# trans-Bis(2,2′-bipyridine-4,4′-dicarboxylic acid-κ²N,N′)dichloridoruthenium(III) perchlorate

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In the crystal structure of the ruthenium(III) complex, trans-[Ru$^{III}$(dcbpy)$_2$Cl$_2$]ClO$_4$ (dcbpy = 2,2′-bipyridine-4,4′-dicarboxylic acid, C$_{12}$H$_8$N$_2$O$_4$), the Ru$^{III}$ atom lies on an inversion centre, showing a small distortion in its octahedral environment. The Ru—Cl bond lengths are shorter than those present in the analogous trans-ruthenium(II) compound containing the bipyridine ligand. The C—O distances in the two symmetry-independent carboxylic acid moieties of the ligand are similar in one group, but different in the other. This is probably due to the different intermolecular interactions they experience with neighbouring cationic complexes. The hydrogen-bonding interactions in which they are involved form a three-dimensional structure, similar to those found in coordination polymers.

**3D view**



**Chemical scheme**
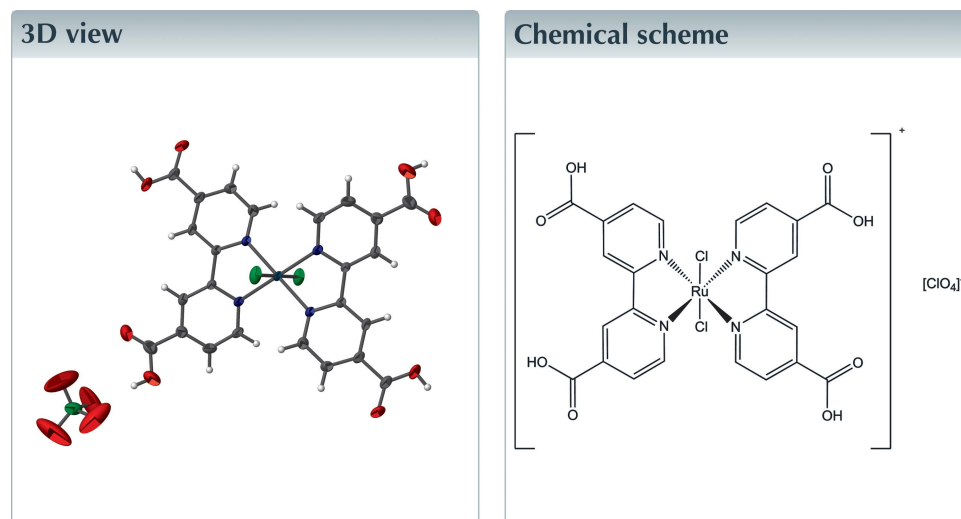


## Structure description

Complexes of ruthenium(III) have been described in the literature for several purposes, such as: anticancer agents (Shoair et al., 2015; Zeng et al., 2017), water-oxidation catalysts (WOC) (Liu et al., 2018), precursors for new oxidants (Seok et al., 2012) and for their catalytic and biological activity (Thangadurai & Natarajan, 2001). Ruthenium complexes with polypyridine ligands in a trans configuration have been mostly designed for dye-sensitized solar cells (DSSC) applications (Barolo et al., 2013). In DSSC, ruthenium complexes are used as dyes, and are responsible for the electron injection into the conduction band of the semiconductor (usually TiO$_2$). Ligands in these complexes may have different functions, such as ancillary or anchoring. Anchoring ligands may present functional groups able to covalently bond to the semiconductor surface. The most often synthetically employed are phosphonic and carboxylic groups that guarantee the adsorption of the coordination compound on the desired surface (Pashaei et al., 2016).
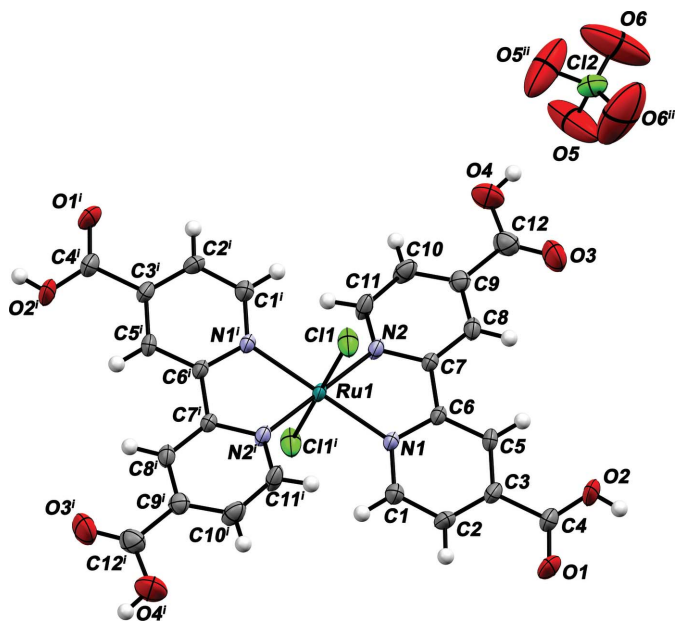
**Table 1**
Selected bond lengths (Å).

| Ru1—Cl1 | 2.2865 (13) | O1—C4 | 1.253 (6) |
|---|---|---|---|
| Ru1—N2 | 2.082 (3) | O3—C12 | 1.195 (7) |
| Ru1—N1 | 2.090 (3) | O2—C4 | 1.253 (6) |
| Cl2—O5 | 1.424 (7) | O4—C12 | 1.316 (6) |
| Cl2—O6 | 1.295 (6) | | |

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

| D—H⋯A | D—H | H⋯A | D⋯A | D—H⋯A |
|---|---|---|---|---|
| O2—H2⋯O1[i] | 0.82 | 1.90 | 2.698 (5) | 165.1 |
| O4—H4⋯O5 | 0.82 | 1.93 | 2.752 (7) | 175.5 |

Symmetry code: (i) $-x, 1-y, 1-z$.

On the other hand, ancillary ligands are employed to finely modulate the redox potential of the central metal cation.

In this work, the molecular and crystal structures of the complex *trans*-Bis(2,2′-bipyridine-4,4′-dicarboxylic acid-$\kappa^2 N,N′$)dichloridoruthenium(III) perchlorate are described (Fig. 1). The ruthenium(III) ion, which lies on an inversion centre, is coordinated by two molecules of dcbpy and two chloride ions, showing a distorted $N_4Cl_2$ octahedral geometry. This mononuclear cationic complex was isolated with perchlorate as counter-ion.

The Ru1—Cl1 bond length (Table 1) is 2.2865 (13) Å, and is shorter than the value of 2.4123 (4) Å present in the *cis*-Ru$^{II}$ analogue *cis*-[Ru$^{II}$(dcbpy)$_2$Cl$_2$] (Fujihara *et al.*, 2004). This difference may be due to either the oxidation state of the central metal cation, as has been reported before (Seok *et al.*, 2012), or to the configuration around the metal (*cis* or *trans*). The Ru1—Cl1 distance in the complex *trans*-[Ru$^{II}$(bpy)$_2$Cl$_2$] [2.3893 (6) Å, Klüfers & Zangl, 2007] shows a higher value than that of the title complex. This is observed because ruthenium(III) is a better Lewis acid than ruthenium(II), attracting the electrons and shortening the bond.

The Ru1—N1 and Ru1—N2 bond lengths are 2.090 (3) Å and 2.082 (3) Å, respectively, and are similar to the values reported for the analogous complex *trans*-[Ru$^{II}$(bpy)$_2$Cl$_2$] in
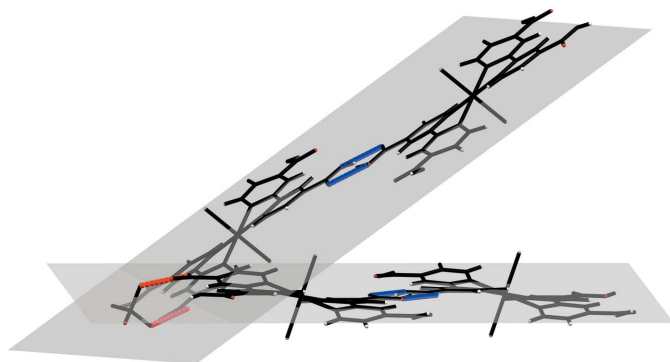
which Ru1—N1 = 2.0632 (18) Å and Ru1—N2 = 2.0560 (19) Å (Klüfers & Zangl, 2007). In general, Ru—N values are comparable with the average bond lengths in similar complexes with a *cis* configuration: *cis*-[Ru$^{II}$(dcbpy)$_2$Cl$_2$] (Fujihara *et al.*, 2004), *cis*-[Ru$^{III}$(bpy)$_2$Cl$_2$]Cl·2H$_2$O (Eggleston *et al.*, 1985) and *cis*-[Ru$^{III}$(dmbpy)$_2$Cl$_2$](PF$_6$) (dmbpy: 2,2′-bi-pyridine-4,4′-dimethyl) (Seok *et al.*, 2012). The N2—Ru—N1 angle is 76.47 (13)°, which is a smaller bite angle than the ideal 90°, as expected for bipyridines, because of the chelate constraints (Schwalbe *et al.*, 2008). The average Cl—Ru—N angle is close to 90°, similar to what is reported for the complex *trans*-[Ru$^{II}$(bpy)$_2$Cl$_2$] (Klüfers & Zangl, 2007), showing a distortion in the octahedral coordination environment.

The angle between the mean planes of the two pyridine rings shows very different values depending on the configuration around the metal cation. In the title compound, this angle is 14.26 (16)°, which is higher than the average value of 9 (2)° in the *cis* complex, *cis*-[Ru$^{II}$(dcbpy)$_2$Cl$_2$] (Fujihara *et al.*, 2004), but lower than the value of 23.8 (1)° in *trans*-[Ru$^{II}$(bpy)$_2$Cl$_2$] (Klüfers & Zangl, 2007).

The angle between the mean planes passing through Ru1—N1—N2—N1$^i$—N2$^i$ [symmetry code: (i) $\frac{1}{2} - x, -\frac{1}{2} - y, 1 - z$) and N1—C6—C7—N2 (involved in the bite angle) is 18.9 (3)°, which is close to the value of 20.4997 (4)° reported for *trans*-[Ru$^{II}$(bpy)$_2$Cl$_2$] (Klüfers & Zangl, 2007).

The carboxylic group C4O1O2H2 shows very similar C—O bond lengths: C4—O2: 1.253 (6) Å and C4—O1: 1.253 (6) Å. This fact can be explained considering that it forms two hydrogen bonds (one as donor with O2—H2 and one as acceptor with O1) with the same group of a neighbouring complex. This is not observed for C12O3O4H4, in which only O4—H4 acts as hydrogen-bond donor towards the O5 atom of one perchlorate anion, while O3 is not involved in any interactions. This explains the lengthening of the C12—O4 bond [1.316 (6) Å], with respect to C12—O3, which shows a value of 1.195 (7) Å.

The hydrogen-bonding interactions between the carboxylic C4O1O2H2 of two neighbouring complexes (Table 2) form a linear ribbon aligned with the Ru1—N1 bond. On the other side, the carboxylic groups aligned with the Ru1—N2 bond (C12O3O4H4) and the perchlorate anions are also involved in hydrogen bonding; both the symmetry-related O5 atoms of the perchlorate anion interact with two cationic complexes in two different set of planes. These planes form an angle of 33.7 (3)° (Fig. 2; the angle has been calculated considering the mean planes passing through sets of O1—C4—O1 atoms) and comprise two sets of ribbons formed by the H-bonded C4O1O2H2 carboxylic groups (Fig. 3).



**Figure 1**
The structures of the molecular entities in the title compound. Displacement ellipsoids are drawn at the 50% probability level [symmetry codes: (i) $\frac{1}{2} - x, -\frac{1}{2} - y, 1 - z$; (ii) $1 - x, +y, \frac{3}{2} - z$].
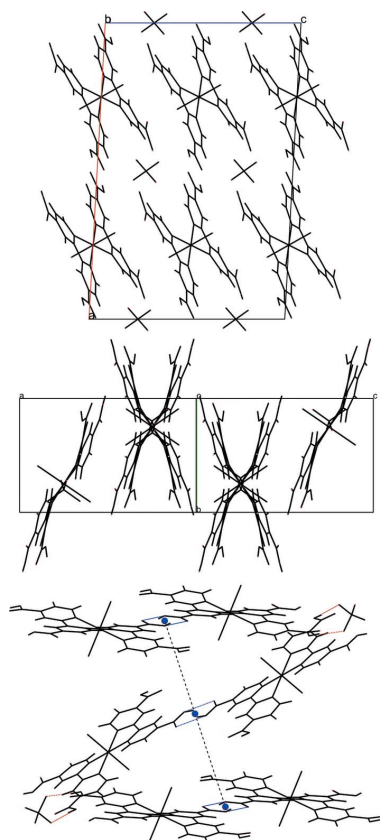
**Figure 2**
View of the planes along which two sets of ribbons formed by the hydrogen-bonded carboxylic groups C4O1O2H2 propagate (hydrogen bonds are represented by blue dashed lines). Red dashed lines show the interactions between the perchlorate anion and the C12O3O4H4 carboxylate group.

The distance between the closest O2—C4—O1 centroids is 7.3833 (7) Å, while the distance between two adjacent ruthenium(III) atoms is 16.5316 (10) Å, and that of the closest ruthenium(III) atoms in the two different planes is of 13.0452 (10) Å.

Focusing on the dcbpy ligand, Fujihara *et al.* (2004) described the analogous *cis* compound, *cis*-[Ru$^{II}$(dcbpy)$_2$Cl$_2$].



**Figure 3**
Crystal packing of [Ru$^{III}$(dcbpy)$_2$Cl$_2$]ClO$_4$ (top, middle), and perpendicular view of the layers in which the ribbons propagate (bottom).

**Table 3**
Experimental details.

| | |
|---|---|
| **Crystal data** | |
| Chemical formula | [RuCl$_2$(C$_{12}$H$_8$N$_2$O$_4$)$_2$]ClO$_4$ |
| $M_r$ | 759.83 |
| Crystal system, space group | Monoclinic, $C2/c$ |
| Temperature (K) | 273 |
| $a$, $b$, $c$ (Å) | 22.3394 (19), 8.1249 (7), 14.7667 (14) |
| $\beta$ (°) | 93.162 (4) |
| $V$ (Å$^3$) | 2676.2 (4) |
| $Z$ | 4 |
| Radiation type | Mo $K\alpha$ |
| $\mu$ (mm$^{-1}$) | 0.96 |
| Crystal size (mm) | 0.24 × 0.10 × 0.06 |
| | |
| **Data collection** | |
| Diffractometer | Bruker D8 Venture |
| Absorption correction | Multi-scan (*SADABS*; Bruker, 2015) |
| $T_{min}$, $T_{max}$ | 0.697, 0.745 |
| No. of measured, independent and observed [$I > 2\sigma(I)$] reflections | 18342, 2741, 2135 |
| $R_{int}$ | 0.080 |
| $(\sin\theta/\lambda)_{max}$ (Å$^{-1}$) | 0.626 |
| | |
| **Refinement** | |
| $R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, $S$ | 0.047, 0.112, 1.07 |
| No. of reflections | 2741 |
| No. of parameters | 202 |
| H-atom treatment | H-atom parameters constrained |
| $\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å$^{-3}$) | 0.92, −0.63 |

Computer programs: *APEX2* and *SAINT* (Bruker, 2015), *SHELXT2018* (Sheldrick, 2015*a*), *SHELXL* (Sheldrick, 2015*b*), *OLEX2* (Dolomanov *et al.*, 2009), *Mercury* (Macrae *et al.*, 2006).

Analyzing ruthenium(III) complexes, only two similar compounds have been found in the literature: *cis*-[Ru$^{III}$(bpy)$_2$Cl$_2$]Cl·2H$_2$O (bpy: 2,2′-bipyridine) (Eggleston *et al.*, 1985) and *cis*-[Ru$^{III}$(dmbpy)$_2$Cl$_2$](PF$_6$) (Seok *et al.*, 2012). In addition, Klüfers & Zangl (2007) presented a ruthenium(III) complex in a *trans* configuration with 2,2′-bipyridine, *trans*-[Ru$^{III}$(bpy)$_2$Cl$_2$]. To the best of our knowledge, these are the only few examples of crystal structures of *trans*-ruthenium(III) complexes comprising bipyridine and a monodentate halogenido group as ligands.

## Synthesis and crystallization

While attempting to synthesize the complex *cis*-[Ru$^{II}$(dcbpy)$_2$(4m4but)] (4m4but = *N*-butyl-4′-methyl-[2,2′-bipyridine]-4-methanamine), a mixture of *cis*-[Ru$^{II}$(dcbpy)$_2$Cl$_2$] and 4m4but (1:1) in MeOH/NaOH solution was refluxed for 3 h, in the dark, under an argon atmosphere. After this time, the solvent was removed under reduced pressure, and a red solid was obtained. Orange single crystals of the title *trans* complex were serendipitously obtained by recrystallization of this solid from a HClO$_4$ solution (1.5 *M*) after several months.

IR (cm$^{-1}$, CsI): 3449 (*m*), 2928 (*w*), 2855 (*w*), 1725 (*m*), 1697 (*sh*), 1619 (*w*), 1556 (*w*), 1448 (*sh*), 1408 (*w*), 1370 (*w*), 1318 (*w*), 1266 (*w*), 1233, 1105 (*s*), 1084 (*sh*), 1023 (*w*), 901 (*w*), 818 (*w*), 769 (*w*), 630 (*s*). Diffuse reflectance (nm, BaSO$_4$): 248, 293, 467, 540 (*sh*), 679 (*sh*).

# data reports

## Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3.

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# full crystallographic data

# *trans*-Bis(2,2′-bipyridine-4,4′-dicarboxylic acid-$\kappa^2N,N'$)dichloridoruthenium(III) perchlorate

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***trans*-Bis(2,2′-bipyridine-4,4′-dicarboxylic acid-$\kappa^2N,N'$)dichloridoruthenium(III) perchlorate**

*Crystal data*

| | |
|---|---|
| $[RuCl_2(C_{12}H_8N_2O_4)_2]ClO_4$ | $F(000) = 1516$ |
| $M_r = 759.83$ | $D_x = 1.886$ Mg m$^{-3}$ |
| Monoclinic, $C2/c$ | Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å |
| $a = 22.3394\,(19)$ Å | Cell parameters from 4234 reflections |
| $b = 8.1249\,(7)$ Å | $\theta = 2.7$–$26.0°$ |
| $c = 14.7667\,(14)$ Å | $\mu = 0.96$ mm$^{-1}$ |
| $\beta = 93.162\,(4)°$ | $T = 273$ K |
| $V = 2676.2\,(4)$ Å$^3$ | Irregular, orange |
| $Z = 4$ | $0.24 \times 0.10 \times 0.06$ mm |

*Data collection*

| | |
|---|---|
| Bruker D8 Venture diffractometer | 2741 independent reflections |
| $\varphi$ and $\omega$ scans | 2135 reflections with $I > 2\sigma(I)$ |
| Absorption correction: multi-scan (SADABS; Bruker, 2015) | $R_{int} = 0.080$ |
| | $\theta_{max} = 26.4°$, $\theta_{min} = 2.7°$ |
| $T_{min} = 0.697$, $T_{max} = 0.745$ | $h = -27 \rightarrow 27$ |
| 18342 measured reflections | $k = -10 \rightarrow 10$ |
| | $l = -18 \rightarrow 18$ |

*Refinement*

| | |
|---|---|
| Refinement on $F^2$ | Hydrogen site location: inferred from neighbouring sites |
| Least-squares matrix: full | |
| $R[F^2 > 2\sigma(F^2)] = 0.047$ | H-atom parameters constrained |
| $wR(F^2) = 0.112$ | $w = 1/[\sigma^2(F_o^2) + (0.0449P)^2 + 15.531P]$ where $P = (F_o^2 + 2F_c^2)/3$ |
| $S = 1.07$ | |
| 2741 reflections | $(\Delta/\sigma)_{max} < 0.001$ |
| 202 parameters | $\Delta\rho_{max} = 0.92$ e Å$^{-3}$ |
| 0 restraints | $\Delta\rho_{min} = -0.63$ e Å$^{-3}$ |
| Primary atom site location: dual | |

*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* | $U_{iso}*/U_{eq}$ |
|---|---|---|---|---|
| Ru1 | 0.250000 | −0.250000 | 0.500000 | 0.02162 (16) |
| Cl1 | 0.29145 (6) | −0.09129 (15) | 0.39197 (9) | 0.0401 (3) |
| Cl2 | 0.500000 | 0.6986 (3) | 0.750000 | 0.0497 (5) |
| N2 | 0.28196 (15) | −0.0850 (4) | 0.5991 (2) | 0.0246 (8) |
| N1 | 0.17958 (15) | −0.0825 (4) | 0.5090 (2) | 0.0233 (8) |
| O1 | 0.00398 (16) | 0.2932 (5) | 0.4656 (3) | 0.0535 (11) |
| C7 | 0.25357 (18) | 0.0625 (5) | 0.5975 (3) | 0.0216 (9) |
| C6 | 0.19433 (18) | 0.0614 (5) | 0.5491 (3) | 0.0224 (9) |
| O3 | 0.3334 (2) | 0.4578 (5) | 0.7421 (3) | 0.0662 (13) |
| O2 | 0.07193 (17) | 0.4483 (5) | 0.5417 (4) | 0.0696 (15) |
| H2 | 0.047154 | 0.520833 | 0.530143 | 0.104* |
| C5 | 0.1549 (2) | 0.1923 (5) | 0.5500 (3) | 0.0270 (10) |
| H5 | 0.166383 | 0.291296 | 0.577413 | 0.032* |
| C8 | 0.2776 (2) | 0.1957 (5) | 0.6436 (3) | 0.0272 (10) |
| H8 | 0.257691 | 0.296196 | 0.641492 | 0.033* |
| C11 | 0.3307 (2) | −0.1043 (6) | 0.6549 (3) | 0.0338 (12) |
| H11 | 0.346985 | −0.209010 | 0.662892 | 0.041* |
| C9 | 0.3318 (2) | 0.1797 (6) | 0.6932 (3) | 0.0291 (10) |
| O4 | 0.41452 (19) | 0.3021 (6) | 0.7693 (4) | 0.0716 (14) |
| H4 | 0.431618 | 0.390156 | 0.778970 | 0.107* |
| C3 | 0.0978 (2) | 0.1736 (6) | 0.5094 (3) | 0.0290 (10) |
| C2 | 0.0818 (2) | 0.0235 (6) | 0.4735 (4) | 0.0334 (11) |
| H2A | 0.043392 | 0.006857 | 0.447597 | 0.040* |
| C1 | 0.1231 (2) | −0.1027 (6) | 0.4759 (3) | 0.0325 (11) |
| H1 | 0.111260 | −0.205576 | 0.453870 | 0.039* |
| C10 | 0.3574 (2) | 0.0258 (6) | 0.7008 (3) | 0.0373 (12) |
| H10 | 0.392536 | 0.010067 | 0.736548 | 0.045* |
| C12 | 0.3593 (2) | 0.3296 (7) | 0.7372 (4) | 0.0418 (13) |
| C4 | 0.0543 (2) | 0.3163 (6) | 0.5054 (4) | 0.0372 (12) |
| O5 | 0.4698 (3) | 0.5970 (9) | 0.8115 (5) | 0.140 (3) |
| O6 | 0.5377 (4) | 0.7789 (11) | 0.8031 (6) | 0.181 (4) |

*Atomic displacement parameters (Å²)*

|  | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| Ru1 | 0.0194 (2) | 0.0161 (2) | 0.0290 (3) | 0.0071 (2) | −0.00141 (18) | −0.0053 (2) |
| Cl1 | 0.0533 (8) | 0.0254 (6) | 0.0429 (7) | 0.0029 (5) | 0.0158 (6) | −0.0004 (5) |
| Cl2 | 0.0304 (9) | 0.0567 (12) | 0.0608 (13) | 0.000 | −0.0079 (9) | 0.000 |
| N2 | 0.0227 (19) | 0.0222 (19) | 0.028 (2) | 0.0088 (15) | −0.0035 (16) | −0.0064 (15) |
| N1 | 0.0201 (18) | 0.0184 (18) | 0.031 (2) | 0.0059 (14) | −0.0016 (15) | −0.0044 (15) |
| O1 | 0.0272 (19) | 0.040 (2) | 0.091 (3) | 0.0158 (16) | −0.014 (2) | −0.008 (2) |
| C7 | 0.019 (2) | 0.018 (2) | 0.027 (2) | 0.0042 (17) | 0.0004 (18) | −0.0015 (17) |
| C6 | 0.020 (2) | 0.020 (2) | 0.027 (2) | 0.0056 (17) | 0.0014 (18) | −0.0033 (18) |
| O3 | 0.065 (3) | 0.037 (2) | 0.094 (3) | 0.000 (2) | −0.021 (3) | −0.022 (2) |
| O2 | 0.036 (2) | 0.028 (2) | 0.143 (4) | 0.0180 (17) | −0.018 (2) | −0.022 (2) |

| | | | | | | |
|------|-------------|-------------|-------------|--------------|--------------|---------------|
| C5 | 0.027 (2) | 0.017 (2) | 0.038 (3) | 0.0061 (18) | 0.003 (2) | −0.0054 (18) |
| C8 | 0.030 (2) | 0.020 (2) | 0.032 (3) | 0.0054 (18) | 0.002 (2) | −0.0040 (18) |
| C11 | 0.034 (3) | 0.030 (3) | 0.036 (3) | 0.017 (2) | −0.010 (2) | −0.009 (2) |
| C9 | 0.027 (2) | 0.031 (2) | 0.029 (2) | 0.001 (2) | 0.002 (2) | −0.007 (2) |
| O4 | 0.046 (3) | 0.066 (3) | 0.100 (4) | −0.009 (2) | −0.022 (3) | −0.024 (3) |
| C3 | 0.022 (2) | 0.024 (2) | 0.041 (3) | 0.0083 (19) | 0.004 (2) | 0.000 (2) |
| C2 | 0.018 (2) | 0.033 (3) | 0.049 (3) | 0.0047 (19) | −0.002 (2) | −0.008 (2) |
| C1 | 0.025 (2) | 0.027 (3) | 0.046 (3) | 0.0035 (19) | 0.000 (2) | −0.011 (2) |
| C10 | 0.028 (3) | 0.047 (3) | 0.035 (3) | 0.012 (2) | −0.009 (2) | −0.014 (2) |
| C12 | 0.038 (3) | 0.046 (3) | 0.041 (3) | −0.005 (3) | −0.002 (2) | −0.013 (3) |
| C4 | 0.028 (3) | 0.025 (2) | 0.059 (3) | 0.009 (2) | 0.002 (2) | 0.000 (2) |
| O5 | 0.163 (7) | 0.147 (6) | 0.115 (5) | −0.105 (5) | 0.060 (5) | −0.055 (5) |
| O6 | 0.168 (7) | 0.224 (9) | 0.142 (7) | −0.132 (7) | −0.063 (6) | 0.025 (6) |

*Geometric parameters (Å, º)*

| | | | |
|----------------------|--------------|------------|------------|
| Ru1—Cl1[i] | 2.2865 (13) | O2—H2 | 0.8200 |
| Ru1—Cl1 | 2.2865 (13) | O2—C4 | 1.253 (6) |
| Ru1—N2[i] | 2.082 (3) | C5—H5 | 0.9300 |
| Ru1—N2 | 2.082 (3) | C5—C3 | 1.388 (6) |
| Ru1—N1 | 2.090 (3) | C8—H8 | 0.9300 |
| Ru1—N1[i] | 2.090 (3) | C8—C9 | 1.385 (6) |
| Cl2—O5[ii] | 1.424 (6) | C11—H11 | 0.9300 |
| Cl2—O5 | 1.424 (7) | C11—C10 | 1.374 (7) |
| Cl2—O6 | 1.295 (6) | C9—C10 | 1.378 (7) |
| Cl2—O6[ii] | 1.295 (6) | C9—C12 | 1.496 (7) |
| N2—C7 | 1.356 (5) | O4—H4 | 0.8200 |
| N2—C11 | 1.338 (5) | O4—C12 | 1.316 (6) |
| N1—C6 | 1.344 (5) | C3—C2 | 1.369 (7) |
| N1—C1 | 1.338 (5) | C3—C4 | 1.511 (6) |
| O1—C4 | 1.253 (6) | C2—H2A | 0.9300 |
| C7—C6 | 1.469 (6) | C2—C1 | 1.378 (6) |
| C7—C8 | 1.372 (6) | C1—H1 | 0.9300 |
| C6—C5 | 1.382 (6) | C10—H10 | 0.9300 |
| O3—C12 | 1.195 (7) | | |
| | | | |
| Cl1—Ru1—Cl1[i] | 180.00 (6) | C4—O2—H2 | 109.5 |
| N2—Ru1—Cl1 | 89.48 (11) | C6—C5—H5 | 120.5 |
| N2—Ru1—Cl1[i] | 90.51 (11) | C6—C5—C3 | 118.9 (4) |
| N2[i]—Ru1—Cl1[i] | 89.49 (11) | C3—C5—H5 | 120.5 |
| N2[i]—Ru1—Cl1 | 90.51 (11) | C7—C8—H8 | 120.2 |
| N2—Ru1—N2[i] | 180.0 | C7—C8—C9 | 119.7 (4) |
| N2—Ru1—N1[i] | 103.53 (13) | C9—C8—H8 | 120.2 |
| N2[i]—Ru1—N1[i] | 76.47 (13) | N2—C11—H11 | 119.0 |
| N2[i]—Ru1—N1 | 103.53 (13) | N2—C11—C10 | 122.0 (4) |
| N2—Ru1—N1 | 76.47 (13) | C10—C11—H11 | 119.0 |
| N1[i]—Ru1—Cl1[i] | 90.70 (11) | C8—C9—C12 | 118.6 (4) |
| N1—Ru1—Cl1 | 90.70 (11) | C10—C9—C8 | 118.4 (4) |

| | | | |
|---|---|---|---|
| N1i—Ru1—Cl1 | 89.30 (11) | C10—C9—C12 | 123.0 (4) |
| N1—Ru1—Cl1i | 89.30 (11) | C12—O4—H4 | 109.5 |
| N1i—Ru1—N1 | 180.00 (12) | C5—C3—C4 | 120.4 (4) |
| O5—Cl2—O5ii | 109.1 (6) | C2—C3—C5 | 118.6 (4) |
| O6ii—Cl2—O5ii | 102.8 (4) | C2—C3—C4 | 121.0 (4) |
| O6ii—Cl2—O5 | 111.3 (6) | C3—C2—H2A | 120.2 |
| O6—Cl2—O5ii | 111.3 (6) | C3—C2—C1 | 119.5 (4) |
| O6—Cl2—O5 | 102.8 (4) | C1—C2—H2A | 120.2 |
| O6ii—Cl2—O6 | 119.5 (9) | N1—C1—C2 | 122.3 (4) |
| C7—N2—Ru1 | 114.5 (3) | N1—C1—H1 | 118.9 |
| C11—N2—Ru1 | 126.4 (3) | C2—C1—H1 | 118.9 |
| C11—N2—C7 | 118.6 (4) | C11—C10—C9 | 119.4 (4) |
| C6—N1—Ru1 | 115.3 (3) | C11—C10—H10 | 120.3 |
| C1—N1—Ru1 | 126.5 (3) | C9—C10—H10 | 120.3 |
| C1—N1—C6 | 118.1 (4) | O3—C12—C9 | 123.2 (5) |
| N2—C7—C6 | 114.3 (4) | O3—C12—O4 | 124.9 (5) |
| N2—C7—C8 | 121.2 (4) | O4—C12—C9 | 111.9 (5) |
| C8—C7—C6 | 124.3 (4) | O1—C4—O2 | 125.6 (4) |
| N1—C6—C7 | 114.4 (4) | O1—C4—C3 | 117.5 (5) |
| N1—C6—C5 | 122.2 (4) | O2—C4—C3 | 116.9 (4) |
| C5—C6—C7 | 123.3 (4) | | |
| | | | |
| Ru1—N2—C7—C6 | 19.6 (5) | C5—C3—C2—C1 | −2.0 (8) |
| Ru1—N2—C7—C8 | −164.9 (3) | C5—C3—C4—O1 | 178.1 (5) |
| Ru1—N2—C11—C10 | 162.3 (4) | C5—C3—C4—O2 | −1.4 (8) |
| Ru1—N1—C6—C7 | −13.0 (5) | C8—C7—C6—N1 | −179.7 (4) |
| Ru1—N1—C6—C5 | 171.6 (4) | C8—C7—C6—C5 | −4.4 (7) |
| Ru1—N1—C1—C2 | −170.4 (4) | C8—C9—C10—C11 | 3.8 (8) |
| N2—C7—C6—N1 | −4.3 (6) | C8—C9—C12—O3 | 10.4 (8) |
| N2—C7—C6—C5 | 171.0 (4) | C8—C9—C12—O4 | −169.8 (5) |
| N2—C7—C8—C9 | −0.4 (7) | C11—N2—C7—C6 | −168.0 (4) |
| N2—C11—C10—C9 | 3.5 (8) | C11—N2—C7—C8 | 7.6 (7) |
| N1—C6—C5—C3 | 1.1 (7) | C3—C2—C1—N1 | −2.9 (8) |
| C7—N2—C11—C10 | −9.2 (7) | C2—C3—C4—O1 | −2.1 (8) |
| C7—C6—C5—C3 | −173.9 (4) | C2—C3—C4—O2 | 178.4 (6) |
| C7—C8—C9—C10 | −5.3 (7) | C1—N1—C6—C7 | 169.6 (4) |
| C7—C8—C9—C12 | 175.5 (4) | C1—N1—C6—C5 | −5.9 (7) |
| C6—N1—C1—C2 | 6.8 (7) | C10—C9—C12—O3 | −168.8 (6) |
| C6—C7—C8—C9 | 174.7 (4) | C10—C9—C12—O4 | 11.1 (8) |
| C6—C5—C3—C2 | 2.9 (7) | C12—C9—C10—C11 | −177.1 (5) |
| C6—C5—C3—C4 | −177.3 (4) | C4—C3—C2—C1 | 178.2 (5) |

Symmetry codes: (i) −x+1/2, −y−1/2, −z+1; (ii) −x+1, y, −z+3/2.

*Hydrogen-bond geometry ()*

| D—H···A |
|---|
| O1—H2···O2iii |

O4—H4⋯O5

Symmetry code: (iii) −$x$, −$y$+1, −$z$+1.