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Crystal structure of chlorido-(η^5 -pentamethylcyclopentadienyl)-(4-chloro-4-pyridyl-2,2':6',2''-terpyridine- κ^2 N,N') rhodium(III) hexafluorophosphate, $C_{31}H_{29}Cl_2F_6N_3PRh$

Table 1: Data collection and handling.

Crystal:	Red block
Size:	0.17 × 0.14 × 0.01 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	0.83 mm ⁻¹
Diffractometer, scan mode:	Bruker D8 Venture, φ and ω
$\theta_{\max}$, completeness:	28.4°, >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	106148, 7840, 0.086
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 6280
$N(\text{param})_{\text{refined}}$:	462
Programs:	Bruker [1], SHELX [2, 3], Mercury [4]

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Abstract

$C_{31}H_{29}Cl_2F_6N_3PRh$, monoclinic, $P2_1/c$ (no. 14), $a = 7.4069(7)$ Å, $b = 13.245(1)$ Å, $c = 32.141(3)$ Å, $\beta = 93.924(2)^\circ$, $V = 3145.8(5)$ Å³, $Z = 4$, $R_{\text{gt}}(F) = 0.0386$, $wR_{\text{ref}}(F^2) = 0.0962$, $T = 123.15$ K.

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The molecular structure is shown in the figure. 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 $[Cp^*RhCl]_2$ precursor (0.055 mmol), the terpyridine ligand (0.110 mmol) and NH_4PF_6 (0.110 mmol) which was stirred in a mixture of methanol (10 mL) and acetone (10 mL) for six hours, where upon the orange yellow product separated out. The product was filtered,

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

Atom	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Rh1	0.35399(3)	0.61736(2)	0.17484(2)	0.02190(7)
Cl1	0.64792(9)	0.54011(6)	0.18257(2)	0.03255(16)
Cl2	0.16921(14)	1.21428(8)	−0.05374(3)	0.0578(3)
N1	0.4818(3)	0.74575(17)	0.19989(7)	0.0249(5)
N2	0.3991(3)	0.70877(18)	0.11964(7)	0.0249(5)
N3	0.2482(4)	0.5638(2)	0.02937(8)	0.0380(6)
C1	0.5551(4)	0.7531(2)	0.23915(9)	0.0310(6)
H1	0.551244	0.696073	0.256987	0.037*
C2	0.6353(4)	0.8402(2)	0.25443(10)	0.0342(7)
H2	0.684397	0.843651	0.282484	0.041*
C3	0.6436(4)	0.9228(2)	0.22838(10)	0.0340(7)
H3	0.697733	0.984075	0.238295	0.041*
C4	0.5720(4)	0.9149(2)	0.18768(9)	0.0313(6)
H4	0.578098	0.970487	0.169148	0.038*
C5	0.4912(4)	0.8254(2)	0.17406(8)	0.0251(6)
C6	0.4212(4)	0.8075(2)	0.13068(8)	0.0257(6)
C7	0.3852(4)	0.8861(2)	0.10347(9)	0.0305(6)
H7	0.402080	0.953760	0.112751	0.037*
C8	0.3237(4)	0.8667(2)	0.06226(9)	0.0305(6)
C9	0.3142(4)	0.7658(2)	0.05017(9)	0.0323(6)
H9	0.279075	0.749186	0.022017	0.039*
C10	0.3553(4)	0.6890(2)	0.07882(9)	0.0281(6)
C11	0.2771(4)	0.9506(2)	0.03298(9)	0.0320(6)
C12	0.2161(5)	1.0424(3)	0.04783(11)	0.0418(8)
H12	0.199048	1.049633	0.076703	0.050*
C13	0.1801(5)	1.1229(3)	0.02143(11)	0.0443(8)
H13	0.137995	1.185160	0.031824	0.053*
C14	0.2063(4)	1.1115(3)	−0.02037(10)	0.0393(7)

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Table 2 (continued)

Atom	x	y	z	U_{iso}^*/U_{eq}
C15	0.2620(5)	1.0215(3)	−0.03637(10)	0.0412(8)
H15	0.276358	1.014631	−0.065378	0.049*
C16	0.2970(4)	0.9408(3)	−0.00958(10)	0.0361(7)
H16	0.335044	0.878083	−0.020375	0.043*
C17	0.3606(4)	0.5836(2)	0.06309(9)	0.0304(6)
C18	0.4811(4)	0.5137(2)	0.08066(10)	0.0365(7)
H18	0.559117	0.530843	0.104304	0.044*
C19	0.4865(5)	0.4182(3)	0.06322(12)	0.0477(9)
H19	0.569107	0.368817	0.074495	0.057*
C20	0.3701(6)	0.3962(3)	0.02935(12)	0.0494(9)
H20	0.368958	0.330979	0.017036	0.059*
C21	0.2552(5)	0.4704(3)	0.01360(11)	0.0474(9)
H21	0.175754	0.454511	−0.009941	0.057*
C22	0.0676(4)	0.6341(2)	0.17758(10)	0.0310(6)
C23	0.1452(4)	0.6142(2)	0.21877(9)	0.0286(6)
C24	0.2377(4)	0.5199(2)	0.21831(9)	0.0270(6)
C25	0.2054(4)	0.4766(2)	0.17706(9)	0.0293(6)
C26	0.0969(4)	0.5454(2)	0.15284(9)	0.0304(6)
C27	−0.0390(4)	0.7258(3)	0.16382(12)	0.0475(9)
H27A	−0.168145	0.712908	0.166194	0.071*
H27B	−0.017515	0.741202	0.134748	0.071*
H27C	−0.000970	0.783263	0.181531	0.071*
C28	0.1291(5)	0.6799(3)	0.25585(11)	0.0428(8)
H28A	0.014193	0.666036	0.268151	0.064*
H28B	0.132788	0.750883	0.247368	0.064*
H28C	0.229702	0.666033	0.276466	0.064*
C29	0.3392(4)	0.4705(3)	0.25474(10)	0.0380(7)
H29A	0.379934	0.522118	0.275127	0.057*
H29B	0.444408	0.434666	0.245149	0.057*
H29C	0.259752	0.422485	0.267764	0.057*
C30	0.2692(5)	0.3753(2)	0.16410(12)	0.0430(8)
H30A	0.194066	0.322743	0.175681	0.065*
H30B	0.395543	0.365782	0.174512	0.065*
H30C	0.259975	0.370662	0.133597	0.065*
C31	0.0121(5)	0.5271(3)	0.10996(11)	0.0504(10)
H31A	0.081349	0.475522	0.096057	0.076*
H31B	0.011896	0.589936	0.093894	0.076*
H31C	−0.112669	0.503695	0.111828	0.076*
P1A ^a	−0.1674(6)	1.1542(3)	0.14000(11)	0.0354(8)
F1A ^a	−0.1339(10)	1.0388(4)	0.1372(2)	0.0486(15)
F2A ^a	−0.2191(8)	1.2758(4)	0.1437(2)	0.0547(15)
F3A ^a	0.0245(8)	1.1699(6)	0.1625(2)	0.0577(16)
F4A ^a	−0.0949(7)	1.1756(6)	0.09570(17)	0.0494(14)
F5A ^a	−0.2394(10)	1.1303(6)	0.1850(2)	0.0497(15)
F6A ^a	−0.3768(10)	1.1419(5)	0.1174(3)	0.0699(18)
P1B ^b	−0.1878(12)	1.1753(6)	0.1362(3)	0.059(2)
F1B ^b	−0.2047(14)	1.0555(7)	0.1301(3)	0.0765(9)
F2B ^b	−0.3482(12)	1.1829(8)	0.1015(3)	0.0765(9)
F3B ^b	−0.3210(14)	1.1649(9)	0.1734(3)	0.0765(9)
F4B ^b	−0.1669(15)	1.2924(7)	0.1428(4)	0.0765(9)
F5B ^b	−0.0387(14)	1.1821(9)	0.1024(3)	0.0765(9)
F6B ^b	−0.0200(15)	1.1704(10)	0.1715(3)	0.0765(9)
P1C ^b	−0.2175(7)	1.1704(5)	0.13740(17)	0.0328(12)
F1C ^b	−0.1132(18)	1.0631(8)	0.1302(4)	0.0765(9)

Table 2 (continued)

Atom	x	y	z	U_{iso}^*/U_{eq}
F2C ^b	−0.1752(14)	1.2003(8)	0.0922(3)	0.0765(9)
F3C ^b	−0.3785(15)	1.1065(8)	0.1213(4)	0.0765(9)
F4C ^b	−0.279(2)	1.1430(13)	0.1826(4)	0.0765(9)
F5C ^b	−0.0336(13)	1.2123(8)	0.1593(3)	0.0765(9)
F6C ^b	−0.3080(13)	1.2728(7)	0.1445(3)	0.0765(9)

^aOccupancy: 0.4, ^bOccupancy: 0.3.

washed with diethyl ether and dried under vacuum. ¹H NMR (400 MHz, d₆-DMSO): δ = 1.14 ppm (s, 15 H, C₅Me₅), 7.23–7.74 ppm (m, 2H), 8.52–8.55 ppm (m, 2H), 9.14–9.16 ppm (m, 2H), 9.17–9.18 ppm (m, 2H), ¹³C NMR (400 MHz, d₆-DMSO): δ = 156.0 ppm, 155.0 ppm, 140.4 ppm, 138.0, 135.0 ppm, 129.0 ppm, 124.0 ppm, 121.0 ppm, 117.0, 95.36 ppm.

Experimental details

Crystal evaluation and data collection were done on a Bruker Smart APEX2 diffractometer [1]. The structure was solved by the direct method using the *SHELXS* [2] program and refined (*SHELXL*) [3]. The visual crystal structure information was performed using *MERCURY* [4] system software. All C–H_{aromatic} and C–H_{methyl} bond distances were restrained to 0.95 Å, 0.98 Å with $U_{iso}(H_{aromatic}) = 1.2U_{eq}$ and $U_{iso}(H_{methyl}) = 1.5U_{eq}$ of parent atom, respectively. The PF₆[−] anion was found to be disordered over three parts with the major component having 40% site occupancy.

Comment

The pentamethyl cyclopentadienyl ligand has a wide application in organometallic chemistry. The η⁵-pentamethylcyclopentadienyl rhodium complexes have found utility in coordination chemistry and catalysis [5–7]. The reactions of the chloride-bridged rhodium dimer [Cp⁺RhCl₂]₂ with a variety of ligands to form monomeric complexes via cleavage of the bridging species readily incorporate many different ligands [5–7]. One of the most commonly used ligands are the nitrogen containing ligands. In organometallic chemistry, nitrogen containing ligands can coordinate with various transition metals because of the inherent lone pair of electrons [8–13]. Thus N-containing ligands are a crucial component in coordination chemistry. Among the ligand systems the 2,2':6',2''-terpyridine is one fascinating ligand. As an N-,N'-N''-tridentate ligand the 2,2':6',2''-terpyridine ligand plays an important role in coordination chemistry with three coordination sites and low LUMO. Terpyridine and its derivatives are among the typical pincer ligands and/or non-innocent ligands in transition metal catalysis [8–13]. The multidentate terpyridine based ligands have been extensively investigated, modified and utilized in various works

in organic and inorganic supramolecular chemistry [8–13]. This is due to the relative ease of synthesizing and modifying the terpyridine moiety, with π -stacking ability, directional hydrogen-bonding, conjugated aromatic cores and coordination properties amongst other structural features [8–13].

In the title compound, the rhodium metal centre is coordinated *via* the nitrogen atoms of the ligand, five carbon atoms of the Cp* moiety and Cl of the metal centre. This gives the pseudo-octahedral piano-stool conformation around the rhodium centres in the complex. The N–Rh–N angle is $76.80(8)^\circ$ and is in agreement with related complexes reported in the literature [5, 7, 14–16]. The N–Rh–N bite angle is 84.36° which is similar to those reported for other Rh complexes with N–N-bidentate ligands [5, 7, 14–16]. The Rh–N distances in the complex are 2.1082(2) and 2.192(2) Å and they are comparable to those previously reported in the literature [5, 7, 14–16]. The Rh–Cl bond length for this complex is 2.4028(5) Å which is comparable to the Rh–Cl bond length of related complexes with N–N-bidentate ligands [5, 7, 14–16]. Non-classical, intermolecular C–H...Cl and C–H...F hydrogen bonds were observed in the crystal packing of the title compound.

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