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Crystal structure of bis(η^6 -cymene)-tri- μ_2 -chlorido-ruthenium(II) tetrafluoroborate, $C_{20}H_{28}BCl_3F_4Ru_2$

Table 1: Data collection and handling.

Crystal:	Prism, brown
Size:	0.37 × 0.29 × 0.25 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	1.58 mm ⁻¹
Diffractometer, scan mode:	Bruker APEX, φ and ω -scans
$\theta_{\max}$, completeness:	27°, >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	12865, 5645, 0.043
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 4085
$N(\text{param})_{\text{refined}}$:	277
Programs:	Bruker programs [1], SHELX [2], Diamond [3]

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Abstract

$C_{20}H_{28}BCl_3F_4Ru_2$, triclinic, $P\bar{1}$ (no. 2), $a = 7.7061(15)$ Å, $b = 12.654(3)$ Å, $c = 13.993(3)$ Å, $\alpha = 68.25(3)^\circ$, $\beta = 78.71(3)^\circ$, $\gamma = 88.89(3)^\circ$, $V = 1240.8(5)$ Å³, $Z = 2$, $R_{\text{gt}}(F) = 0.0686$, $wR_{\text{ref}}(F^2) = 0.2017$, $T = 293(2)$ K.

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The title crystal structure is shown using a ball-and-stick scheme in the figure. Tables 1 and 2 contain details of the measurement method and a list of the atoms including atomic coordinates and displacement parameters.

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Ru1	0.63390(9)	0.83339(5)	0.32977(5)	0.0493(2)
Ru2	0.87897(8)	0.73838(5)	0.16257(4)	0.0431(2)
F1	0.6329(17)	0.7830(12)	0.8392(8)	0.190(4)
F2	0.653(2)	0.7577(13)	0.7077(11)	0.210(4)
F3	0.838(2)	0.8518(15)	0.6974(15)	0.257(6)
F4	0.8349(18)	0.6733(11)	0.8029(9)	0.186(4)
Cl1	0.7510(3)	0.64761(17)	0.34953(16)	0.0607(5)
Cl2	0.5924(3)	0.8222(2)	0.16694(16)	0.0591(5)
Cl3	0.9368(3)	0.88996(18)	0.22385(16)	0.0566(5)
B1	0.754(5)	0.754(3)	0.778(3)	0.185(6)
C1	0.733(2)	1.0912(15)	0.3235(15)	0.154(7)
H1A	0.8424	1.0729	0.3477	0.231*
H1B	0.6796	1.1493	0.3460	0.231*
H1C	0.7569	1.1181	0.2481	0.231*
C2	0.6072(17)	0.9843(9)	0.3691(10)	0.085(4)
C3	0.6457(16)	0.8903(12)	0.4554(9)	0.088(3)
H3	0.7555	0.8899	0.4809	0.105*
C4	0.5262(16)	0.7870(10)	0.4931(6)	0.079(3)
H4	0.5600	0.7159	0.5430	0.095*
C5	0.3829(12)	0.7828(8)	0.4426(7)	0.062(2)
C6	0.3626(15)	0.8780(11)	0.3619(8)	0.082(3)
H6	0.2845	0.8727	0.3161	0.098*
C7	0.4727(17)	0.9746(10)	0.3281(10)	0.086(3)
H7	0.4676	1.0326	0.2591	0.104*
C8	0.2688(18)	0.6694(12)	0.4850(11)	0.100(4)
H8	0.3289	0.6115	0.5340	0.120*

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Table 2 (continued)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} [*] / <i>U</i> _{eq}
C9	0.0927(19)	0.6877(15)	0.5479(12)	0.134(6)
H9A	0.0288	0.7421	0.5012	0.201*
H9B	0.1152	0.7157	0.5996	0.201*
H9C	0.0234	0.6167	0.5823	0.201*
C10	0.2405(17)	0.6271(11)	0.4076(10)	0.097(4)
H10A	0.1641	0.6757	0.3657	0.146*
H10B	0.1861	0.5512	0.4417	0.146*
H10C	0.3520	0.6258	0.3633	0.146*
C11	1.2548(14)	0.8827(10)	0.0064(9)	0.084(3)
H11A	1.3585	0.8714	−0.0386	0.127*
H11B	1.2872	0.8894	0.0668	0.127*
H11C	1.2025	0.9512	−0.0313	0.127*
C12	1.1220(10)	0.7818(8)	0.0415(6)	0.055(2)
C13	1.1419(11)	0.6813(8)	0.1245(7)	0.060(2)
H13	1.2289	0.6810	0.1672	0.072*
C14	1.0157(14)	0.5893(8)	0.1598(7)	0.067(2)
H14	1.0180	0.5273	0.2270	0.081*
C15	0.8661(12)	0.5936(8)	0.1147(8)	0.062(2)
C16	0.8517(12)	0.6970(9)	0.0303(7)	0.062(2)
H16	0.7391	0.7103	0.0063	0.074*
C17	0.9771(12)	0.7888(8)	−0.0044(6)	0.060(2)
H17	0.9491	0.8634	−0.0517	0.071*
C18	0.7286(14)	0.4964(10)	0.1569(11)	0.089(4)
H18	0.7380	0.4521	0.2296	0.106*
C19	0.546(2)	0.5285(13)	0.1587(15)	0.137(6)
H19A	0.5219	0.5809	0.1940	0.206*
H19B	0.4673	0.4617	0.1952	0.206*
H19C	0.5281	0.5641	0.0879	0.206*
C20	0.7728(19)	0.4199(11)	0.0962(13)	0.118(5)
H20A	0.7025	0.3494	0.1321	0.178*
H20B	0.8962	0.4048	0.0906	0.178*
H20C	0.7480	0.4565	0.0272	0.178*

Source of materials

To a solution containing [(η⁶-p-cymene)RuCl₂] in CH₃OH and CH₂Cl₂, excessive NaBF₄ and moderate dilute hydrochloric acid were added successively. The reaction mixture was stirred at ambient temperature for over 12 h and filtered to remove NaCl. The solvents were removed from the filtrate on a rotary evaporator and the residue was recrystallized from 1:1 CH₂Cl₂/ether to afford dark red crystals with high yield.

Experimental details

All hydrogen atoms were positioned geometrically and allowed to ride on their parent atoms.

Comment

The dinuclear triply chlorido bridged arene ruthenium(II) complexes receive widely attention [4, 5], because they can

provide diverse coordination environments to develop metal-mediated catalyst [6] and for medicinal applications [7]. Its structure was first determined nearly 40 years ago with the very large BPh₄[−] as counter ion [8]. With the research going on, the tri-μ-chloro-bis[(η⁶-p-arene)ruthenium(II)]⁺ ion (TCRu) was observed in more and more cases [8, 10–12]. From the literature, we found the TCRu can be easily obtained by reacting the starting materials [(η⁶-p-arene)RuCl(μ-Cl)]₂ with excessive alkali metal salts which have weakly coordinating anions, such as BF₄[−] [8], BPh₄[−] [9], AsF₆[−] [10], [Hg₂Cl₆]^{2−} [11], BAr₄[−] (Ar = p-tolyl) [12].

The title complex crystallizes in the space group *P* $\bar{1}$, which is different from its structural isomer which has the space group *Pccn*, orthorhombic [8]. The molecular structure, depicted in the figure, consists of one TCRu cation and one tetrafluoroborate anion. In the cation the [Ru(η⁶-p-cymene)] fragments are linked by three bridging Cl atoms, with an average Ru–Cl bond distance of 2.440(2) Å and an average Ru1–Cl–Ru2 bond angle of 84.4(7)°. Each Ru atom exhibits a distorted octahedral coordination with the arene ring of the p-cymene ligand formally occupying three sites. The Cl–Ru–Cl angles are considerably reduced (average 79.79(7)°) because of steric interactions. The separation between two Ru atoms is 3.2787(13) Å, which agrees with the previous studies [8–11], but still beyond direct metal-metal bond [13]. The tetrahedral BF₄[−] anion is ordered with average B–F bond lengths of 1.266(2)°.

Apparently, the sandwich structure of the title structure between the two benzene rings of the p-cymene ligands is nearly parallel with the corresponding torsion angle about 6.42°, however the sandwich structure of the isomer [8] is staggered with the corresponding torsion angle about 56°. The influence of this configuration change led to the separation between two Ru atoms of the isomer getting closer than the title complex. This could be reasonably explained by the steric hindrance effect of the isopropyl group. That's the main difference between the title structure and the orthorhombic analogon.

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