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cis-Bis(2,2′-bipyridyl-κ^2N,N')chloro(1-phenyl-4,4′-bipyridinium-$\kappa N^{1'}$)ruthenium(II) bis(hexafluorophosphate)

Benjamin J. Coe,[a]* Naomi R. M. Curati,[a] Simon R. Grabowski,[a] Peter N. Horton[b] and Michael B. Hursthouse[b]

[a]Department of Chemistry, University of Manchester, Manchester M13 9PL, England, and [b]EPSRC National Crystallography Service, School of Chemistry, University of Southampton, Highfield, Southampton SO17 1BJ, England

Correspondence e-mail: b.coe@man.ac.uk

Key indicators

Single-crystal X-ray study
T = 120 K
Mean σ(C–C) = 0.007 Å
Disorder in solvent or counterion
R factor = 0.060
wR factor = 0.128
Data-to-parameter ratio = 13.1

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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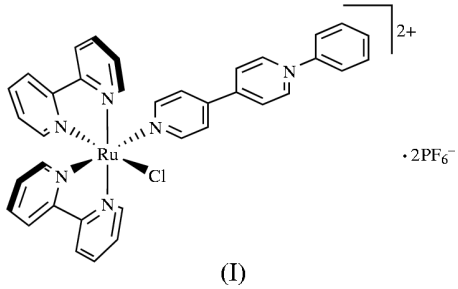
The crystal structure of the title compound, [RuCl($C_{16}H_{13}N_2$)($C_{10}H_8N_2$)$_2$](PF_6)$_2$, is described. Although related compounds are known to display nonlinear optical (NLO) properties, the present salt crystallizes in the centrosymmetric space group $P2_1/c$, so is not expected to show bulk NLO effects.

Comment

Investigations into new molecular materials having nonlinear optical (NLO) properties are important for the development of emerging optoelectronic and photonic technologies (Bosshard *et al.*, 1995; Nalwa & Miyata, 1997). Recent studies in this field have involved a wide range of organotransition metal complexes, which can show very pronounced NLO effects (Di Bella, 2001; Coe, 2004). Previous studies from our laboratory have included ruthenium(II) ammine complexes of *N*-arylated pyridinium ligands, such as *N*-phenyl-4,4′-bipyridinium (PhQ^+; Coe *et al.*, 1998, 2002; Coe, Jones *et al.*, 2003). The creation of potentially useful quadratic NLO materials requires the optimization of both molecular and macroscopic properties. Active chromophores must be arranged non-centrosymmetrically for bulk quadratic NLO effects, such as frequency doubling (second harmonic generation, SHG), to be observed.

We have recently studied a series of complex salts containing *cis*-$[Ru(NH_3)_4(L)_2]^{4+}$ (L = PhQ^+ *etc.*), which have strongly two-dimensional molecular NLO responses (Coe, Harris & Brunschwig, 2003). The investigation of related compounds is clearly of interest, and readily accessible targets include species in which the ammine ligands are replaced by the classical chelating 2,2′-bipyridyl (bpy) ligand. The new compound, (I), was synthesized as an intermediate on the route to *cis*-$[Ru(bpy)_2(PhQ^+)_2]^{4+}$, by the reaction of *cis*-$RuCl_2(bpy)_2\cdot 2H_2O$ (Lay *et al.*, 1986) with $[PhQ^+]PF_6$ (Coe *et al.*, 2000).



(I)

The complex salt, (I), shows an intense broad visible absorption band at λ_{max} = 498 nm in acetonitrile. This absorption is attributable to $d \rightarrow \pi^*$ metal-to-ligand charge-

transfer (MLCT) transitions from the Ru-based HOMO to the LUMOs localized on the bpy and PhQ^+ ligands. PhQ^+ is expected to be a stronger electron acceptor than bpy, so it is likely that the low-energy tail of the MLCT band corresponds to Ru→ PhQ^+ excitations. Such low-energy MLCT bands are typically associated with large molecular quadratic NLO responses (Di Bella, 2001; Coe, 2004). Cyclic voltammetric studies reveal a reversible $Ru^{III/II}$ wave at $E_{1/2}$ = 0.88 V *versus* Ag–AgCl, together with several irreversible ligand-based reduction processes, the first of which has an E_{pc} value of −0.63 V *versus* Ag–AgCl (most likely attributable to a $PhQ^{+/0}$ process).

The molecular structure of the complex cation in (I) is as indicated by ^{1}NMR spectroscopy, with an approximately octahedral metal centre and a *cis* arrangement of the bpy ligands (Fig. 1). The PhQ^+ ligand is highly twisted, with a dihedral angle of 37.5 (3)° defined by the ring planes N1/C1–C5 and N2/C9/C10/C6–C8, and an angle of 47.0 (3)° between the planes N2/C9/C10/C6–C8 and C11–C16. Smaller twists between the pyridyl and pyridinium rings of PhQ^+ have been observed in the compounds *trans*-$[Ru(NH_3)_4(PTZ)(PhQ^+)](PF_6)_3\cdot Et_2O$ (PTZ = S-coordinated phenothiazine; Coe *et al.*, 1998) and *trans*-$[RuCl(pdma)_2(PhQ^+)](PF_6)_3\cdot MeCN$ [pdma = 1,2-phenylenebis(dimethylarsine); Coe *et al.*, 2000], whilst *fac*-$[Re(CO)_3(L–L)(PhQ^+)](PF_6)_2$ (*L–L* = *N*,*N*′-bis-isopropyl-1,4-diazabutadiene) also shows a highly twisted ligand structure (Busby *et al.*, 2004).

The crystal packing of (I) is of interest with regard to quadratic NLO properties. Unfortunately, (I) adopts the centrosymmetric space group $P2_1/c$ and is therefore not expected to display bulk NLO effects. Nevertheless, it is quite possible that metathesis of the hexafluorophosphate counter-anions may cause the complex cations to adopt a more favourable crystal structure.

Experimental

A solution of *cis*-$RuCl_2(bpy)_2\cdot 2H_2O$ (100 mg. 0.192 mmol) and $[PhQ^+]PF_6$ (280 mg, 0.740 mmol) in degassed 2:1 ethanol/acetone (60 ml) was heated at reflux in the dark under Ar for 2.5 h. The resulting red–purple solution was reduced in volume on a rotary evaporator, and addition of aqueous NH_4PF_6 produced a purple precipitate, which was filtered off, washed with water and dried. Excess $[PhQ^+]PF_6$ was removed by washing several times with methanol to afford a dark-purple solid. Yield 102 mg (55%). The product (29 mg) was further purified by vapour diffusion of diethyl ether into a concentrated acetone solution, giving 22 mg of dark-purple crystals. Analysis calculated for $C_{36}H_{29}ClF_{12}N_6P_2Ru$: C 44.48, H 3.01, N 8.65%; found: C 44.50, H 2.86, N 8.51%. ^{1}H NMR (300 MHz, CD_3COCD_3, p.p.m.): 10.10 (1H, *d*, *J* = 5.7 Hz, bpy H^6), 9.52 (2H, *d*, *J* = 7.0 Hz, C_5H_4N), 9.11 (2H, *br s*, C_5H_4N), 8.80 (4H, *d*, *J* = 6.9 Hz, C_5H_4N), 8.73 (1H, *d*, *J* = 8.2 Hz, bpy H^3), 8.67 (1H, *d*, *J* = 7.8 Hz, bpy H^3), 8.64 (1H, *d*, *J* = 7.8 Hz, bpy H^3), 8.26 (2H, *m*, bpy H^4 and H^3), 8.18 (1H, *d*, *J* = 5.1 Hz, bpy H^6), 8.08–7.94 (7H, *m*, 2 Ph, 3bpy H^4 and 2bpy H^6), 7.84 (4H, *m*, 3 Ph and bpy H^5), 7.76 (1H, *m*, *J* = 1.5, 5.8 and 7.5 Hz, bpy H^5), 7.45 (1H, *m*, *J* = 1.5, 5.9 and 7.1 Hz, bpy H^5), 7.37 (1H, *m*, *J* = 1.3, 5.9 and 7.6 Hz, bpy H^5). ES–MS *m*/*z* = 995 ($\{M + Na^+\}^+$), 827 ($\{M - PF_6^-\}^+$). Crystals were obtained by slow diffusion of diethyl ether vapour into an acetone solution at 277 K.

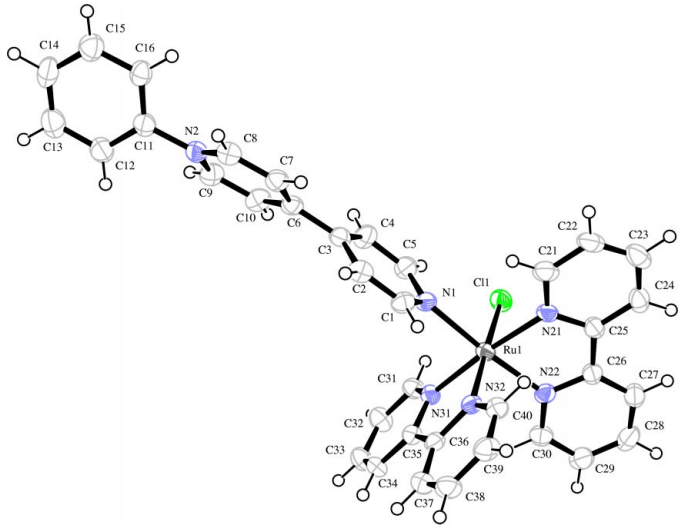


Figure 1
View of the complex cation in salt (I) (35% probability displacement ellipsoids).

Crystal data

$[RuCl(C_{16}H_{13}N_2)(C_{10}H_8N_2)_2](PF_6)_2$	D_x = 1.735 Mg m^{-3}
M_r = 972.11	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 8598 reflections
a = 12.687 (3) Å	θ = 2.9–27.5°
b = 23.424 (17) Å	μ = 0.68 mm^{-1}
c = 12.956 (8) Å	T = 120 (2) K
β = 104.80 (4)°	Plate, dark purple
V = 3722 (4) Å^3	0.38 × 0.22 × 0.03 mm
Z = 4	

Data collection

Nonius KappaCCD area-detector diffractometer	8537 independent reflections
	5485 reflections with $I > 2\sigma(I)$
φ and ω scans	R_{int} = 0.097
Absorption correction: multi-scan (*SORTAV*; Blessing, 1995, 1997)	θ_{max} = 27.5°
	$h = -16 \rightarrow 15$
T_{min} = 0.783, T_{max} = 0.980	$k = -30 \rightarrow 30$
50 477 measured reflections	$l = -16 \rightarrow 16$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0483P)^2 + 5.3619P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)]$ = 0.060	
$wR(F^2)$ = 0.128	
S = 1.03	$(\Delta/\sigma)_{max} < 0.001$
8537 reflections	$\Delta\rho_{max}$ = 1.40 e Å^{-3}
651 parameters	$\Delta\rho_{min}$ = −0.49 e Å^{-3}
H-atom parameters constrained	

Table 1
Selected geometric parameters (Å, °).

Ru1—N32	2.029 (3)	Ru1—N31	2.057 (3)
Ru1—N22	2.038 (3)	Ru1—N1	2.125 (3)
Ru1—N21	2.053 (3)	Ru1—Cl1	2.4059 (16)
N32—Ru1—N22	91.32 (13)	N21—Ru1—N1	97.65 (13)
N32—Ru1—N21	98.91 (14)	N31—Ru1—N1	87.81 (13)
N22—Ru1—N21	78.99 (14)	N32—Ru1—Cl1	173.48 (10)
N32—Ru1—N31	79.60 (15)	N22—Ru1—Cl1	84.68 (10)
N22—Ru1—N31	95.61 (13)	N21—Ru1—Cl1	85.41 (11)
N21—Ru1—N31	174.40 (13)	N31—Ru1—Cl1	95.63 (11)
N32—Ru1—N1	92.09 (13)	N1—Ru1—Cl1	92.18 (10)
N22—Ru1—N1	175.56 (13)		

The two hexafluorophosphate anions were both disordered over two main sites [site-occupancy factors: (i) PF_6 0.45 (2):0.55 (2) P1:P101; (ii) PF_6 0.581 (5):0.419 (2) P11:P111]. To simplify the modelling, the P—F bonds were restrained to be similar in length, with angles close to 90°. These restraints have resulted in some closer contacts than expected. All H atoms were included in idealized positions, with C—H = 0.95 Å and U_{iso}(H) values set at $1.2U_{eq}$(C). The maximum electron-density peak is 2.23 Å from atom H39.

Data collection: *DENZO* (Otwinowski & Minor, 1997); cell refinement: *DENZO* and *COLLECT* (Hooft, 1998); data reduction: *DENZO* and *COLLECT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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(I)

Crystal data

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$M_r = 972.11$
Monoclinic, $P2_1/c$
$a = 12.687$ (3) Å
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$c = 12.956$ (8) Å
$\beta = 104.80$ (4)°
$V = 3722$ (4) Å^3
$Z = 4$
$F(000) = 1944$
$D_x = 1.735$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 8598 reflections
$\theta = 2.9$–27.5°
$\mu = 0.68$ mm^{-1}
$T = 120$ K
Plate, red
0.38 × 0.22 × 0.03 mm

Data collection

Nonius KappaCCD area-detector diffractometer
Radiation source: Nonius FR591 rotating anode
Graphite monochromator
Detector resolution: 9.091 pixels mm^{-1}
φ and ω scans to fill Ewald Sphere
Absorption correction: multi-scan (SORTAV, Blessing, 1995, 1997)
$T_{min} = 0.783$, $T_{max} = 0.980$
50477 measured reflections
8537 independent reflections
5485 reflections with $I > 2\sigma(I)$
$R_{int} = 0.097$
$\theta_{max} = 27.5°$, $\theta_{min} = 3.1°$
$h = -16 \rightarrow 15$
$k = -30 \rightarrow 30$
$l = -16 \rightarrow 16$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.060$
$wR(F^2) = 0.128$
$S = 1.03$
8537 reflections
651 parameters
612 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0483P)^2 + 5.3619P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 1.40$ e Å^{-3}
$\Delta\rho_{min} = -0.49$ e Å^{-3}

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
Ru1	0.75061 (3)	0.111296 (13)	0.21958 (3)	0.02808 (11)	
Cl1	0.64391 (9)	0.04872 (4)	0.08574 (9)	0.0369 (3)	
C1	0.9900 (3)	0.11951 (17)	0.2087 (3)	0.0333 (10)	
H1	1.0009	0.1338	0.2793	0.040*	
C2	1.0783 (3)	0.11734 (17)	0.1661 (3)	0.0336 (10)	
H2	1.1479	0.1298	0.2066	0.040*	
C3	1.0648 (3)	0.09659 (17)	0.0622 (3)	0.0308 (10)	
C4	0.9614 (3)	0.07829 (19)	0.0102 (4)	0.0373 (11)	
H4	0.9484	0.0632	−0.0600	0.045*	
C5	0.8782 (4)	0.08157 (18)	0.0581 (4)	0.0362 (10)	
H5	0.8084	0.0683	0.0200	0.043*	
C6	1.1534 (3)	0.09743 (17)	0.0066 (3)	0.0313 (10)	
C7	1.2622 (3)	0.08703 (17)	0.0571 (3)	0.0331 (10)	
H7	1.2821	0.0765	0.1304	0.040*	
C8	1.3411 (3)	0.09177 (18)	0.0027 (3)	0.0344 (10)	
H8	1.4152	0.0844	0.0381	0.041*	
C9	1.2097 (4)	0.11577 (18)	−0.1524 (4)	0.0364 (10)	
H9	1.1916	0.1257	−0.2260	0.044*	
C10	1.1287 (4)	0.11082 (19)	−0.1009 (3)	0.0370 (10)	
H10	1.0549	0.1166	−0.1391	0.044*	
C11	1.3976 (3)	0.11371 (18)	−0.1598 (3)	0.0346 (10)	
C12	1.3931 (4)	0.1609 (2)	−0.2240 (4)	0.0431 (11)	
H12	1.3387	0.1893	−0.2285	0.052*	
C13	1.4703 (4)	0.1655 (2)	−0.2816 (4)	0.0506 (13)	
H13	1.4696	0.1978	−0.3262	0.061*	
C14	1.5476 (4)	0.1243 (2)	−0.2752 (4)	0.0493 (13)	
H14	1.5998	0.1278	−0.3160	0.059*	
C15	1.5501 (4)	0.0781 (2)	−0.2104 (4)	0.0458 (12)	
H15	1.6049	0.0499	−0.2057	0.055*	
C16	1.4748 (3)	0.07181 (19)	−0.1519 (3)	0.0357 (10)	
H16	1.4760	0.0395	−0.1073	0.043*	
N1	0.8894 (3)	0.10280 (13)	0.1574 (3)	0.0303 (8)	
N2	1.3138 (3)	0.10693 (14)	−0.1012 (3)	0.0318 (8)	
C21	0.8645 (4)	0.00676 (18)	0.3363 (4)	0.0398 (11)	
H21	0.9263	0.0183	0.3128	0.048*	

C22	0.8682 (4)	−0.04451 (19)	0.3905 (4)	0.0443 (12)	
H22	0.9321	−0.0674	0.4040	0.053*	
C23	0.7811 (5)	−0.0620 (2)	0.4243 (4)	0.0486 (13)	
H23	0.7822	−0.0974	0.4602	0.058*	
C24	0.6908 (4)	−0.02721 (19)	0.4056 (3)	0.0411 (11)	
H24	0.6287	−0.0386	0.4287	0.049*	
C25	0.6903 (4)	0.02437 (18)	0.3530 (3)	0.0355 (10)	
C26	0.6005 (4)	0.06549 (18)	0.3333 (3)	0.0342 (10)	
C27	0.5062 (4)	0.0586 (2)	0.3675 (4)	0.0415 (11)	
H27	0.4951	0.0248	0.4037	0.050*	
C28	0.4289 (4)	0.1013 (2)	0.3483 (4)	0.0453 (12)	
H28	0.3644	0.0972	0.3721	0.054*	
C29	0.4453 (4)	0.1496 (2)	0.2947 (4)	0.0427 (11)	
H29	0.3931	0.1796	0.2815	0.051*	
C30	0.5389 (3)	0.15359 (19)	0.2607 (3)	0.0358 (10)	
H30	0.5498	0.1869	0.2229	0.043*	
N21	0.7769 (3)	0.04043 (14)	0.3160 (3)	0.0319 (8)	
N22	0.6160 (3)	0.11275 (14)	0.2780 (3)	0.0312 (8)	
C31	0.6522 (3)	0.18837 (18)	0.0307 (3)	0.0340 (10)	
H31	0.6265	0.1541	−0.0066	0.041*	
C32	0.6250 (4)	0.23930 (19)	−0.0205 (4)	0.0403 (11)	
H32	0.5789	0.2403	−0.0909	0.048*	
C33	0.6650 (4)	0.28928 (19)	0.0308 (4)	0.0397 (11)	
H33	0.6482	0.3251	−0.0037	0.048*	
C34	0.7295 (3)	0.28589 (17)	0.1329 (4)	0.0341 (10)	
H34	0.7587	0.3198	0.1695	0.041*	
C35	0.7525 (3)	0.23367 (17)	0.1832 (3)	0.0308 (9)	
C36	0.8151 (3)	0.22600 (17)	0.2942 (3)	0.0293 (9)	
C37	0.8586 (4)	0.27001 (19)	0.3628 (4)	0.0378 (11)	
H37	0.8500	0.3084	0.3385	0.045*	
C38	0.9141 (4)	0.25818 (19)	0.4658 (4)	0.0416 (11)	
H38	0.9450	0.2882	0.5133	0.050*	
C39	0.9246 (4)	0.2024 (2)	0.4997 (3)	0.0394 (11)	
H39	0.9629	0.1933	0.5708	0.047*	
C40	0.8789 (3)	0.16000 (18)	0.4291 (3)	0.0343 (10)	
H40	0.8852	0.1216	0.4535	0.041*	
N31	0.7130 (3)	0.18468 (13)	0.1306 (3)	0.0288 (8)	
N32	0.8261 (3)	0.17033 (14)	0.3281 (3)	0.0281 (8)	
F1	1.3343 (12)	0.1808 (5)	0.4946 (14)	0.081 (5)	0.45 (2)
F2	1.2107 (13)	0.1984 (7)	0.5870 (11)	0.074 (4)	0.45 (2)
F3	1.1527 (10)	0.2741 (5)	0.4872 (17)	0.097 (5)	0.45 (2)
F4	1.1588 (13)	0.1890 (8)	0.4098 (12)	0.117 (6)	0.45 (2)
F5	1.2749 (13)	0.2566 (7)	0.3927 (18)	0.124 (6)	0.45 (2)
F6	1.3279 (8)	0.2662 (5)	0.569 (2)	0.105 (6)	0.45 (2)
P1	1.2432 (9)	0.2276 (4)	0.4897 (12)	0.072 (3)	0.45 (2)
F101	1.3098 (7)	0.2751 (3)	0.4877 (12)	0.080 (3)	0.55 (2)
F102	1.2117 (11)	0.2166 (7)	0.5690 (9)	0.071 (3)	0.55 (2)
F103	1.1430 (8)	0.1748 (4)	0.4139 (9)	0.060 (3)	0.55 (2)

F104	1.1295 (8)	0.2679 (5)	0.4225 (14)	0.092 (4)	0.55 (2)
F105	1.2439 (7)	0.2296 (5)	0.3349 (8)	0.078 (3)	0.55 (2)
F106	1.3239 (8)	0.1792 (4)	0.4792 (11)	0.059 (3)	0.55 (2)
P101	1.2279 (5)	0.2245 (3)	0.4527 (7)	0.0457 (16)	0.55 (2)
F11	1.2027 (7)	−0.0807 (4)	0.2224 (7)	0.054 (2)	0.581 (5)
F12	1.0650 (8)	−0.0206 (6)	0.2242 (11)	0.038 (3)	0.581 (5)
F13	1.1163 (4)	−0.0208 (3)	0.4038 (4)	0.0532 (17)	0.581 (5)
F14	1.2366 (4)	0.0037 (2)	0.3098 (5)	0.0577 (18)	0.581 (5)
F15	1.2575 (4)	−0.0787 (2)	0.4007 (3)	0.0438 (14)	0.581 (5)
F16	1.0847 (4)	−0.10382 (18)	0.3157 (4)	0.0492 (15)	0.581 (5)
P11	1.1611 (4)	−0.0492 (2)	0.3136 (4)	0.0307 (10)	0.581 (5)
F111	1.1848 (13)	−0.0931 (5)	0.2491 (11)	0.091 (6)	0.419 (5)
F112	1.0578 (11)	−0.0255 (9)	0.2354 (15)	0.047 (5)	0.419 (5)
F113	1.1773 (7)	0.0282 (3)	0.3503 (5)	0.062 (2)	0.419 (5)
F114	1.2220 (5)	−0.0060 (3)	0.2088 (6)	0.059 (2)	0.419 (5)
F115	1.3033 (6)	−0.0400 (4)	0.3723 (5)	0.063 (2)	0.419 (5)
F116	1.1404 (8)	−0.0588 (5)	0.3988 (7)	0.078 (3)	0.419 (5)
P111	1.1815 (6)	−0.0333 (3)	0.3028 (6)	0.0393 (17)	0.419 (5)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ru1	0.0348 (2)	0.02182 (17)	0.0286 (2)	−0.00108 (15)	0.00990 (14)	−0.00148 (15)
Cl1	0.0439 (6)	0.0312 (6)	0.0360 (6)	−0.0081 (5)	0.0110 (5)	−0.0054 (5)
C1	0.034 (2)	0.035 (2)	0.030 (2)	0.0032 (19)	0.007 (2)	−0.0032 (19)
C2	0.035 (2)	0.032 (2)	0.029 (2)	0.0009 (19)	0.0006 (19)	−0.0024 (19)
C3	0.037 (2)	0.025 (2)	0.030 (2)	0.0036 (17)	0.008 (2)	0.0003 (17)
C4	0.039 (3)	0.044 (3)	0.030 (2)	−0.007 (2)	0.010 (2)	−0.011 (2)
C5	0.034 (2)	0.036 (3)	0.039 (3)	−0.0059 (19)	0.010 (2)	−0.007 (2)
C6	0.037 (3)	0.027 (2)	0.030 (2)	−0.0001 (17)	0.008 (2)	−0.0063 (18)
C7	0.039 (3)	0.031 (2)	0.030 (2)	−0.0003 (19)	0.008 (2)	−0.0025 (19)
C8	0.033 (2)	0.034 (2)	0.033 (3)	0.0007 (18)	0.002 (2)	−0.0026 (19)
C9	0.041 (3)	0.039 (3)	0.028 (2)	0.000 (2)	0.007 (2)	−0.005 (2)
C10	0.034 (2)	0.043 (3)	0.032 (3)	−0.001 (2)	0.005 (2)	−0.009 (2)
C11	0.039 (2)	0.033 (2)	0.033 (2)	−0.009 (2)	0.010 (2)	−0.008 (2)
C12	0.053 (3)	0.037 (3)	0.042 (3)	−0.005 (2)	0.018 (2)	−0.002 (2)
C13	0.062 (3)	0.047 (3)	0.045 (3)	−0.010 (3)	0.018 (3)	0.004 (2)
C14	0.047 (3)	0.059 (3)	0.047 (3)	−0.016 (2)	0.024 (3)	−0.003 (3)
C15	0.042 (3)	0.048 (3)	0.049 (3)	−0.005 (2)	0.015 (2)	−0.003 (2)
C16	0.032 (2)	0.040 (3)	0.035 (3)	−0.007 (2)	0.009 (2)	−0.003 (2)
N1	0.036 (2)	0.0267 (19)	0.029 (2)	0.0030 (15)	0.0105 (16)	−0.0019 (15)
N2	0.037 (2)	0.0274 (19)	0.032 (2)	−0.0028 (15)	0.0104 (17)	−0.0031 (16)
C21	0.050 (3)	0.032 (2)	0.037 (3)	0.005 (2)	0.011 (2)	−0.006 (2)
C22	0.070 (3)	0.028 (2)	0.033 (3)	0.013 (2)	0.011 (2)	−0.003 (2)
C23	0.084 (4)	0.028 (3)	0.032 (3)	−0.004 (3)	0.013 (3)	−0.002 (2)
C24	0.061 (3)	0.037 (3)	0.027 (3)	−0.011 (2)	0.015 (2)	−0.003 (2)
C25	0.053 (3)	0.029 (2)	0.026 (2)	−0.004 (2)	0.013 (2)	−0.0019 (19)
C26	0.047 (3)	0.031 (2)	0.027 (2)	−0.007 (2)	0.013 (2)	−0.0050 (19)

C27	0.054 (3)	0.038 (3)	0.036 (3)	−0.010 (2)	0.018 (2)	−0.002 (2)
C28	0.044 (3)	0.057 (3)	0.040 (3)	−0.011 (2)	0.021 (2)	−0.011 (2)
C29	0.040 (3)	0.043 (3)	0.047 (3)	−0.002 (2)	0.014 (2)	−0.008 (2)
C30	0.036 (3)	0.033 (2)	0.036 (3)	−0.0007 (19)	0.006 (2)	−0.005 (2)
N21	0.050 (2)	0.0221 (18)	0.0258 (19)	0.0033 (16)	0.0131 (17)	−0.0030 (15)
N22	0.034 (2)	0.0311 (19)	0.031 (2)	−0.0042 (16)	0.0113 (16)	−0.0072 (17)
C31	0.036 (2)	0.031 (2)	0.034 (3)	−0.0028 (18)	0.007 (2)	−0.004 (2)
C32	0.043 (3)	0.038 (3)	0.035 (3)	−0.001 (2)	0.001 (2)	0.005 (2)
C33	0.046 (3)	0.032 (2)	0.040 (3)	0.004 (2)	0.010 (2)	0.010 (2)
C34	0.041 (3)	0.022 (2)	0.041 (3)	−0.0016 (18)	0.013 (2)	0.0003 (19)
C35	0.031 (2)	0.029 (2)	0.035 (3)	−0.0016 (18)	0.013 (2)	−0.0017 (19)
C36	0.028 (2)	0.030 (2)	0.033 (2)	0.0002 (17)	0.0131 (19)	−0.0044 (19)
C37	0.044 (3)	0.031 (2)	0.039 (3)	−0.003 (2)	0.013 (2)	−0.003 (2)
C38	0.046 (3)	0.036 (3)	0.043 (3)	−0.005 (2)	0.012 (2)	−0.013 (2)
C39	0.046 (3)	0.045 (3)	0.026 (2)	0.002 (2)	0.008 (2)	−0.004 (2)
C40	0.042 (3)	0.031 (2)	0.031 (3)	0.0005 (19)	0.013 (2)	−0.002 (2)
N31	0.0317 (19)	0.0272 (18)	0.028 (2)	0.0002 (14)	0.0081 (16)	0.0010 (15)
N32	0.0308 (19)	0.0281 (18)	0.027 (2)	−0.0017 (14)	0.0111 (16)	−0.0047 (15)
F1	0.112 (11)	0.060 (9)	0.064 (9)	0.018 (7)	0.009 (7)	−0.016 (6)
F2	0.104 (8)	0.056 (8)	0.064 (7)	0.028 (6)	0.021 (6)	0.009 (5)
F3	0.082 (7)	0.051 (6)	0.146 (13)	0.011 (5)	0.005 (8)	0.030 (7)
F4	0.151 (12)	0.115 (12)	0.066 (8)	−0.051 (9)	−0.005 (8)	0.003 (8)
F5	0.165 (13)	0.089 (11)	0.134 (14)	−0.008 (9)	0.065 (12)	0.055 (11)
F6	0.092 (7)	0.062 (6)	0.155 (16)	−0.010 (5)	0.018 (8)	−0.049 (8)
P1	0.088 (5)	0.034 (3)	0.095 (7)	−0.001 (3)	0.024 (4)	0.008 (4)
F101	0.083 (5)	0.048 (4)	0.101 (9)	−0.022 (3)	0.009 (6)	0.002 (5)
F102	0.089 (6)	0.081 (9)	0.055 (6)	0.008 (5)	0.038 (5)	−0.006 (5)
F103	0.065 (5)	0.046 (4)	0.060 (5)	−0.019 (3)	−0.001 (4)	0.009 (3)
F104	0.073 (5)	0.058 (5)	0.144 (11)	0.021 (4)	0.027 (6)	0.034 (6)
F105	0.087 (5)	0.093 (7)	0.057 (5)	−0.009 (4)	0.024 (4)	0.023 (4)
F106	0.054 (5)	0.052 (7)	0.080 (7)	0.005 (4)	0.032 (5)	−0.001 (5)
P101	0.046 (2)	0.031 (2)	0.063 (4)	−0.0042 (15)	0.018 (2)	0.005 (2)
F11	0.032 (3)	0.087 (6)	0.042 (4)	0.015 (3)	0.006 (3)	−0.017 (4)
F12	0.051 (5)	0.031 (4)	0.027 (5)	0.010 (4)	0.002 (4)	0.003 (3)
F13	0.050 (3)	0.071 (4)	0.036 (3)	0.016 (3)	0.005 (2)	−0.021 (3)
F14	0.052 (3)	0.039 (3)	0.079 (5)	−0.016 (3)	0.011 (3)	0.002 (3)
F15	0.048 (3)	0.043 (3)	0.033 (3)	0.011 (2)	−0.005 (2)	−0.010 (2)
F16	0.053 (3)	0.037 (3)	0.053 (3)	−0.008 (2)	0.006 (2)	0.009 (2)
P11	0.0355 (18)	0.031 (2)	0.0245 (19)	0.0020 (15)	0.0053 (13)	−0.0040 (15)
F111	0.149 (13)	0.028 (5)	0.080 (10)	0.025 (6)	−0.002 (7)	−0.021 (6)
F112	0.040 (6)	0.066 (10)	0.036 (8)	−0.009 (5)	0.014 (5)	−0.008 (6)
F113	0.086 (6)	0.046 (4)	0.045 (4)	0.005 (4)	−0.003 (4)	−0.016 (3)
F114	0.056 (5)	0.079 (5)	0.045 (5)	0.007 (4)	0.023 (4)	0.020 (4)
F115	0.062 (5)	0.083 (6)	0.040 (4)	0.016 (4)	0.006 (4)	−0.005 (4)
F116	0.083 (7)	0.104 (8)	0.047 (5)	−0.028 (6)	0.017 (5)	0.027 (6)
P111	0.053 (4)	0.034 (4)	0.034 (2)	0.006 (3)	0.015 (2)	0.002 (2)

Geometric parameters (Å, º)

Ru1—N32	2.029 (3)	C27—H27	0.9500
Ru1—N22	2.038 (3)	C28—C29	1.371 (6)
Ru1—N21	2.053 (3)	C28—H28	0.9500
Ru1—N31	2.057 (3)	C29—C30	1.372 (6)
Ru1—N1	2.125 (3)	C29—H29	0.9500
Ru1—Cl1	2.4059 (16)	C30—N22	1.345 (5)
C1—N1	1.338 (5)	C30—H30	0.9500
C1—C2	1.371 (6)	C31—N31	1.330 (5)
C1—H1	0.9500	C31—C32	1.366 (6)
C2—C3	1.400 (6)	C31—H31	0.9500
C2—H2	0.9500	C32—C33	1.377 (6)
C3—C4	1.381 (6)	C32—H32	0.9500
C3—C6	1.481 (6)	C33—C34	1.368 (6)
C4—C5	1.357 (6)	C33—H33	0.9500
C4—H4	0.9500	C34—C35	1.382 (6)
C5—N1	1.352 (5)	C34—H34	0.9500
C5—H5	0.9500	C35—N31	1.363 (5)
C6—C10	1.383 (6)	C35—C36	1.465 (6)
C6—C7	1.390 (6)	C36—N32	1.372 (5)
C7—C8	1.368 (6)	C36—C37	1.381 (6)
C7—H7	0.9500	C37—C38	1.370 (6)
C8—N2	1.349 (5)	C37—H37	0.9500
C8—H8	0.9500	C38—C39	1.373 (6)
C9—N2	1.334 (5)	C38—H38	0.9500
C9—C10	1.367 (6)	C39—C40	1.375 (6)
C9—H9	0.9500	C39—H39	0.9500
C10—H10	0.9500	C40—N32	1.331 (5)
C11—C16	1.372 (6)	C40—H40	0.9500
C11—C12	1.375 (6)	F1—P1	1.581 (11)
C11—N2	1.464 (5)	F2—P1	1.579 (10)
C12—C13	1.380 (6)	F3—P1	1.578 (11)
C12—H12	0.9500	F4—P1	1.570 (11)
C13—C14	1.363 (7)	F5—P1	1.568 (10)
C13—H13	0.9500	F6—P1	1.569 (10)
C14—C15	1.366 (7)	F101—P101	1.565 (8)
C14—H14	0.9500	F102—P101	1.583 (8)
C15—C16	1.370 (6)	F103—P101	1.579 (9)
C15—H15	0.9500	F104—P101	1.578 (9)
C16—H16	0.9500	F105—P101	1.596 (8)
C21—N21	1.332 (5)	F106—P101	1.586 (9)
C21—C22	1.386 (6)	F11—P11	1.593 (7)
C21—H21	0.9500	F12—P11	1.600 (8)
C22—C23	1.352 (7)	F13—P11	1.572 (6)
C22—H22	0.9500	F14—P11	1.575 (5)
C23—C24	1.375 (7)	F15—P11	1.594 (6)
C23—H23	0.9500	F16—P11	1.609 (6)

C24—C25	1.386 (6)	F111—P111	1.570 (10)
C24—H24	0.9500	F112—P111	1.600 (11)
C25—N21	1.360 (5)	F113—P111	1.571 (8)
C25—C26	1.463 (6)	F114—P111	1.575 (8)
C26—N22	1.360 (5)	F115—P111	1.585 (9)
C26—C27	1.387 (6)	F116—P111	1.583 (8)
C27—C28	1.379 (7)		

N32—Ru1—N22	91.32 (13)	C25—N21—Ru1	114.7 (3)
N32—Ru1—N21	98.91 (14)	C30—N22—C26	118.1 (4)
N22—Ru1—N21	78.99 (14)	C30—N22—Ru1	126.3 (3)
N32—Ru1—N31	79.60 (15)	C26—N22—Ru1	115.4 (3)
N22—Ru1—N31	95.61 (13)	N31—C31—C32	122.8 (4)
N21—Ru1—N31	174.40 (13)	N31—C31—H31	118.6
N32—Ru1—N1	92.09 (13)	C32—C31—H31	118.6
N22—Ru1—N1	175.56 (13)	C31—C32—C33	119.5 (4)
N21—Ru1—N1	97.65 (13)	C31—C32—H32	120.3
N31—Ru1—N1	87.81 (13)	C33—C32—H32	120.3
N32—Ru1—Cl1	173.48 (10)	C34—C33—C32	118.2 (4)
N22—Ru1—Cl1	84.68 (10)	C34—C33—H33	120.9
N21—Ru1—Cl1	85.41 (11)	C32—C33—H33	120.9
N31—Ru1—Cl1	95.63 (11)	C33—C34—C35	120.6 (4)
N1—Ru1—Cl1	92.18 (10)	C33—C34—H34	119.7
N1—C1—C2	124.3 (4)	C35—C34—H34	119.7
N1—C1—H1	117.9	N31—C35—C34	120.2 (4)
C2—C1—H1	117.9	N31—C35—C36	115.2 (4)
C1—C2—C3	119.2 (4)	C34—C35—C36	124.6 (4)
C1—C2—H2	120.4	N32—C36—C37	120.8 (4)
C3—C2—H2	120.4	N32—C36—C35	114.6 (3)
C4—C3—C2	116.4 (4)	C37—C36—C35	124.6 (4)
C4—C3—C6	120.7 (4)	C38—C37—C36	119.9 (4)
C2—C3—C6	122.7 (4)	C38—C37—H37	120.1
C5—C4—C3	120.8 (4)	C36—C37—H37	120.1
C5—C4—H4	119.6	C37—C38—C39	119.2 (4)
C3—C4—H4	119.6	C37—C38—H38	120.4
N1—C5—C4	123.4 (4)	C39—C38—H38	120.4
N1—C5—H5	118.3	C38—C39—C40	119.0 (4)
C4—C5—H5	118.3	C38—C39—H39	120.5
C10—C6—C7	117.1 (4)	C40—C39—H39	120.5
C10—C6—C3	119.2 (4)	N32—C40—C39	122.9 (4)
C7—C6—C3	123.7 (4)	N32—C40—H40	118.5
C8—C7—C6	120.8 (4)	C39—C40—H40	118.5
C8—C7—H7	119.6	C31—N31—C35	118.7 (4)
C6—C7—H7	119.6	C31—N31—Ru1	126.4 (3)
N2—C8—C7	120.0 (4)	C35—N31—Ru1	114.9 (3)
N2—C8—H8	120.0	C40—N32—C36	118.2 (3)
C7—C8—H8	120.0	C40—N32—Ru1	126.0 (3)
N2—C9—C10	121.1 (4)	C36—N32—Ru1	115.8 (3)

N2—C9—H9	119.5	F5—P1—F6	90.0 (6)
C10—C9—H9	119.5	F5—P1—F4	89.6 (7)
C9—C10—C6	120.4 (4)	F6—P1—F4	179.6 (8)
C9—C10—H10	119.8	F5—P1—F3	91.0 (6)
C6—C10—H10	119.8	F6—P1—F3	89.3 (6)
C16—C11—C12	122.6 (4)	F4—P1—F3	90.8 (6)
C16—C11—N2	118.9 (4)	F5—P1—F2	179.7 (9)
C12—C11—N2	118.5 (4)	F6—P1—F2	90.2 (6)
C11—C12—C13	117.7 (4)	F4—P1—F2	90.2 (7)
C11—C12—H12	121.1	F3—P1—F2	88.7 (6)
C13—C12—H12	121.1	F5—P1—F1	89.9 (7)
C14—C13—C12	120.7 (5)	F6—P1—F1	90.1 (6)
C14—C13—H13	119.7	F4—P1—F1	89.8 (7)
C12—C13—H13	119.7	F3—P1—F1	178.8 (8)
C13—C14—C15	120.1 (4)	F2—P1—F1	90.3 (7)
C13—C14—H14	119.9	F101—P101—F104	90.6 (6)
C15—C14—H14	119.9	F101—P101—F103	178.0 (7)
C14—C15—C16	121.0 (5)	F104—P101—F103	88.0 (5)
C14—C15—H15	119.5	F101—P101—F102	92.9 (7)
C16—C15—H15	119.5	F104—P101—F102	91.4 (6)
C15—C16—C11	117.8 (4)	F103—P101—F102	88.5 (6)
C15—C16—H16	121.1	F101—P101—F106	91.5 (5)
C11—C16—H16	121.1	F104—P101—F106	177.6 (8)
C1—N1—C5	115.8 (3)	F103—P101—F106	89.9 (6)
C1—N1—Ru1	124.2 (3)	F102—P101—F106	89.7 (6)
C5—N1—Ru1	119.9 (3)	F101—P101—F105	89.0 (5)
C9—N2—C8	120.5 (4)	F104—P101—F105	90.0 (6)
C9—N2—C11	118.8 (4)	F103—P101—F105	89.6 (6)
C8—N2—C11	120.7 (4)	F102—P101—F105	177.6 (7)
N21—C21—C22	122.1 (4)	F106—P101—F105	88.8 (6)
N21—C21—H21	118.9	F13—P11—F14	91.6 (4)
C22—C21—H21	118.9	F13—P11—F11	177.1 (6)
C23—C22—C21	120.1 (5)	F14—P11—F11	91.3 (5)
C23—C22—H22	120.0	F13—P11—F15	90.8 (4)
C21—C22—H22	120.0	F14—P11—F15	90.1 (4)
C22—C23—C24	118.5 (4)	F11—P11—F15	89.2 (4)
C22—C23—H23	120.8	F13—P11—F12	90.4 (6)
C24—C23—H23	120.8	F14—P11—F12	90.2 (6)
C23—C24—C25	120.2 (4)	F11—P11—F12	89.5 (6)
C23—C24—H24	119.9	F15—P11—F12	178.7 (7)
C25—C24—H24	119.9	F13—P11—F16	89.4 (4)
N21—C25—C24	120.7 (4)	F14—P11—F16	178.9 (5)
N21—C25—C26	114.8 (4)	F11—P11—F16	87.7 (4)
C24—C25—C26	124.5 (4)	F15—P11—F16	90.0 (3)
N22—C26—C27	121.0 (4)	F12—P11—F16	89.7 (6)
N22—C26—C25	114.7 (4)	F111—P111—F113	176.8 (8)
C27—C26—C25	124.3 (4)	F111—P111—F114	88.2 (7)
C28—C27—C26	119.4 (4)	F113—P111—F114	88.9 (5)

C28—C27—H27	120.3	F111—P111—F116	93.6 (8)
C26—C27—H27	120.3	F113—P111—F116	89.3 (6)
C29—C28—C27	119.8 (4)	F114—P111—F116	178.2 (7)
C29—C28—H28	120.1	F111—P111—F115	91.7 (7)
C27—C28—H28	120.1	F113—P111—F115	89.7 (5)
C28—C29—C30	118.4 (4)	F114—P111—F115	90.9 (5)
C28—C29—H29	120.8	F116—P111—F115	89.2 (6)
C30—C29—H29	120.8	F111—P111—F112	89.6 (10)
N22—C30—C29	123.4 (4)	F113—P111—F112	89.0 (9)
N22—C30—H30	118.3	F114—P111—F112	90.0 (9)
C29—C30—H30	118.3	F116—P111—F112	89.9 (9)
C21—N21—C25	118.4 (4)	F115—P111—F112	178.4 (10)
C21—N21—Ru1	126.6 (3)		