Joel M. Gichumbi, Sizwe J. Zamisa* and Holger B. Friedrich

Crystal structure of chlorido-(η^5 -pentamethylcyclopentadienyl)-((bis-pyrazol-1-yl)methane- $\kappa^2 N, N'$) rhodium(III) hexafluorophosphate. ($C_{17}H_{23}ClN_4RhF_6P$)

Table 1: Data collection and handling.

Crystal:	Orange block
Size:	0.35 × 0.31 × 0.23 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	1.09 mm ⁻¹
Diffractometer, scan mode:	Bruker APEX-II, φ and ω
$\theta_{\max}$, completeness:	28.3°, >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	31369, 5166, 0.017
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 4994
$N(\text{param})_{\text{refined}}$:	276
Programs:	Bruker [1], SHELX [2, 3], Mercury [4]

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

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} */ <i>U</i> _{eq}
Rh1	0.69970(2)	0.11853(2)	0.33986(2)	0.01016(6)
Cl1	0.67376(5)	0.10711(4)	0.52789(4)	0.01562(10)
N1	0.70574(17)	−0.01726(12)	0.33402(14)	0.0138(4)
N2	0.80103(18)	−0.06209(12)	0.28963(15)	0.0148(4)
N3	0.96207(17)	0.03978(12)	0.32904(15)	0.0141(3)
N4	0.89583(17)	0.10842(12)	0.36637(15)	0.0135(3)
C1	0.6225(2)	−0.07659(15)	0.36404(18)	0.0177(4)
H1	0.5459	−0.0641	0.3983	0.021*
C2	0.6641(2)	−0.15980(16)	0.33783(19)	0.0202(5)
H2	0.6222	−0.2133	0.3499	0.024*
C3	0.7783(2)	−0.14813(15)	0.29097(18)	0.0187(4)
H3	0.8313	−0.1925	0.2645	0.022*
C4	0.9074(2)	−0.01508(15)	0.24775(18)	0.0158(4)
H4A	0.9708	−0.0569	0.2223	0.019*
H4B	0.8801	0.0211	0.1869	0.019*
C5	1.0774(2)	0.03702(16)	0.37305(19)	0.0178(4)
H5	1.1401	−0.0052	0.3594	0.021*
C6	1.0876(2)	0.10634(16)	0.44118(19)	0.0184(4)
H6	1.1580	0.1221	0.4835	0.022*
C7	0.9719(2)	0.14879(15)	0.43480(18)	0.0164(4)
H7	0.9505	0.1994	0.4738	0.020*
C8	0.5812(2)	0.12664(14)	0.20087(17)	0.0125(4)
C9	0.6921(2)	0.17742(14)	0.18605(17)	0.0133(4)
C10	0.6934(2)	0.24515(14)	0.26632(17)	0.0151(4)
C11	0.5842(2)	0.23564(14)	0.32890(17)	0.0150(4)
C12	0.5168(2)	0.15966(14)	0.29214(17)	0.0134(4)
C13	0.5399(2)	0.05056(15)	0.13573(18)	0.0170(4)
H13A	0.6129	0.0235	0.1028	0.026*
H13B	0.4816	0.0702	0.0803	0.026*

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Abstract

$C_{17}H_{23}ClN_4RhF_6P$, monoclinic, $P2_1/c$ (no. 14), $a = 10.6954(2)$ Å, $b = 15.3868(3)$ Å, $c = 12.6130(2)$ Å, $\beta = 90.5590(10)^\circ$, $V = 2075.60(7)$ Å³, $Z = 4$, $R_{\text{gt}}(F) = 0.0296$, $wR_{\text{ref}}(F^2) = 0.0727$, $T = 100(2)$ K.

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The asymmetric unit of the salt title structure is shown in the figure (hydrogen atoms are omitted for clarity). Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Source of material

The title compound was synthesized using a mixture of the rhodium dimer pentamethylcyclopentadienyl

*Corresponding author: Sizwe J. Zamisa, University of KwaZulu-Natal, School of Chemistry and Physics, Private Bag X54001, Westville Campus, Westville, 4000 Durban, South Africa, e-mail: Zamisas@ukzn.ac.za. <https://orcid.org/0000-0003-1968-381X>

Joel M. Gichumbi and Holger B. Friedrich: University of KwaZulu-Natal, School of Chemistry and Physics, Private Bag X54001, Westville Campus, Westville, 4000 Durban, South Africa

Table 2 (continued)

Atom	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
H13C	0.4983	0.0081	0.1813	0.026*
C14	0.7856(2)	0.16944(16)	0.09947(18)	0.0181(4)
H14A	0.8701	0.1746	0.1294	0.027*
H14B	0.7717	0.2158	0.0473	0.027*
H14C	0.7762	0.1128	0.0648	0.027*
C15	0.7914(2)	0.31409(16)	0.2772(2)	0.0224(5)
H15A	0.7962	0.3335	0.3511	0.034*
H15B	0.7697	0.3634	0.2314	0.034*
H15C	0.8726	0.2904	0.2561	0.034*
C16	0.5413(2)	0.29392(16)	0.41568(19)	0.0214(5)
H16A	0.5349	0.2606	0.4816	0.032*
H16B	0.4593	0.3181	0.3970	0.032*
H16C	0.6015	0.3413	0.4255	0.032*
C17	0.3963(2)	0.12866(17)	0.33710(19)	0.0190(4)
H17A	0.3269	0.1616	0.3055	0.029*
H17B	0.3972	0.1373	0.4141	0.029*
H17C	0.3856	0.0667	0.3213	0.029*
P1	0.84478(6)	−0.13070(4)	−0.03400(5)	0.02066(13)
F1	0.72533(18)	−0.13738(13)	−0.10906(16)	0.0413(5)
F2	0.91255(16)	−0.20669(13)	−0.10006(16)	0.0412(5)
F3	0.7831(2)	−0.20471(13)	0.03929(17)	0.0485(5)
F4	0.96244(18)	−0.12937(15)	0.04689(18)	0.0502(6)
F5	0.77755(16)	−0.05845(11)	0.03655(14)	0.0324(4)
F6	0.9090(3)	−0.06062(15)	−0.10376(19)	0.0627(7)

rhodium(III) dichloride (0.055 mmol), bis(pyrazol-1-yl) methane (0.110 mmol) and NH₄PF₆ (0.110 mmol) which were stirred in methanol (10 mL) for six hours, where upon the orange yellow product separated out. The product was filtered, washed with diethyl ether and dried under vacuum. X-ray quality, orange block crystals were grown by vapour diffusion of diethyl ether into an acetone solution. **m.p.** = >300 °C (decomposition); **IR** ν(cm^{−1}): 1519, 1429, 1401 (C=N), 832 (PF₆); **¹H NMR** (400 MHz, *d*₆-DMSO): δ(ppm) = 8.23 (d, 2H, *J* = 2.40 Hz, Pyrazole), 7.90 (s, 2H, Pyrazole), 7.09 (s, 1H, Pyrazole), 7.05 (s, 1H, Pyrazole), 6.63 (t, 2H, *J* = 2.12 Hz, −CH₂), **¹³C NMR** (400 MHz, *d*₆-DMSO): δ(ppm) = 146.39, 145.27, 135.47, 108.81, 106.69, 97.26, 9.24.

Experimental details

The structure was solved by the direct method using the *SHELXS* [2] program and refined. The visual crystal structure information was performed using *Mercury* [4] system software. All C—H_{aromatic}, C—H_{methyl} and C—H_{methylene} bond distances were restrained to 0.95 Å, 0.98 Å and 0.99 Å with $U_{\text{iso}}(\text{H}_{\text{aromatic}})$ and $U_{\text{iso}}(\text{H}_{\text{methylene}}) = 1.2U_{\text{eq}}$ and $U_{\text{iso}}(\text{H}_{\text{methyl}}) = 1.5U_{\text{eq}}$ of parent atom, respectively. Some larger electron density peaks are located near the PF₆[−] anion.

These peaks may be the result of a minor disorder of this anion.

Comment

The pyrazole nucleus has been widely used as core motif for a large number of compounds with various applications and especially in coordination chemistry [5, 6]. Bis(pyrazolyl) alkanes are one of the most fascinating family of stable and flexible ligands and they are isoelectronic and isosteric with the well-known bis(pyrazolyl)borates. The coordinating properties of bis(pyrazol-1-yl)alkanes can be varied over wide range by introduction of various substituents into the pyrazole rings which are able to modify steric and electronic properties [7]. The bis(pyrazol-1-yl)alkanes are neutral ligands containing two pyrazole cycles linked by an aliphatic spacer and are related in concept to the heteroscorpionate ligands. The coordination properties of bis(pyrazol-1-yl)alkanes may be varied in wide range by introducing substituents into the pyrazole rings. Generally, two major coordination modes can be expected for bis(pyrazol-1-yl)alkanes, namely bidentate chelating and bidentate bridging. Bis(pyrazol-1-yl)methanes and 1,2-bis (pyrazol-1-yl)ethanes usually act as bidentate chelating ligands forming boat-shaped six- and seven-membered rings, respectively. 1,3-Bis(pyrazol-1-yl) propane forms eight-membered metallocycles or acts as a bidentate bridging ligand, whereas bis(pyrazol-1-yl)alkanes with four and more methylene groups in the spacer coordinate in a bridging mode to give coordination compounds of intriguing architectures and topologies [8–10]. We have prepared the title compound as part of our ongoing studies of Rh complexes with bidentate ligands [11, 12].

The asymmetric unit of the title compound consists of an cationic Rh(III) complex with a PF₆[−] anion. The Rh complex exists in the piano-stool conformation with a six-membered metallocycle (Rh1–N1–N2–C4–N3–N4) formed by coordination of the bidentate ligand. Furthermore, the metallocycle adopts a distorted boat conformation with a dihedral angle of 274(1)° between the N1–N2–N3–N4 and N1–Rh1–N4 planes. Upon coordination of the ligand, the dihedral angle between the pyrazolyl rings significantly decreased from 72.8(2)–73.06(9)° (observed in the free ligand [13, 14]) to 56.85(9)°. All bond distances and angles were found to be in agreement with closely related complexes reported in the literature [15–17]. Intermolecular, very weak π⋯π interactions between pyrazolyl rings N3–N4–C5–C6–C7 of neighbouring molecules were observed in the crystal packing of the title compound (π⋯π = 3.899(1) Å; symmetry code: 2 − *x*, −*y*, 1 − *z*). C–H⋯π intermolecular interactions were also observed between the H6 atom and the center of gravity of the N1–N2–C1–C2–C3 ring

(H6... π = 2.82 Å; C6... π = 3.638(2) Å; C6—H6... π = 145°; symmetry code: 2 - x, -y, 1 - z).

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