Acta Cryst. (1999). C**55**, IUC9900108 [**doi:10.1107/S0108270199098881**]

Bis(2,2'-bipyridine)(pyridine-2-carboxylate)ruthenium(II) hexafluorophosphate at 173K

K. Lashgari, R. Norrestam and B. Åkermark

Abstract

The structure of the title compound, [(bis(2,2'-bipyridine) (pyridine-2-carboxylate)ruthenium(II)] hexafluorophosphate, with the composition $[Ru(C_{10}H_8N_2)_2(C_6H_4NO_2)]PF_6$ was determined at 173 K. The result of the present study is in good agreement with the previously determined structure at 295 K (Canty *et al.*, 1997). The coordination formed by five N atoms and one O atom, around the Ru(II) ion deviate substantially from octahedral symmetry. The Ru—N distances is in the range 2.032 (2)–2.070 (2) Å while the Ru—O distance is 2.100 (2) Å. The bite angles of each bidentate ligand at the Ru atom is in the range 78.82 (10)–78.97 (11)°. The relatively large thermal parameters of the F atoms in the PF_6 anion can be assumed as being due to substantial rigid group vibrations.

Comment

As part of a project investigating artificial photosynthesis systems based on ruthenium polypyridine complexes as photo-active complex (Juris *et al.*, 1988), we have concentrated our attention to ruthenium polypyridine complexes with metal-co-ordinating substituents on *ortho* position to the N atom (Norrby *et al.*, 1997). Our structural study is providing necessary structural information for explanation of the different photophysical behaviour of the complexes and how different substituents affect the metal to ligand charge transfer (MLCT) process (Kalyanasundaram,1992; Roundhill, 1994).

The present work describes a single-crystal X-ray structure determination of the title compound [bis(2,2'-bipyridine)(pyridine-2-carboxylate) ruthenium(II)] hexafluorophosphate, abbrev. $[Ru(bpy)_2(pic)]PF_6$ at 173 K. The obtained result is in good agreement with a former structural study carried out by Canty *et al.* (1997) at ambient temperature (295 K). Although the present study provide a low temperature data set, which is considered to be more accurate. Other chemical studies on $[Ru(bpy)_2(pic)]PF_6$ include spectroscopical and electrochemical studies which have been carried out by two independent groups (Norrby *et al.*, 1997; Couchman *et al.*, 1998).

As expected, the unit cell volume for the present study is smaller (about 2.6%), compared to the unit cell volume observed for the room temperature study. A TLS-analysis performed on $[Ru(bpy)_2(pic)]PF_6$, shows that the PF_6^- molecule displacement clearly has considerable contribution from rigid body thermal motions. The corrections of the P—F bond distances is about 0.086 Å, which is significant and implies that the average P—F distances increase from 1.56 to 1.64 Å.

Experimental

The preparation and characterization of $[Ru(bpy)_2(pic)]PF_6$ by NMR, MS and UV spectroscopy is described in an article by Norrby *et al.*, (1997). Red crystals were obtained by slow evaporation of a methanol solution of $[Ru(bpy)_2(pic)]PF_6$ at room temperature. Experimental details are presented below. Selected bond lengths and bond angles for the coordination around Ru are given in Table 1.

CIF access

Refinement

Data collection began with a θ limit of 30°, but this was subseqently reduced to 25° because of the low observed intensity of the higher-angle data. The data set is complete up to 25° in θ and partial between 25 and 30°.

Computing details

Data collection: *DIF4* (Stoe & Cie, 1985); cell refinement: *DIF4* (Stoe & Cie, 1985); data reduction: *REDU4* (Stoe & Cie, 1985); program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); software used to prepare material for publication: *PLATON98* (Spek, 1990).

[bis(2,2'-bipyridine)(pyridine-2-carboxylato)ruthenium(II)] hexafluorophosphate

Crystal data

$[Ru(C_6H_4O_2)(C_{10}H_8N_2)_2]P_1F_6$	$V = 2547\ (2)$ Å^3
$M_r = 680.51$	$Z = 4$
Monoclinic, $P2_1/n$	Mo $K\alpha$
$a = 14.373\ (7)$ Å	$\mu = 0.76$ mm^{-1}
$b = 11.078\ (7)$ Å	$T = 173\ (2)$ K
$c = 16.788\ (8)$ Å	0.65 × 0.36 × 0.08 mm
β = 107.67 (5)º	

Data collection

STOE 4-circle diffractometer	5097 reflections with $I > 2\sigma(I)$
Absorption correction: Numerical (X-RED; Stoe & Cie, 1997)	$R_{int} = 0.021$
$T_{min} = 0.806$, $T_{max} = 0.919$	3 standard reflections
8171 measured reflections	every 360 min
6867 independent reflections	intensity decay: 10%

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.036$	370 parameters
$wR(F^2) = 0.105$	H-atom parameters constrained
$S = 1.00$	$\Delta\rho_{max} = 1.40$ e Å^{-3}
6867 reflections	$\Delta\rho_{min} = -1.19$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °)

Ru1—N1	2.063 (2)	Ru1—N21'	2.070 (2)
Ru1—O8	2.100 (2)	Ru1—N31	2.033 (2)

Ru1—N21	2.052 (3)	Ru1—N31'	2.038 (2)
N1—Ru1—O8	78.82 (9)	N31—Ru1—N31'	78.99 (10)
N21—Ru1—N21'	78.95 (10)		

Acknowledgements

The authors would like to thank Dr Thomas Norrby for preparing the compound studied in this paper. This work was supported by a grant from the Swedish Natural Science Research Council. K·*L*. would like to thank Dr J·C. Huffman for giving the opportunity to finish the present work at IUMSC.

References

Canty, A. J., Traill, P. R., Skelton, B. W. & White, A. H. (1997). *Inorg. Chim. Acta*, **255**, 117–123.

Couchman, S., Dominguez-Vera, J. M., Jeffery, J. C., McKee, C. A., Nevitt, S., Pohlman, M., White, C. M. & Ward, M. D. (1998). *Polyhedron*, **17**, 3541–3550.

Juris, A., Balzani, V., Barigelletti, F., Campagna, S., Belser, P. & von Zelewsky, A. (1988). *Coord. Chem. Rev.* **84**, 85–277.

Kalyanasundaram, K. (1992). Photochemistry of Polypyridine and Porphyrin Complexes. London: Academic Press.

Norrby, T., Börje, A., Åkermark, B., Hammarström, L., Alsins, J., Lashgari, K., Norrestam, R., Mårtensson, J. & Stenhagen, G. (1997). *Inorg. Chem.* **36**, 5850–5858.

Roundhill, D. M. (1994). Photochemistry and Photophysics of Metal Complexes. New York, USA: Plenum Press.

Sheldrick, G. M. (1985). *SHELXS86*. Program for crystal structure solution. University of Göttingen, Germany.

Sheldrick, G. M. (1997). *SHELXL97*. Program for crystal structure refinement. University of Göttingen, Germany.

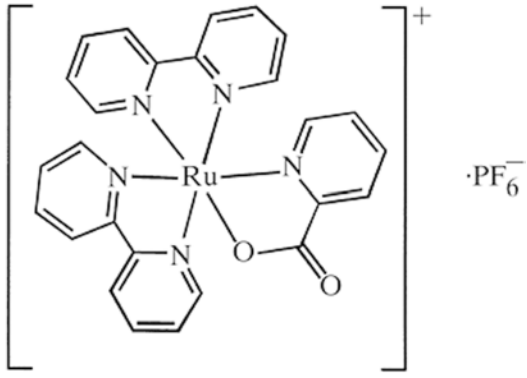
Spek, A. L. (1990). *PLATON98*, Acta Cryst. A46, C-34.

Stoe & Cie (1985). *DIF4* and *REDU4*. Stoe 4-circle diffractometer software. Stoe & Cie GmbH, Darmstadt, Germany.

Stoe & Cie (1997). *X-RED*. Data Reduction and Absorption Correction Program. Version 1.09. Stoe & Cie GmbH, Darmstadt, Germany.

CIF access

Scheme 1



supplementary materials

[bis(2,2'-bipyridine)(pyridine-2-carboxylato)ruthenium(II)] hexafluorophosphate

Crystal data

$[Ru(C_6H_4O_2)(C_{10}H_8N_2)_2]P_1F_6$	F_{000} = 1360
M_r = 680.51	D_x = 1.775 Mg m^{-3}
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation λ = 0.71073 Å
a = 14.373 (7) Å	Cell parameters from 22 reflections
b = 11.078 (7) Å	θ = 18.0–24.5º
c = 16.788 (8) Å	μ = 0.76 mm^{-1}
β = 107.67 (5)º	T = 173 (2) K
V = 2547 (2) Å^3	Thin flake, red
Z = 4	0.65 × 0.36 × 0.08 mm

Data collection

STOE 4-circle diffractometer	R_{int} = 0.021
Radiation source: fine-focus sealed tube	θ_{max} = 30.0º
Monochromator: graphite	θ_{min} = 1.6º
T = 173(2) K	h = −17→17
ω–2θ scans	k = −1→13
Absorption correction: Numerical (X-RED; Stoe & Cie, 1997)	l = −1→20
T_{min} = 0.806, T_{max} = 0.919	3 standard reflections
8171 measured reflections	every 360 min
6867 independent reflections	intensity decay: 10%
5097 reflections with $I > 2\sigma(I)$	

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)]$ = 0.036	H-atom parameters constrained
$wR(F^2)$ = 0.105	$w = 1/[\sigma^2(F_o^2) + (0.0567P)^2 + 3.8959P]$ where $P = (F_o^2 + 2F_c^2)/3$
S = 1.00	$(\Delta/\sigma)_{max}$ = 0.001
6867 reflections	$\Delta\rho_{max}$ = 1.40 e Å^{-3}
370 parameters	$\Delta\rho_{min}$ = −1.19 e Å^{-3}
Primary atom site location: patt	Extinction correction: none

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* andgoodness 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

$F^2 > 2\text{sigma}(F^2)$ 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.

The initial position of the Ru atom on a general position was found by interpretation of a calculated Patterson map (Sheldrick, 1985). The positions of the remaining non-hydrogen atoms were located by subsequent difference electron density maps and refined by full-matrix least squares techniques (Sheldrick, 1997).

Treatment of H-atoms: The aromatic hydrogen atoms were placed at calculated positions and later refined by applying the same coordinate shift as their parent carbon atoms and with their thermal parameters 1.3 times larger than those of the parent carbon atoms. The structure was refined with all the non-hydrogen atoms having anisotropic thermal parameters.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($Å^2$)

	x	*y*	*z*	U_{iso}*/U_{eq}
Ru1	0.267007 (14)	0.008616 (18)	0.115398 (12)	0.01662 (7)
P1	0.73637 (7)	0.01010 (10)	0.37607 (6)	0.0395 (2)
F1	0.7340 (2)	0.1195 (3)	0.4370 (2)	0.0771 (9)
F2	0.7405 (3)	−0.0990 (4)	0.3174 (2)	0.0954 (12)
F3	0.6233 (2)	0.0212 (4)	0.3374 (3)	0.1090 (14)
F4	0.8498 (2)	0.0071 (4)	0.4139 (4)	0.143 (2)
F5	0.7200 (5)	−0.0817 (3)	0.4407 (2)	0.136 (2)
F6	0.7506 (4)	0.1045 (5)	0.3111 (3)	0.1353 (18)
N1	0.32232 (16)	−0.0081 (2)	0.24354 (14)	0.0187 (4)
C2	0.26556 (19)	0.0437 (3)	0.28571 (16)	0.0203 (5)
C3	0.2882 (2)	0.0362 (3)	0.37159 (18)	0.0260 (6)
H3	0.2462	0.0708	0.3994	0.034*
C4	0.3732 (2)	−0.0227 (3)	0.41690 (18)	0.0292 (6)
H4	0.3905	−0.0287	0.4760	0.038*
C5	0.4321 (2)	−0.0723 (3)	0.37385 (19)	0.0277 (6)
H5	0.4915	−0.1111	0.4035	0.036*
C6	0.40443 (19)	−0.0653 (3)	0.28792 (18)	0.0234 (5)
H6	0.4445	−0.1021	0.2590	0.030*
C7	0.1783 (2)	0.1139 (3)	0.23238 (17)	0.0236 (5)
O8	0.17192 (14)	0.12113 (18)	0.15484 (12)	0.0226 (4)
O9	0.12222 (16)	0.1603 (2)	0.26584 (14)	0.0344 (5)
N21	0.19650 (16)	0.0171 (2)	−0.01061 (14)	0.0196 (4)
C22	0.12022 (19)	−0.0605 (3)	−0.03955 (16)	0.0205 (5)

C23	0.0735 (2)	−0.0755 (3)	−0.12451 (18)	0.0282 (6)
H23	0.0207	−0.1305	−0.1433	0.037*
C24	0.1051 (2)	−0.0095 (3)	−0.18126 (19)	0.0327 (7)
H24	0.0757	−0.0207	−0.2396	0.043*
C25	0.1799 (2)	0.0731 (3)	−0.15205 (19)	0.0312 (6)
H25	0.2009	0.1219	−0.1899	0.041*
C26	0.2238 (2)	0.0834 (3)	−0.06682 (18)	0.0248 (6)
H26	0.2755	0.1397	−0.0471	0.032*
N21'	0.15930 (15)	−0.1203 (2)	0.10309 (14)	0.0189 (4)
C22'	0.09308 (19)	−0.1269 (2)	0.02599 (16)	0.0201 (5)
C23'	0.00545 (19)	−0.1887 (3)	0.01160 (17)	0.0233 (5)
H23'	−0.0401	−0.1909	−0.0429	0.030*
C24'	−0.0150 (2)	−0.2471 (3)	0.07756 (19)	0.0251 (6)
H24'	−0.0748	−0.2891	0.0691	0.033*
C25'	0.0533 (2)	−0.2428 (3)	0.15545 (18)	0.0239 (5)
H25'	0.0417	−0.2832	0.2014	0.031*
C26'	0.1391 (2)	−0.1790 (2)	0.16612 (17)	0.0213 (5)
H26'	0.1857	−0.1765	0.2202	0.028*
N31	0.37594 (17)	−0.0892 (2)	0.09280 (14)	0.0210 (4)
C32	0.4635 (2)	−0.0308 (3)	0.11060 (18)	0.0255 (6)
C33	0.5479 (2)	−0.0925 (3)	0.1127 (2)	0.0386 (8)
H33	0.6089	−0.0517	0.1279	0.050*
C34	0.5430 (3)	−0.2137 (4)	0.0926 (3)	0.0468 (10)
H34	0.6006	−0.2574	0.0949	0.061*
C35	0.4533 (3)	−0.2709 (3)	0.0692 (2)	0.0414 (8)
H35	0.4480	−0.3533	0.0526	0.054*
C36	0.3714 (2)	−0.2063 (3)	0.0704 (2)	0.0299 (6)
H36	0.3099	−0.2458	0.0548	0.039*
N31'	0.36773 (16)	0.1400 (2)	0.11984 (14)	0.0214 (5)
C32'	0.4585 (2)	0.0999 (3)	0.12403 (17)	0.0246 (6)
C33'	0.5356 (2)	0.1801 (3)	0.1351 (2)	0.0365 (8)
H33'	0.5993	0.1510	0.1402	0.047*
C34'	0.5192 (3)	0.3020 (3)	0.1388 (2)	0.0408 (8)
H34'	0.5717	0.3575	0.1469	0.053*
C35'	0.4262 (3)	0.3432 (3)	0.1307 (2)	0.0372 (7)
H35'	0.4133	0.4272	0.1311	0.048*
C36'	0.3522 (2)	0.2600 (3)	0.12194 (18)	0.0271 (6)
H36'	0.2884	0.2881	0.1173	0.035*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ru1	0.01214 (10)	0.02258 (11)	0.01474 (10)	−0.00218 (8)	0.00347 (6)	0.00043 (8)
P1	0.0287 (4)	0.0583 (6)	0.0336 (5)	0.0063 (4)	0.0126 (3)	−0.0043 (4)
F1	0.0694 (19)	0.0647 (18)	0.102 (2)	0.0189 (15)	0.0327 (17)	−0.0263 (17)
F2	0.091 (2)	0.123 (3)	0.092 (2)	−0.033 (2)	0.058 (2)	−0.066 (2)
F3	0.0351 (16)	0.122 (3)	0.158 (4)	−0.0047 (17)	0.013 (2)	−0.011 (3)
F4	0.0424 (17)	0.126 (3)	0.222 (5)	0.0338 (19)	−0.016 (2)	−0.100 (3)

F5	0.297 (7)	0.070 (2)	0.071 (2)	0.036 (3)	0.100 (3)	0.0197 (18)
F6	0.171 (4)	0.152 (4)	0.107 (3)	−0.046 (4)	0.077 (3)	0.022 (3)
N1	0.0147 (9)	0.0227 (11)	0.0175 (10)	−0.0039 (8)	0.0028 (7)	0.0000 (8)
C2	0.0174 (12)	0.0249 (12)	0.0182 (12)	−0.0031 (9)	0.0047 (9)	−0.0024 (9)
C3	0.0286 (14)	0.0289 (14)	0.0215 (14)	−0.0027 (11)	0.0090 (11)	−0.0020 (10)
C4	0.0338 (16)	0.0341 (16)	0.0170 (13)	−0.0037 (12)	0.0038 (11)	0.0031 (11)
C5	0.0241 (14)	0.0300 (15)	0.0245 (14)	−0.0002 (11)	0.0007 (11)	0.0072 (11)
C6	0.0176 (12)	0.0268 (14)	0.0240 (14)	−0.0007 (10)	0.0034 (10)	0.0013 (10)
C7	0.0192 (13)	0.0291 (14)	0.0215 (13)	−0.0003 (10)	0.0049 (10)	−0.0032 (10)
O8	0.0181 (9)	0.0278 (10)	0.0212 (10)	0.0035 (7)	0.0051 (7)	0.0003 (7)
O9	0.0253 (11)	0.0489 (14)	0.0292 (12)	0.0078 (10)	0.0086 (9)	−0.0081 (10)
N21	0.0154 (10)	0.0266 (11)	0.0171 (10)	−0.0003 (8)	0.0052 (7)	0.0012 (8)
C22	0.0163 (12)	0.0271 (13)	0.0170 (12)	−0.0008 (10)	0.0034 (9)	−0.0016 (10)
C23	0.0236 (14)	0.0369 (16)	0.0214 (14)	−0.0015 (11)	0.0025 (10)	−0.0043 (11)
C24	0.0304 (15)	0.0485 (19)	0.0174 (13)	−0.0009 (14)	0.0045 (10)	−0.0004 (12)
C25	0.0268 (15)	0.0459 (18)	0.0231 (15)	0.0015 (13)	0.0110 (11)	0.0066 (12)
C26	0.0177 (12)	0.0360 (15)	0.0223 (14)	−0.0008 (10)	0.0085 (10)	0.0035 (11)
N21'	0.0147 (10)	0.0231 (11)	0.0181 (11)	−0.0021 (8)	0.0038 (8)	−0.0004 (8)
C22'	0.0161 (12)	0.0243 (12)	0.0182 (12)	−0.0002 (9)	0.0026 (9)	−0.0005 (9)
C23'	0.0178 (12)	0.0253 (13)	0.0241 (15)	−0.0027 (10)	0.0022 (10)	−0.0033 (10)
C24'	0.0181 (13)	0.0245 (13)	0.0330 (15)	−0.0033 (10)	0.0079 (11)	−0.0026 (11)
C25'	0.0246 (14)	0.0231 (13)	0.0262 (14)	−0.0034 (10)	0.0109 (11)	0.0013 (10)
C26'	0.0207 (13)	0.0240 (13)	0.0185 (12)	−0.0024 (10)	0.0052 (9)	0.0008 (9)
N31	0.0191 (11)	0.0278 (12)	0.0179 (11)	0.0009 (8)	0.0081 (8)	0.0027 (8)
C32	0.0196 (13)	0.0380 (16)	0.0208 (13)	0.0005 (11)	0.0089 (10)	0.0016 (11)
C33	0.0222 (15)	0.051 (2)	0.046 (2)	0.0036 (14)	0.0162 (14)	0.0048 (16)
C34	0.038 (2)	0.050 (2)	0.063 (3)	0.0160 (16)	0.0315 (18)	0.0105 (19)
C35	0.053 (2)	0.0317 (17)	0.053 (2)	0.0096 (15)	0.0356 (19)	0.0059 (15)
C36	0.0340 (16)	0.0296 (15)	0.0312 (16)	−0.0016 (12)	0.0175 (13)	0.0005 (12)
N31'	0.0169 (10)	0.0288 (12)	0.0177 (11)	−0.0068 (8)	0.0040 (8)	0.0009 (8)
C32'	0.0179 (13)	0.0369 (15)	0.0197 (13)	−0.0055 (11)	0.0066 (10)	−0.0005 (11)
C33'	0.0243 (15)	0.053 (2)	0.0356 (18)	−0.0155 (14)	0.0136 (13)	−0.0074 (15)
C34'	0.0397 (19)	0.046 (2)	0.0400 (19)	−0.0254 (15)	0.0170 (15)	−0.0081 (15)
C35'	0.046 (2)	0.0303 (16)	0.0368 (18)	−0.0144 (14)	0.0143 (15)	−0.0006 (13)
C36'	0.0281 (15)	0.0277 (14)	0.0237 (14)	−0.0032 (11)	0.0054 (11)	0.0012 (11)

Geometric parameters (Å, °)

Ru1—N1	2.063 (2)	C22—C22'	1.472 (4)
Ru1—O8	2.100 (2)	C23—C24	1.382 (4)
Ru1—N21	2.052 (3)	C24—C25	1.384 (5)
Ru1—N21'	2.070 (2)	C25—C26	1.382 (4)
Ru1—N31	2.033 (2)	N21'—C26'	1.346 (3)
Ru1—N31'	2.038 (2)	N21'—C22'	1.356 (3)
P1—F5	1.556 (4)	C22'—C23'	1.388 (4)
P1—F3	1.561 (3)	C23'—C24'	1.389 (4)
P1—F4	1.561 (4)	C24'—C25'	1.377 (4)
P1—F6	1.568 (4)	C25'—C26'	1.386 (4)
P1—F2	1.572 (3)	N31—C36	1.346 (4)

P1—F1	1.593 (3)	N31—C32	1.365 (4)
N1—C6	1.348 (3)	C32—C33	1.384 (4)
N1—C2	1.359 (3)	C32—C32'	1.471 (4)
C2—C3	1.381 (4)	C33—C34	1.381 (6)
C2—C7	1.516 (4)	C34—C35	1.382 (6)
C3—C4	1.390 (4)	C35—C36	1.383 (5)
C4—C5	1.382 (5)	N31'—C36'	1.350 (4)
C5—C6	1.377 (4)	N31'—C32'	1.359 (4)
C7—O9	1.226 (3)	C32'—C33'	1.389 (4)
C7—O8	1.279 (3)	C33'—C34'	1.375 (5)
N21—C26	1.344 (4)	C34'—C35'	1.380 (5)
N21—C22	1.361 (3)	C35'—C36'	1.380 (4)
C22—C23	1.390 (4)		
N1—Ru1—O8	78.82 (9)	O8—C7—C2	115.1 (2)
N21—Ru1—N21'	78.95 (10)	C7—O8—Ru1	115.56 (18)
N31—Ru1—N31'	78.99 (10)	C26—N21—C22	118.0 (2)
N31—Ru1—N21	89.97 (10)	C26—N21—Ru1	126.21 (19)
N31'—Ru1—N21	97.35 (10)	C22—N21—Ru1	115.55 (18)
N31—Ru1—N1	94.13 (10)	N21—C22—C23	121.9 (3)
N31'—Ru1—N1	88.93 (9)	N21—C22—C22'	114.6 (2)
N21—Ru1—N1	173.07 (8)	C23—C22—C22'	123.5 (3)
N31—Ru1—N21'	102.04 (10)	C24—C23—C22	119.1 (3)
N31'—Ru1—N21'	176.13 (9)	C23—C24—C25	119.2 (3)
N1—Ru1—N21'	94.71 (9)	C26—C25—C24	118.8 (3)
N31—Ru1—O8	170.91 (9)	N21—C26—C25	122.9 (3)
N31'—Ru1—O8	95.02 (10)	C26'—N21'—C22'	117.9 (2)
N21—Ru1—O8	97.63 (9)	C26'—N21'—Ru1	125.98 (18)
N21'—Ru1—O8	84.39 (9)	C22'—N21'—Ru1	114.82 (18)
F5—P1—F3	89.0 (3)	N21'—C22'—C23'	122.0 (3)
F5—P1—F4	93.6 (3)	N21'—C22'—C22	114.7 (2)
F3—P1—F4	176.6 (3)	C23'—C22'—C22	123.3 (2)
F5—P1—F6	178.5 (3)	C22'—C23'—C24'	119.4 (3)
F3—P1—F6	89.8 (3)	C25'—C24'—C23'	118.6 (3)
F4—P1—F6	87.5 (3)	C24'—C25'—C26'	119.4 (3)
F5—P1—F2	88.7 (2)	N21'—C26'—C25'	122.7 (3)
F3—P1—F2	91.9 (2)	C36—N31—C32	118.7 (3)
F4—P1—F2	90.3 (2)	C36—N31—Ru1	126.3 (2)
F6—P1—F2	92.2 (3)	C32—N31—Ru1	114.67 (19)
F5—P1—F1	90.7 (2)	N31—C32—C33	121.0 (3)
F3—P1—F1	89.1 (2)	N31—C32—C32'	114.6 (2)
F4—P1—F1	88.72 (19)	C33—C32—C32'	124.4 (3)
F6—P1—F1	88.4 (2)	C34—C33—C32	119.6 (3)
F2—P1—F1	178.8 (2)	C35—C34—C33	119.3 (3)
C6—N1—C2	118.3 (2)	C34—C35—C36	118.9 (3)
C6—N1—Ru1	127.9 (2)	N31—C36—C35	122.3 (3)
C2—N1—Ru1	113.78 (18)	C36'—N31'—C32'	118.9 (2)
N1—C2—C3	122.0 (3)	C36'—N31'—Ru1	125.7 (2)
N1—C2—C7	115.4 (2)	C32'—N31'—Ru1	115.3 (2)
C3—C2—C7	122.6 (3)	N31'—C32'—C33'	120.8 (3)

C2—C3—C4	119.3 (3)	N31'—C32'—C32	113.9 (2)
C5—C4—C3	118.4 (3)	C33'—C32'—C32	125.2 (3)
C6—C5—C4	119.8 (3)	C34'—C33'—C32'	119.5 (3)
N1—C6—C5	122.1 (3)	C33'—C34'—C35'	119.6 (3)
O9—C7—O8	125.9 (3)	C34'—C35'—C36'	118.8 (3)
O9—C7—C2	119.0 (3)	N31'—C36'—C35'	122.2 (3)