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Crystal structure of chlorido-(η^6 -toluene) (5,5'-dimethyl-2,2'-bipyridine- $\kappa^2 N, N'$) ruthenium(II) hexafluoridophosphate(V) – acetone (1/1) $C_{22}H_{26}ClN_2ORuPF_6$

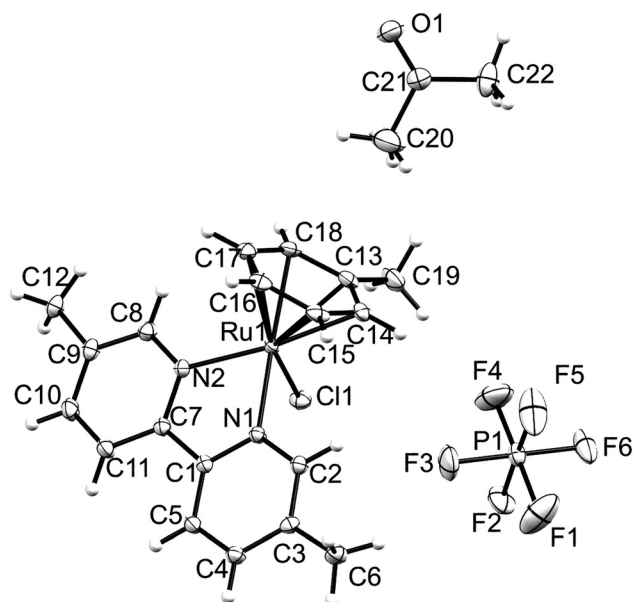


Table 1: Data collection and handling.

Crystal:	Orange block
Size:	0.29 × 0.25 × 0.18 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	0.87 mm ⁻¹
Diffractometer, scan mode:	Bruker Kappa Apex II, 0.5° φ and ω
$\theta_{\max}$, completeness:	28.3°, >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	23,856, 6080, 0.026
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 5787
$N(\text{param})_{\text{refined}}$:	312
Programs:	Bruker [1], SHELX [2, 4], Mercury [3]

Source of material

To a solution of $[(\eta^6\text{-toluene})Ru(\mu\text{-Cl})Cl]_2$ (0.2 mmol) in acetonitrile (20 mL) was added 5,5'-dimethyl-2,2'-bipyridine (0.42 mmol). The mixture was stirred for 3 h followed by the reduction in the volume of the solvent *in vacuo* to about (10 mL) before adding NH_4PF_6 (0.42 mmol) and then cooled in an ice bath while stirring for 2 h leading to a precipitate which was collected by filtration. The filtrate was washed with diethyl ether and dried *in vacuo*. Crystals were grown by layering an acetone solution with hexane and left undisturbed for 2 days. Orange yellow, yield 84%, m.p. 189 °C (decomp.). 1H NMR (400 MHz, DMSO- d_6) δ_{ppm} = 9.37 (s, 2H, Py); 8.45 (d, J_{HH} = 8.32 Hz, 2H, Py); 8.08 (t, J_{HHH} = 6.8 Hz, 2H, Py); 6.33 (t, J_{HHH} = 6.08 Hz, 2H, Arene); 5.95 (t, J_{HH} = 6.12 Hz, 2H, Arene); 5.79 (t, J_{HHH} = 5.68 Hz, 1H, Arene); 2.51 (s, 6H, Me), 2.23 (s, 3H, Me-Toluene)), ^{13}C NMR (400 MHz, DMSO- d_6) δ_{ppm} = 155.82 (Py), 154.53 (Py), 140.0 (Py); 127.40 (Py); 123.65 (Py); 105.88 (Ar); 90.54 (Ar); 82.94 (Ar); 79.74 (Ar); 23.21 (Me); 18.74 (Me). MS (ESI, m/z): 413.04 $[C_{19}H_{20}ClN_2Ru]^+$.

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Abstract

$C_{22}H_{26}ClN_2ORuPF_6$, triclinic, $P\bar{1}$ (no. 2), $a = 10.2106(4)$ Å, $b = 10.8139(4)$ Å, $c = 11.1963(4)$ Å, $\alpha = 93.765(2)^\circ$, $\beta = 90.418(1)^\circ$, $\gamma = 94.324(2)^\circ$, $V = 1229.98(8)$ Å³, $Z = 2$, $R_{\text{gt}}(F) = 0.0251$, $wR_{\text{ref}}(F^2) = 0.0683$, $T = 100$ K.

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Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

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Experimental details

A Bruker APEX2 diffractometer was used for crystal evaluation and data collection [1]. The structure was

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}
Ru1	0.21980 (2)	0.24581 (2)	0.72509 (2)	0.01259 (5)
Cl1	0.06511 (4)	0.37191 (4)	0.82106 (4)	0.01933 (9)
N1	0.15098 (14)	0.31223 (13)	0.56692 (13)	0.0139 (3)
N2	0.05198 (14)	0.12801 (13)	0.68370 (13)	0.0147 (3)
C1	0.03457 (16)	0.25935 (15)	0.52316 (15)	0.0144 (3)
C2	0.21107 (17)	0.40672 (16)	0.51077 (16)	0.0161 (3)
H2	0.292011	0.444267	0.542798	0.019*
C3	0.16042 (17)	0.45190 (16)	0.40837 (15)	0.0161 (3)
C4	0.03954 (18)	0.39924 (16)	0.36574 (16)	0.0179 (3)
H4	0.000393	0.429437	0.297250	0.022*
C5	−0.02407 (17)	0.30243 (16)	0.42327 (16)	0.0175 (3)
H5	−0.106892	0.266004	0.394600	0.021*
C6	0.23689 (19)	0.55247 (18)	0.34559 (17)	0.0224 (4)
H6A	0.302126	0.515322	0.293508	0.034*
H6B	0.281598	0.611871	0.405119	0.034*
H6C	0.176702	0.595694	0.297266	0.034*
C7	−0.02176 (16)	0.15619 (15)	0.58980 (15)	0.0151 (3)
C8	0.00643 (17)	0.03719 (16)	0.75297 (16)	0.0169 (3)
H8	0.058291	0.019096	0.819492	0.020*
C9	−0.11314 (17)	−0.03105 (16)	0.73116 (16)	0.0179 (3)
C10	−0.18761 (18)	−0.00250 (17)	0.63383 (17)	0.0211 (4)
H10	−0.269687	−0.047547	0.616054	0.025*
C11	−0.14270 (18)	0.09144 (17)	0.56249 (17)	0.0197 (3)
H11	−0.193538	0.111400	0.496006	0.024*
C12	−0.15876 (18)	−0.12986 (17)	0.81292 (17)	0.0209 (4)
H12A	−0.099881	−0.125836	0.882808	0.031*
H12B	−0.157959	−0.211768	0.770046	0.031*
H12C	−0.248211	−0.116431	0.839240	0.031*
C13	0.35618 (18)	0.30426 (18)	0.87878 (17)	0.0208 (4)
C14	0.40903 (17)	0.35019 (17)	0.77203 (18)	0.0209 (4)
H14	0.434652	0.436224	0.769123	0.025*
C15	0.42374 (17)	0.26846 (18)	0.66997 (17)	0.0208 (4)
H15	0.457507	0.300623	0.598506	0.025*
C16	0.38902 (17)	0.13980 (18)	0.67260 (17)	0.0210 (4)
H16	0.402972	0.084641	0.605087	0.025*
C17	0.33313 (17)	0.09503 (17)	0.77782 (17)	0.0204 (4)
H17	0.305394	0.009326	0.779605	0.024*
C18	0.31767 (17)	0.17542 (17)	0.88058 (17)	0.0196 (3)
H18	0.281417	0.143196	0.951080	0.024*
C19	0.3356 (2)	0.3900 (2)	0.98671 (19)	0.0316 (5)
H19A	0.406301	0.384209	1.045235	0.047*
H19B	0.250892	0.366190	1.022627	0.047*
H19C	0.335998	0.475575	0.962770	0.047*
P1	0.45704 (5)	0.75864 (5)	0.68457 (5)	0.02172 (10)
F1	0.4662 (2)	0.85292 (15)	0.57965 (16)	0.0648 (5)
F2	0.30983 (12)	0.79529 (14)	0.70704 (14)	0.0384 (3)
F3	0.40696 (16)	0.64846 (13)	0.58997 (13)	0.0453 (4)
F4	0.4440 (2)	0.66610 (15)	0.78859 (14)	0.0569 (5)
F5	0.60260 (15)	0.72622 (17)	0.6580 (2)	0.0699 (6)
F6	0.50717 (13)	0.86903 (14)	0.77859 (15)	0.0474 (4)
O1	0.82456 (17)	0.08082 (14)	1.03257 (14)	0.0335 (3)
C20	0.6867 (3)	0.1968 (3)	0.9219 (3)	0.0631 (10)
H20A	0.654335	0.114992	0.886144	0.095*
H20B	0.721624	0.248561	0.859076	0.095*
H20C	0.614474	0.236729	0.962119	0.095*

Table 2: (continued)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} */ <i>U</i> _{eq}
C21	0.7926 (2)	0.18194 (18)	1.01063 (17)	0.0230 (4)
C22	0.8576 (2)	0.2991 (2)	1.0697 (2)	0.0355 (5)
H22A	0.924525	0.278377	1.126812	0.053*
H22B	0.791761	0.345996	1.112198	0.053*
H22C	0.899213	0.349566	1.008892	0.053*

solved by the direct method using the *SHELXS* [2] program and refined. The visual crystal structure information was performed using *Mercury* [3] system software. All non-hydrogen atoms were refined isotropically and then by anisotropic refinement using *SHELXL* [4].

Comment

Half-sandwich complexes are versatile and highly modifiable organometallics, which contain a π -bonded neutral arene or negatively charged cyclopentadienyl ligand, and, usually, one monodentate and one bidentate ligand. The monodentate and bidentate ligands allow further structural and electronic control of reactivity, including the incorporation of bio-active moieties [5–7]. The complexes have found application as good catalysts in transfer hydrogenation and aerobic alcohol oxidation [5–8]. In addition, the complexes have found biological applications as anticancer agents and antibacterial agents [5].

The asymmetric unit of the title structure contains one cationic ruthenium complex and one [PF₆][−] anion. The cationic ruthenium(II) complex possesses a piano stool geometry, where the chelating ligand and the chlorido ligand occupy the position of three legs of a piano-stool and the arene ring occupies the remaining coordination sites as the seat of the stool [9–16]. The Ru–N bond lengths are 2.091(1) and 2.087(1) Å. These distances are comparable to those reported for other arene ruthenium complexes with N,N'-donor ligands [9–15]. The N–Ru–N bond angle was derived to be 76.96(6)°. The N–Ru–Cl bond angles are 82.65(4)° and 84.96(4)°. These values were close to those reported for related compounds [9–15]. All C–C, C–N and P–F bond lengths and angles are in the expected range. Non-classical intermolecular hydrogen bonds were found in the crystal packing of the title compound.

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