Tetra-\(\mu\)-acetato-\(\kappa^8O:O'\)-bis[(3-chloropyridine-\(\kappa^N\))ruthenium(II,III)](Ru—Ru) hexafluorido-phosphate 1,2-dichloroethane monosolvate

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The title compound, [Ru\(_2(\mu\text{-O}_2\text{CCH}_3)\text{C}_5\text{H}_4\text{ClN})_2\text{PF}_6\text{C}_2\text{H}_4\text{Cl}_2], was obtained via a rapid substitution reaction of 3-chloropyridine for water in [Ru\(_2(\mu\text{-O}_2\text{CCH}_3)\text{C}_5\text{H}_4\text{O}_2\text{CCH}_3)_2\text{PF}_6\text{C}_2\text{H}_4\text{Cl}_2] in 2-propanol and subsequent crystallization from a dichloroethane solution. The cationic diruthenium(II,III) tetraacetate core lies on a crystallographic inversion center with Ru—Ru and Ru—N bond lengths of 2.2738 (3) and 2.2920 (17) Å, respectively. The Ru—Ru—N bond angle is close to linear at 176.48 (4)°, and a significant \(\pi\)-stacking interaction of 3.5649 (16) Å is seen between overlapping pyridine rings of adjacent cations.

Structure description

Earlier research in our lab dealt with the chemistry of various mixed-valent diruthenium(II,III) tetraacetate complexes incorporating substituted pyridines and other, biologically relevant, heterocyclic N-donors in the axial coordination positions (Bland et al., 2005; Gilfoy et al., 2001; Minaker et al., 2011; Vamvounis et al., 2000). At that time we were unable to obtain structures of amino- or chloro-pyridine diadducts. Recently, we have been able to characterize both a 3-aminopyridine diadduct (Aquino et al., 2021) and the 3-chloropyridine diadduct is reported here. This is the first crystal structure of a chloro-pyridine diadduct of a diruthenium(II,III) tetracarboxylate that we are aware of.

The solvated title salt consists of a complex cation with a diruthenium (II,III) tetraacetate core and 3-chloropyridine in the axial positions, a hexafluoridophosphate anion, and a 1,2-dichloroethane molecule of solvation (Fig. 1). The cation displays the classic Chinese lantern or paddlewheel shape with each ruthenium atom at the center of a
Slightly distorted octahedron. The Ru1—Ru1(−x + 1, −y, −z) and Ru1—N1 bond lengths are 2.2738 (3) and 2.2920 (17) Å, and are similar to those in the 3-cyanopyridine diadduct [2.2702 (6) and 2.295 (3) Å; Minaker et al., 2011]. The Ru1(−x + 1, −y, −z)−Ru1—N1 bond angle of 176.48 (4)° is also comparable to the 174.27 (7)°/C14 of the 3-cyanopyridine adduct, showing essentially linear coordination. While no substantial hydrogen bonding was detected in the title compound, showing essentially linear coordination. While no substantial hydrogen bonding was detected in the title compound, showing essentially linear coordination.

Synthesis and crystallization

Synthesis of the title compound followed an earlier method developed in our lab (Vamvounis et al., 2011). The Ru1(−x + 1, −y, −z)−Ru1—N1 bond angle of 176.48 (4)° is also comparable to the 174.27 (7)°/C14 of the 3-cyanopyridine adduct, showing essentially linear coordination. While no substantial hydrogen bonding was detected in the title compound, showing essentially linear coordination.

Figure 2

Packing diagram viewed approximately along [001] showing the π–π stacking interactions (dashed lines).

Table 1

| Crystal data            | Chemical formula | [Ru₂(C₃H₂O₂)₄(C₅H₄ClN)₂]PF₆ |
|-------------------------|------------------|--------------------------------|
| M_r                     |                  | 909.32                         |
| Crystal system, space group |                | Triclinic, P̅T                 |
| Temperature (K)         |                  | 293                            |
| a, b, c (Å)             |                  | 8.2737 (1), 10.5784 (3), 11.5534 (1) |
| α, β, γ (°)             |                  | 100.764 (7), 108.980 (8), 110.525 (7) |
| V (Å³)                  |                  | 842.27 (6)                      |
| Z                       |                  | 1                              |
| μ (mm⁻¹)                |                  | 1.34                           |
| Crystal size (mm)       |                  | 0.43 × 0.20 × 0.07             |

Data collection

| Diffractometer          | Rigaku R-AXIS RAPID |
|-------------------------|---------------------|
| Radiation type          | Mo Kα               |
| No. of measured, independent and observed [I > 2σ(I)] reflections | 4084 |
| Rint (sin θ/λ)max (Å⁻¹) | 0.687               |

Refinement

| R[F² > 2σ(F²)], wR(F²), S | 0.024, 0.069, 1.10 |
|---------------------------|--------------------|
| No. of reflections        | 4084               |
| No. of parameters         | 250                |
| No. of restraints         | 99                 |
| H-atoms treatment         | H-atom parameters constrained |
| Δρmax, Δρmin (e Å⁻³)      | 0.49, −0.52        |

Computer programs: CrystalStructure (Rigaku, 2007), SIR2004 (Burla et al., 2005), SHELXL (Sheldrick, 2015), Merdury (Maezoe et al., 2020) and pubICIF (Westrip, 2010).

278 K overnight. The crystalline product was collected via suction filtration. Yield = 0.098 g (63%). Crystals suitable for X-ray diffraction were obtained by slow diffusion of diethyl ether into a 1,2-dichloroethane solution of the complex. IR (cm⁻¹): 2947 (υC–H), 1447 (asym. υC=O), 1396 (sym. υC=O), 841 (υPF₆), 766 (υC–Cl), 692 (δC–CH₃). UV–vis (λ nm, (log ε)): 427 (2.95), 263 (4.05), 210 (4.33).

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1. Two reflections were removed from the refinement because of poor agreements between F² (obs) and F² (calc), 775 and 826. In the cation, the methyl groups of the acetate ligands were modeled in the refinement as idealized disordered methyl groups with the two sets of positions rotated from each other by 60°. The crystal structure was found to contain solvent molecules. The recrystallization solvents were dichloroethylene and diethyl ether. The SQUEEZE routine (Spek, 2015) in PLATON (Spek, 2020) was used to get an estimate of the void volumes and of the unaccounted electron density in them. The unit cell was found to contain one void of 228 Å³ with 50 electrons per void. This suggested that there was one molecule of dichloroethylene in each void and it was modeled as such. The disorder in the solvent was modeled by two equally occupied parts, which were then also split again across an inversion center, giving all

Figure 1

The molecular structure of the title compound with displacement ellipsoids at the 50% probability level. Unlabeled atoms are generated by the symmetry operations (i) (−x + 1, −y, −z) and (ii) (−x + 2, −y, −z + 1). Only one orientation of the disordered methyl groups and the disordered C₅H₄Cl solvent molecule is shown.

Figure 2

Packing diagram viewed approximately along [001] showing the π–π stacking interactions (dashed lines).
atoms an occupancy of 0.25. The geometries of all the parts were restrained to be similar. In addition the C—C and the C—Cl bond lengths were restrained to reasonable values. The heavy atoms of the same type in the solvent were restrained to have similar displacement parameters and the carbon atoms were restrained to have more isotropic ellipsoids. Finally, rigid-bond restraints were placed over each solvent part.

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full crystallographic data

*IUCrData* (2022). 7, x220249  [https://doi.org/10.1107/S2414314622002498]

**Tetra-μ-acetato-κ²O:O’-bis[(3-chloropyridine-κN)ruthenium(II,III)](Ru—Ru) hexafluoridophosphate 1,2-dichloroethane monosolvate**

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**Crystal data**

\[\text{[Ru}_2(C_2H_3O_2)_4(C_5H_4ClN)_2]\text{PF}_6\]

\[M_r = 909.32\]

Triclinic, \(P\bar{1}\)

\[a = 8.2737 (1) \text{ Å}\]

\[b = 10.5784 (3) \text{ Å}\]

\[c = 11.5534 (1) \text{ Å}\]

\[α = 100.764 (7)°\]

\[β = 108.980 (8)°\]

\[γ = 110.525 (7)°\]

\[V = 842.27 (6) \text{ Å}^3\]

\[Z = 1\]

\[F(000) = 447\]

\[D_x = 1.793 \text{ Mg m}^{-3}\]

Mo \(Kα\) radiation, \(λ = 0.71075 \text{ Å}\)

Cell parameters from 8636 reflections

\[θ = 2.7–58.1°\]

\[µ = 1.34 \text{ mm}^{-1}\]

\[T = 293 \text{ K}\]

Needle plate, light brown

0.43 × 0.20 × 0.07 mm

**Data collection**

Rigaku R-AXIS RAPID
diffractometer

Detector resolution: 10.00 pixels mm\(^{-1}\)

\(ω\) scans

Absorption correction: multi-scan

\((ABSCOR; Higashi, 1995).\)

\(T_{\text{min}} = 0.702, T_{\text{max}} = 0.921\)

23200 measured reflections

4084 independent reflections

4084 reflections with \(I > 2σ(I)\)

\(R_{\text{int}} = 0.084\)

\(θ_{\text{max}} = 29.2°\)

\(h = −11→11\)

\(k = −14→14\)

\(l = −15→15\)

**Refinement**

Refinement on \(F^2\)

Least-squares matrix: full

\(R[F^2 > 2σ(F^2)] = 0.024\)

\(wR(F^2) = 0.069\)

\(S = 1.10\)

4084 reflections

250 parameters

99 restraints

Primary atom site location: structure-invariant direct methods

Secondary atom site location: iterative

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

\(w = 1/[σ^2(F_c)^2 + (0.0183P)^2]\) 

where \(P = (F_c^2 + 2F_s^2)/3\)

\((Δ/σ)_{\text{max}} = 0.002\)

\(Δρ_{\text{max}} = 0.49 \text{ e Å}^{-3}\)

\(Δρ_{\text{min}} = −0.51 \text{ e Å}^{-3}\)
Special details

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

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

|   | x     | y     | z     | U_iso* Å² | Occ. (<1) |
|---|-------|-------|-------|-----------|-----------|
| Ru1 | 0.53229 (2) | 0.11769 (2) | 0.03458 (2) | 0.03317 (6) | |
| Cl1 | 0.94986 (12) | 0.69082 (8) | 0.05336 (11) | 0.0947 (3) | |
| P1  | 1.000000 | 0.000000 | 0.500000 | 0.0569 (2) | |
| F1  | 0.9249 (3) | 0.0893 (2) | 0.57695 (18) | 0.0917 (6) | |
| F2  | 0.8293 (3) | -0.1428 (2) | 0.4802 (2) | 0.0949 (6) | |
| F3  | 0.8683 (2) | 0.0034 (2) | 0.36556 (16) | 0.0862 (5) | |
| O1  | 0.5024 (2) | 0.09675 (16) | 0.19771 (13) | 0.0425 (3) | |
| O2  | 0.5603 (2) | 0.13381 (16) | -0.13033 (14) | 0.0416 (3) | |
| O3  | 0.81269 (19) | 0.16819 (15) | 0.12454 (14) | 0.0415 (3) | |
| O4  | 0.25099 (19) | 0.06299 (16) | -0.05668 (14) | 0.0410 (3) | |
| N1  | 0.6166 (2) | 0.35849 (18) | 0.10681 (18) | 0.0427 (4) | |
| C1  | 0.7380 (3) | 0.4444 (2) | 0.0712 (3) | 0.0544 (5) | |
| H1  | 0.787140 | 0.404761 | 0.020620 | 0.065* | |
| C2  | 0.7934 (3) | 0.5901 (2) | 0.1069 (2) | 0.0541 (5) | |
| C3  | 0.7242 (4) | 0.6514 (2) | 0.1813 (3) | 0.0615 (6) | |
| H3  | 0.759615 | 0.749444 | 0.205596 | 0.074* | |
| C4  | 0.6005 (4) | 0.5631 (3) | 0.2192 (3) | 0.0692 (7) | |
| H4  | 0.550116 | 0.600878 | 0.269981 | 0.083* | |
| C5  | 0.5508 (4) | 0.4172 (3) | 0.1814 (2) | 0.0564 (5) | |
| H5  | 0.468896 | 0.358717 | 0.209032 | 0.068* | |
| C6  | 0.4646 (3) | -0.0242 (2) | 0.21398 (18) | 0.0417 (4) | |
| C7  | 0.4480 (4) | -0.0360 (3) | 0.3375 (2) | 0.0600 (6) | |
| H7A | 0.470433 | 0.055322 | 0.390462 | 0.090* | 0.5 |
| H7B | 0.322347 | -0.106306 | 0.316927 | 0.090* | 0.5 |
| H7C | 0.540552 | -0.064512 | 0.384004 | 0.090* | 0.5 |
| H7D | 0.418455 | -0.132319 | 0.337133 | 0.090* | 0.5 |
| H7E | 0.566541 | 0.029309 | 0.410669 | 0.090* | 0.5 |
| H7F | 0.348336 | -0.012486 | 0.343592 | 0.090* | 0.5 |
| C8  | 0.1350 (3) | -0.0685 (2) | -0.11919 (18) | 0.0402 (4) | |
| C9  | -0.0728 (3) | -0.1078 (3) | -0.1872 (2) | 0.0562 (5) | |
| H9A | -0.143002 | -0.209827 | -0.230077 | 0.084* | 0.5 |
| H9B | -0.116969 | -0.078012 | -0.124702 | 0.084* | 0.5 |
| H9C | -0.091531 | -0.060687 | -0.250386 | 0.084* | 0.5 |
| H9D | -0.091332 | -0.022523 | -0.173366 | 0.084* | 0.5 |
| H9E | -0.117366 | -0.154338 | -0.278742 | 0.084* | 0.5 |
| H9F | -0.142804 | -0.171664 | -0.153057 | 0.084* | 0.5 |
| C11A | 0.138 (5) | 0.586 (4) | 0.499 (3) | 0.162 (8) | 0.25 |
| H11A | 0.241338 | 0.623432 | 0.584600 | 0.194* | 0.25 |
### Atomic displacement parameters (Å²)

|   | \(U_{11}^1\) | \(U_{22}^1\) | \(U_{33}^1\) | \(U_{12}^1\) | \(U_{13}^1\) | \(U_{23}^1\) |
|---|--------------|--------------|--------------|--------------|--------------|--------------|
| Ru | 0.03692 (9)  | 0.03044 (9)  | 0.03524 (9)  | 0.01429 (7)  | 0.01879 (7)  | 0.01260 (7)  |
| Cl1| 0.0931 (5)   | 0.0526 (4)   | 0.1638 (9)   | 0.0269 (4)   | 0.0820 (6)   | 0.0510 (5)   |
| P1 | 0.0473 (4)   | 0.0698 (5)   | 0.0440 (4)   | 0.0201 (4)   | 0.0198 (3)   | 0.0101 (4)   |
| F1 | 0.0812 (12)  | 0.1152 (16)  | 0.0748 (11)  | 0.0509 (11)  | 0.0357 (9)   | 0.0047 (10)  |
| F2 | 0.0731 (11)  | 0.0886 (13)  | 0.0909 (14)  | 0.0053 (10)  | 0.0353 (10)  | 0.0225 (11)  |
| F3 | 0.0722 (10)  | 0.1275 (16)  | 0.0568 (9)   | 0.0446 (11)  | 0.0237 (8)   | 0.0392 (10)  |
| O1 | 0.0500 (8)   | 0.0477 (8)   | 0.0356 (7)   | 0.0228 (6)   | 0.0237 (6)   | 0.0144 (6)   |
| O2 | 0.0478 (7)   | 0.0434 (7)   | 0.0423 (7)   | 0.0192 (6)   | 0.0257 (6)   | 0.0234 (6)   |
| O3 | 0.0348 (6)   | 0.0399 (7)   | 0.0453 (7)   | 0.0123 (5)   | 0.0165 (6)   | 0.0142 (6)   |
| O4 | 0.0402 (7)   | 0.0439 (7)   | 0.0471 (8)   | 0.0224 (6)   | 0.0220 (6)   | 0.0190 (6)   |
| N1 | 0.0444 (9)   | 0.0320 (8)   | 0.0489 (9)   | 0.0155 (7)   | 0.0197 (7)   | 0.0111 (7)   |
| C1 | 0.0560 (12)  | 0.0392 (10)  | 0.0764 (15)  | 0.0215 (9)   | 0.0368 (11)  | 0.0211 (10)  |
| C2 | 0.0475 (11)  | 0.0378 (10)  | 0.0696 (14)  | 0.0139 (8)   | 0.0207 (10)  | 0.0197 (10)  |
| C3 | 0.0679 (15)  | 0.0365 (10)  | 0.0662 (15)  | 0.0200 (10)  | 0.0193 (12)  | 0.0108 (10)  |
| C4 | 0.0924 (19)  | 0.0481 (13)  | 0.0720 (17)  | 0.0325 (13)  | 0.0450 (15)  | 0.0100 (12)  |
| C5 | 0.0654 (14)  | 0.0451 (11)  | 0.0606 (13)  | 0.0210 (10)  | 0.0344 (11)  | 0.0150 (10)  |
| C6 | 0.0390 (9)   | 0.0567 (11)  | 0.0375 (9)   | 0.0219 (8)   | 0.0214 (7)   | 0.0220 (8)   |
| C7 | 0.0685 (14)  | 0.0859 (18)  | 0.0451 (11)  | 0.0377 (13)  | 0.0361 (11)  | 0.0348 (12)  |
| C8 | 0.0371 (8)   | 0.0506 (10)  | 0.0391 (9)   | 0.0195 (8)   | 0.0206 (7)   | 0.0201 (8)   |
| C9 | 0.0382 (10)  | 0.0688 (15)  | 0.0622 (13)  | 0.0222 (10)  | 0.0211 (9)   | 0.0270 (11)  |
| Cl2A| 0.219 (10)  | 0.219 (11)   | 0.261 (16)   | 0.095 (8)    | 0.117 (11)   | 0.061 (12)   |
| Cl1A| 0.159 (9)   | 0.158 (9)    | 0.161 (9)    | 0.072 (7)    | 0.059 (6)    | 0.051 (7)    |
| Cl1A| 0.154 (8)   | 0.153 (9)    | 0.156 (8)    | 0.073 (7)    | 0.061 (6)    | 0.056 (7)    |
| Cl3A| 0.38 (2)    | 0.29 (2)     | 0.204 (12)   | 0.23 (2)     | 0.084 (16)   | 0.008 (13)   |
| Cl2B| 0.245 (12)  | 0.171 (9)    | 0.239 (16)   | 0.097 (8)    | 0.135 (10)   | 0.043 (10)   |
| Cl1B| 0.156 (8)   | 0.153 (8)    | 0.158 (9)    | 0.075 (7)    | 0.060 (6)    | 0.053 (6)    |
| Cl2B| 0.156 (9)   | 0.157 (9)    | 0.161 (9)    | 0.076 (7)    | 0.053 (6)    | 0.056 (7)    |
| Cl3B| 0.34 (2)    | 0.339 (19)   | 0.128 (8)    | 0.22 (2)     | 0.080 (12)   | 0.071 (10)   |
### Geometric parameters (Å, °)

| Bond/Angle          | Distance/Angle  | Distance/Angle  | Value  |
|---------------------|-----------------|-----------------|--------|
| Ru1—O1              | 2.0204 (14)     | C7—H7A          | 0.9600 |
| Ru1—O2              | 2.0232 (14)     | C7—H7B          | 0.9600 |
| Ru1—O4              | 2.0235 (13)     | C7—H7C          | 0.9600 |
| Ru1—O3              | 2.0256 (13)     | C7—H7D          | 0.9600 |
| Ru1—Ru1'            | 2.2738 (3)      | C7—H7E          | 0.9600 |
| Ru1—N1              | 2.2920 (17)     | C7—H7F          | 0.9600 |
| C11—C2              | 1.730 (3)       | C8—C9           | 1.498 (3) |
| P1—F2               | 1.5795 (19)     | C9—H9A          | 0.9600 |
| P1—F2               | 1.5795 (19)     | C9—H9B          | 0.9600 |
| P1—F1               | 1.5896 (18)     | C9—H9C          | 0.9600 |
| P1—F1               | 1.5896 (18)     | C9—H9D          | 0.9600 |
| P1—F3               | 1.5965 (16)     | C9—H9E          | 0.9600 |
| O1—C6               | 1.272 (2)       | C11A—C11A       | 1.803 (16) |
| O2—C6               | 1.267 (3)       | C11A—C12A       | 1.493 (13) |
| O3—C8               | 1.272 (2)       | C11A—H11A       | 0.9700 |
| O4—C8               | 1.271 (2)       | C11A—H11B       | 0.9700 |
| N1—C5               | 1.329 (3)       | C12A—C13A       | 1.811 (16) |
| N1—C1               | 1.331 (3)       | C12A—H12A       | 0.9700 |
| C1—C2               | 1.379 (3)       | C12A—H12B       | 0.9700 |
| C1—H1               | 0.9300          | C12B—C11B       | 1.826 (16) |
| C2—C3               | 1.364 (4)       | C11B—C12B       | 1.476 (13) |
| C3—C4               | 1.373 (4)       | C11B—H11C       | 0.9700 |
| C3—H3               | 0.9300          | C11B—H11D       | 0.9700 |
| C4—C5               | 1.389 (3)       | C12B—C13B       | 1.805 (16) |
| C4—H4               | 0.9300          | C12B—H12C       | 0.9700 |
| C5—H5               | 0.9300          | C12B—H12D       | 0.9700 |
| C6—C7               | 1.501 (3)       |                 |        |
| O1—Ru1—O2           | 178.70 (5)      | N1—C5—H5       | 119.0  |
| O1—Ru1—O4           | 90.18 (6)       | C4—C5—H5       | 119.0  |
| O2—Ru1—O4           | 89.69 (6)       | O2'—C6—O1      | 122.70 (17) |
| O1—Ru1—O3           | 89.85 (6)       | O2'—C6—C7      | 119.34 (19) |
| O2—Ru1—O3           | 90.25 (6)       | O1—C6—C7       | 117.96 (19) |
| O4—Ru1—O3           | 178.83 (5)      | C6—C7—H7A      | 109.5  |
| O1—Ru1—Ru1'         | 89.66 (4)       | C6—C7—H7B      | 109.5  |
| O2—Ru1—Ru1'         | 89.04 (4)       | H7A—C7—H7B     | 109.5  |
| O4—Ru1—Ru1'         | 89.73 (4)       | C6—C7—H7C      | 109.5  |
| O3—Ru1—Ru1'         | 89.11 (4)       | H7A—C7—H7C     | 109.5  |
| O1—Ru1—N1           | 91.38 (6)       | H7B—C7—H7C     | 109.5  |
| O2—Ru1—N1           | 89.92 (6)       | H7D—C7—H7E     | 109.5  |
| O4—Ru1—N1           | 93.63 (6)       | H7D—C7—H7F     | 109.5  |
| O3—Ru1—N1           | 87.53 (6)       | H7E—C7—H7F     | 109.5  |
| Ru1'—Ru1—N1         | 176.48 (4)      | O4—C8—O3'      | 122.84 (17) |
| F2'i—P1—F2          | 180.0           | O4—C8—C9       | 118.51 (18) |
| F2'i—P1—F1'         | 89.08 (12)      | O3'—C8—C9      | 118.64 (18) |
| Bond/ Angle/ Distance | Value (uncertainty) |
|----------------------|---------------------|
| F2—P1—F1           | 90.92 (12)          |
| C8—C9—H9A         | 109.5               |
| F2—P1—F1           | 90.92 (12)          |
| C8—C9—H9B         | 109.5               |
| F2—P1—F1           | 90.08 (12)          |
| H9A—C9—H9B       | 109.5               |
| F1—P1—F1           | 180.00 (15)         |
| C8—C9—H9C         | 109.5               |
| F2—P1—F1           | 89.49 (11)          |
| H9B—C9—H9C       | 109.5               |
| F1—P1—F1           | 91.11 (11)          |
| H9D—C9—H9E       | 109.5               |
| F2—P1—F1           | 88.89 (11)          |
| C12A—C11A—C12B   | 104.0 (18)          |
| F1—P1—F1           | 89.29 (11)          |
| Cl2A—C11A—C12B   | 111.0               |
| F1—P1—F1           | 90.71 (11)          |
| Cl2A—C11A—C12B   | 111.0               |
| F2—P1—F1           | 90.00 (12)          |
| C12A—C11A—Cl3A   | 99.1 (17)           |
| F1—P1—F1           | 89.49 (11)          |
| C12A—C11A—C12B   | 112.0               |
| C1—N1—C5           | 1.9 (4)             |
| Ru1—N1—C5—C4      | -177.7 (2)          |
| C5—N1—C1           | -1.4 (4)            |
| Cl2A—C11A—C12B   | 109.8               |
| C5—N1—C1           | 123.95 (15)         |
| Cl2A—C11A—C12B   | 112.0               |
| C5—N1—Ru1          | 118.99 (13)         |
| Cl2A—C11A—C12B   | 112.0               |
| C5—N1—Ru1          | 117.87 (15)         |
| Cl2A—C11A—C12B   | 112.0               |
| N1—C1—H1           | 118.9               |
| C12B—C11B—C12B   | 114.2 (2)           |
| N1—C1—H1           | 122.2 (2)           |
| C12B—C11B—C12B   | 109.6               |
| C3—C2—C1           | 120.3 (2)           |
| Cl2B—C11B—C12B   | 108.8               |
| C3—C2—C1           | 121.60 (19)         |
| Cl2B—C11B—H11D   | 108.8               |
| C3—C2—C1           | 118.1 (2)           |
| Cl2B—C11B—H11D   | 108.8               |
| C3—C4—C5           | 119.7 (2)           |
| C3B—C12B—H12C   | 111.3               |
| C5—C4—C3           | 121.2               |
| Cl3B—C12B—C12B   | 102.6 (18)          |
| N1—C5—C4           | 122.1 (2)           |
| H12C—C12B—H12D   | 109.2               |
| N1—C5—C4           | 121.2               |
| Cl3B—C12B—C12B   | 111.3               |
| C5—N1—C1—C2       | -1.4 (4)            |
| Ru1—N1—C5—C4      | -177.7 (2)          |
| N1—C1—C2—C3       | 0.2 (4)             |
| Ru1—O1—C6—O2[i]  | -1.9 (3)            |
| N1—C1—C2—C3       | -179.25 (19)        |
| Ru1—O1—C6—C7     | 178.49 (14)         |
| C1—C2—C3—C4       | 0.5 (4)             |
| Ru1—O4—C8—O3[i]  | 1.7 (3)             |
| C1—C2—C3—C4       | 179.9 (2)           |
| Ru1—O4—C8—C9     | -179.58 (14)        |
| C2—C3—C4—C5       | 0.1 (4)             |
| Cl2A—C11A—C12A—Cl3A | -164 (3)          |
| C1—N1—C5—C4       | 1.9 (4)             |
| Cl2B—C11B—C12B—Cl3B | -154 (3)          |

Symmetry codes: (i) −x+1, −y, −z; (ii) −x+2, −y, −z+1.