# metal-organic compounds

## Bis(2-phenyl-4,6-di-2-pyridyl-1,3,5-triazine-$\kappa^3 N^4,N^5,N^6$)ruthenium(II) bis(hexafluoridophosphate)

**Matthew I. J. Polson[a]\* and Garry S. Hanan[b]**

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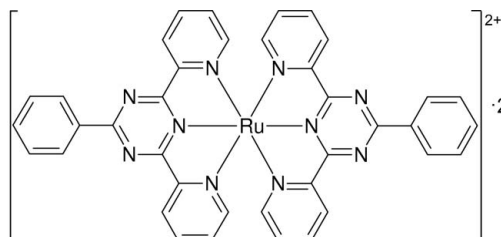Correspondence e-mail: matthew.polson@canterbury.ac.nz

The asymmetric unit of the title compound, [Ru(C₁₉H₁₃N₅)₂]-(PF₆)₂, consists of an Ru$^{II}$ complex cation and two hexafluoridophosphate anions. The Ru$^{II}$ atom is coordinated by three N atoms from the two outer pyridine and the central triazine rings of each of two tridentate ligands in a distorted octahedral environment. The ligands are approximately orthogonal to one another, with a dihedral angle of 88.34 (2)° between planes through the three six-membered rings of the two ligands. The pendant phenyl substituents are almost coplanar with the triazine rings to which they are bound, with dihedral angles of 5.41 (9) and 14.90 (10)°. This is reflected in the previously reported photophysical results with an increased lifetime of the triplet metal to ligand charge transfer ($^3$MLCT) excited state [Fang, Taylor, Hanan, Loiseau, Passalacqua, Campagna, Nierengarten & Van Dorsselaer (2002). *J. Am. Chem. Soc.* **124**, 7912–7913].

### Related literature

For related synthetic details, see: Polson et al. (2002, 2004). For related structures, see: Polson et al. (2002). For general background on the photophysics of ruthenium polypyridyl complexes, see: Kalyanasundaram (1991); Barigelletti et al. (1995). For background on C—H···N interactions in α-diimines, see: Fitchett et al. (2005). For related literature, see: Beley et al. (1991); Fang et al. (2002).



## Experimental

### Crystal data

| | |
|---|---|
| [Ru(C₁₉H₁₃N₅)₂](PF₆)₂ | $V$ = 3897.3 (2) Å³ |
| $M_r$ = 1013.70 | $Z$ = 4 |
| Monoclinic, $P2_1/n$ | Mo $K\alpha$ radiation |
| $a$ = 9.0995 (3) Å | $\mu$ = 0.59 mm⁻¹ |
| $b$ = 32.5979 (11) Å | $T$ = 93 (2) K |
| $c$ = 13.1451 (5) Å | 0.30 × 0.13 × 0.08 mm |
| $\beta$ = 91.774 (2)° | |

### Data collection

| | |
|---|---|
| Bruker APEXII CCD area-detector diffractometer | 75901 measured reflections |
| | 8114 independent reflections |
| Absorption correction: multi-scan (*SADABS*; Bruker, 2007) | 6511 reflections with $I > 2\sigma(I)$ |
| $T_{min}$ = 0.822, $T_{max}$ = 0.950 | $R_{int}$ = 0.060 |

### Refinement

| | |
|---|---|
| $R[F^2 > 2\sigma(F^2)]$ = 0.027 | 568 parameters |
| $wR(F^2)$ = 0.066 | H-atom parameters constrained |
| $S$ = 0.99 | $\Delta\rho_{max}$ = 0.55 e Å⁻³ |
| 8114 reflections | $\Delta\rho_{min}$ = −0.56 e Å⁻³ |

**Table 1**
Selected geometric parameters (Å, °).

| | | | |
|---|---|---|---|
| Ru1—N10 | 2.0982 (16) | Ru1—N50 | 2.0967 (16) |
| Ru1—N20 | 1.9773 (15) | Ru1—N60 | 1.9723 (15) |
| Ru1—N30 | 2.0990 (16) | Ru1—N70 | 2.0939 (17) |
| | | | |
| N10—Ru1—N30 | 154.76 (6) | N50—Ru1—N30 | 92.35 (6) |
| N60—Ru1—N20 | 179.28 (7) | N60—Ru1—N50 | 77.85 (6) |
| N70—Ru1—N50 | 155.22 (6) | N60—Ru1—N70 | 77.42 (6) |
| N20—Ru1—N70 | 103.31 (6) | N60—Ru1—N10 | 102.25 (6) |
| N20—Ru1—N50 | 101.42 (6) | N60—Ru1—N30 | 102.98 (6) |
| N20—Ru1—N10 | 77.77 (6) | N70—Ru1—N10 | 91.67 (6) |
| N20—Ru1—N30 | 77.00 (6) | N70—Ru1—N30 | 94.71 (6) |
| N50—Ru1—N10 | 91.99 (6) | | |

**Table 2**
Hydrogen-bond geometry (Å, °).

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| C41—H41···N21 | 0.95 | 2.47 | 2.793 (3) | 100 |
| C45—H45···N22 | 0.95 | 2.52 | 2.826 (3) | 99 |
| C81—H81···N61 | 0.95 | 2.47 | 2.797 (2) | 100 |
| C85—H85···N62 | 0.95 | 2.50 | 2.823 (3) | 100 |

Data collection: *APEX2* (Bruker, 2007); cell refinement: *SAINT* (Bruker, 2007); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *publCIF* (Westrip, 2008).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: SJ2423).

## References

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# supporting information

## Bis(2-phenyl-4,6-di-2-pyridyl-1,3,5-triazine-$\kappa^3N^4$,$N^5$,$N^6$)ruthenium(II) bis-(hexafluoridophosphate)

### Matthew I. J. Polson and Garry S. Hanan

### S1. Comment

The structure of the title compound reveals the ruthenium(II) atom to be in a distorted octahedral environment, Table 1. The Ru—N bond lengths to the central triazine ring are significantly shortened when compared to those of the outer pyridine rings. The angles between the coordinating pyridine N atoms also deviate significantly from 180 ° indicating considerable distortion.

Ruthenium complexes of this type have long been known to exhibit surprisingly short lived excited states. This is due to rapid deactivation of the excited state through a low lying metal centred state (Kalyanasundaram, 1991; Barigelletti *et al.*, 1995). By lowering the energy of the triplet metal to ligand charge transfer ³MLCT state, this exchange can be slowed and the lifetime of the excited state is extended (Fang *et al.*, 2002). In the title compound (1) replacement of a the central pyridine ring with a triazine ring in complex with a 4-phenyl substituent allows the pendant phenyl ring to adopt an arrangement in which it is approximately co-planar with the rest of the ligand. This results from the removal of sterically conflicting C—H···H—C interactions and the addition of attractive intramolecular C—H···N interactions. Although the C—H···N angles are acute (approximately 100 °) they are typical of interactions in molecules of this kind (Fitchett *et al.*, 2005) with N···H lengths of 2.47 to 2.52 Å, Table 2. The greater overall planarity of the ligands extends the HOMO orbital (predominately $\pi^*$ in nature) over more of the ligand surface, decreasing the energy of the ³MLCT state (Beley *et al.*, 1991; Polson *et al.*, 2002).

### S2. Experimental

The complex was prepared as described by Polson *et al.* (2004). Crystals suitable for X-ray crystallography were prepared by the diffusion of diisopropyl ether into an acetonitrile solution of the complex over a week.

### S3. Refinement

All H-atoms were positioned geometrically and refined using a riding model with d(C—H) = 0.93 Å, $U_{iso}$=1.2$U_{eq}$ (C).
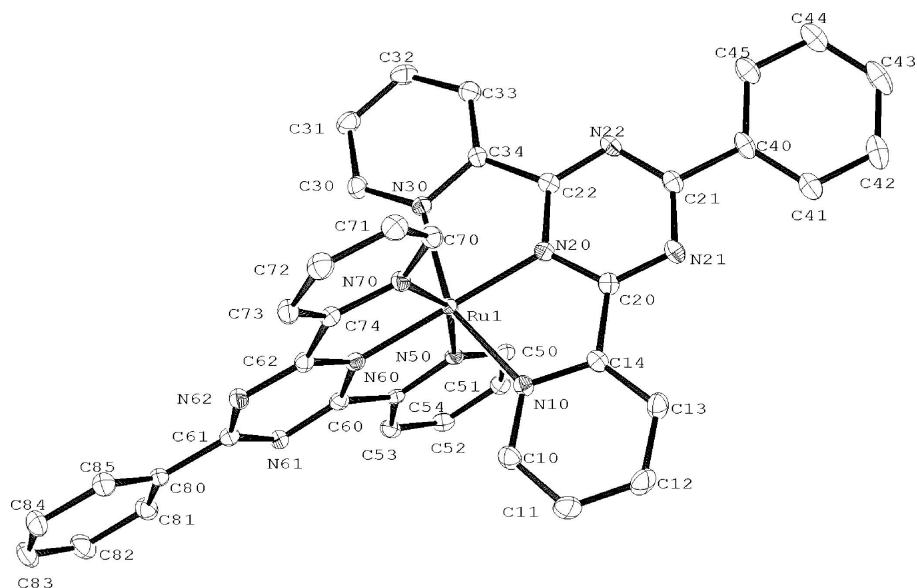
**Figure 1**

The molecular structure of (1), showing displacement ellipsoids at the 50% probability level. All H atoms have been omitted for clarity.

**Bis(2-phenyl-4,6-di-2-pyridyl-1,3,5-triazine- $\kappa^3 N^4, N^5, N^6$)ruthenium(II) bis(hexafluoridophosphate)**

*Crystal data*

[Ru($C_{19}H_{13}N_5$)$_2$](PF$_6$)$_2$
$M_r = 1013.70$
Monoclinic, $P2_1/n$
Hall symbol: -P 2yn
$a = 9.0995 (3)$ Å
$b = 32.5979 (11)$ Å
$c = 13.1451 (5)$ Å
$\beta = 91.774 (2)°$
$V = 3897.3 (2)$ Å$^3$
$Z = 4$

$F(000) = 2024$
$D_x = 1.728$ Mg m$^{-3}$
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 7650 reflections
$\theta = 4.7–53.0°$
$\mu = 0.59$ mm$^{-1}$
$T = 93$ K
Needle, red
$0.30 \times 0.13 \times 0.08$ mm

*Data collection*

Bruker APEXII CCD area-detector diffractometer
Radiation source: sealed tube
Graphite monochromator
$\omega$ scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2007)
$T_{min} = 0.822$, $T_{max} = 0.950$

75901 measured reflections
8114 independent reflections
6511 reflections with $I > 2\sigma(I)$
$R_{int} = 0.060$
$\theta_{max} = 26.6°$, $\theta_{min} = 2.5°$
$h = -11\rightarrow11$
$k = -40\rightarrow40$
$l = -16\rightarrow15$

*Refinement*

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.027$
$wR(F^2) = 0.066$
$S = 0.99$
8114 reflections

568 parameters
0 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

$w = 1/[\sigma^2(F_o^2) + (0.0562P)^2 + 0.5007P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.55$ e Å$^{-3}$
$\Delta\rho_{min} = -0.57$ 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* | $U_{iso}$*/$U_{eq}$ |
|------|------|------|------|------|
| Ru1  | 0.511004 (17) | 0.118305 (4) | 0.711838 (12) | 0.01108 (5) |
| N10  | 0.71581 (17) | 0.12419 (5) | 0.64422 (12) | 0.0136 (4) |
| C10  | 0.8068 (2) | 0.09472 (6) | 0.61281 (16) | 0.0179 (5) |
| H10  | 0.7805 | 0.0669 | 0.6231 | 0.021* |
| C11  | 0.9375 (2) | 0.10327 (6) | 0.56596 (17) | 0.0232 (5) |
| H11  | 0.9978 | 0.0815 | 0.5433 | 0.028* |
| C12  | 0.9798 (2) | 0.14335 (6) | 0.55231 (17) | 0.0240 (5) |
| H12  | 1.0700 | 0.1496 | 0.5212 | 0.029* |
| C13  | 0.8884 (2) | 0.17461 (6) | 0.58476 (16) | 0.0192 (5) |
| H13  | 0.9150 | 0.2026 | 0.5765 | 0.023* |
| C14  | 0.7588 (2) | 0.16422 (5) | 0.62909 (15) | 0.0141 (4) |
| N20  | 0.53678 (17) | 0.17849 (5) | 0.70707 (12) | 0.0123 (3) |
| N21  | 0.67356 (18) | 0.23500 (5) | 0.65306 (13) | 0.0158 (4) |
| N22  | 0.44719 (18) | 0.24472 (5) | 0.73807 (12) | 0.0148 (4) |
| C20  | 0.6545 (2) | 0.19520 (6) | 0.66416 (15) | 0.0137 (4) |
| C21  | 0.5662 (2) | 0.25871 (6) | 0.69099 (15) | 0.0147 (4) |
| C22  | 0.4357 (2) | 0.20427 (6) | 0.74240 (15) | 0.0132 (4) |
| N30  | 0.31752 (18) | 0.14032 (5) | 0.77547 (12) | 0.0130 (3) |
| C30  | 0.2009 (2) | 0.11839 (6) | 0.80597 (16) | 0.0177 (4) |
| H30  | 0.2042 | 0.0893 | 0.8016 | 0.021* |
| C31  | 0.0766 (2) | 0.13690 (6) | 0.84348 (17) | 0.0220 (5) |
| H31  | −0.0040 | 0.1205 | 0.8633 | 0.026* |
| C32  | 0.0698 (2) | 0.17918 (6) | 0.85204 (17) | 0.0221 (5) |
| H32  | −0.0141 | 0.1921 | 0.8790 | 0.027* |
| C33  | 0.1878 (2) | 0.20221 (6) | 0.82050 (15) | 0.0180 (4) |
| H33  | 0.1858 | 0.2313 | 0.8247 | 0.022* |
| C34  | 0.3083 (2) | 0.18235 (6) | 0.78291 (15) | 0.0133 (4) |
| C40  | 0.5820 (2) | 0.30342 (6) | 0.67733 (16) | 0.0172 (4) |
| C41  | 0.6825 (2) | 0.31883 (6) | 0.60975 (17) | 0.0223 (5) |
| H41  | 0.7451 | 0.3007 | 0.5747 | 0.027* |

| | | | |
|---|---|---|---|
| C42 | 0.6911 (3) | 0.36089 (6) | 0.59355 (18) | 0.0268 (5) |
| H42 | 0.7585 | 0.3715 | 0.5464 | 0.032* |
| C43 | 0.6018 (3) | 0.38746 (6) | 0.64602 (18) | 0.0263 (5) |
| H43 | 0.6081 | 0.4162 | 0.6349 | 0.032* |
| C44 | 0.5033 (2) | 0.37218 (6) | 0.71460 (18) | 0.0237 (5) |
| H44 | 0.4433 | 0.3905 | 0.7513 | 0.028* |
| C45 | 0.4920 (2) | 0.33042 (6) | 0.72995 (17) | 0.0207 (5) |
| H45 | 0.4232 | 0.3200 | 0.7763 | 0.025* |
| N50 | 0.40436 (17) | 0.10703 (5) | 0.57094 (12) | 0.0124 (3) |
| C50 | 0.3662 (2) | 0.13390 (6) | 0.49749 (15) | 0.0141 (4) |
| H50 | 0.3903 | 0.1620 | 0.5073 | 0.017* |
| C51 | 0.2932 (2) | 0.12242 (6) | 0.40811 (16) | 0.0162 (4) |
| H51 | 0.2681 | 0.1424 | 0.3579 | 0.019* |
| C52 | 0.2572 (2) | 0.08161 (6) | 0.39243 (16) | 0.0172 (4) |
| H52 | 0.2063 | 0.0732 | 0.3318 | 0.021* |
| C53 | 0.2965 (2) | 0.05329 (6) | 0.46646 (15) | 0.0161 (4) |
| H53 | 0.2732 | 0.0251 | 0.4572 | 0.019* |
| C54 | 0.3700 (2) | 0.06633 (5) | 0.55407 (15) | 0.0120 (4) |
| N60 | 0.48400 (17) | 0.05829 (5) | 0.71489 (12) | 0.0129 (3) |
| N61 | 0.40078 (18) | −0.00188 (5) | 0.63404 (12) | 0.0143 (4) |
| N62 | 0.51801 (18) | −0.00465 (5) | 0.79959 (13) | 0.0147 (4) |
| C60 | 0.4180 (2) | 0.03841 (6) | 0.63663 (15) | 0.0137 (4) |
| C61 | 0.4496 (2) | −0.02227 (6) | 0.71801 (15) | 0.0148 (4) |
| C62 | 0.5347 (2) | 0.03559 (6) | 0.79454 (15) | 0.0143 (4) |
| N70 | 0.61068 (17) | 0.10207 (5) | 0.85180 (12) | 0.0136 (4) |
| C70 | 0.6809 (2) | 0.12700 (6) | 0.91947 (15) | 0.0158 (4) |
| H70 | 0.6798 | 0.1557 | 0.9076 | 0.019* |
| C71 | 0.7543 (2) | 0.11210 (6) | 1.00527 (16) | 0.0187 (4) |
| H71 | 0.8037 | 0.1305 | 1.0508 | 0.022* |
| C72 | 0.7560 (2) | 0.07045 (6) | 1.02492 (16) | 0.0197 (5) |
| H72 | 0.8068 | 0.0599 | 1.0835 | 0.024* |
| C73 | 0.6820 (2) | 0.04436 (6) | 0.95750 (16) | 0.0173 (4) |
| H73 | 0.6803 | 0.0156 | 0.9695 | 0.021* |
| C74 | 0.6111 (2) | 0.06077 (6) | 0.87298 (15) | 0.0145 (4) |
| C80 | 0.4271 (2) | −0.06706 (6) | 0.71991 (15) | 0.0155 (4) |
| C81 | 0.3459 (2) | −0.08622 (6) | 0.64177 (16) | 0.0194 (5) |
| H81 | 0.3037 | −0.0703 | 0.5878 | 0.023* |
| C82 | 0.3265 (2) | −0.12824 (6) | 0.64252 (18) | 0.0236 (5) |
| H82 | 0.2722 | −0.1411 | 0.5886 | 0.028* |
| C83 | 0.3860 (2) | −0.15176 (6) | 0.72169 (18) | 0.0237 (5) |
| H83 | 0.3720 | −0.1806 | 0.7221 | 0.028* |
| C84 | 0.4651 (2) | −0.13302 (6) | 0.79949 (17) | 0.0227 (5) |
| H84 | 0.5049 | −0.1490 | 0.8541 | 0.027* |
| C85 | 0.4873 (2) | −0.09084 (6) | 0.79877 (16) | 0.0197 (5) |
| H85 | 0.5435 | −0.0782 | 0.8522 | 0.024* |
| P10 | 0.21119 (6) | 0.252045 (16) | 0.48554 (4) | 0.02011 (13) |
| F10 | 0.18421 (15) | 0.22740 (4) | 0.58837 (10) | 0.0386 (4) |
| F11 | 0.26219 (15) | 0.29172 (4) | 0.54874 (10) | 0.0327 (3) |

| F12 | 0.04573 (14) | 0.26820 (4) | 0.48256 (10) | 0.0362 (3) |
| F13 | 0.23965 (14) | 0.27617 (3) | 0.38108 (9) | 0.0250 (3) |
| F14 | 0.16179 (15) | 0.21244 (4) | 0.42100 (10) | 0.0339 (3) |
| F15 | 0.37791 (14) | 0.23611 (4) | 0.48793 (11) | 0.0353 (3) |
| P20 | 0.01052 (6) | 0.008488 (16) | 0.76644 (5) | 0.02301 (14) |
| F20 | −0.05493 (16) | −0.01201 (4) | 0.86490 (11) | 0.0395 (4) |
| F21 | −0.04478 (14) | 0.05249 (3) | 0.80299 (10) | 0.0278 (3) |
| F22 | −0.14343 (15) | 0.00207 (4) | 0.70590 (11) | 0.0369 (4) |
| F23 | 0.07743 (16) | 0.02936 (4) | 0.66771 (11) | 0.0399 (4) |
| F24 | 0.06484 (16) | −0.03543 (4) | 0.72907 (12) | 0.0396 (4) |
| F25 | 0.16550 (15) | 0.01533 (4) | 0.82574 (13) | 0.0452 (4) |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| Ru1 | 0.01126 (9) | 0.00884 (8) | 0.01317 (9) | −0.00001 (6) | 0.00056 (6) | −0.00003 (6) |
| N10 | 0.0122 (9) | 0.0126 (8) | 0.0159 (9) | 0.0005 (6) | −0.0007 (7) | 0.0005 (7) |
| C10 | 0.0173 (11) | 0.0149 (10) | 0.0214 (12) | 0.0028 (8) | −0.0001 (9) | 0.0018 (8) |
| C11 | 0.0189 (12) | 0.0222 (11) | 0.0288 (13) | 0.0087 (9) | 0.0053 (10) | 0.0020 (9) |
| C12 | 0.0129 (11) | 0.0274 (12) | 0.0320 (14) | 0.0020 (9) | 0.0074 (10) | 0.0044 (10) |
| C13 | 0.0155 (11) | 0.0182 (10) | 0.0240 (12) | −0.0028 (8) | 0.0010 (9) | 0.0028 (9) |
| C14 | 0.0149 (11) | 0.0135 (9) | 0.0135 (11) | −0.0004 (8) | −0.0032 (8) | −0.0011 (8) |
| N20 | 0.0124 (9) | 0.0125 (8) | 0.0120 (9) | −0.0001 (6) | −0.0015 (7) | −0.0014 (6) |
| N21 | 0.0170 (9) | 0.0124 (8) | 0.0178 (10) | −0.0018 (7) | −0.0025 (7) | −0.0012 (7) |
| N22 | 0.0182 (9) | 0.0106 (8) | 0.0153 (9) | 0.0016 (7) | −0.0031 (7) | −0.0012 (7) |
| C20 | 0.0127 (10) | 0.0152 (10) | 0.0130 (11) | −0.0019 (8) | −0.0031 (8) | −0.0006 (8) |
| C21 | 0.0166 (11) | 0.0133 (9) | 0.0140 (11) | −0.0020 (8) | −0.0047 (8) | −0.0014 (8) |
| C22 | 0.0112 (10) | 0.0144 (9) | 0.0136 (11) | 0.0006 (8) | −0.0033 (8) | −0.0012 (8) |
| N30 | 0.0139 (9) | 0.0137 (8) | 0.0114 (9) | −0.0001 (7) | −0.0002 (7) | −0.0005 (6) |
| C30 | 0.0181 (11) | 0.0163 (10) | 0.0189 (11) | −0.0040 (8) | 0.0010 (9) | −0.0006 (8) |
| C31 | 0.0174 (12) | 0.0256 (11) | 0.0234 (13) | −0.0048 (9) | 0.0069 (9) | −0.0032 (9) |
| C32 | 0.0176 (11) | 0.0258 (11) | 0.0233 (13) | 0.0045 (9) | 0.0055 (9) | −0.0038 (9) |
| C33 | 0.0198 (11) | 0.0168 (10) | 0.0174 (11) | 0.0017 (8) | 0.0010 (9) | −0.0008 (8) |
| C34 | 0.0149 (10) | 0.0131 (9) | 0.0116 (10) | −0.0011 (8) | −0.0022 (8) | 0.0004 (8) |
| C40 | 0.0189 (11) | 0.0118 (9) | 0.0203 (12) | −0.0021 (8) | −0.0091 (9) | 0.0007 (8) |
| C41 | 0.0276 (13) | 0.0157 (10) | 0.0233 (13) | −0.0021 (9) | −0.0030 (10) | −0.0006 (9) |
| C42 | 0.0321 (14) | 0.0194 (11) | 0.0283 (14) | −0.0084 (10) | −0.0078 (11) | 0.0061 (9) |
| C43 | 0.0321 (14) | 0.0129 (10) | 0.0329 (14) | −0.0011 (9) | −0.0184 (11) | 0.0019 (9) |
| C44 | 0.0225 (12) | 0.0155 (10) | 0.0326 (14) | 0.0019 (9) | −0.0093 (10) | −0.0031 (9) |
| C45 | 0.0195 (12) | 0.0162 (10) | 0.0260 (13) | −0.0004 (8) | −0.0067 (9) | −0.0020 (9) |
| N50 | 0.0096 (8) | 0.0120 (8) | 0.0156 (9) | 0.0008 (6) | 0.0028 (7) | −0.0017 (6) |
| C50 | 0.0124 (10) | 0.0136 (9) | 0.0164 (11) | 0.0022 (8) | 0.0038 (8) | 0.0010 (8) |
| C51 | 0.0140 (10) | 0.0165 (10) | 0.0182 (11) | 0.0045 (8) | 0.0019 (8) | 0.0029 (8) |
| C52 | 0.0164 (11) | 0.0210 (10) | 0.0143 (11) | 0.0026 (8) | 0.0006 (9) | −0.0026 (8) |
| C53 | 0.0138 (10) | 0.0142 (9) | 0.0202 (12) | 0.0006 (8) | 0.0016 (9) | −0.0032 (8) |
| C54 | 0.0087 (10) | 0.0133 (9) | 0.0142 (11) | 0.0018 (7) | 0.0041 (8) | −0.0002 (8) |
| N60 | 0.0119 (9) | 0.0139 (8) | 0.0128 (9) | 0.0010 (6) | 0.0019 (7) | 0.0000 (7) |
| N61 | 0.0152 (9) | 0.0123 (8) | 0.0154 (9) | 0.0002 (7) | 0.0028 (7) | 0.0004 (7) |

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|---|---|---|---|---|---|
| N62 | 0.0139 (9) | 0.0123 (8) | 0.0180 (10) | −0.0002 (6) | 0.0026 (7) | 0.0007 (7) |
| C60 | 0.0100 (10) | 0.0145 (9) | 0.0168 (11) | −0.0007 (8) | 0.0033 (8) | −0.0020 (8) |
| C61 | 0.0127 (10) | 0.0142 (9) | 0.0177 (11) | 0.0010 (8) | 0.0047 (8) | 0.0004 (8) |
| C62 | 0.0114 (10) | 0.0148 (9) | 0.0171 (11) | 0.0019 (8) | 0.0032 (8) | 0.0028 (8) |
| N70 | 0.0125 (9) | 0.0119 (8) | 0.0166 (9) | −0.0002 (7) | 0.0021 (7) | −0.0002 (7) |
| C70 | 0.0156 (11) | 0.0142 (10) | 0.0177 (11) | −0.0022 (8) | 0.0016 (9) | −0.0021 (8) |
| C71 | 0.0185 (11) | 0.0209 (11) | 0.0165 (11) | −0.0018 (9) | −0.0016 (9) | −0.0021 (8) |
| C72 | 0.0212 (12) | 0.0219 (10) | 0.0160 (12) | 0.0020 (9) | −0.0003 (9) | 0.0026 (9) |
| C73 | 0.0180 (11) | 0.0146 (10) | 0.0194 (12) | −0.0006 (8) | 0.0024 (9) | 0.0024 (8) |
| C74 | 0.0140 (10) | 0.0142 (9) | 0.0154 (11) | 0.0001 (8) | 0.0040 (8) | 0.0005 (8) |
| C80 | 0.0138 (11) | 0.0124 (9) | 0.0208 (12) | 0.0015 (8) | 0.0069 (9) | 0.0002 (8) |
| C81 | 0.0175 (11) | 0.0166 (10) | 0.0242 (12) | 0.0018 (8) | 0.0020 (9) | 0.0008 (9) |
| C82 | 0.0228 (12) | 0.0163 (10) | 0.0318 (14) | −0.0018 (9) | 0.0008 (10) | −0.0053 (9) |
| C83 | 0.0224 (12) | 0.0108 (10) | 0.0382 (15) | −0.0009 (9) | 0.0062 (10) | 0.0008 (9) |
| C84 | 0.0247 (13) | 0.0158 (10) | 0.0280 (14) | 0.0038 (9) | 0.0044 (10) | 0.0068 (9) |
| C85 | 0.0194 (11) | 0.0171 (10) | 0.0228 (13) | −0.0001 (9) | 0.0034 (9) | 0.0005 (9) |
| P10 | 0.0221 (3) | 0.0165 (3) | 0.0213 (3) | −0.0062 (2) | −0.0066 (2) | 0.0052 (2) |
| F10 | 0.0444 (9) | 0.0439 (8) | 0.0267 (8) | −0.0221 (7) | −0.0129 (7) | 0.0191 (6) |
| F11 | 0.0482 (9) | 0.0203 (6) | 0.0289 (8) | −0.0060 (6) | −0.0121 (7) | −0.0017 (6) |
| F12 | 0.0238 (8) | 0.0526 (9) | 0.0321 (8) | 0.0031 (6) | −0.0023 (6) | 0.0042 (7) |
| F13 | 0.0325 (8) | 0.0205 (6) | 0.0221 (7) | −0.0048 (5) | −0.0007 (6) | 0.0061 (5) |
| F14 | 0.0488 (9) | 0.0168 (6) | 0.0350 (8) | −0.0108 (6) | −0.0161 (7) | 0.0028 (6) |
| F15 | 0.0278 (8) | 0.0266 (7) | 0.0510 (9) | 0.0031 (6) | −0.0085 (7) | 0.0075 (6) |
| P20 | 0.0197 (3) | 0.0132 (3) | 0.0362 (4) | 0.0013 (2) | 0.0028 (3) | 0.0045 (2) |
| F20 | 0.0471 (9) | 0.0261 (7) | 0.0462 (9) | 0.0023 (6) | 0.0159 (7) | 0.0127 (6) |
| F21 | 0.0287 (7) | 0.0152 (6) | 0.0396 (8) | −0.0012 (5) | 0.0023 (6) | −0.0028 (5) |
| F22 | 0.0330 (8) | 0.0214 (7) | 0.0556 (10) | −0.0009 (6) | −0.0114 (7) | −0.0082 (6) |
| F23 | 0.0446 (9) | 0.0280 (7) | 0.0483 (10) | 0.0128 (6) | 0.0215 (7) | 0.0156 (7) |
| F24 | 0.0415 (9) | 0.0165 (6) | 0.0616 (10) | 0.0101 (6) | 0.0152 (7) | 0.0042 (6) |
| F25 | 0.0277 (8) | 0.0321 (8) | 0.0746 (12) | −0.0004 (6) | −0.0156 (8) | 0.0129 (8) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| Ru1—N10 | 2.0982 (16) | C50—H50 | 0.9500 |
| Ru1—N20 | 1.9773 (15) | C51—C52 | 1.384 (3) |
| Ru1—N30 | 2.0990 (16) | C51—H51 | 0.9500 |
| Ru1—N50 | 2.0967 (16) | C52—C53 | 1.380 (3) |
| Ru1—N60 | 1.9723 (15) | C52—H52 | 0.9500 |
| Ru1—N70 | 2.0939 (17) | C53—C54 | 1.381 (3) |
| N10—C10 | 1.342 (2) | C53—H53 | 0.9500 |
| N10—C14 | 1.378 (2) | C54—C60 | 1.472 (3) |
| C10—C11 | 1.385 (3) | N60—C60 | 1.342 (2) |
| C10—H10 | 0.9500 | N60—C62 | 1.351 (2) |
| C11—C12 | 1.375 (3) | N61—C60 | 1.323 (2) |
| C11—H11 | 0.9500 | N61—C61 | 1.352 (2) |
| C12—C13 | 1.390 (3) | N62—C62 | 1.323 (2) |
| C12—H12 | 0.9500 | N62—C61 | 1.351 (3) |
| C13—C14 | 1.374 (3) | C61—C80 | 1.475 (3) |

| | | | |
|---|---|---|---|
| C13—H13 | 0.9500 | C62—C74 | 1.475 (3) |
| C14—C20 | 1.470 (3) | N70—C70 | 1.351 (2) |
| N20—C22 | 1.340 (2) | N70—C74 | 1.375 (2) |
| N20—C20 | 1.341 (2) | C70—C71 | 1.381 (3) |
| N21—C20 | 1.318 (2) | C70—H70 | 0.9500 |
| N21—C21 | 1.353 (3) | C71—C72 | 1.382 (3) |
| N22—C22 | 1.324 (2) | C71—H71 | 0.9500 |
| N22—C21 | 1.344 (3) | C72—C73 | 1.388 (3) |
| C21—C40 | 1.476 (3) | C72—H72 | 0.9500 |
| C22—C34 | 1.475 (3) | C73—C74 | 1.376 (3) |
| N30—C30 | 1.351 (2) | C73—H73 | 0.9500 |
| N30—C34 | 1.376 (2) | C80—C85 | 1.393 (3) |
| C30—C31 | 1.386 (3) | C80—C81 | 1.394 (3) |
| C30—H30 | 0.9500 | C81—C82 | 1.381 (3) |
| C31—C32 | 1.384 (3) | C81—H81 | 0.9500 |
| C31—H31 | 0.9500 | C82—C83 | 1.389 (3) |
| C32—C33 | 1.385 (3) | C82—H82 | 0.9500 |
| C32—H32 | 0.9500 | C83—C84 | 1.376 (3) |
| C33—C34 | 1.378 (3) | C83—H83 | 0.9500 |
| C33—H33 | 0.9500 | C84—C85 | 1.390 (3) |
| C40—C41 | 1.388 (3) | C84—H84 | 0.9500 |
| C40—C45 | 1.400 (3) | C85—H85 | 0.9500 |
| C41—C42 | 1.390 (3) | P10—F12 | 1.5943 (14) |
| C41—H41 | 0.9500 | P10—F10 | 1.5980 (13) |
| C42—C43 | 1.386 (3) | P10—F11 | 1.5981 (13) |
| C42—H42 | 0.9500 | P10—F14 | 1.6015 (13) |
| C43—C44 | 1.383 (3) | P10—F15 | 1.6029 (14) |
| C43—H43 | 0.9500 | P10—F13 | 1.6104 (13) |
| C44—C45 | 1.380 (3) | P20—F20 | 1.5887 (14) |
| C44—H44 | 0.9500 | P20—F24 | 1.5970 (13) |
| C45—H45 | 0.9500 | P20—F21 | 1.5988 (13) |
| N50—C50 | 1.341 (2) | P20—F23 | 1.6022 (14) |
| N50—C54 | 1.380 (2) | P20—F22 | 1.6033 (15) |
| C50—C51 | 1.383 (3) | P20—F25 | 1.6056 (15) |
| | | | |
| N10—Ru1—N30 | 154.76 (6) | C52—C51—H51 | 120.3 |
| N60—Ru1—N20 | 179.28 (7) | C53—C52—C51 | 118.88 (19) |
| N70—Ru1—N50 | 155.22 (6) | C53—C52—H52 | 120.6 |
| N20—Ru1—N70 | 103.31 (6) | C51—C52—H52 | 120.6 |
| N20—Ru1—N50 | 101.42 (6) | C52—C53—C54 | 119.35 (18) |
| N20—Ru1—N10 | 77.77 (6) | C52—C53—H53 | 120.3 |
| N20—Ru1—N30 | 77.00 (6) | C54—C53—H53 | 120.3 |
| N50—Ru1—N10 | 91.99 (6) | N50—C54—C53 | 122.12 (18) |
| N50—Ru1—N30 | 92.35 (6) | N50—C54—C60 | 114.54 (17) |
| N60—Ru1—N50 | 77.85 (6) | C53—C54—C60 | 123.34 (17) |
| N60—Ru1—N70 | 77.42 (6) | C60—N60—C62 | 117.61 (16) |
| N60—Ru1—N10 | 102.25 (6) | C60—N60—Ru1 | 121.10 (13) |
| N60—Ru1—N30 | 102.98 (6) | C62—N60—Ru1 | 121.27 (13) |

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| N70—Ru1—N10 | 91.67 (6) | C60—N61—C61 | 115.55 (17) |
| N70—Ru1—N30 | 94.71 (6) | C62—N62—C61 | 115.62 (17) |
| C10—N10—C14 | 116.93 (17) | N61—C60—N60 | 123.30 (18) |
| C10—N10—Ru1 | 129.03 (13) | N61—C60—C54 | 124.22 (18) |
| C14—N10—Ru1 | 114.03 (12) | N60—C60—C54 | 112.47 (16) |
| N10—C10—C11 | 122.65 (18) | N62—C61—N61 | 124.81 (17) |
| N10—C10—H10 | 118.7 | N62—C61—C80 | 117.91 (18) |
| C11—C10—H10 | 118.7 | N61—C61—C80 | 117.28 (18) |
| C12—C11—C10 | 119.80 (19) | N62—C62—N60 | 123.03 (18) |
| C12—C11—H11 | 120.1 | N62—C62—C74 | 124.68 (18) |
| C10—C11—H11 | 120.1 | N60—C62—C74 | 112.28 (16) |
| C11—C12—C13 | 118.93 (19) | C70—N70—C74 | 117.23 (17) |
| C11—C12—H12 | 120.5 | C70—N70—Ru1 | 127.56 (13) |
| C13—C12—H12 | 120.5 | C74—N70—Ru1 | 115.09 (13) |
| C14—C13—C12 | 118.61 (19) | N70—C70—C71 | 122.21 (18) |
| C14—C13—H13 | 120.7 | N70—C70—H70 | 118.9 |
| C12—C13—H13 | 120.7 | C71—C70—H70 | 118.9 |
| C13—C14—N10 | 123.06 (18) | C70—C71—C72 | 120.02 (19) |
| C13—C14—C20 | 122.33 (17) | C70—C71—H71 | 120.0 |
| N10—C14—C20 | 114.62 (17) | C72—C71—H71 | 120.0 |
| C22—N20—C20 | 117.20 (16) | C71—C72—C73 | 118.71 (19) |
| C22—N20—Ru1 | 121.87 (13) | C71—C72—H72 | 120.6 |
| C20—N20—Ru1 | 120.87 (12) | C73—C72—H72 | 120.6 |
| C20—N21—C21 | 114.99 (17) | C74—C73—C72 | 118.93 (18) |
| C22—N22—C21 | 115.08 (16) | C74—C73—H73 | 120.5 |
| N21—C20—N20 | 123.77 (18) | C72—C73—H73 | 120.5 |
| N21—C20—C14 | 123.59 (18) | C73—C74—N70 | 122.87 (18) |
| N20—C20—C14 | 112.63 (16) | C73—C74—C62 | 123.19 (17) |
| N22—C21—N21 | 125.27 (17) | N70—C74—C62 | 113.88 (17) |
| N22—C21—C40 | 118.31 (17) | C85—C80—C81 | 119.08 (18) |
| N21—C21—C40 | 116.42 (18) | C85—C80—C61 | 120.80 (19) |
| N22—C22—N20 | 123.61 (18) | C81—C80—C61 | 120.12 (18) |
| N22—C22—C34 | 124.21 (17) | C82—C81—C80 | 120.3 (2) |
| N20—C22—C34 | 112.13 (16) | C82—C81—H81 | 119.9 |
| C30—N30—C34 | 117.11 (16) | C80—C81—H81 | 119.9 |
| C30—N30—Ru1 | 127.86 (13) | C81—C82—C83 | 120.4 (2) |
| C34—N30—Ru1 | 114.98 (12) | C81—C82—H82 | 119.8 |
| N30—C30—C31 | 122.18 (18) | C83—C82—H82 | 119.8 |
| N30—C30—H30 | 118.9 | C84—C83—C82 | 119.66 (19) |
| C31—C30—H30 | 118.9 | C84—C83—H83 | 120.2 |
| C32—C31—C30 | 120.11 (19) | C82—C83—H83 | 120.2 |
| C32—C31—H31 | 119.9 | C83—C84—C85 | 120.5 (2) |
| C30—C31—H31 | 119.9 | C83—C84—H84 | 119.8 |
| C33—C32—C31 | 118.56 (19) | C85—C84—H84 | 119.8 |
| C33—C32—H32 | 120.7 | C84—C85—C80 | 120.1 (2) |
| C31—C32—H32 | 120.7 | C84—C85—H85 | 119.9 |
| C34—C33—C32 | 119.07 (18) | C80—C85—H85 | 119.9 |
| C34—C33—H33 | 120.5 | F12—P10—F10 | 90.99 (8) |

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|---|---|---|---|
| C32—C33—H33 | 120.5 | F12—P10—F11 | 90.25 (8) |
| N30—C34—C33 | 122.95 (17) | F10—P10—F11 | 90.97 (7) |
| N30—C34—C22 | 114.00 (16) | F12—P10—F14 | 90.22 (8) |
| C33—C34—C22 | 122.99 (17) | F10—P10—F14 | 89.70 (7) |
| C41—C40—C45 | 119.70 (18) | F11—P10—F14 | 179.17 (9) |
| C41—C40—C21 | 120.25 (18) | F12—P10—F15 | 179.52 (9) |
| C45—C40—C21 | 120.01 (19) | F10—P10—F15 | 89.46 (8) |
| C40—C41—C42 | 119.8 (2) | F11—P10—F15 | 89.57 (7) |
| C40—C41—H41 | 120.1 | F14—P10—F15 | 89.95 (8) |
| C42—C41—H41 | 120.1 | F12—P10—F13 | 89.68 (7) |
| C43—C42—C41 | 120.2 (2) | F10—P10—F13 | 178.99 (8) |
| C43—C42—H42 | 119.9 | F11—P10—F13 | 89.79 (7) |
| C41—C42—H42 | 119.9 | F14—P10—F13 | 89.53 (7) |
| C44—C43—C42 | 120.07 (19) | F15—P10—F13 | 89.87 (7) |
| C44—C43—H43 | 120.0 | F20—P20—F24 | 90.05 (7) |
| C42—C43—H43 | 120.0 | F20—P20—F21 | 90.18 (7) |
| C45—C44—C43 | 120.2 (2) | F24—P20—F21 | 179.50 (9) |
| C45—C44—H44 | 119.9 | F20—P20—F23 | 179.55 (10) |
| C43—C44—H44 | 119.9 | F24—P20—F23 | 90.15 (7) |
| C44—C45—C40 | 120.0 (2) | F21—P20—F23 | 89.63 (7) |
| C44—C45—H45 | 120.0 | F20—P20—F22 | 90.33 (8) |
| C40—C45—H45 | 120.0 | F24—P20—F22 | 90.25 (8) |
| C50—N50—C54 | 117.38 (17) | F21—P20—F22 | 89.31 (7) |
| C50—N50—Ru1 | 128.60 (13) | F23—P20—F22 | 90.08 (8) |
| C54—N50—Ru1 | 114.01 (13) | F20—P20—F25 | 90.50 (9) |
| N50—C50—C51 | 122.80 (18) | F24—P20—F25 | 89.90 (8) |
| N50—C50—H50 | 118.6 | F21—P20—F25 | 90.54 (7) |
| C51—C50—H50 | 118.6 | F23—P20—F25 | 89.10 (9) |
| C50—C51—C52 | 119.45 (19) | F22—P20—F25 | 179.16 (9) |
| C50—C51—H51 | 120.3 | | |

*Hydrogen-bond geometry (Å, º)*

| D—H···A | D—H | H···A | D···A | D—H···A |
|---|---|---|---|---|
| C41—H41···N21 | 0.95 | 2.47 | 2.793 (3) | 100 |
| C45—H45···N22 | 0.95 | 2.52 | 2.826 (3) | 99 |
| C81—H81···N61 | 0.95 | 2.47 | 2.797 (2) | 100 |
| C85—H85···N62 | 0.95 | 2.50 | 2.823 (3) | 100 |