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Crystal structure of chlorido-(η^6 -toluene)(2,2'-bipyridine- κ^2N,N')ruthenium(II) hexafluorophosphate, $C_{17}H_{16}ClN_2RuPF_6$

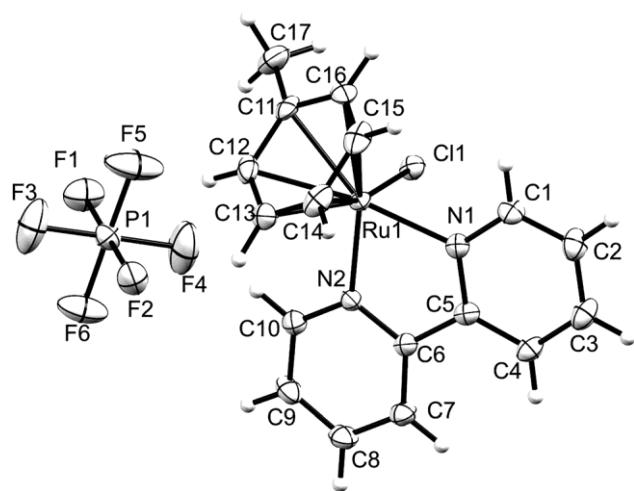


Table 1: Data collection and handling.

Crystal:	Gold block
Size:	0.11 × 0.09 × 0.03 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	1.13 mm ⁻¹
Diffractometer, scan mode:	Bruker Kappa Duo Apex II, 0.5% φ and ω
θ_{\max} , completeness:	28.4°, >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	39733, 4658, 0.072
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 3770
$N(\text{param})_{\text{refined}}$:	254
Programs:	Bruker [1], SHELX [2, 4], Mercury [3]

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Abstract

$C_{17}H_{16}ClN_2RuPF_6$, monoclinic, $P2_1/c$ (no. 14), $a = 14.4426(9)$ Å, $b = 8.3311(5)$ Å, $c = 16.413(1)$ Å, $\beta = 109.2690^\circ$, $V = 1864.2(2)$ Å³, $Z = 4$, $R_{\text{gt}}(F) = 0.0309$, $wR_{\text{ref}}(F^2) = 0.0697$, $T = 173$ 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

To a suspension of $[(\eta^6\text{-toluene})Ru(m\text{-Cl})Cl]_2$ (0.2 mmol) in methanol (20 mL) was added the 2,2'-bipyridine ligand

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(0.42 mmol). The mixture was stirred at room temperature for 3 h followed by the reduction of the volume of the solvent in vacuo to about (10 mL) before adding NH_4PF_6 (0.42 mmol). The mixture was 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 solutions of the compounds in acetone with hexane and leaving undisturbed for two days. Orange solid, yield 84%, m.p. 190 °C (decomp.). ¹H NMR (400 MHz, DMSO-*d*₆). δ (ppm) = 9.55 (d, $J_{\text{HH}} = 5.48$ Hz, 2H, Py); 8.62 (d, $J_{\text{HH}} = 8.04$ Hz, 2H, Py); 8.28 (t, $J_{\text{HHH}} = 7.76$ Hz, 2H, Py); 7.79 (d, $J_{\text{HH}} = 6.48$ Hz, 2H, Py); 6.31 (t, $J_{\text{HHH}} = 5.88$ Hz, 2H, Arene); 5.95 (d, $J_{\text{HH}} = 6.04$ Hz, 2H, Arene); 5.83 (t, $J_{\text{HHH}} = 5.64$ Hz, 1H, Arene); 2.23 (s, 3H, Arene), ¹³C NMR (400 MHz, DMSO-*d*₆). δ (ppm) = 155.819 (Py), 154.52 (Py), 139.81 (Py); 127.35 (Py); 123.64 (Py); 105.87 (Py); 105.87 (Ar); 90.53 (Ar); 82.93 (Ar); 79.73 (Ar); 18.73 (Me). MS (ESI, m/z): 385.0061 [$C_{17}H_{16}ClN_2Ru$]⁺.

Experimental details

A Bruker Smart APEX2 diffractometer was used for crystal evaluation and data collection [1]. The structure was solved by the direct method using the *SHELXS* [2] program and refined. The visual crystal structure information was performed using *Mercury* [3] system software.

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

Atom	x	y	z	U_{iso}^*/U_{eq}
Ru1	0.22422 (2)	0.15753 (2)	0.36493 (2)	0.01760 (6)
Cl1	0.36280 (4)	0.25838 (8)	0.33130 (4)	0.02259 (14)
N1	0.31536 (15)	0.1738 (3)	0.49283 (14)	0.0202 (5)
N2	0.29840 (15)	-0.0597 (3)	0.38481 (14)	0.0198 (5)
C1	0.3230 (2)	0.3052 (3)	0.54244 (18)	0.0243 (6)
H1	0.285391	0.397606	0.518325	0.029*
C2	0.3837 (2)	0.3095 (4)	0.62705 (19)	0.0302 (7)
H2	0.386517	0.402744	0.661125	0.036*
C3	0.4406 (2)	0.1766 (4)	0.66206 (19)	0.0304 (7)
H3	0.483063	0.177441	0.720296	0.036*
C4	0.43469 (19)	0.0428 (4)	0.61085 (18)	0.0251 (6)
H4	0.473521	-0.049288	0.633305	0.030*
C5	0.37137 (18)	0.0443 (3)	0.52623 (17)	0.0201 (5)
C6	0.36048 (18)	-0.0896 (3)	0.46538 (17)	0.0197 (5)
C7	0.40899 (19)	-0.2357 (3)	0.48628 (19)	0.0256 (6)
H7	0.451568	-0.255689	0.543333	0.031*
C8	0.3945 (2)	-0.3516 (3)	0.4230 (2)	0.0298 (6)
H8	0.425962	-0.452986	0.436329	0.036*
C9	0.3340 (2)	-0.3181 (3)	0.3406 (2)	0.0293 (7)
H9	0.324206	-0.395402	0.296019	0.035*
C10	0.2877 (2)	-0.1713 (3)	0.32342 (19)	0.0258 (6)
H10	0.246745	-0.148367	0.266159	0.031*
C11	0.12364 (18)	0.2654 (3)	0.24319 (18)	0.0248 (6)
C12	0.10172 (19)	0.1014 (3)	0.24589 (19)	0.0261 (6)
H12	0.098012	0.034328	0.198108	0.031*
C13	0.08508 (19)	0.0354 (4)	0.3198 (2)	0.0284 (6)
H13	0.074184	-0.076683	0.322249	0.034*
C14	0.0845 (2)	0.1331 (4)	0.3891 (2)	0.0318 (7)
H14	0.070426	0.089113	0.437075	0.038*
C15	0.1053 (2)	0.2987 (4)	0.3863 (2)	0.0319 (7)
H15	0.105352	0.366382	0.432865	0.038*
C16	0.12569 (19)	0.3634 (3)	0.3153 (2)	0.0272 (6)
H16	0.141165	0.474185	0.315069	0.033*
C17	0.1480 (2)	0.3351 (4)	0.1683 (2)	0.0369 (7)
H17A	0.164750	0.248265	0.135374	0.055*
H17B	0.204027	0.408136	0.189877	0.055*
H17C	0.091277	0.394326	0.130936	0.055*
P1	0.15802 (6)	-0.21417 (9)	0.05156 (5)	0.02626 (17)
F1	0.18238 (15)	-0.1686 (2)	-0.03407 (12)	0.0444 (5)
F2	0.13395 (13)	-0.2577 (2)	0.13774 (11)	0.0371 (4)
F3	0.05123 (14)	-0.2670 (3)	-0.00468 (14)	0.0667 (7)
F4	0.26593 (16)	-0.1622 (3)	0.10806 (15)	0.0692 (7)
F5	0.1218 (2)	-0.0359 (3)	0.05619 (16)	0.0756 (8)
F6	0.19604 (17)	-0.3911 (2)	0.04708 (15)	0.0559 (6)

All non-hydrogen atoms were refined isotropically and then by anisotropic refinement using *SHELXL* [4].

Comment

Half-sandwich arene ruthenium(II) complexes of the type [(η⁶-arene) Ru(XY)Z] are referred to as piano stool structures, where XY is a bidentate chelating ligand and Z is a leaving

group [5-7]. These half-sandwich complexes contain the arene ring which is hydrophobic and can be derivatized to finetune the properties. For instance, the biological and physicochemical properties of the complexes can be modified by the exchange of the arene ligand. Making it more hydrophobic facilitates the admittance of Ru(II) complexes into cells and this contributes to their stability [5-7]. The arene half-sandwich complexes are also attractive due to their diverse possibilities of applications [5-8], made possible by introduction of various bidentate and monodentate ligands at the XY-site.

The asymmetric unit of the title structure contains one cationic ruthenium complex and one [PF₆]⁻ counter 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 [9-13]. The Ru-N bond strengths of the complex are 2.073(2) and 2.082(2) Å. These distances are comparable to those reported for other arene ruthenium complexes with *N,N'*-donor ligands [8-12]. The N-Ru-N bond angle was derived to be 77.07(8)°. These values, including other intramolecular bond parameters, are close to those reported for related compounds [9-15]. Non-classical intermolecular hydrogen bonds were found in the crystal packing of the title compound.

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