

Cobaltocenium trifluoromethanesulfonate

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Key indicators

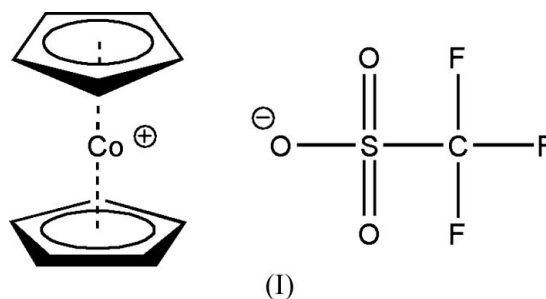
Single-crystal X-ray study
 $T = 173$ K
Mean $\sigma(\text{C}-\text{C}) = 0.012$ Å
 R factor = 0.072
 wR factor = 0.212
Data-to-parameter ratio = 15.9For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.

In the structure of cobaltocenium trifluoromethanesulfonate [systematic name: bis(η^5 -cyclopentadienyl)cobalt(III) trifluoromethanesulfonate], $[\text{Co}(\text{C}_5\text{H}_5)_2](\text{CF}_3\text{O}_3\text{S})$ or $[\text{CoCp}_2][\text{OTf}]$, the asymmetric unit contains three independent anions, together with two full and two half-cations. Two of the cations reside on crystallographic inversion centers.

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Comment

The title compound, (I), was isolated in quantitative yield from the reaction of cobaltocene with indium(I) trifluoromethanesulfonate ($[\text{In}][\text{OTf}]$) during an investigation of the reactivity of the indium reagent with some transition metal metallocenes (Andrews & Macdonald, 2005).



The asymmetric unit of (I) contains three anions, in which all atoms are located in general positions, and a total of three $[\text{CoCp}_2]$ cations. Two of the $[\text{CoCp}_2]$ cations (containing atoms

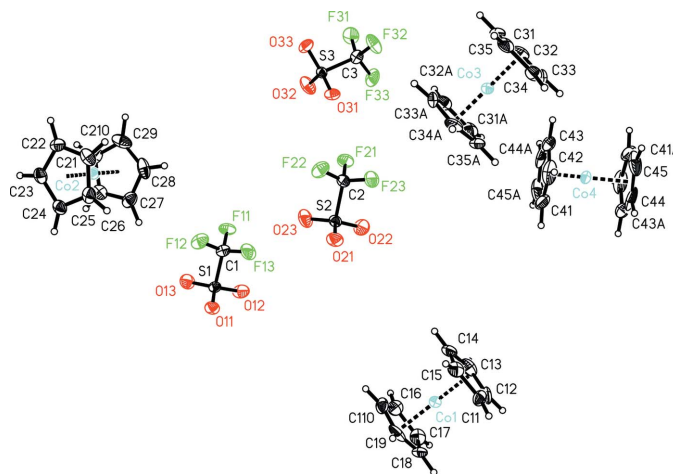


Figure 1

A view of the contents of the asymmetric unit of (I), with the two centrosymmetric cations completed by inversion symmetry. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry codes: (A) $-x, 1 - y, -z$ for the Co3 cation; $-x, -y, -z$ for the Co4 cation.]

Co1 and Co2) are also situated in general positions, and two half-cations (containing atoms Co3 and Co4) are located such that the Co atoms are on the inversion centers at $(0, \frac{1}{2}, 0)$ (atom Co3) and $(0, 0, 0)$ (atom Co4). The contents of the asymmetric unit (including complete symmetry-generated cations) are depicted in Fig. 1, and a diagram of the packing of the unit cell is presented in Fig. 2.

The indistinguishable S—O distances within each of the trifluoromethanesulfonate anions are consistent with the completely delocalized structure expected for an unperturbed trifluoromethanesulfonate anion. While the Cp-centroid—Co distances are essentially the same for all of the cations [1.629 (4)–1.637 (4) Å], the conformations of the cations differ slightly depending on their locations in the unit cell. The cations containing atoms Co3 and Co4 have perfectly staggered Cp rings enforced by the $\bar{1}$ symmetry. In contrast, the cations containing atoms Co1 and Co2 are not subject to symmetry constraints and the rings are rotated slightly (*ca* 10° for Co1 and *ca* 7° for Co2) from a staggered arrangement. Overall, the structures of both components are consistent with those reported previously in the Cambridge Structural Database (Version 5.26; Allen, 2002).

In the crystal structure of (I), there are numerous weak C—H...O interactions (Table 2).

Experimental

The title salt, bis(η^5 -cyclopentadienyl)cobalt(III) trifluoromethanesulfonate, was obtained in quantitative yield from the reaction of bis(η^5 -cyclopentadienyl)cobalt(II) with indium(I) trifluoromethanesulfonate, as described previously by Andrews & Macdonald (2005). Suitable crystals of (I) were obtained by the slow evaporation of a dichloromethane solution of the salt in a nitrogen-filled glove box.

Crystal data

| | |
|----------------------------------------------------------------------|-------------------------------------------|
| $[\text{Co}(\text{C}_5\text{H}_5)_2](\text{CF}_3\text{O}_3\text{S})$ | $D_x = 1.856 \text{ Mg m}^{-3}$ |
| $M_r = 338.18$ | Mo $K\alpha$ radiation |
| Monoclinic, $P2_1/c$ | Cell parameters from 5242 reflections |
| $a = 16.326 (3) \text{ \AA}$ | $\theta = 3.0\text{--}27.3^\circ$ |
| $b = 13.119 (3) \text{ \AA}$ | $\mu = 1.63 \text{ mm}^{-1}$ |
| $c = 17.644 (3) \text{ \AA}$ | $T = 173 (2) \text{ K}$ |
| $\beta = 106.069 (2)^\circ$ | Block, yellow |
| $V = 3631.4 (12) \text{ \AA}^3$ | $0.40 \times 0.30 \times 0.30 \text{ mm}$ |
| $Z = 12$ | |

Data collection

| | |
|----------------------------------------------------------|----------------------------------------|
| Bruker SMART CCD area-detector diffractometer | 8245 independent reflections |
| φ and ω scans | 3836 reflections with $I > 2\sigma(I)$ |
| Absorption correction: multi-scan (SADABS; Bruker, 2000) | $R_{\text{int}} = 0.111$ |
| $T_{\text{min}} = 0.466, T_{\text{max}} = 0.614$ | $\theta_{\text{max}} = 27.5^\circ$ |
| 39731 measured reflections | $h = -20 \rightarrow 20$ |
| | $k = -16 \rightarrow 17$ |
| | $l = -22 \rightarrow 22$ |

Refinement

| | |
|---------------------------------|------------------------------------------------------|
| Refinement on F^2 | $w = 1/[\sigma^2(F_o^2) + (0.077P)^2 + 11.3024P]$ |
| $R[F^2 > 2\sigma(F^2)] = 0.072$ | where $P = (F_o^2 + 2F_c^2)/3$ |
| $wR(F^2) = 0.212$ | $(\Delta/\sigma)_{\text{max}} = 0.001$ |
| $S = 1.04$ | $\Delta\rho_{\text{max}} = 1.39 \text{ e \AA}^{-3}$ |
| 8245 reflections | $\Delta\rho_{\text{min}} = -0.73 \text{ e \AA}^{-3}$ |
| 517 parameters | |
| H-atom parameters constrained | |

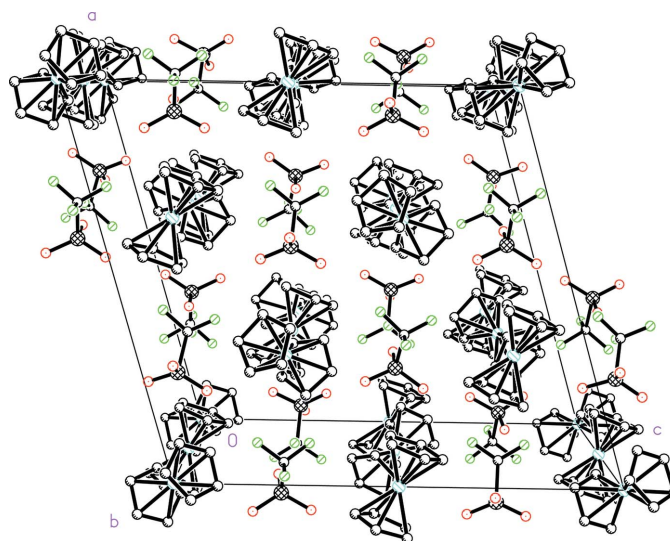


Figure 2
A plot, viewed down the *b* axis, of the unit-cell contents of (I). H atoms have been omitted for clarity.

Table 1
Selected bond distances (Å).

| | | | |
|----------|-----------|---------|-----------|
| Co1—C11 | 2.029 (7) | Co3—C31 | 2.035 (7) |
| Co1—C12 | 2.025 (7) | Co3—C32 | 2.022 (7) |
| Co1—C13 | 2.012 (8) | Co3—C33 | 2.023 (7) |
| Co1—C14 | 2.027 (7) | Co3—C34 | 2.020 (7) |
| Co1—C15 | 2.031 (7) | Co3—C35 | 2.019 (7) |
| Co1—C16 | 2.028 (8) | Co4—C41 | 2.017 (9) |
| Co1—C17 | 2.034 (7) | Co4—C42 | 2.022 (8) |
| Co1—C18 | 2.011 (8) | Co4—C43 | 2.010 (7) |
| Co1—C19 | 2.022 (8) | Co4—C44 | 2.007 (8) |
| Co1—C110 | 2.038 (7) | Co4—C45 | 2.010 (8) |
| Co2—C21 | 2.023 (7) | S1—O11 | 1.439 (5) |
| Co2—C22 | 2.020 (7) | S1—O12 | 1.434 (5) |
| Co2—C23 | 2.027 (7) | S1—O13 | 1.434 (6) |
| Co2—C24 | 2.038 (7) | S2—O21 | 1.446 (5) |
| Co2—C25 | 2.020 (7) | S2—O22 | 1.441 (5) |
| Co2—C26 | 2.018 (7) | S2—O23 | 1.431 (6) |
| Co2—C27 | 2.032 (7) | S3—O31 | 1.431 (5) |
| Co2—C28 | 2.029 (8) | S3—O32 | 1.431 (6) |
| Co2—C29 | 2.011 (8) | S3—O33 | 1.438 (5) |
| Co2—C210 | 2.016 (7) | | |

Table 2
Hydrogen-bond 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> |
|--------------------------------|-------------|---------------|-----------------------|-------------------------|
| C11—H11...O12 ⁱ | 0.95 | 2.43 | 3.285 (10) | 149 |
| C16—H16...O22 ⁱⁱ | 0.95 | 2.56 | 3.474 (11) | 161 |
| C17—H17...O31 ⁱⁱⁱ | 0.95 | 2.48 | 3.203 (10) | 133 |
| C19—H19...O13 ⁱ | 0.95 | 2.56 | 3.429 (10) | 152 |
| C21—H21...O21 ⁱⁱⁱ | 0.95 | 2.58 | 3.221 (10) | 125 |
| C23—H23...O11 ⁱⁱⁱ | 0.95 | 2.43 | 3.347 (10) | 162 |
| C24—H24...O33 ^{iv} | 0.95 | 2.55 | 3.465 (10) | 161 |
| C26—H26...O31 ^{iv} | 0.95 | 2.57 | 3.249 (10) | 128 |
| C28—H28...O21 ^v | 0.95 | 2.36 | 3.243 (10) | 154 |
| C29—H29...O22 ⁱⁱⁱ | 0.95 | 2.57 | 3.438 (11) | 152 |
| C32—H32...O33 ⁱ | 0.95 | 2.47 | 3.245 (10) | 138 |
| C41—H41...O12 ⁱⁱ | 0.95 | 2.53 | 3.332 (12) | 142 |
| C42—H42...O32 ⁱ | 0.95 | 2.45 | 3.334 (11) | 155 |
| C210—H210...O12 ⁱⁱⁱ | 0.95 | 2.57 | 3.425 (9) | 151 |

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

H atoms were placed in calculated positions, with C–H distances of 0.95 Å. They were included in the refinement in the riding-model approximation, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. The top three peaks in the final difference Fourier map are all above 1.0 e \AA^{-3} . The most intense peak has an electron density of 1.39 e \AA^{-3} and is located 1.045 Å from atom Co3 toward the centroid of the C_5H_5 ring. Similarly, the other two peaks are located at distances of 1.085 Å (1.28 e \AA^{-3}) and 1.043 Å (1.25 e \AA^{-3}) from atom Co1 and are also oriented toward the centroids of the C_5H_5 rings labeled C16–C110 and C11–C15, respectively. The high value of R_{int} is due to the poor quality of the crystal. Numerous attempted recrystallizations failed to yield crystals of superior quality.

Data collection: *SMART* (Bruker, 1997); cell refinement: *SAINTE-Plus* (Bruker, 1997); data reduction: *SAINTE-Plus*; program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1997); software used to prepare material for publication: *SHELXTL*, *PLATON* (Spek, 2003) and *WinGX* (Farrugia, 1999).

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