 544
D_x = 1.841 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 9062 reflections
θ = 2.6–27.5°
μ = 1.97 mm^{-1}
T = 193 K
Platelet, yellow
0.18 × 0.14 × 0.14 mm

Data collection

Bruker D8 QUEST PHOTON 100 diffractometer
Radiation source: Incoatec Microfocus
Multi layered optics monochromator
Detector resolution: 10.4 pixels mm^{-1}
φ and ω scans
Absorption correction: multi-scan (DIFABS; Walker & Stuart, 1983)
T_{min} = 0.676, T_{max} = 0.790
22746 measured reflections
2116 independent reflections
2032 reflections with $I > 2\sigma(I)$
R_{int} = 0.025
θ_{max} = 27.0°, θ_{min} = 2.6°
h = −9→9
k = −16→16
l = −12→12

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.020
$wR(F^2)$ = 0.054
S = 1.08
2116 reflections
136 parameters
0 restraints
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0286P)^2 + 0.5214P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.24 e Å^{-3}
$\Delta\rho_{min}$ = −0.43 e Å^{-3}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. Hydrogen atoms were located in the difference Fourier syntheses and included and refined as riding atoms in their calculated positions.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
Co1	0.72231 (2)	0.58762 (2)	0.24293 (2)	0.01743 (8)
S1	0.83395 (5)	0.69190 (3)	0.55827 (4)	0.02232 (10)
O1	0.76626 (18)	0.67652 (11)	0.69286 (13)	0.0405 (3)
O2	1.00545 (15)	0.64785 (10)	0.54789 (15)	0.0381 (3)
O3	0.81863 (18)	0.79505 (9)	0.50811 (15)	0.0398 (3)
C1	0.8206 (2)	0.68857 (14)	0.10960 (19)	0.0355 (4)
H1	0.7914	0.7586	0.1010	0.043*
C2	0.7347 (2)	0.60824 (16)	0.03566 (17)	0.0367 (4)
H2	0.6381	0.6148	−0.0315	0.044*
C3	0.8179 (2)	0.51592 (14)	0.07925 (18)	0.0357 (4)
H3	0.7868	0.4497	0.0466	0.043*
C4	0.9564 (2)	0.54022 (14)	0.18074 (18)	0.0323 (4)
H4	1.0340	0.4931	0.2279	0.039*
C5	0.9578 (2)	0.64712 (14)	0.19881 (18)	0.0322 (4)
H5	1.0368	0.6844	0.2600	0.039*
C6	0.54570 (19)	0.66101 (12)	0.35710 (15)	0.0222 (3)
H6	0.5113	0.7304	0.3503	0.027*
C7	0.4639 (2)	0.57829 (13)	0.28320 (16)	0.0260 (3)
H7	0.3653	0.5829	0.2176	0.031*
C8	0.5545 (2)	0.48737 (12)	0.32406 (15)	0.0252 (3)
H8	0.5264	0.4209	0.2908	0.030*
C9	0.69493 (19)	0.51320 (11)	0.42370 (15)	0.0209 (3)
H9	0.7769	0.4673	0.4684	0.025*
C10	0.68939 (18)	0.62079 (11)	0.44371 (14)	0.0187 (3)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Co1	0.01734 (12)	0.01810 (12)	0.01726 (11)	−0.00121 (7)	0.00411 (7)	−0.00056 (6)
S1	0.02178 (18)	0.01959 (18)	0.02482 (18)	0.00203 (13)	−0.00344 (14)	−0.00436 (13)
O1	0.0459 (8)	0.0523 (8)	0.0231 (6)	−0.0119 (6)	0.0008 (5)	−0.0104 (5)
O2	0.0212 (6)	0.0373 (7)	0.0541 (8)	0.0067 (5)	−0.0086 (5)	−0.0140 (6)
O3	0.0454 (8)	0.0187 (6)	0.0526 (8)	−0.0002 (5)	−0.0145 (6)	−0.0005 (5)
C1	0.0388 (10)	0.0295 (8)	0.0406 (10)	0.0021 (7)	0.0199 (8)	0.0123 (7)
C2	0.0333 (9)	0.0581 (11)	0.0195 (7)	−0.0007 (8)	0.0080 (7)	0.0048 (7)
C3	0.0426 (10)	0.0357 (9)	0.0314 (8)	−0.0064 (8)	0.0200 (7)	−0.0119 (7)
C4	0.0258 (8)	0.0370 (9)	0.0360 (9)	0.0071 (7)	0.0153 (7)	0.0050 (7)
C5	0.0247 (8)	0.0383 (9)	0.0352 (9)	−0.0103 (7)	0.0120 (6)	−0.0022 (7)
C6	0.0177 (7)	0.0285 (8)	0.0208 (7)	0.0049 (6)	0.0036 (5)	0.0003 (5)
C7	0.0163 (7)	0.0404 (9)	0.0213 (7)	−0.0040 (6)	0.0026 (5)	0.0017 (6)
C8	0.0267 (8)	0.0261 (7)	0.0233 (7)	−0.0102 (6)	0.0055 (6)	−0.0005 (6)
C9	0.0231 (7)	0.0207 (7)	0.0192 (6)	−0.0007 (5)	0.0035 (5)	0.0017 (5)
C10	0.0182 (7)	0.0205 (7)	0.0176 (6)	0.0021 (5)	0.0028 (5)	−0.0003 (5)

Geometric parameters (Å, º)

Co1—C4	2.0230 (16)	C2—C3	1.419 (3)
Co1—C3	2.0245 (16)	C2—H2	0.9500
Co1—C10	2.0251 (14)	C3—C4	1.425 (3)
Co1—C9	2.0288 (14)	C3—H3	0.9500
Co1—C5	2.0320 (16)	C4—C5	1.416 (3)
Co1—C1	2.0323 (16)	C4—H4	0.9500
Co1—C2	2.0333 (16)	C5—H5	0.9500
Co1—C8	2.0345 (15)	C6—C7	1.421 (2)
Co1—C7	2.0399 (15)	C6—C10	1.431 (2)
Co1—C6	2.0452 (14)	C6—H6	0.9500
S1—O2	1.4402 (12)	C7—C8	1.422 (2)
S1—O3	1.4425 (12)	C7—H7	0.9500
S1—O1	1.4499 (14)	C8—C9	1.429 (2)
S1—C10	1.7717 (15)	C8—H8	0.9500
C1—C2	1.410 (3)	C9—C10	1.4289 (19)
C1—C5	1.416 (3)	C9—H9	0.9500
C1—H1	0.9500		
C4—Co1—C3	41.22 (8)	Co1—C1—H1	126.4
C4—Co1—C10	121.73 (7)	C1—C2—C3	108.00 (16)
C3—Co1—C10	158.16 (7)	C1—C2—Co1	69.67 (10)
C4—Co1—C9	104.88 (7)	C3—C2—Co1	69.20 (10)
C3—Co1—C9	121.06 (7)	C1—C2—H2	126.0
C10—Co1—C9	41.28 (5)	C3—C2—H2	126.0
C4—Co1—C5	40.89 (7)	Co1—C2—H2	126.7
C3—Co1—C5	68.94 (7)	C2—C3—C4	107.79 (16)
C10—Co1—C5	106.99 (7)	C2—C3—Co1	69.86 (10)
C9—Co1—C5	121.02 (7)	C4—C3—Co1	69.33 (9)
C4—Co1—C1	68.77 (7)	C2—C3—H3	126.1
C3—Co1—C1	68.70 (7)	C4—C3—H3	126.1
C10—Co1—C1	123.10 (7)	Co1—C3—H3	126.3
C9—Co1—C1	158.23 (7)	C5—C4—C3	107.83 (16)
C5—Co1—C1	40.76 (8)	C5—C4—Co1	69.90 (9)
C4—Co1—C2	69.01 (7)	C3—C4—Co1	69.45 (10)
C3—Co1—C2	40.95 (8)	C5—C4—H4	126.1
C10—Co1—C2	159.39 (7)	C3—C4—H4	126.1
C9—Co1—C2	158.48 (7)	Co1—C4—H4	126.1
C5—Co1—C2	68.64 (7)	C1—C5—C4	107.95 (16)
C1—Co1—C2	40.58 (8)	C1—C5—Co1	69.63 (9)
C4—Co1—C8	120.58 (7)	C4—C5—Co1	69.22 (9)
C3—Co1—C8	105.84 (7)	C1—C5—H5	126.0
C10—Co1—C8	69.11 (6)	C4—C5—H5	126.0
C9—Co1—C8	41.17 (6)	Co1—C5—H5	126.7
C5—Co1—C8	157.06 (7)	C7—C6—C10	107.52 (13)
C1—Co1—C8	160.03 (7)	C7—C6—Co1	69.45 (9)
C2—Co1—C8	122.90 (7)	C10—C6—Co1	68.66 (8)

C4—Co1—C7	157.47 (7)	C7—C6—H6	126.2
C3—Co1—C7	121.97 (7)	C10—C6—H6	126.2
C10—Co1—C7	68.91 (6)	Co1—C6—H6	127.2
C9—Co1—C7	69.16 (6)	C6—C7—C8	108.50 (13)
C5—Co1—C7	160.70 (7)	C6—C7—Co1	69.85 (8)
C1—Co1—C7	124.53 (7)	C8—C7—Co1	69.37 (9)
C2—Co1—C7	108.17 (7)	C6—C7—H7	125.8
C8—Co1—C7	40.85 (7)	C8—C7—H7	125.8
C4—Co1—C6	159.40 (7)	Co1—C7—H7	126.6
C3—Co1—C6	158.66 (7)	C7—C8—C9	108.21 (13)
C10—Co1—C6	41.16 (6)	C7—C8—Co1	69.78 (9)
C9—Co1—C6	69.40 (6)	C9—C8—Co1	69.20 (8)
C5—Co1—C6	123.96 (7)	C7—C8—H8	125.9
C1—Co1—C6	108.84 (7)	C9—C8—H8	125.9
C2—Co1—C6	123.38 (7)	Co1—C8—H8	126.7
C8—Co1—C6	68.87 (6)	C8—C9—C10	107.38 (13)
C7—Co1—C6	40.70 (6)	C8—C9—Co1	69.63 (8)
O2—S1—O3	113.96 (9)	C10—C9—Co1	69.22 (8)
O2—S1—O1	113.04 (9)	C8—C9—H9	126.3
O3—S1—O1	114.09 (9)	C10—C9—H9	126.3
O2—S1—C10	105.68 (7)	Co1—C9—H9	126.4
O3—S1—C10	104.73 (7)	C9—C10—C6	108.39 (13)
O1—S1—C10	104.05 (7)	C9—C10—S1	125.74 (11)
C2—C1—C5	108.43 (16)	C6—C10—S1	125.87 (11)
C2—C1—Co1	69.75 (10)	C9—C10—Co1	69.50 (8)
C5—C1—Co1	69.61 (9)	C6—C10—Co1	70.17 (8)
C2—C1—H1	125.8	S1—C10—Co1	126.80 (8)
C5—C1—H1	125.8		

C5—C1—C2—C3	0.29 (19)	Co1—C8—C9—C10	59.15 (10)
Co1—C1—C2—C3	−58.76 (12)	C7—C8—C9—Co1	−59.05 (10)
C5—C1—C2—Co1	59.04 (12)	C8—C9—C10—C6	0.20 (16)
C1—C2—C3—C4	−0.12 (19)	Co1—C9—C10—C6	59.61 (10)
Co1—C2—C3—C4	−59.17 (11)	C8—C9—C10—S1	179.33 (11)
C1—C2—C3—Co1	59.05 (12)	Co1—C9—C10—S1	−121.26 (11)
C2—C3—C4—C5	−0.09 (18)	C8—C9—C10—Co1	−59.41 (10)
Co1—C3—C4—C5	−59.59 (11)	C7—C6—C10—C9	−0.42 (16)
C2—C3—C4—Co1	59.50 (12)	Co1—C6—C10—C9	−59.19 (10)
C2—C1—C5—C4	−0.34 (18)	C7—C6—C10—S1	−179.55 (11)
Co1—C1—C5—C4	58.79 (11)	Co1—C6—C10—S1	121.68 (12)
C2—C1—C5—Co1	−59.13 (12)	C7—C6—C10—Co1	58.77 (10)
C3—C4—C5—C1	0.26 (18)	O2—S1—C10—C9	39.68 (15)
Co1—C4—C5—C1	−59.05 (11)	O3—S1—C10—C9	160.34 (13)
C3—C4—C5—Co1	59.31 (11)	O1—S1—C10—C9	−79.61 (14)
C10—C6—C7—C8	0.49 (17)	O2—S1—C10—C6	−141.34 (13)
Co1—C6—C7—C8	58.77 (11)	O3—S1—C10—C6	−20.68 (15)
C10—C6—C7—Co1	−58.28 (10)	O1—S1—C10—C6	99.37 (14)
C6—C7—C8—C9	−0.37 (17)	O2—S1—C10—Co1	−50.30 (11)

Co1—C7—C8—C9	58.69 (10)	O3—S1—C10—Co1	70.37 (11)
C6—C7—C8—Co1	−59.06 (11)	O1—S1—C10—Co1	−169.58 (10)
C7—C8—C9—C10	0.10 (17)		