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Compositional disorder in *trans*-$[RhBr_{0.26}Cl_{0.74}H(PMe_3)_4]$-$[B(1,2\text{-}O_2C_6Br_4)]\cdot CH_2Cl_2$

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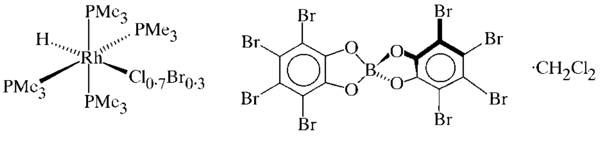
The structure of *trans*-(bromo/chloro)hydridotetrakis(trimethylphosphine)rhodium(III) bis(tetrabromopyrocatecholato-*O,O′*)borate dichloromethane solvate, $[RhCl_{0.74}Br_{0.26}H(C_3H_9P)_4](C_{12}BBr_8O_4)\cdot CH_2Cl_2$, is reported. The Rh^{III} complex shows bromine/chlorine compositional disorder with a *trans* arrangement of the hydride and halide ligands. The anion has approximate D_{2d} symmetry, with a central spiro-B atom distorted from regular tetrahedral geometry by the small chelating O—B—O angles.

Comment

The compound *trans*-$[RhBr_{0.26}Cl_{0.74}H(PMe_3)_4][B(1,2\text{-}O_2C_6Br_4)_2]\cdot CH_2Cl_2$, (I), was obtained as a by-product from the reaction between $[Rh(PMe_3)_4]Cl$ and $B_2(1,2\text{-}O_2C_6Br_4)_2$. A number of structures of the bis(catecholato)borate anion, $[B(cat)_2]^-$ (cat = $1,2\text{-}O_2C_6H_4$), have been reported both with organic cations (Clegg, Scott *et al.*, 1998) and with metal complex cations (Clegg *et al.*, 1999), and this anion seems to be a favoured product in many reactions involving H(Bcat), $B_2(cat)_2$ and $B_2(cat)_3$.



(I)

The geometry of the anion in this salt is similar to those of the unsubstituted anion in previously reported structures. Thus, B—O distances in (I) are in the range 1.453 (11)–1.486 (11) Å {*cf.* 1.452–1.519 Å in $[B(cat)_2]^-$ anions}. The O—C distances [1.330 (9)–1.339 (8) Å] are similar to those in other $[B(cat)_2]^-$ anions (1.338–1.375 Å). The B—O and O—C distances in these tetrahedral anions are longer than those in the diborane(4) compound $B_2(1,2\text{-}O_2C_6H_4)_2$ [B—O = 1.382 (2)–1.394 (2) Å and O = 1.386 (2)–1.387 (2) Å; Clegg *et al.*, 1999], consistent with an increased coordination number and hybridization change at boron. The structure of $B_2(1,2\text{-}O_2C_6Br_4)_2$ has not been characterized to date. The coordination around boron is slightly elongated from tetrahedral with two small O—B—O chelating angles [105.1 (6) and 103.9 (6)°]. The rings are close to planar [torsion angles O1—C51—C52—O2 = 4.1 (11)° and O3—C61—C62—O4 = 0.9 (9)°]. In other $[B(cat)_2]^-$ anions, slight folding is reported about the O···O vector, with dihedral angles between the BO_2 and O_2C_2 planes of up to 13.9 (2)° (Clegg *et al.*, 1999), however, in the anion of (I) these angles are only 2.4 (2) and 4.6 (2)°. The anion has approximate D_{2d} symmetry (see Fig. 1).

The hydride and halide ligands in the cation of (I), which contains four phosphine ligands, are *trans* to each other, consistent with the relative high and low *trans* influences of hydride and halide ligands, respectively. Compositional disorder was observed in the halide site and was modelled with

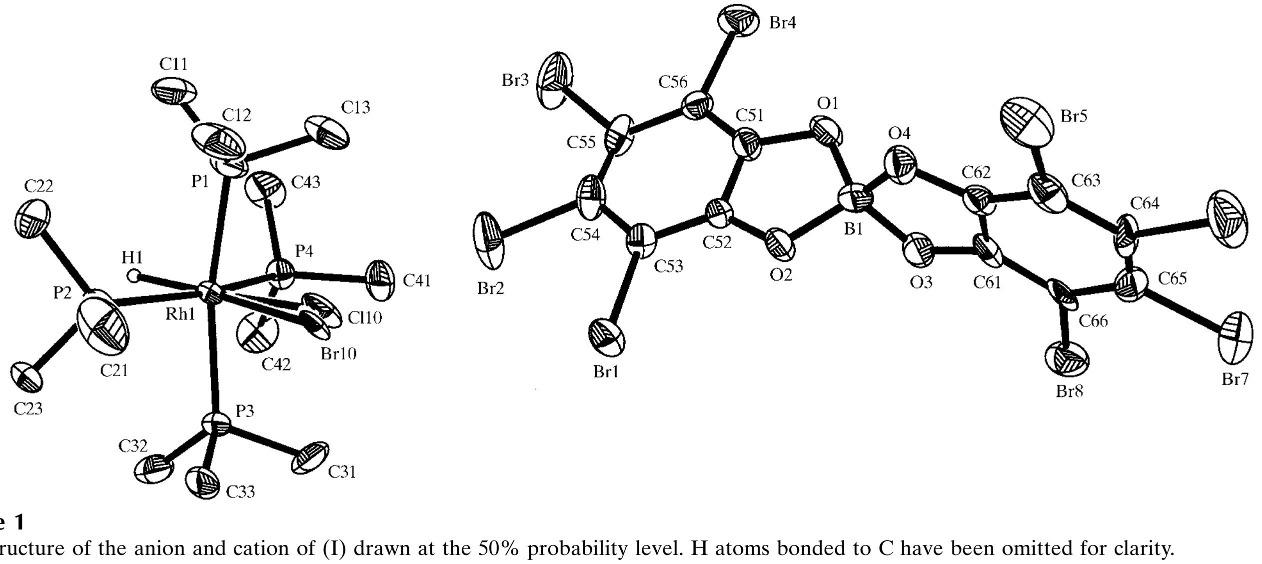


Figure 1
The structure of the anion and cation of (I) drawn at the 50% probability level. H atoms bonded to C have been omitted for clarity.

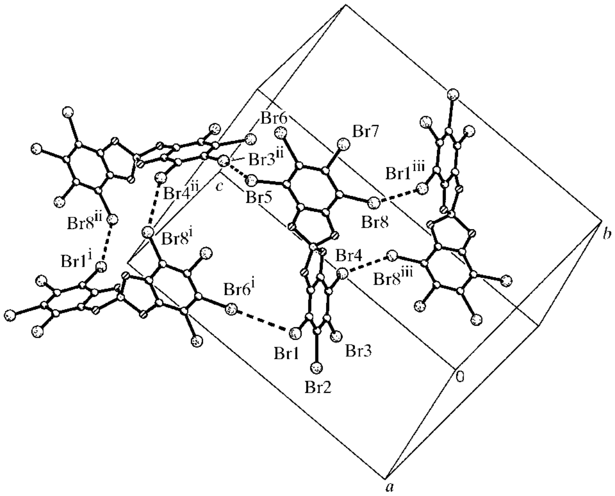


Figure 2

The packing of anions of (I) showing Br···Br interactions. [Symmetry codes: (i) $-x, -\frac{1}{2}+y, \frac{3}{2}-z$; (ii) $-\frac{1}{2}-x, 2-y, \frac{1}{2}+z$; (iii) $-\frac{1}{2}+x, \frac{5}{2}-y, 1-z$.]

components of bromine and chlorine in the ratio *ca* 3:1 (see *Experimental*). Presumably the source of the bromine here is the catecholate 1,2-$O_2C_6Br_4$. The Rh—PMe_3 distances [2.322 (2)–2.357 (2) Å] are similar to those of other Rh^{III} cations [2.281 (3)–2.397 (3) Å; Marder *et al.*, 1987; Westcott *et al.*, 1993]. Ignoring the Br/Cl disorder, the geometry around rhodium is octahedral with *cis*-P—Rh—P bond angles in the range 90.57 (8)–91.45 (8)°, though the *trans*-P—Rh—P angles are somewhat distorted from linearity [P1—Rh1—P3 166.27 (9) and P2—Rh1—P4 159.16 (9)°].

The $[B(1,2\text{-}O_2C_6Br_4)_2]^-$ anions form an intricate packing supported by Br···Br interactions. The interactions, shown in Fig. 2, include the unique contacts: Br1···$Br6^{i}$ = 3.656 (2), Br5···$Br3^{ii}$ = 3.287 (2), Br4···$Br8^{iii}$ = 3.617 (1) and Br8···$Br1^{iii}$ = 3.519 (1) Å [symmetry codes: (i) $-x, y-\frac{1}{2}, \frac{3}{2}-z$; (ii) $-\frac{1}{2}-x, 2-y, \frac{1}{2}+z$; (iii) $x-\frac{1}{2}, \frac{5}{2}-y, 1-z$] (van der Waals radius of bromine = 1.85 Å; Bondi, 1964). The shortest published Br···Br interaction is 3.202 (3) Å in CPh_3Br (Desiraju, 1989, and references therein). Database studies on Cl···Cl, Br···Br and I···I interactions have shown that these contacts are generally of two types (Ramasubbu *et al.*, 1986). Either both C—*X*···*X* (*X* = halide) angles are equal and around 160 (10)° or one of the angles is about 175° and the other around 80°. As shown in Table 1, both of these types are observed. That these contacts have specific directional effects appears to dominate in the packing in (I), whereas classic hydrogen bonding between organic cations and the O atoms in $[B(cat)_2]^-$, forming ion pairs, is found in salts of this anion (Clegg, Scott *et al.*, 1998).

Experimental

$B_2(1,2\text{-}O_2C_6Br_4)_2$ was prepared as described by Clegg, Lawlor *et al.* (1998). Compound (I) was obtained as a minor by-product from the reaction between $[Rh(PMe_3)_4]Cl$ and $B_2(1,2\text{-}O_2C_6Br_4)_2$ in CH_2Cl_2 after the addition of pentane. $^{31}P\{^1H\}$ NMR ($CDCl_3$): multiplet at δ −10.6 p.p.m; $^{11}B\{^1H\}$ NMR: δ 12.3 p.p.m. Crystals of (I) suitable for X-ray diffraction were grown from a CH_2Cl_2 solution layered with hexane at 243 K.

Crystal data

$[RhCl_{0.74}Br_{0.26}H(C_3H_9P)_4]$-
$(C_{12}BBr_8O_4)\cdot CH_2Cl_2$
$M_r = 1398.57$
Orthorhombic, $P2_12_12_1$
$a = 13.0140$ (9) Å
$b = 16.3990$ (15) Å
$c = 20.726$ (3) Å
$V = 4423.3$ (8) Å^3
$Z = 4$
$D_x = 2.100$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 462 reflections
$\theta = 5$–25°
$\mu = 8.191$ mm^{-1}
$T = 173$ (2) K
Rhomb, pale yellow
0.80 × 0.30 × 0.30 mm

Data collection

Siemens SMART area-detector diffractometer
ω rotation with narrow frame scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.026$, $T_{max} = 0.086$
28 033 measured reflections
5613 independent reflections (plus 4511 Friedel-related reflections)
7391 reflections with $I > 2\sigma(I)$
$R_{int} = 0.050$
$\theta_{max} = 27.51°$
$h = -16 \rightarrow 16$
$k = -19 \rightarrow 21$
$l = -15 \rightarrow 26$
Intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.049$
$wR(F^2) = 0.113$
$S = 1.154$
10 124 reflections
430 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0570P)^2]$ where $P = [\max(F_o^2,0) + 2F_c^2]/3$
$(\Delta/\sigma)_{max} = -0.002$
$\Delta\rho_{max} = 1.44$ e Å^{-3}
$\Delta\rho_{min} = -1.10$ e Å^{-3}
Absolute structure: Flack (1983)
Flack parameter = 0.486 (10)

Table 1

Selected geometric parameters (Å, °).

Rh1—P4	2.322 (2)	Br6—C64	1.883 (9)
Rh1—P2	2.345 (2)	Br7—C65	1.886 (7)
Rh1—P3	2.346 (2)	Br8—C66	1.848 (9)
Rh1—P1	2.357 (2)	B1—O2	1.453 (11)
Rh1—Cl10	2.507 (14)	B1—O3	1.478 (10)
Rh1—Br10	2.531 (12)	B1—O1	1.482 (10)
Br1—C53	1.889 (7)	B1—O4	1.486 (11)
Br2—C54	1.903 (9)	O1—C51	1.335 (9)
Br3—C55	1.891 (8)	O2—C52	1.330 (9)
Br4—C56	1.879 (7)	O3—C61	1.333 (8)
Br5—C63	1.887 (8)	O4—C62	1.339 (8)
P4—Rh1—P2	159.16 (9)	C43—P4—C42	96.3 (5)
P4—Rh1—P3	91.04 (8)	C41—P4—C42	104.0 (5)
P2—Rh1—P3	91.45 (8)	O2—B1—O3	112.2 (7)
P4—Rh1—P1	90.57 (8)	O2—B1—O1	105.1 (6)
P2—Rh1—P1	91.88 (8)	O3—B1—O1	111.3 (8)
P3—Rh1—P1	166.27 (9)	O2—B1—O4	112.3 (8)
C11—P1—C13	104.6 (4)	O3—B1—O4	103.9 (6)
C11—P1—C12	103.8 (6)	O1—B1—O4	112.4 (7)
C13—P1—C12	96.0 (5)	C53—Br1···$Br8^{i}$	156.0 (3)
C21—P2—C23	101.7 (5)	C53—Br1···$Br6^{ii}$	84.9 (2)
C21—P2—C22	101.8 (6)	C55—Br3···$Br5^{iii}$	168.3 (3)
C23—P2—C22	97.8 (5)	C56—Br4···$Br8^{iv}$	153.6 (3)
C32—P3—C31	102.5 (5)	C63—Br5···$Br3^{v}$	137.1 (3)
C32—P3—C33	103.5 (5)	C64—Br6···$Br1^{vi}$	176.5 (3)
C31—P3—C33	99.9 (4)	C66—Br8···$Br1^{iv}$	111.9 (2)
C43—P4—C41	104.2 (4)	C66—Br8···$Br4^{i}$	116.4 (2)

Symmetry codes: (i) $\frac{1}{2}+x, \frac{5}{2}-y, 1-z$; (ii) $-x, y-\frac{1}{2}, \frac{3}{2}-z$; (iii) $-\frac{1}{2}-x, 2-y, z-\frac{1}{2}$; (iv) $x-\frac{1}{2}, \frac{5}{2}-y, 1-z$; (v) $-\frac{1}{2}-x, 2-y, \frac{1}{2}+z$; (vi) $-x, \frac{1}{2}+y, \frac{3}{2}-z$.

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The data showed inversion twinning with the Flack parameter (Flack, 1983) refining to 0.486 (10).

The position of the hydride was located in the electron-density difference map and was refined with fixed coordinates and $U_{\rm iso}$. Other H atoms were constrained to idealized geometries and assigned isotropic displacement parameters $1.5U_{\rm eq}$ of their attached carbon (or $1.2U_{\rm eq}$ for CH_2Cl_2).

Compositional disorder was suspected in the halide as unaccounted electron density was present when it was modelled as pure chloride. Both components of the disorder were refined anisotropically and the site occupancies refined to 0.74 (1) and 0.26 (1) for Cl and Br, respectively. The Rh—Cl and Rh—Br distances were constrained to standard bond distances (Rh—Cl 2.44 and Rh—Br 2.56 Å; Orpen *et al.*, 1989) and the anisotropic displacement parameters of the Cl and Br atoms were constrained to be the same.

The CH_2Cl_2 solvent molecule was disordered and modelled with two images of equal occupancy ratio, with their C atom in the same location. The C—Cl distances were constrained.

Data collection: *SMART* (Siemens, 1995*a*); cell refinement: *SAINT* (Siemens, 1995*a*); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Siemens, 1995*b*); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD1060). Services for accessing these data are described at the back of the journal.

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