

A highly disordered cobaltocenium salt

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Key indicators

Single-crystal X-ray study

T = 213 K

Mean $\sigma(F-B) = 0.002 \text{ \AA}$

Disorder in main residue

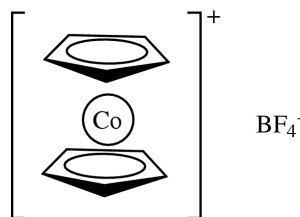
R factor = 0.028

wR factor = 0.084

Data-to-parameter ratio = 12.1

For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.Cobaltocenium tetrafluoroborate, $[\text{Co}(\text{C}_5\text{H}_5)_2]\text{BF}_4$, crystallizes in space group *Cccm* and packs in a way that causes the Cp_2Co moiety to sit just off of the mirror plane, causing extreme disorder.

Comment

Cobaltocene has often been used as a convenient, mild reducing agent (Connelly & Geiger, 1996), thus leading to the appearance of the cobaltocenium cation in many crystal structures [over 80 times in the Cambridge Database (Allen & Kennard, 1993)]. We have also found the cobaltocenium cation to be useful as a mild oxidizing agent, and often use the BF_4^- salt whenever a weakly coordinating anion is desired in the target synthetic product. While structures of the Cp_2Co^+ ion with many different anions are known, the BF_4^- salt, (I), is not, and its structure is reported here.

(I)

Space group *Cccm* was strongly indicated by intensity statistics, and while the solution and refinement of the structure was expected to be straightforward, the initial solution from direct methods suggested a position for the Co atom that was on the twofold axis at $1/4, 1/4, z$ but only approximately 0.2 \AA from the $2/m$ site at $1/4, 1/4, 1/2$. (The BF_4^- anion resides on a site of 222 symmetry at $0, 1/2, 1/4$ in a way that generates an almost perfectly tetrahedral moiety.) Fourier peaks corresponding to the C atoms of the Cp rings were therefore badly mixed by the symmetry operations. At this point, it seemed apparent that the mirror plane should be removed to reduce the symmetry and change the space group to *Ccc2*. However, two slightly separated positions for the Co atom persisted and the Cp rings continued to appear as a badly disordered cluster of atoms. The solution and refinement were therefore continued in space group *Cccm*, using a disordered model in which the Cp_2Co^+ unit resides on a twofold axis perpendicular to the main axis of the molecule, but slightly displaced from the mirror plane which almost contains the main molecular axis. A view of the model showing one orientation of the Cp_2Co group is shown in Fig. 1.

In order to refine the model effectively, the Cp ring was constrained to be exactly pentagonal, but was allowed to

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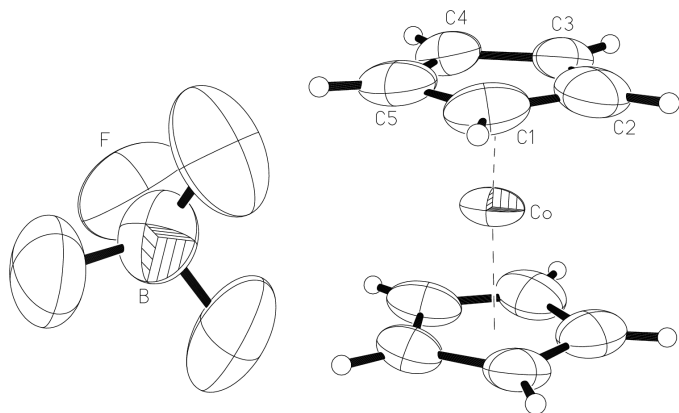


Figure 1
The molecular structure of $[(C_5H_5)_2Co]BF_4$, drawn with 40% displacement ellipsoids.

shrink or expand freely. This resulted in a C—C distance of 1.397 (4) Å, which is shorter than the expected distance for π -bonded Cp, but is due to librational error. Librational analysis (Schomaker & Trueblood, 1968) of the Cp ring gives corrected C—C bond lengths of 1.42 Å, which is the expected value of the distances.

Atom C1 lies almost on the mirror plane and appears to be shared by both orientations (see Fig. 2), although it is actually not. The Cp plane is 1.634 (1) Å from the Co atom, and the two Cp rings form an angle of 1.5 (4)°. The Cp rings are slightly staggered, with an approximate offset of 21°.

Experimental

All synthetic procedures were carried out under a nitrogen atmosphere. Cobaltocene (51 mg, 0.27 mmol) and $AgBF_4$ (52 mg, 0.27 mmol) were weighed into separate Schlenk flasks. Methylene chloride (10 ml) was added to each flask, and the cobaltocene solution was transferred to the flask containing the $AgBF_4$ *via* cannula. The mixture was allowed to react, with stirring, for 1 h. The solution was then transferred with a filter-equipped cannula into a 50 ml Schlenk tube and layered with 20 ml hexanes. Crystals formed after one week.

Crystal data

$[Co(C_5H_5)_2] \cdot BF_4$
 $M_r = 275.92$
 Orthorhombic, *Cc**cm*
 $a = 7.3586$ (7) Å
 $b = 11.9176$ (11) Å
 $c = 12.4369$ (13) Å
 $V = 1090.68$ (18) Å³
 $Z = 4$
 $D_x = 1.680$ Mg m⁻³

Mo $K\alpha$ radiation
 Cell parameters from 1619 reflections
 $\theta = 2.4$ – 27.4°
 $\mu = 1.59$ mm⁻¹
 $T = 213$ (2) K
 Block, yellow
 $0.30 \times 0.28 \times 0.20$ mm

Data collection

Bruker SMART diffractometer
 ω scans
 Absorption correction: multi-scan (*SADABS*; Blessing, 1995)
 $T_{min} = 0.609$, $T_{max} = 0.727$
 3263 measured reflections
 665 independent reflections

485 reflections with $I > 2\sigma(I)$
 $R_{int} = 0.018$
 $\theta_{max} = 27.5^\circ$
 $h = -9 \rightarrow 9$
 $k = -15 \rightarrow 10$
 $l = -16 \rightarrow 13$

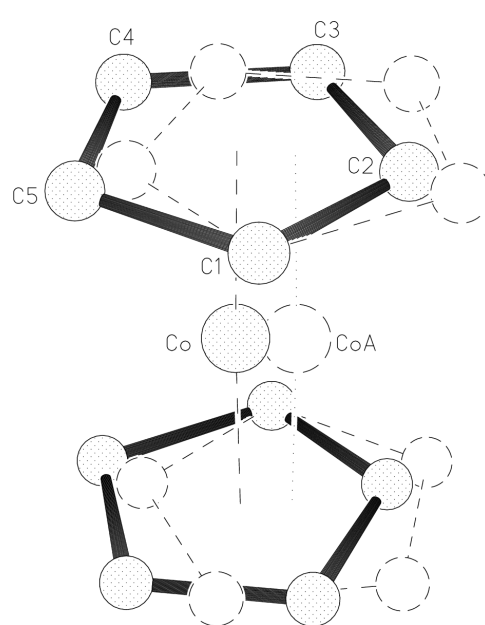


Figure 2
A representation of the entire model used in the refinement of the disordered structure. The twofold axis is horizontal in this view, passing through the Co atoms. The mirror is vertical, perpendicular to the plane of the drawing, passing between the Co atoms.

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.028$
 $wR(F^2) = 0.084$
 $S = 1.09$
 665 reflections
 55 parameters
 H-atom parameters not refined

$$w = 1/[\sigma^2(F_o^2) + (0.036P)^2 + 0.6P]$$

$$\text{where } P = (F_o^2 + 2F_c^2)/3$$

$$(\Delta/\sigma)_{max} = 0.003$$

$$\Delta\rho_{max} = 0.19 \text{ e \AA}^{-3}$$

$$\Delta\rho_{min} = -0.18 \text{ e \AA}^{-3}$$

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Siemens, 1996); software used to prepare material for publication: *SHELXL97*.

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