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Crystal structure and near-infrared emission of *trans*-dichlorido(dimethoxyphenylphosphine)-[4,4′,4″-tris(methoxycarbonyl)-2,2′:6′,2″-terpyridine]ruthenium(II) monohydrate

Takumi Kinoshita[a]* and Hiroshi Segawa[a,b]

[a]Department of General Systems Studies, Graduate School of Arts and Sciences, The University of Tokyo, 3-8-1 Komaba, Meguro-ku, Tokyo, 153-8902, Japan, and [b]Research Center for Advanced Science and Technology (RCAST), The University of Tokyo 4-6-1, Komaba, Meguro-ku, Tokyo, 153-8904, Japan. *Correspondence e-mail: utkino@mail.ecc.u-tokyo.ac.jp

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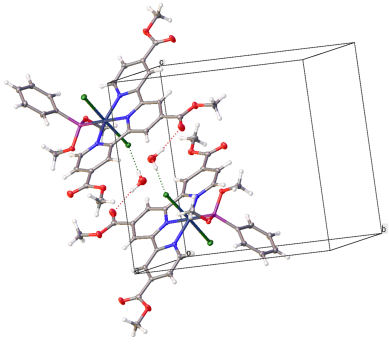
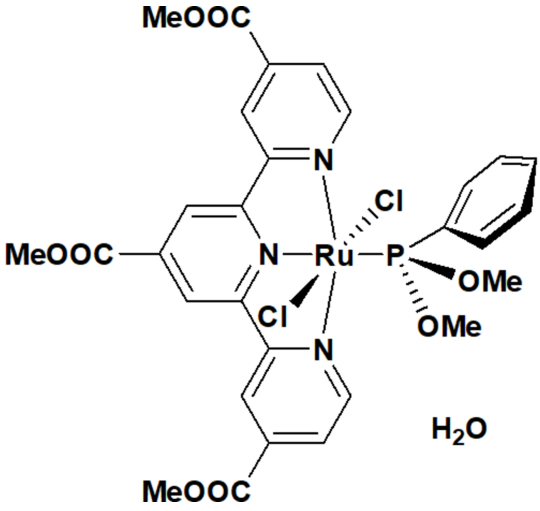
In the title compound, $[RuCl_2(C_{21}H_{17}N_3O_6)(C_8H_{11}O_2P)]\cdot H_2O$, the Ru^{II} atom is coordinated by three N atoms of a meridionally bound 4,4′,4″-tris(methoxycarbonyl)-2,2′:6′,2″-terpyridine ligand, a phosphinite P donor and two chloride ligands in a distorted octahedral geometry. The Ru—N distances lie in the range 1.996 (2)–2.078 (2) Å, with a Ru—P distance of 2.2879 (9) Å and Ru—Cl distances of 2.3713 (8) and 2.4191 (8) Å; the N—Ru—N bite angles are 78.59 (9) and 79.10 (9)°, with an N—Ru—N angle of 157.30 (9)° within the terpyridine chelate. The methyl ester groups adopt conformations that minimize steric interactions with the phosphinite phenyl ring and provide potential anchoring sites in the corresponding carboxylic acid dye. In the crystal, pairs of complex molecules are linked into discrete hydrogen-bonded dimers by the water molecule of crystallization: one H atom forms an O—H···O contact to a methyl carbonyl O atom [H···O = 2.17 Å] and the other H atom forms an O—H···Cl contact to a *trans* chloride ligand of a neighbouring complex [H···Cl = 2.40 Å].

1. Chemical context

Ruthenium(II) polypyridyl complexes remain among the most widely studied sensitizers for dye-sensitized solar cells (DSSCs) because they combine intense metal-to-ligand charge-transfer (MLCT) absorption with favourable redox properties and robust synthetic tunability (Grätzel, 2005; Qin *et al.*, 2012). Within this family, strongly σ-donating phosphine or phosphinite co-ligands have been used to modulate the ligand field at the Ru^{II} atom, alter the energy and composition of the frontier *d* orbitals and, in some cases, to enable spin-forbidden singlet–triplet excitations that extend the spectroscopic response into the near-infrared region (Kinoshita *et al.*, 2013; De Angelis, 2014; Kinoshita *et al.*, 2015; Swetha *et al.*, 2015; Kinoshita, 2022; Juwita *et al.*, 2024). A notable example is the phosphine-coordinated sensitizer DX1, which employs a tricarboxy-substituted terpyridine ligand to anchor onto TiO_2 and displays an unusually broad photoresponse that has been attributed to spin-forbidden singlet–triplet absorption (Kinoshita *et al.*, 2013, 2019; Kinoshita, 2022). Reliable structural information on such systems is desirable in order to benchmark quantum-chemical calculations, to assess how the strong σ-donor phosphinite perturbs the RuN_3PCl_2 coordination environment, and to relate the conformation of the extended π system and the ester groups to the photophysical behaviour of the dye (Fantacci *et al.*, 2014; Mishima *et al.*, 2015; Imamura *et al.*, 2015; Kanno *et al.*, 2016; Kinoshita *et al.*, 2024;



Juwita *et al.*, 2024). To date, a single-crystal X-ray structure has been reported only for a thiophene-extended tricarboxy ester analogue (DX4m) (Kinoshita *et al.*, 2021), and that study focused mainly on the crystal packing rather than on a detailed analysis of the RuN_3PCl_2 coordination geometry or the terpyridine conformation in a DX1-type core. The title compound, $[RuCl_2(C_{21}H_{17}N_3O_6)(C_8H_{11}O_2P)]\cdot H_2O$, is the methyl ester analogue of DX1 and contains a 4,4′,4″-tris-(methoxycarbonyl)-2,2′:6′,2″-terpyridine ligand (tcTpy) (Nazeeruddin *et al.*, 2001; Dehaudt *et al.*, 2011) and a dimethoxyphenylphosphine co-ligand. Its crystal structure therefore provides the first detailed crystallographic insight into the coordination geometry and molecular conformation of a DX1-type Ru^{II} sensitizer.



2. Structural commentary

The molecular structure of the title complex, $[RuCl_2(tcTpy)(PPh(OMe)_2)]\cdot H_2O$, is shown in Fig. 1. The Ru^{II} atom (Ru1) is six-coordinated in a slightly distorted octahedral environment defined by three N atoms (N39, N40 and N41) of the meridionally bound tcTpy ligand, one P atom (P1) of the dimethoxyphenylphosphine ligand and two chlorido ligands (Cl1 and Cl2). The two Cl ligands occupy mutually *trans* positions [Cl2—Ru1—Cl1 = 174.94 (2)°], while the phosphinite donor P1 is *trans* to the central tcTpy N atom N39 [P1—Ru1—N39 = 177.03 (6)°].

The Ru—N bond lengths are Ru1—N39 = 1.996 (2) Å, Ru1—N40 = 2.078 (2) Å and Ru1—N41 = 2.054 (2) Å, with the shortest distance to the central tcTpy N atom N39. The chelating bite angles within the tcTpy ligand are N39—Ru1—N40 = 79.10 (9)° and N39—Ru1—N41 = 78.59 (9)°, and the corresponding N—Ru—N angle involving the two terminal N donors is N40—Ru1—N41 = 157.30 (9)°, indicating the usual meridional terpyridine binding mode with a modest opening of the N—Ru—N angle opposite the phosphinite ligand. The Ru—P bond length is Ru1—P1 = 2.2879 (9) Å, and the Ru—Cl distances are Ru1—Cl1 = 2.4191 (8) Å and Ru1—Cl2 = 2.3713 (8) Å, all of which are within the ranges commonly observed for Ru^{II} terpyridine–

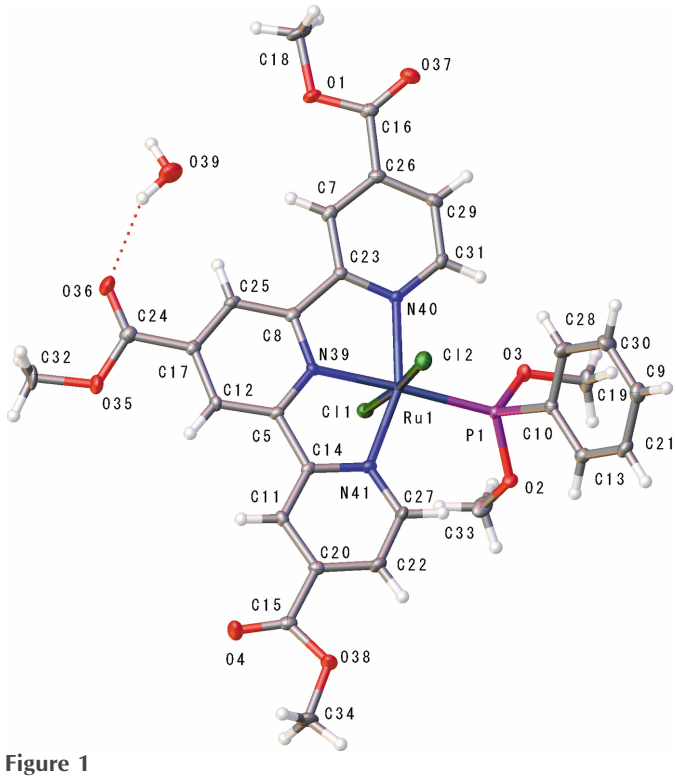


Figure 1
The molecular structure of the title complex, $[RuCl_2(tcTpy)(PPh(OMe)_2)]\cdot H_2O$, showing the atom-labelling scheme and 50% probability displacement ellipsoids for non-H atoms. The O39—H hydrogen bond is indicated by a dashed line.

phosphine complexes. The coordination geometry around the Ru^{II} atom can thus be described as a slightly distorted octahedron, with the primary distortion arising from the constrained tcTpy bite angles. The tcTpy ligand is close to planar within each pyridyl ring, but the terpyridine unit as a whole shows a slight bowl-shaped curvature, with the terminal rings tilted by about 7.6 and 5.7° with respect to the central ring plane. This curvature most likely reflects steric repulsion between the 4,4′,4″-methoxycarbonyl substituents and the dimethoxyphenylphosphine co-ligand, and it propagates to the metal coordination sphere: as a result, the Cl1—Ru1—Cl2 axis is not exactly perpendicular to the tcTpy mean plane, but is inclined by about 11° from the normal

The three methoxycarbonyl substituents at the 4,4′,4″ positions are rotated out of the terpyridine mean plane by 1about 0.7, 12.2 and 7.7°, respectively, to relieve steric crowding around the RuN_3PCl_2 core and the phosphinite phenyl.The dimethoxyphenylphosphine ligand adopts a conformation in which the phenyl ring is roughly orthogonal to the Ru—P bond, while the two methoxy groups project away from the metal centre and from the tcTpy core, further minimizing steric congestion around the coordination sphere.

3. Supramolecular features

The dominant intermolecular interactions in the crystal are mediated by the water molecule of crystallization (O39), which acts as a hydrogen-bond donor to two adjacent accep-

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O39—H39B···O36	0.90	2.17	3.00	154.2
O39—H39A···Cl1^{i}	0.85	2.40	3.24	176.3

Symmetry code: (i) $-x+1, -y+2, -z+1$.

tors (Fig. 2). One H atom, H39*B*, forms an O39—H39*B*···O36 hydrogen bond to a methylcarbonyl O atom of the tcTpy ligand of its own complex, whereas the other H atom, H39*A*, forms an O39—H39*A*···Cl1 hydrogen bond to the *trans* chlorido ligand (Cl1) of a neighbouring complex. These contacts link two symmetry-related complexes into a discrete centrosymmetric dimer in which the water molecule bridges between a tcTpy ester group on one molecule and the Ru—Cl fragment of the other. The H···O and H···Cl separations are 2.17 and 2.40 Å, respectively, and the complete hydrogen-bond geometry is given in Table 1. Apart from this motif, only relatively long C—H···O and C—H···Cl contacts are observed between neighbouring molecules, and no extended hydrogen-bonded or π–π-stacked network is formed; the remaining packing is governed mainly by van der Waals contacts between the aromatic ligands.

To relate these structural features to the functional behaviour of the complex, low-temperature single-crystal emission measurements at 77 K show a near-infrared band with a maximum around 974 nm, which can be assigned to a $Ru^{II}\rightarrow$tcTpy triplet MLCT transition (Fig. 3). The presence of this MLCT-type NIR emission reflects the relatively strong ligand field at the Ru^{II} atom imposed by the meridionally bound tcTpy ligand and the phosphinite ligand trans to its central nitrogen donor. The band is noticeably sharper than in fluid solution, and its maximum at 974 nm is only slightly red-shifted relative to the solution spectrum, suggesting that crystal-packing effects on the emissive state are modest. This modest perturbation is consistent with the absence of extended π–π stacking and the limited supramolecular interactions beyond the discrete hydrogen-bonded dimers, which restrict intermolecular quenching pathways and allow the MLCT excited state to be preserved in the solid state.

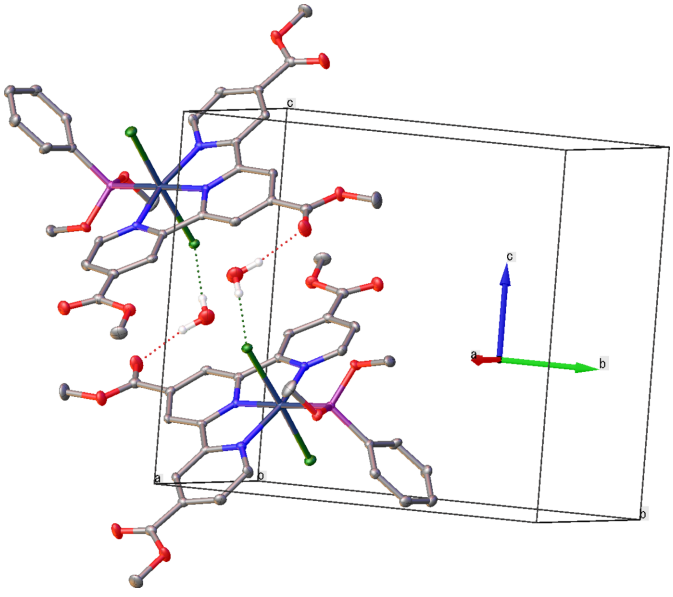


Figure 2
The molecular structure of the title complex with displacement ellipsoids drawn at the 50% probability level. The O39—H39*B*···O36 and O39—H39*A*···Cl1 hydrogen bonds are indicated by dashed lines; other H atoms are omitted for clarity.

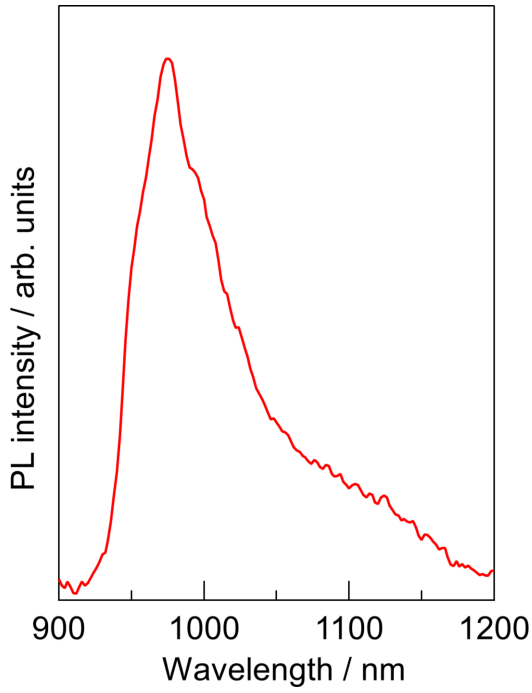


Figure 3
Low-temperature (77 K) single-crystal emission spectrum of the title complex in the near-infrared region (λ_{ex} = 532 nm).

4. Database survey

Inspection of the Cambridge Structural Database (WebCSD, November 2025; Groom *et al.*, 2016) was carried out for mononuclear Ru^{II} complexes containing the tcTpy ligand, defined here as 4,4′,4″-tris(methoxycarbonyl)-2,2′:6′,2″-terpyridine coordinated in the usual meridional fashion. In this subset, crystal structures have been reported only in combination with neutral or anionic N-donor or carbon-donor co-ligands (Schulze *et al.*, 2012; Breivogel *et al.*, 2013; Yao *et al.*, 2014; Shao *et al.*, 2015); no tcTpy complexes bearing a monodentate κP-bound phosphorus ligand or a terminal halide ligand at the Ru^{II} centre are represented. For comparison, we also searched for mononuclear Ru^{II} complexes with a *trans*-{$RuCl_2$(Tpy)(P-donor)} core, defined as an *N*^*N*^*N* terpyridine ligand (parent tpy or 4-substituted derivatives), two mutually *trans* chlorido ligands and a monodentate κP-bound phosphine, phosphinite or phosphite ligand. Under these criteria, only a single crystal structure with a *trans*-{$RuCl_2$(tpy-type)(P-donor)} core is currently deposited in the CSD, namely our previously reported thiophene-extended DX4m complex (CSD refcode EVOQEO; Kinoshita

Table 2
Experimental details.

Crystal data	
Chemical formula	$[Ru(C_8H_{11}O_2P)Cl_2(C_{21}H_{17}N_3O_6)]\cdot H_2O$
M_r	767.50
Crystal system, space group	Triclinic, $P\overline{1}$
Temperature (K)	273
a, b, c (Å)	10.472 (4), 12.777 (4), 12.973 (4)
α, β, γ (°)	92.254 (3), 108.118 (3), 105.483 (4)
V (Å^3)	1575.7 (9)
Z	2
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.78
Crystal size (mm)	0.11 × 0.04 × 0.03
Data collection	
Diffractometer	Rigaku Saturn724+ (4x4 bin mode)
Absorption correction	Multi-scan (*REQAB*; Rigaku, 2008)
T_{min}, T_{max}	0.900, 0.977
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	12392, 6845, 5862
R_{int}	0.029
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.649
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.037, 0.078, 1.05
No. of reflections	6845
No. of parameters	414
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.48, −0.98

Computer programs: *CrysAlis PRO* (Rigaku OD, 2025), *SIR2011* (Burla *et al.*, 2012), *SHELXL* 2018/3 (Sheldrick, 2015) and *OLEX2* (Dolomanov *et al.*, 2009).

et al., 2021). Thus, while such *trans*-{$RuCl_2$(tpy-type)(P-donor)} species are very rare, no examples incorporating the tcTpy ligand are known, and the title compound represents the first crystallographically characterized Ru^{II} complex of the trans-{$RuCl_2$(tcTpy)(P-donor)} type.

5. Synthesis and crystallization

The methyl ester analogue of DX1 (DX1m) was prepared according to a published procedure (Kinoshita *et al.*, 2013). A sample of DX1m was dissolved in dichloromethane to give a *ca.* 5 mg mL^{-1} solution, which was filtered and transferred to a small glass tube. Diethyl ether was then carefully layered on top of the CH_2Cl_2 solution and allowed to diffuse slowly at room temperature. After several days, black needle-like single crystals of the title complex suitable for X-ray diffraction were obtained from the interface between the two solvents.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. Hydrogen atoms bonded to carbon were placed in calculated positions and refined using a riding model, with C—H = 0.95–0.99 Å and U_{iso}(H) = 1.2U_{eq}(C) for aromatic and methine H atoms, and C—H = 0.98 Å and U_{iso}(H) = 1.5U_{eq}(C) for methyl groups; methyl groups were refined as rotating groups. The H atoms of the water molecule of crystallization were located in a difference-Fourier map and refined with restrained O—H and H···H distances, with U_{iso}(H) = 1.5U_{eq}(O). The largest residual electron-density peak and hole are located in the vicinity of the Ru atom and are not chemically significant.

Acknowledgements

The authors thank Dr Hiroyasu Sato (Rigaku Corp.) for support with the crystallographic measurements and structural analysis.

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Crystal structure and near-infrared emission of *trans*-dichlorido(dimethoxyphenylphosphine)[4,4′,4′′-tris(methoxycarbonyl)-2,2′:6′,2′′-terpyridine]ruthenium(II) monohydrate

Takumi Kinoshita and Hiroshi Segawa

Computing details

***trans*-Dichlorido(dimethoxyphenylphosphine)[4,4′,4′′-tris(methoxycarbonyl)-2,2′:6′,2′′-terpyridine]ruthenium(II) monohydrate**

Crystal data

$[Ru(C_8H_{11}O_2P)Cl_2(C_{21}H_{17}N_3O_6)]\cdot H_2O$
$M_r = 767.50$
Triclinic, $P\overline{1}$
$a = 10.472$ (4) Å
$b = 12.777$ (4) Å
$c = 12.973$ (4) Å
$\alpha = 92.254$ (3)°
$\beta = 108.118$ (3)°
$\gamma = 105.483$ (4)°
$V = 1575.7$ (9) Å^3
$Z = 2$
$F(000) = 780$
$D_x = 1.618$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71075$ Å
Cell parameters from 4786 reflections
$\theta = 3.0$–27.5°
$\mu = 0.78$ mm^{-1}
$T = 273$ K
Prism, colourless
0.11 × 0.04 × 0.03 mm

Data collection

Rigaku Saturn724+ (4x4 bin mode) diffractometer
Detector resolution: 7.1429 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (*REQAB*; Rigaku, 2008)
$T_{min} = 0.900$, $T_{max} = 0.977$
12392 measured reflections
6845 independent reflections
5862 reflections with $I > 2\sigma(I)$
$R_{int} = 0.029$
$\theta_{max} = 27.5°$, $\theta_{min} = 3.0°$
$h = -12 \rightarrow 13$
$k = -15 \rightarrow 16$
$l = -16 \rightarrow 16$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.037$
$wR(F^2) = 0.078$
$S = 1.05$
6845 reflections
414 parameters
0 restraints
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0275P)^2 + 1.6521P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.002$
$\Delta\rho_{max} = 0.48$ e Å^{-3}
$\Delta\rho_{min} = -0.98$ 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.

Refinement. The structure was solved by direct methods with SIR2011 and refined by full-matrix least squares on F^2 using SHELXL (Burla *et al.*, 2012) (Sheldrick, 2015). All non-hydrogen atoms were refined with anisotropic displacement parameters.

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

	x	*y*	*z*	U_{iso}*/U_{eq}
Ru1	0.26693 (2)	0.75898 (2)	0.76612 (2)	0.00940 (6)
Cl1	0.10372 (6)	0.81480 (5)	0.61763 (5)	0.01324 (13)
Cl2	0.44238 (7)	0.71836 (5)	0.91122 (5)	0.01578 (14)
P1	0.11296 (7)	0.58928 (6)	0.75016 (5)	0.01076 (14)
O1	0.6970 (2)	0.81833 (16)	0.44551 (16)	0.0178 (4)
O2	−0.03404 (19)	0.58173 (15)	0.77135 (15)	0.0136 (4)
O3	0.0654 (2)	0.51917 (15)	0.63157 (15)	0.0147 (4)
O4	0.2132 (2)	1.14384 (17)	1.14372 (18)	0.0265 (5)
O35	0.5711 (2)	1.30809 (16)	0.80683 (17)	0.0204 (4)
O36	0.6939 (2)	1.25636 (16)	0.71037 (18)	0.0261 (5)
O37	0.6454 (2)	0.63475 (17)	0.43124 (17)	0.0220 (5)
O38	0.1028 (2)	0.98566 (16)	1.18854 (17)	0.0224 (5)
N39	0.3927 (2)	0.91008 (17)	0.77744 (17)	0.0099 (4)
N40	0.3718 (2)	0.73341 (18)	0.65974 (17)	0.0107 (4)
N41	0.2247 (2)	0.84184 (18)	0.88451 (17)	0.0115 (4)
C5	0.3846 (3)	0.9919 (2)	0.8413 (2)	0.0105 (5)
C7	0.5464 (3)	0.8264 (2)	0.5828 (2)	0.0130 (5)
H7	0.605083	0.891751	0.574081	0.016*
C8	0.4690 (3)	0.9284 (2)	0.7096 (2)	0.0118 (5)
C9	0.2509 (3)	0.3439 (2)	0.9794 (2)	0.0186 (6)
H9	0.279488	0.294123	1.025057	0.022*
C10	0.1647 (3)	0.4936 (2)	0.8425 (2)	0.0120 (5)
C11	0.2783 (3)	1.0195 (2)	0.9870 (2)	0.0117 (5)
H11	0.323981	1.094341	0.999595	0.014*
C12	0.4567 (3)	1.0995 (2)	0.8393 (2)	0.0115 (5)
H12	0.452975	1.156562	0.884038	0.014*
C13	0.0967 (3)	0.4548 (2)	0.9162 (2)	0.0143 (5)
H13	0.021542	0.478658	0.919836	0.017*
C14	0.2931 (3)	0.9527 (2)	0.9071 (2)	0.0107 (5)
C15	0.1730 (3)	1.0460 (2)	1.1314 (2)	0.0146 (6)
C16	0.6331 (3)	0.7202 (2)	0.4641 (2)	0.0154 (6)
C17	0.5348 (3)	1.1204 (2)	0.7687 (2)	0.0127 (5)
C18	0.7931 (3)	0.8219 (3)	0.3847 (2)	0.0238 (7)
H18A	0.833338	0.896435	0.375922	0.029*
H18B	0.866577	0.792261	0.423871	0.029*
H18C	0.742827	0.779332	0.313966	0.029*

C19	0.2771 (3)	0.4562 (2)	0.8382 (2)	0.0178 (6)
H19	0.323914	0.481674	0.789706	0.021*
C20	0.1946 (3)	0.9736 (2)	1.0481 (2)	0.0126 (5)
C21	0.1401 (3)	0.3811 (2)	0.9842 (2)	0.0168 (6)
H21	0.094324	0.356359	1.033467	0.020*
C22	0.1310 (3)	0.8609 (2)	1.0290 (2)	0.0155 (6)
H22	0.077372	0.827601	1.070490	0.019*
C23	0.4629 (3)	0.8268 (2)	0.6475 (2)	0.0111 (5)
C24	0.6104 (3)	1.2341 (2)	0.7585 (2)	0.0159 (6)
C25	0.5422 (3)	1.0340 (2)	0.7035 (2)	0.0129 (5)
H25	0.595205	1.047261	0.657045	0.015*
C26	0.5412 (3)	0.7274 (2)	0.5312 (2)	0.0140 (5)
C27	0.1487 (3)	0.7992 (2)	0.9479 (2)	0.0154 (6)
H27	0.105727	0.723964	0.936109	0.018*
C28	−0.0272 (3)	0.4072 (2)	0.6091 (2)	0.0202 (6)
H28A	−0.044857	0.377658	0.535097	0.024*
H28B	0.016741	0.363179	0.658489	0.024*
H28C	−0.114471	0.406906	0.618844	0.024*
C29	0.4494 (3)	0.6319 (2)	0.5438 (2)	0.0153 (6)
H29	0.444090	0.564498	0.510108	0.018*
C30	0.3193 (3)	0.3817 (2)	0.9055 (2)	0.0200 (6)
H30	0.393494	0.356678	0.901450	0.024*
C31	0.3659 (3)	0.6376 (2)	0.6070 (2)	0.0136 (5)
H31	0.303253	0.573209	0.613413	0.016*
C32	0.6376 (3)	1.4223 (2)	0.8022 (3)	0.0264 (7)
H32A	0.601879	1.468134	0.839231	0.032*
H32B	0.737438	1.439128	0.837117	0.032*
H32C	0.617604	1.435000	0.727169	0.032*
C33	−0.1313 (3)	0.6341 (3)	0.7058 (3)	0.0254 (7)
H33A	−0.211998	0.621524	0.729132	0.030*
H33B	−0.086307	0.711477	0.714307	0.030*
H33C	−0.160483	0.604241	0.630237	0.030*
C34	0.0660 (3)	1.0450 (3)	1.2671 (2)	0.0232 (7)
H34A	0.015956	0.993960	1.303651	0.028*
H34B	0.150140	1.092666	1.319989	0.028*
H34C	0.007692	1.087802	1.229786	0.028*
O39	0.7618 (3)	1.1027 (2)	0.5693 (2)	0.0318 (6)
H39A	0.800 (4)	1.127 (3)	0.523 (3)	0.044 (12)*
H39B	0.767 (4)	1.163 (3)	0.610 (3)	0.048 (13)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ru1	0.00922 (10)	0.00957 (12)	0.00963 (10)	0.00205 (8)	0.00404 (8)	0.00137 (8)
Cl1	0.0132 (3)	0.0157 (3)	0.0118 (3)	0.0058 (3)	0.0041 (2)	0.0032 (2)
Cl2	0.0129 (3)	0.0169 (4)	0.0142 (3)	0.0038 (3)	0.0003 (3)	0.0033 (3)
P1	0.0107 (3)	0.0108 (4)	0.0114 (3)	0.0030 (3)	0.0046 (3)	0.0018 (3)
O1	0.0184 (10)	0.0198 (11)	0.0202 (10)	0.0045 (9)	0.0139 (9)	0.0041 (8)

O2	0.0105 (9)	0.0143 (10)	0.0176 (10)	0.0048 (8)	0.0054 (8)	0.0044 (8)
O3	0.0173 (10)	0.0114 (10)	0.0119 (9)	−0.0004 (8)	0.0044 (8)	−0.0014 (7)
O4	0.0421 (14)	0.0127 (12)	0.0300 (12)	0.0031 (10)	0.0241 (11)	−0.0007 (9)
O35	0.0239 (11)	0.0109 (10)	0.0261 (11)	0.0000 (9)	0.0124 (9)	0.0002 (8)
O36	0.0307 (12)	0.0153 (11)	0.0349 (13)	−0.0021 (9)	0.0223 (11)	0.0019 (9)
O37	0.0265 (11)	0.0211 (12)	0.0253 (11)	0.0103 (9)	0.0153 (9)	0.0023 (9)
O38	0.0333 (12)	0.0153 (11)	0.0263 (11)	0.0055 (9)	0.0223 (10)	0.0014 (9)
N39	0.0103 (10)	0.0100 (11)	0.0102 (10)	0.0045 (9)	0.0030 (9)	0.0013 (8)
N40	0.0112 (10)	0.0114 (12)	0.0094 (10)	0.0027 (9)	0.0038 (9)	0.0014 (9)
N41	0.0110 (10)	0.0137 (12)	0.0100 (10)	0.0037 (9)	0.0038 (9)	0.0014 (9)
C5	0.0086 (12)	0.0133 (14)	0.0091 (12)	0.0026 (10)	0.0027 (10)	0.0012 (10)
C7	0.0112 (12)	0.0156 (14)	0.0102 (12)	0.0022 (11)	0.0021 (10)	0.0037 (10)
C8	0.0084 (12)	0.0148 (14)	0.0111 (12)	0.0030 (10)	0.0021 (10)	0.0026 (10)
C9	0.0210 (14)	0.0151 (15)	0.0185 (14)	0.0051 (12)	0.0045 (12)	0.0054 (11)
C10	0.0121 (12)	0.0107 (14)	0.0114 (12)	0.0024 (10)	0.0022 (10)	0.0011 (10)
C11	0.0121 (12)	0.0101 (14)	0.0113 (12)	0.0034 (10)	0.0016 (10)	−0.0002 (10)
C12	0.0120 (12)	0.0092 (13)	0.0111 (12)	0.0013 (10)	0.0026 (10)	−0.0003 (10)
C13	0.0132 (13)	0.0140 (14)	0.0150 (13)	0.0024 (11)	0.0053 (11)	0.0007 (11)
C14	0.0088 (12)	0.0139 (14)	0.0103 (12)	0.0040 (10)	0.0034 (10)	0.0044 (10)
C15	0.0119 (12)	0.0199 (16)	0.0135 (13)	0.0063 (11)	0.0048 (11)	0.0018 (11)
C16	0.0132 (13)	0.0202 (16)	0.0135 (13)	0.0050 (11)	0.0053 (11)	0.0017 (11)
C17	0.0109 (12)	0.0141 (14)	0.0133 (13)	0.0041 (11)	0.0036 (10)	0.0043 (10)
C18	0.0194 (15)	0.0362 (19)	0.0223 (16)	0.0075 (14)	0.0158 (13)	0.0083 (13)
C19	0.0194 (14)	0.0227 (16)	0.0167 (14)	0.0089 (12)	0.0102 (12)	0.0096 (12)
C20	0.0117 (12)	0.0152 (14)	0.0114 (12)	0.0050 (11)	0.0038 (10)	0.0011 (10)
C21	0.0161 (13)	0.0162 (15)	0.0166 (14)	0.0000 (11)	0.0072 (11)	0.0039 (11)
C22	0.0152 (13)	0.0183 (15)	0.0150 (13)	0.0032 (11)	0.0090 (11)	0.0040 (11)
C23	0.0104 (12)	0.0120 (14)	0.0113 (12)	0.0035 (10)	0.0039 (10)	0.0014 (10)
C24	0.0145 (13)	0.0181 (15)	0.0138 (13)	0.0031 (11)	0.0041 (11)	0.0024 (11)
C25	0.0112 (12)	0.0172 (15)	0.0121 (12)	0.0042 (11)	0.0061 (10)	0.0049 (10)
C26	0.0128 (12)	0.0184 (15)	0.0125 (13)	0.0063 (11)	0.0052 (11)	0.0022 (11)
C27	0.0159 (13)	0.0107 (14)	0.0196 (14)	−0.0009 (11)	0.0100 (11)	0.0009 (11)
C28	0.0251 (15)	0.0117 (15)	0.0163 (14)	−0.0014 (12)	0.0029 (12)	−0.0014 (11)
C29	0.0165 (13)	0.0166 (15)	0.0148 (13)	0.0077 (11)	0.0057 (11)	−0.0005 (11)
C30	0.0232 (15)	0.0204 (16)	0.0223 (15)	0.0125 (13)	0.0102 (13)	0.0059 (12)
C31	0.0136 (13)	0.0112 (14)	0.0158 (13)	0.0023 (11)	0.0057 (11)	0.0043 (11)
C32	0.0299 (17)	0.0077 (15)	0.0361 (18)	−0.0034 (13)	0.0115 (15)	0.0004 (13)
C33	0.0145 (14)	0.0282 (18)	0.0385 (19)	0.0119 (13)	0.0096 (14)	0.0182 (14)
C34	0.0298 (16)	0.0267 (17)	0.0218 (15)	0.0105 (14)	0.0189 (14)	0.0025 (13)
O39	0.0415 (15)	0.0330 (15)	0.0318 (14)	0.0118 (12)	0.0258 (12)	0.0120 (11)

Geometric parameters (Å, º)

Ru1—Cl1	2.4191 (8)	C11—C20	1.391 (4)
Ru1—Cl2	2.3713 (8)	C12—H12	0.9300
Ru1—P1	2.2879 (9)	C12—C17	1.396 (4)
Ru1—N39	1.996 (2)	C13—H13	0.9300
Ru1—N40	2.078 (2)	C13—C21	1.384 (4)

Ru1—N41	2.054 (2)	C15—C20	1.503 (4)
P1—O2	1.6250 (19)	C16—C26	1.502 (4)
P1—O3	1.6107 (19)	C17—C24	1.490 (4)
P1—C10	1.814 (3)	C17—C25	1.399 (4)
O1—C16	1.324 (3)	C18—H18A	0.9600
O1—C18	1.452 (3)	C18—H18B	0.9600
O2—C33	1.442 (3)	C18—H18C	0.9600
O3—C28	1.457 (3)	C19—H19	0.9300
O4—C15	1.194 (3)	C19—C30	1.384 (4)
O35—C24	1.333 (3)	C20—C22	1.392 (4)
O35—C32	1.452 (3)	C21—H21	0.9300
O36—C24	1.207 (3)	C22—H22	0.9300
O37—C16	1.210 (3)	C22—C27	1.377 (4)
O38—C15	1.329 (3)	C25—H25	0.9300
O38—C34	1.450 (3)	C26—C29	1.389 (4)
N39—C5	1.345 (3)	C27—H27	0.9300
N39—C8	1.349 (3)	C28—H28A	0.9600
N40—C23	1.364 (3)	C28—H28B	0.9600
N40—C31	1.356 (3)	C28—H28C	0.9600
N41—C14	1.378 (3)	C29—H29	0.9300
N41—C27	1.348 (3)	C29—C31	1.384 (4)
C5—C12	1.386 (4)	C30—H30	0.9300
C5—C14	1.478 (3)	C31—H31	0.9300
C7—H7	0.9300	C32—H32A	0.9600
C7—C23	1.389 (4)	C32—H32B	0.9600
C7—C26	1.386 (4)	C32—H32C	0.9600
C8—C23	1.476 (4)	C33—H33A	0.9600
C8—C25	1.382 (4)	C33—H33B	0.9600
C9—H9	0.9300	C33—H33C	0.9600
C9—C21	1.383 (4)	C34—H34A	0.9600
C9—C30	1.394 (4)	C34—H34B	0.9600
C10—C13	1.392 (4)	C34—H34C	0.9600
C10—C19	1.399 (4)	O39—H39A	0.85 (4)
C11—H11	0.9300	O39—H39B	0.90 (4)
C11—C14	1.389 (4)		

Cl2—Ru1—Cl1	174.94 (2)	C12—C17—C25	120.3 (2)
P1—Ru1—Cl1	93.19 (3)	C25—C17—C24	117.9 (2)
P1—Ru1—Cl2	91.78 (3)	O1—C18—H18A	109.5
N39—Ru1—Cl1	84.28 (6)	O1—C18—H18B	109.5
N39—Ru1—Cl2	90.78 (7)	O1—C18—H18C	109.5
N39—Ru1—P1	177.03 (6)	H18A—C18—H18B	109.5
N39—Ru1—N40	79.10 (9)	H18A—C18—H18C	109.5
N39—Ru1—N41	78.59 (9)	H18B—C18—H18C	109.5
N40—Ru1—Cl1	88.54 (7)	C10—C19—H19	119.7
N40—Ru1—Cl2	89.49 (7)	C30—C19—C10	120.6 (3)
N40—Ru1—P1	102.43 (7)	C30—C19—H19	119.7
N41—Ru1—Cl1	93.37 (7)	C11—C20—C15	119.8 (2)

N41—Ru1—Cl2	86.67 (7)	C11—C20—C22	118.6 (2)
N41—Ru1—P1	100.04 (7)	C22—C20—C15	121.6 (2)
N41—Ru1—N40	157.30 (9)	C9—C21—C13	120.6 (3)
O2—P1—Ru1	118.31 (8)	C9—C21—H21	119.7
O2—P1—C10	96.43 (11)	C13—C21—H21	119.7
O3—P1—Ru1	113.14 (8)	C20—C22—H22	120.4
O3—P1—O2	104.16 (10)	C27—C22—C20	119.1 (2)
O3—P1—C10	102.62 (11)	C27—C22—H22	120.4
C10—P1—Ru1	119.52 (9)	N40—C23—C7	122.4 (2)
C16—O1—C18	116.4 (2)	N40—C23—C8	115.4 (2)
C33—O2—P1	120.47 (17)	C7—C23—C8	122.1 (2)
C28—O3—P1	120.35 (17)	O35—C24—C17	111.3 (2)
C24—O35—C32	116.4 (2)	O36—C24—O35	124.3 (3)
C15—O38—C34	116.3 (2)	O36—C24—C17	124.4 (3)
C5—N39—Ru1	118.95 (17)	C8—C25—C17	118.4 (2)
C5—N39—C8	122.3 (2)	C8—C25—H25	120.8
C8—N39—Ru1	118.12 (18)	C17—C25—H25	120.8
C23—N40—Ru1	113.65 (16)	C7—C26—C16	122.2 (2)
C31—N40—Ru1	128.71 (18)	C7—C26—C29	118.7 (2)
C31—N40—C23	117.6 (2)	C29—C26—C16	119.1 (2)
C14—N41—Ru1	115.02 (17)	N41—C27—C22	123.7 (3)
C27—N41—Ru1	127.63 (18)	N41—C27—H27	118.2
C27—N41—C14	117.1 (2)	C22—C27—H27	118.2
N39—C5—C12	120.1 (2)	O3—C28—H28A	109.5
N39—C5—C14	112.8 (2)	O3—C28—H28B	109.5
C12—C5—C14	127.1 (2)	O3—C28—H28C	109.5
C23—C7—H7	120.4	H28A—C28—H28B	109.5
C26—C7—H7	120.4	H28A—C28—H28C	109.5
C26—C7—C23	119.3 (2)	H28B—C28—H28C	109.5
N39—C8—C23	113.1 (2)	C26—C29—H29	120.2
N39—C8—C25	120.3 (2)	C31—C29—C26	119.5 (2)
C25—C8—C23	126.7 (2)	C31—C29—H29	120.2
C21—C9—H9	120.3	C9—C30—H30	119.9
C21—C9—C30	119.3 (3)	C19—C30—C9	120.2 (3)
C30—C9—H9	120.3	C19—C30—H30	119.9
C13—C10—P1	123.1 (2)	N40—C31—C29	122.5 (2)
C13—C10—C19	118.7 (2)	N40—C31—H31	118.7
C19—C10—P1	118.2 (2)	C29—C31—H31	118.7
C14—C11—H11	120.3	O35—C32—H32A	109.5
C14—C11—C20	119.5 (2)	O35—C32—H32B	109.5
C20—C11—H11	120.3	O35—C32—H32C	109.5
C5—C12—H12	120.7	H32A—C32—H32B	109.5
C5—C12—C17	118.6 (2)	H32A—C32—H32C	109.5
C17—C12—H12	120.7	H32B—C32—H32C	109.5
C10—C13—H13	119.7	O2—C33—H33A	109.5
C21—C13—C10	120.6 (3)	O2—C33—H33B	109.5
C21—C13—H13	119.7	O2—C33—H33C	109.5
N41—C14—C5	114.1 (2)	H33A—C33—H33B	109.5

N41—C14—C11	121.9 (2)	H33A—C33—H33C	109.5
C11—C14—C5	123.9 (2)	H33B—C33—H33C	109.5
O4—C15—O38	125.2 (3)	O38—C34—H34A	109.5
O4—C15—C20	124.5 (3)	O38—C34—H34B	109.5
O38—C15—C20	110.3 (2)	O38—C34—H34C	109.5
O1—C16—C26	111.5 (2)	H34A—C34—H34B	109.5
O37—C16—O1	125.0 (2)	H34A—C34—H34C	109.5
O37—C16—C26	123.5 (3)	H34B—C34—H34C	109.5
C12—C17—C24	121.8 (2)	H39A—O39—H39B	105 (4)

Ru1—P1—O2—C33	59.1 (2)	C10—P1—O3—C28	46.9 (2)
Ru1—P1—O3—C28	177.04 (17)	C10—C13—C21—C9	−0.6 (4)
Ru1—P1—C10—C13	117.0 (2)	C10—C19—C30—C9	−0.7 (5)
Ru1—P1—C10—C19	−63.9 (2)	C11—C20—C22—C27	−2.4 (4)
Ru1—N39—C5—C12	−171.34 (19)	C12—C5—C14—N41	174.2 (2)
Ru1—N39—C5—C14	7.9 (3)	C12—C5—C14—C11	−7.4 (4)
Ru1—N39—C8—C23	−9.0 (3)	C12—C17—C24—O35	−12.0 (4)
Ru1—N39—C8—C25	170.95 (19)	C12—C17—C24—O36	169.7 (3)
Ru1—N40—C23—C7	177.8 (2)	C12—C17—C25—C8	0.9 (4)
Ru1—N40—C23—C8	−1.0 (3)	C13—C10—C19—C30	0.4 (4)
Ru1—N40—C31—C29	−175.4 (2)	C14—N41—C27—C22	3.2 (4)
Ru1—N41—C14—C5	0.2 (3)	C14—C5—C12—C17	−178.0 (2)
Ru1—N41—C14—C11	−178.35 (19)	C14—C11—C20—C15	−177.4 (2)
Ru1—N41—C27—C22	176.9 (2)	C14—C11—C20—C22	1.7 (4)
P1—C10—C13—C21	179.5 (2)	C15—C20—C22—C27	176.7 (3)
P1—C10—C19—C30	−178.9 (2)	C16—C26—C29—C31	179.0 (2)
O1—C16—C26—C7	−11.2 (4)	C18—O1—C16—O37	−2.6 (4)
O1—C16—C26—C29	169.9 (2)	C18—O1—C16—C26	177.8 (2)
O2—P1—O3—C28	−53.2 (2)	C19—C10—C13—C21	0.3 (4)
O2—P1—C10—C13	−10.8 (2)	C20—C11—C14—N41	1.4 (4)
O2—P1—C10—C19	168.4 (2)	C20—C11—C14—C5	−176.9 (2)
O3—P1—O2—C33	−67.5 (2)	C20—C22—C27—N41	−0.1 (4)
O3—P1—C10—C13	−116.9 (2)	C21—C9—C30—C19	0.4 (4)
O3—P1—C10—C19	62.3 (2)	C23—N40—C31—C29	1.0 (4)
O4—C15—C20—C11	6.8 (4)	C23—C7—C26—C16	−177.2 (2)
O4—C15—C20—C22	−172.3 (3)	C23—C7—C26—C29	1.7 (4)
O37—C16—C26—C7	169.2 (3)	C23—C8—C25—C17	179.7 (2)
O37—C16—C26—C29	−9.8 (4)	C24—C17—C25—C8	−178.0 (2)
O38—C15—C20—C11	−173.4 (2)	C25—C8—C23—N40	−173.6 (2)
O38—C15—C20—C22	7.6 (4)	C25—C8—C23—C7	7.6 (4)
N39—C5—C12—C17	1.1 (4)	C25—C17—C24—O35	166.9 (2)
N39—C5—C14—N41	−5.0 (3)	C25—C17—C24—O36	−11.4 (4)
N39—C5—C14—C11	173.5 (2)	C26—C7—C23—N40	−2.2 (4)
N39—C8—C23—N40	6.3 (3)	C26—C7—C23—C8	176.5 (2)
N39—C8—C23—C7	−172.5 (2)	C26—C29—C31—N40	−1.5 (4)
N39—C8—C25—C17	−0.2 (4)	C27—N41—C14—C5	174.7 (2)
C5—N39—C8—C23	179.9 (2)	C27—N41—C14—C11	−3.8 (4)
C5—N39—C8—C25	−0.2 (4)	C30—C9—C21—C13	0.2 (4)

C5—C12—C17—C24	177.5 (2)	C31—N40—C23—C7	0.9 (4)
C5—C12—C17—C25	−1.4 (4)	C31—N40—C23—C8	−178.0 (2)
C7—C26—C29—C31	0.1 (4)	C32—O35—C24—O36	−1.7 (4)
C8—N39—C5—C12	−0.3 (4)	C32—O35—C24—C17	−179.9 (2)
C8—N39—C5—C14	178.9 (2)	C34—O38—C15—O4	3.9 (4)
C10—P1—O2—C33	−172.3 (2)	C34—O38—C15—C20	−176.0 (2)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O39—H39*B*···O36	0.90	2.17	3.00	154.2
O39—H39*A*···Cl1^{i}	0.85	2.40	3.24	176.3

Symmetry code: (i) −*x*+1, −*y*+2, −*z*+1.