STRUCTURAL CHEMISTRY
ISSN 2053-2296

Polymeric structure of a coproporphyrin I ruthenium(II) complex: a powder diffraction study

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Received 12 November 2016
Accepted 4 December 2016

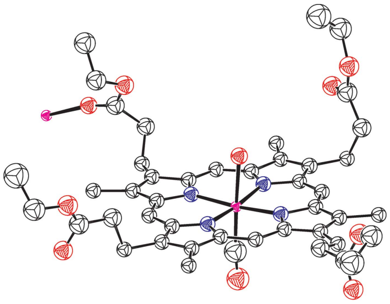
Edited by L. R. Falvello, Universidad de Zaragoza, Spain

Keywords: coproporphyrin I; ruthenium(II) complex; one-dimensional coordination polymer; synchrotron powder diffraction; computational chemistry; molecular cavity.

CCDC reference: 1520660

Supporting information: this article has supporting information at journals.iucr.org/c

Porphyrin complexes of ruthenium are widely used as models for the heme protein system, for modelling naturally occurring iron–porphyrin systems and as catalysts in epoxidation reactions. The structural diversity of ruthenium complexes offers an opportunity to use them in the design of multifunctional supramolecular assemblies. Coproporphyrins and metallocoproporphyrins are used as sensors in bioassay and the potential use of derivatives as multiparametric sensors for oxygen and H^+ is one of the main factors driving a growing interest in the synthesis of new porphyrin derivatives. In the coproporphyrin I Ru^{II} complex *catena*-poly[[carbonylruthenium(II)]-μ-2,7,12,17-tetrakis[2-(ethoxycarbonyl)ethyl]-3,8,13,18-tetramethylporphyrinato-κ^5N,N',N'',-N''':*O*], $[Ru(C_{44}H_{52}N_4O_8)(CO)]_n$, the Ru^{II} centre is coordinated by four N atoms in the basal plane, and by axial C (carbonyl ligand) and O (ethoxycarbonylethyl arm from a neighbouring complex) atoms. The complex adopts a distorted octahedral geometry. Self-assembly of the molecules during crystallization from a methylene chloride–ethanol (1:10 *v*/*v*) solution at room temperature gives one-dimensional polymeric chains.

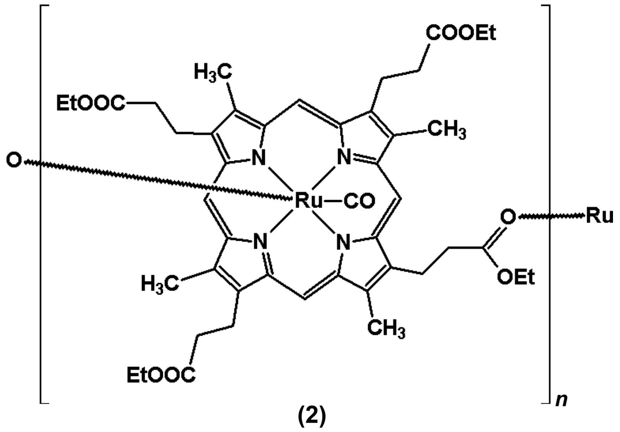


1. Introduction

Porphyrin complexes of ruthenium have been studied actively in recent decades because of their many useful applications. They are widely used as models for the heme protein system (Masuda *et al.*, 1982), for modelling naturally occurring iron–porphyrin systems involved in oxidation processes of the mono- and dioxygenase type (James *et al.*, 1988) and as catalysts in epoxidation reactions (Barona-Castano *et al.*, 2016), including aerobic oxidation tandem epoxidation–isomerization (Jiang *et al.*, 2008). Ruthenium in porphyrinates can exist in a variety of oxidation states, *viz.* Ru^{II} (Ariel *et al.*, 1984), Ru^{III} (James *et al.*, 1984), Ru^{IV} (Maeda *et al.*, 2015) or Ru^{VI} (Katsunori *et al.*, 2012), and it is able to coordinate one or two small axial ligands, such as aqua, hydroxide, dinitrogen, nitrite, nitrosyl, carbonyl, methanol, ethanol, tetrahydrofuran, pyridine and many others, as can be found from a search in the Cambridge Structural Database (*ConQuest*, Version 1.18 with updates; Groom *et al.*, 2016), which gave 225 hits. The structural diversity of ruthenium complexes, which can also form metal–metal bonds (Collman *et al.*, 1984), offers an opportunity to use them in the design of multifunctional supramolecular assemblies (Mamardashvili *et al.*, 2013).

https://doi.org/10.1107/S2053229616019422

Due to their unique photophysical and photochemical properties, coproporphyrins and metallocoproporphyrins have also been used as sensors in bioassay (Papkovsky & O'Riordan, 2005; Dmitriev *et al.*, 2012; Burke *et al.*, 2007). The potential use of derivatives of coproporphyrins as multiparametric sensors for oxygen and H^+ is one of the main factors driving a growing interest in the synthesis of new porphyrin derivatives (Borchert *et al.*, 2011). Recently, we reported synthetic and crystallographic studies of the coproporphyrin I molecular complexes with Pd^{II} (Volov *et al.*, 2014; Tyurin *et al.*, 2015). We report herein the synthesis and structural characterization of the novel ruthenium(II) complex of coproporphyrin I tetraethyl ester, (1), namely *catena*-poly[[carbonylruthenium(II)]-μ-2,7,12,17-tetrakis[2-(ethoxycarbonyl)ethyl]-3,8,13,18-tetramethylporphyrinato-$\kappa^5N,N',N'',N''':O$], (2), which crystallizes with the formation of one-dimensional polymeric chains.



(2)

2. Experimental

Commercial reagents were used without purification. Solvents were purified according to standard procedures: CH_2Cl_2 was distilled over calcium hydride under an argon atmosphere and toluene was dried over magnesium chloride and then distilled over sodium. Coproporphyrin I, (1), was prepared according to a literature procedure (Smith, 1972). Silica gel 40/60 (Merck) was used for column and flash chromatography. For preparative thin-layer chromatography (TLC), silica gel 60 (Merck) 20 × 20 cm plates with a 1 mm layer thickness were used. A mixture of methylene chloride–ethanol was used as solvent for elution. Electronic absorption, NMR and mass spectra for the final product are presented in the *Supporting information*.

2.1. Synthesis and crystallization

To a solution of (1) (50 mg, 0.065 mmol) in dry toluene (15 ml) was added $Ru_3(CO)_{12}$ (83.5 mg, 0.13 mmol). The resulting mixture was refluxed for 24 h. After completion of the reaction, the solvent was evaporated. Purification was carried out by preparative chromatography using an ethanol–dichloromethane (100:1 *v*/*v*) mixture. A powder sample suitable for crystal structure determination was obtained by crystallization from the methylene chloride–ethanol (1:10 *v*/*v*) solvent system at room temperature over a period of 7 d.

Table 1
Experimental details.

Crystal data	
Chemical formula	$[Ru(C_{44}H_{52}N_4O_8)(CO)]$
M_r	893.98
Crystal system, space group	Monoclinic, *C*2/*c*
Temperature (K)	295
a, *b*, *c* (Å)	39.3876 (19), 9.6153 (8), 29.5299 (16)
β (°)	130.719 (7)
V (Å^3)	8476.3 (9)
Z	8
Radiation type	Synchrotron, λ = 0.399927(2) Å
μ (mm^{-1})	0.09
Specimen shape, size (mm)	Cylinder, 15 × 1.0
Data collection	
Diffractometer	ESRF powder diffractometer ID22
Specimen mounting	Specimen was sealed in a 1.0 mm diameter borosilicate glass capillary
Data collection mode	Transmission
Scan method	Continuous
2θ values (°)	$2\theta_{min}$ = 1.000, $2\theta_{max}$ = 20.000, $2\theta_{step}$ = 0.002
Refinement	
R factors and goodness of fit	R_p = 0.031, R_{wp} = 0.040, R_{exp} = 0.013, R_{Bragg} = 0.070, χ^2 = 9.566
No. of parameters	247
No. of restraints	193
H-atom treatment	H-atom parameters not refined

Computer programs: *MRIA* (Zlokazov & Chernyshev, 1992), *FOX* (Favre-Nicolin & Cerný, 2004), *PLATON* (Spek, 2009), *Mercury* (Macrae *et al.*, 2008), *SHELXL97* (Sheldrick, 2008) and *publCIF* (Westrip, 2010).

2.2. Refinement

X-ray powder diffraction measurements were carried out at room temperature at beamline ID22 of the European Synchrotron Radiation Facility (ESRF, Grenoble, France). The instrument is equipped with a cryogenically cooled double-crystal Si 111 monochromator and Si 111 analyzers. The powder was loaded into a 1 mm diameter borosilicate thin-walled glass capillary which was rotated during measurements at a rate of 1200 rpm to improve the powder averaging. Calibration of the instrument and refinement of the X-ray wavelength [0.399927 (3) Å] were performed using NIST silicon standard 640c.

The monoclinic cell dimensions were determined using three indexing programs: *TREOR90* (Werner *et al.*, 1985), *ITO* (Visser, 1969) and *AUTOX* (Zlokazov, 1992, 1995). Based on systematic extinctions and other considerations, the space group was determined as *C*2/*c*. The unit-cell parameters and space group were further tested using a Pawley fit (Pawley, 1981) and confirmed by crystal structure solution. The geometry of the initial molecular model of (2) with the Ru centre coordinated by the four N atoms only, *i.e.* without the carbonyl ligand, was optimized by density functional theory (DFT) calculations *in vacuo* using the quantum-chemical program *PRIRODA* (Laikov, 1997, 2004, 2005; Laikov &

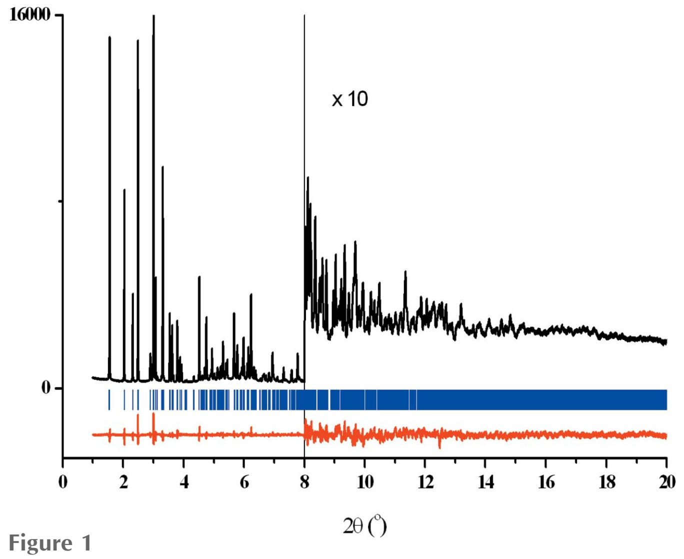


Figure 1
Rietveld plot showing the experimental (black) and difference (red) profiles for (2). The vertical bars (blue) correspond to the positions of the Bragg peaks.

Ustynyuk, 2005), employing the generalized gradient approximation (GGA) and the PBE exchange-correlation function (Perdew *et al.*, 1996). This fragment was used in the crystal structure determination. The crystal structure was solved using two techniques, *viz.* simulated annealing (Zhukov *et al.*, 2001) using the program *MRIA* (Zlokazov & Chernyshev, 1992) and parallel tempering (Favre-Nicolin & Cerný, 2002) using the program *FOX* (Favre-Nicolin & Cerný, 2002, 2004). The carbonyl group was added to the model after the analysis of a difference Fourier map, where axial positive residual electron density was observed at 1.9 Å from the Ru centre. The final Rietveld refinement was performed with the program *MRIA* following the procedure described by us previously (Dorokhov *et al.*, 2007; Logacheva *et al.*, 2009; Chernyshev *et al.*, 2013). In the refinement, anisotropic line broadening was taken into account with the use of nine variables (Popa, 1998). All non-H atoms were refined isotropically. One common $U_{\rm iso}$ parameter was varied for 32 atoms, *i.e.* 24 atoms of the porphyrin core and eight C atoms attached to the core. The maximum difference peak and hole at the end of refinement had densities of 0.61 and −0.89 e Å^{-3}, respectively. Crystal data, data collection and structure refinement details are summarized in Table 1 and the diffraction profiles after the final bond-restrained Rietveld refinement are shown in Fig. 1.

3. Results and discussion

In the title compound, the Ru$^{\rm II}$ centre is coordinated by four N atoms [Ru—N = 2.025 (17)–2.055 (12) Å] in the basal plane and by an axial carbonyl ligand [Ru—C = 1.871 (19) Å]. A carbonyl O atom (O5) of the ethoxycarbonylethyl arm [Ru—O = 2.194 (12) Å] from a neighbouring asymmetric unit completes the distorted octahedral coordination geometry. The metal atom is displaced by 0.11 (1) Å from the mean plane of the porphyrin core, toward the carbonyl ligand. As seen in Fig. 2, just one of four ethyl ester arms serves as a connector between neighbouring molecules *via* the aforementioned axially coordinating atom O5, mediating the formation of polymeric chains running along [010] (Fig. 3). The porphyrin cores of neighbouring links in the chain are inclined to one another by 74.3 (2)°. Examples of metal–porphyrin complexes in which the carbonyl groups of lateral substituents coordinate neighbouring metal centres have been observed, though they are rare; our search in the Cambridge Structural Database (CSD) resulted in just three hits, namely *catena*-(bis{μ_3-5,10,15,20-tetrakis[3′,5′-bis(ethoxycarbonyl)phenyl]porphyrinato}dizinc(II)) (CSD refcode LUBKOI; Bhyrappa *et al.*, 2002), bis{μ_2-diethyl-2,2′-[(porphyrin-5,15-diyl)bis(naphthalene-1,2-diyloxy)]diacetatato}dizinc(II) dichloromethane solvate (MUVQAW; Amaya *et al.*, 2010) and *catena*-[bis{μ-5-*tert*-butyl-*N*,*N*′-bis[2-(10,15,20-triphenylporphyrin-21,23-diyl-5-yl)phenyl]isophthalamide}tetrazinc unknown solvate] (OGUFIH; Fang *et al.*, 2015).

The most interesting feature of the crystal structure of (2) is the formation of a molecular cavity, as the four ethoxycarbonylethyl substituents are located on the same side of the porphyrin plane, like the petals of a tulip. The CSD contains no examples of tetramethyl metalloporphyrins with four ethoxycarbonylethyl branches, and a search for metalloporphyrins with similar substituents yielded the following four structures: {2,7,12,17-tetrakis[2-(isopropyloxycarbonyl)ethyl]-3,8,13,18-tetramethylporphyrinato}platinum(II) and -palladium(II) (KILQIH and KILQON, respectively; Zamilatskov *et al.*, 2012), and chlorido- and (acetato-κ^2O,O')(tetramethyl-3,8,13,18-tetramethylporphyrin-2,7,12,17-tetrapropionato-κ^4N,N',N'',N''')thallium(III) dichloromethane solvate (WECSIG and WECTAZ, respectively; Senge *et al.*, 1993); none of these structures has a molecular cavity. Surprisingly, to provide the axial coordination of the Ru$^{\rm II}$ atom in (2), the flexible ethoxycarbonylethyl branch from the neighbouring segment of the polymer positions its O atom (O5) within the 'tulip petals'. This

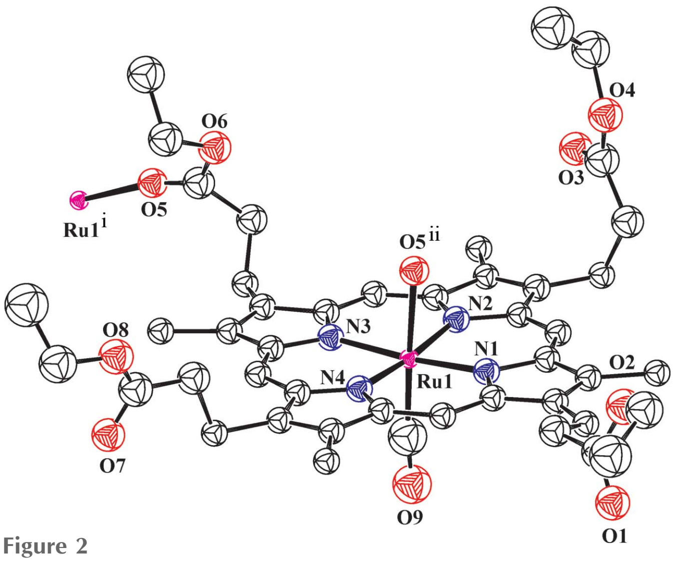


Figure 2
View of (2) showing the atomic numbering and 50% probability displacement spheres. H atoms have been omitted for clarity. [Symmetry codes: (i) $-x+\frac{3}{2}, y+\frac{1}{2}, -z+\frac{3}{2}$; (ii) $-x+\frac{3}{2}, y-\frac{1}{2}, -z+\frac{3}{2}$.]

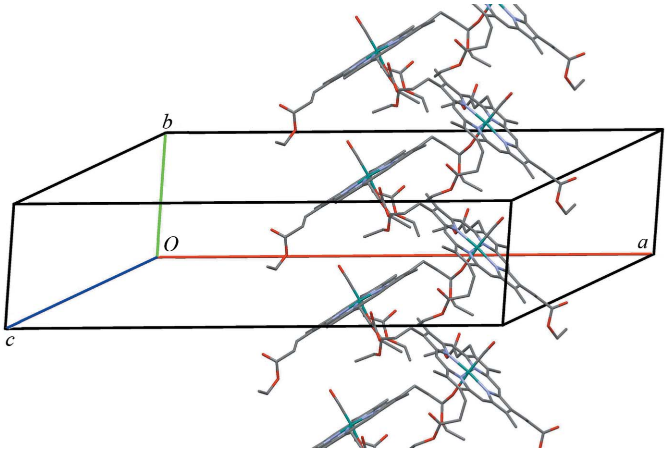


Figure 3
A portion of the polymeric chain in the crystal structure of (2).

fragment of the neighbouring porphyrin core thus penetrates into the 'tulip bowl' of the molecule (Fig. 3).

The aforementioned features of the crystal packing of (2) demonstrate its potential for self-assembling in various modes depending on crystallization and environmental conditions, as has been observed for [tetrakis(pyridin-4-yl)porphyrin]zinc, [Zn(tpyp)]. Several coordination polymers were obtained for [Zn(tpyp)], *viz.* a one-dimensional chain structure (Krupitsky *et al.*, 1994), a one-dimensional ladder structure (Diskin-Posner *et al.*, 2001), a one-dimensional ribbon structure (Ring *et al.*, 2005) and a three-dimensional framework (Krupitsky *et al.*, 1994). For compound (2), we hope to remove the carbonyl fragments either from the solution before crystallization or directly from the solid-state sample to explore other possibilities for self-assembly of the coproporphyrin I tetraethyl ester ruthenium(II) complex.

Acknowledgements

This research was supported by the Russian Ministry of Science and Education (grant No. RFMEFI61616X0069). We also thank ESRF for the access to ID22 station, experiment MA-3313.

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supporting information

Acta Cryst. (2017). C**73**, 47-51   [https://doi.org/10.1107/S2053229616019422]

Polymeric structure of a coproporphyrin I ruthenium(II) complex: a powder diffraction study

Sergey V. Andreev, Sergey A. Zverev, Ilya A. Zamilatskov, Nadezhda M. Kurochkina, Gelii V. Ponomarev, Andrew N. Fitch and Vladimir V. Chernyshev

Computing details

Cell refinement: *MRIA* (Zlokazov & Chernyshev, 1992); program(s) used to solve structure: *MRIA* (Zlokazov & Chernyshev, 1992) and *FOX* (Favre-Nicolin & Cerný, 2004); program(s) used to refine structure: *MRIA* (Zlokazov & Chernyshev, 1992); molecular graphics: *PLATON* (Spek, 2009) and *Mercury* (Macrae *et al.*, 2008); software used to prepare material for publication: *SHELXL97* (Sheldrick, 2008) and *publCIF* (Westrip, 2010).

catena-Poly[[carbonylruthenium(II)]-μ-2,7,12,17-tetrakis[2-(ethoxycarbonyl)ethyl]-3,8,13,18-tetramethylporphyrinato-κ^5*N*,*N*′,*N*′′,*N*′′′:*O*]

Crystal data

$[Ru(C_{44}H_{52}N_4O_8)(CO)]$
$M_r = 893.98$
Monoclinic, $C2/c$
Hall symbol: -C 2yc
$a = 39.3876\ (19)$ Å
$b = 9.6153\ (8)$ Å
$c = 29.5299\ (16)$ Å
$\beta = 130.719\ (7)°$
$V = 8476.3\ (9)$ Å^3
$Z = 8$
$F(000) = 3728$
$D_x = 1.401$ Mg m^{-3}
Synchrotron radiation, $\lambda = 0.399927(2)$ Å
$\mu = 0.09$ mm^{-1}
$T = 295$ K
Particle morphology: no specific habit
colorless
cylinder, 15 × 1.0 mm
Specimen preparation: Prepared at 295 K and 101 kPa

Data collection

ESRF powder diffractometer ID22
Radiation source: ID22 bending magnet at ESRF, synchrotron radiation
Si 111 double crystal monochromator
Specimen mounting: Specimen was sealed in a 1.0 mm diameter borosilicate glass capillary
Data collection mode: transmission
Scan method: continuous
$2\theta_{min} = 1.000°$, $2\theta_{max} = 20.000°$, $2\theta_{step} = 0.002°$

Refinement

Refinement on I_{net}
Least-squares matrix: full with fixed elements per cycle
$R_p = 0.031$
$R_{wp} = 0.040$
$R_{exp} = 0.013$
$R_{Bragg} = 0.070$
9501 data points
Profile function: split-type pseudo-Voigt
247 parameters
193 restraints
21 constraints
H-atom parameters not refined
Weighting scheme based on measured s.u.'s
$(\Delta/\sigma)_{max} = 0.003$
Background function: Chebyshev polynomial up to the 5th order
Preferred orientation correction: none

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	0.88520 (4)	0.5249 (2)	0.82080 (6)	0.0170 (12)*
N1	0.9371 (3)	0.3887 (14)	0.8584 (5)	0.034 (10)*
N2	0.8917 (3)	0.5230 (13)	0.8947 (5)	0.034 (10)*
N3	0.8290 (3)	0.6456 (15)	0.7803 (5)	0.034 (10)*
N4	0.8732 (3)	0.5119 (13)	0.7428 (5)	0.034 (10)*
C1	0.9549 (4)	0.3341 (19)	0.8342 (6)	0.034 (10)*
C2	0.9928 (4)	0.2503 (19)	0.8768 (6)	0.034 (10)*
C3	0.9990 (4)	0.2549 (18)	0.9290 (7)	0.034 (10)*
C4	0.9652 (4)	0.3374 (19)	0.9178 (6)	0.034 (10)*
C5	0.9575 (4)	0.3725 (18)	0.9559 (5)	0.034 (10)*
H5	0.9776	0.3334	0.9938	0.041*
C6	0.9254 (4)	0.4549 (18)	0.9473 (6)	0.034 (10)*
C7	0.9209 (4)	0.4849 (18)	0.9914 (6)	0.034 (10)*
C8	0.8857 (4)	0.5682 (17)	0.9663 (6)	0.034 (10)*
C9	0.8675 (4)	0.5963 (19)	0.9058 (6)	0.034 (10)*
C10	0.8307 (4)	0.6775 (19)	0.8638 (6)	0.034 (10)*
H10	0.8167	0.7226	0.8756	0.041*
C11	0.8129 (4)	0.6974 (17)	0.8053 (6)	0.034 (10)*
C12	0.7734 (4)	0.7848 (19)	0.7630 (6)	0.034 (10)*
C13	0.7672 (4)	0.7845 (18)	0.7121 (6)	0.034 (10)*
C14	0.8005 (4)	0.6945 (18)	0.7212 (6)	0.034 (10)*
C15	0.8070 (4)	0.6615 (19)	0.6821 (5)	0.034 (10)*
H15	0.7866	0.7008	0.6443	0.041*
C16	0.8397 (4)	0.5778 (19)	0.6906 (6)	0.034 (10)*
C17	0.8442 (4)	0.5503 (17)	0.6468 (6)	0.034 (10)*
C18	0.8800 (4)	0.4628 (17)	0.6723 (6)	0.034 (10)*
C19	0.8980 (4)	0.4395 (19)	0.7331 (6)	0.034 (10)*
C20	0.9356 (4)	0.3604 (19)	0.7753 (6)	0.034 (10)*
H20	0.9497	0.3198	0.7628	0.041*
C21	1.0222 (5)	0.1708 (18)	0.8744 (7)	0.034 (10)*
H21A	1.0297	0.0874	0.8978	0.041*
H21B	1.0497	0.2240	0.8954	0.041*
C22	1.0099 (4)	0.126 (2)	0.8183 (6)	0.049 (10)*
H22A	1.0048	0.2078	0.7952	0.059*
H22B	0.9821	0.0744	0.7956	0.059*
C23	1.0462 (4)	0.0347 (18)	0.8273 (7)	0.055 (11)*
C24	1.0564 (5)	−0.214 (2)	0.8123 (6)	0.069 (10)*
H24A	1.0360	−0.2920	0.7966	0.083*
H24B	1.0856	−0.2452	0.8478	0.083*

C25	1.0596 (5)	−0.168 (2)	0.7667 (7)	0.089 (11)*
H25A	1.0699	−0.2447	0.7575	0.134*
H25B	1.0803	−0.0925	0.7823	0.134*
H25C	1.0306	−0.1392	0.7311	0.134*
C26	1.0361 (4)	0.1737 (18)	0.9841 (6)	0.034 (10)*
H26A	1.0538	0.1275	0.9770	0.051*
H26B	1.0233	0.1058	0.9930	0.051*
H26C	1.0547	0.2362	1.0173	0.051*
C27	0.9516 (4)	0.4256 (18)	1.0535 (6)	0.034 (10)*
H27A	0.9472	0.4749	1.0780	0.041*
H27B	0.9825	0.4390	1.0710	0.041*
C28	0.9429 (4)	0.2704 (18)	1.0533 (6)	0.051 (10)*
H28A	0.9447	0.2243	1.0257	0.061*
H28B	0.9669	0.2337	1.0928	0.061*
C29	0.8992 (4)	0.2311 (19)	1.0369 (6)	0.059 (11)*
C30	0.8427 (5)	0.0444 (18)	1.0068 (7)	0.071 (11)*
H30A	0.8262	0.1176	1.0078	0.085*
H30B	0.8528	−0.0222	1.0381	0.085*
C31	0.8128 (4)	−0.0275 (16)	0.9454 (5)	0.091 (12)*
H31A	0.7895	0.0350	0.9158	0.136*
H31B	0.7997	−0.1095	0.9470	0.136*
H31C	0.8306	−0.0529	0.9350	0.136*
C32	0.8667 (4)	0.6283 (19)	0.9920 (6)	0.034 (10)*
H32A	0.8411	0.6845	0.9624	0.051*
H32B	0.8889	0.6848	1.0260	0.051*
H32C	0.8578	0.5545	1.0042	0.051*
C33	0.7508 (4)	0.859 (2)	0.7794 (6)	0.034 (10)*
H33A	0.7311	0.9267	0.7482	0.041*
H33B	0.7734	0.9112	0.8155	0.041*
C34	0.7244 (5)	0.7836 (17)	0.7898 (7)	0.046 (10)*
H34A	0.7200	0.8411	0.8126	0.055*
H34B	0.7402	0.7001	0.8127	0.055*
C35	0.6781 (4)	0.7437 (17)	0.7289 (6)	0.050 (10)*
C36	0.6421 (4)	0.5757 (18)	0.6487 (7)	0.058 (10)*
H36A	0.6347	0.6607	0.6262	0.070*
H36B	0.6569	0.5129	0.6406	0.070*
C37	0.6008 (4)	0.5101 (18)	0.6313 (7)	0.068 (12)*
H37A	0.5807	0.4886	0.5894	0.102*
H37B	0.5865	0.5733	0.6395	0.102*
H37C	0.6086	0.4261	0.6538	0.102*
C38	0.7278 (4)	0.8624 (18)	0.6580 (6)	0.034 (10)*
H38A	0.7279	0.8526	0.6258	0.051*
H38B	0.7300	0.9591	0.6677	0.051*
H38C	0.7004	0.8250	0.6462	0.051*
C39	0.8137 (4)	0.6012 (19)	0.5812 (6)	0.034 (10)*
H39A	0.7997	0.6887	0.5771	0.041*
H39B	0.8313	0.6155	0.5693	0.041*
C40	0.7777 (4)	0.4897 (18)	0.5414 (6)	0.052 (12)*

H40A	0.7921	0.3996	0.5515	0.062*
H40B	0.7576	0.4866	0.5498	0.062*
C41	0.7509 (5)	0.5157 (17)	0.4762 (7)	0.058 (11)*
C42	0.6974 (4)	0.4449 (19)	0.3694 (7)	0.071 (11)*
H42A	0.6946	0.5437	0.3609	0.085*
H42B	0.7114	0.4020	0.3555	0.085*
C43	0.6524 (4)	0.384 (2)	0.3371 (6)	0.094 (11)*
H43A	0.6345	0.3992	0.2950	0.141*
H43B	0.6383	0.4276	0.3504	0.141*
H43C	0.6552	0.2860	0.3449	0.141*
C44	0.8932 (4)	0.4175 (19)	0.6362 (6)	0.034 (10)*
H44A	0.9187	0.3568	0.6600	0.051*
H44B	0.9006	0.4979	0.6249	0.051*
H44C	0.8686	0.3692	0.6010	0.051*
O1	1.0781 (3)	0.0868 (13)	0.8400 (4)	0.058 (7)*
O2	1.0411 (3)	−0.1050 (14)	0.8286 (4)	0.063 (7)*
O3	0.8775 (3)	0.3143 (12)	1.0409 (4)	0.054 (7)*
O4	0.8818 (3)	0.1038 (13)	1.0157 (4)	0.058 (7)*
O5	0.6509 (3)	0.8273 (12)	0.7038 (4)	0.042 (6)*
O6	0.6724 (3)	0.6071 (13)	0.7148 (4)	0.053 (6)*
O7	0.7559 (3)	0.6281 (14)	0.4631 (4)	0.054 (6)*
O8	0.7260 (3)	0.4236 (13)	0.4346 (4)	0.060 (7)*
O9	0.9432 (3)	0.7812 (12)	0.8590 (4)	0.074 (7)*
C45	0.9192 (5)	0.6859 (19)	0.8412 (6)	0.074 (10)*

Geometric parameters (Å, º)

Ru1—C45	1.871 (19)	C25—H25C	0.9600
Ru1—N2	2.025 (17)	C26—H26A	0.9601
Ru1—N4	2.031 (16)	C26—H26B	0.9599
Ru1—N1	2.041 (12)	C26—H26C	0.9600
Ru1—N3	2.055 (12)	C27—C28	1.53 (2)
Ru1—O5$^{\rm i}$	2.194 (12)	C27—H27A	0.9700
N1—C1	1.39 (3)	C27—H27B	0.9700
N1—C4	1.418 (18)	C28—C29	1.50 (3)
N2—C6	1.383 (17)	C28—H28A	0.9700
N2—C9	1.39 (3)	C28—H28B	0.9700
N3—C11	1.34 (3)	C29—O3	1.23 (2)
N3—C14	1.404 (18)	C29—O4	1.34 (2)
N4—C16	1.366 (16)	C30—O4	1.50 (2)
N4—C19	1.37 (3)	C30—C31	1.54 (2)
C1—C20	1.39 (2)	C30—H30A	0.9701
C1—C2	1.418 (19)	C30—H30B	0.9699
C2—C3	1.40 (3)	C31—H31A	0.9600
C2—C21	1.43 (3)	C31—H31B	0.9600
C3—C4	1.39 (3)	C31—H31C	0.9600
C3—C26	1.513 (18)	C32—H32A	0.9600
C4—C5	1.38 (3)	C32—H32B	0.9600

C5—C6	1.37 (2)	C32—H32C	0.9603
C5—H5	0.9300	C33—C34	1.46 (3)
C6—C7	1.45 (3)	C33—H33A	0.9699
C7—C8	1.33 (2)	C33—H33B	0.9700
C7—C27	1.50 (2)	C34—C35	1.558 (16)
C8—C9	1.45 (2)	C34—H34A	0.9702
C8—C32	1.49 (3)	C34—H34B	0.9700
C9—C10	1.380 (19)	C35—O5	1.143 (17)
C10—C11	1.39 (2)	C35—O6	1.35 (2)
C10—H10	0.9299	C36—C37	1.49 (3)
C11—C12	1.467 (19)	C36—O6	1.512 (19)
C12—C13	1.36 (3)	C36—H36A	0.9700
C12—C33	1.45 (3)	C36—H36B	0.9701
C13—C14	1.44 (3)	C37—H37A	0.9601
C13—C38	1.512 (17)	C37—H37B	0.9599
C14—C15	1.37 (3)	C37—H37C	0.9602
C15—C16	1.40 (3)	C38—H38A	0.9600
C15—H15	0.9300	C38—H38B	0.9599
C16—C17	1.44 (3)	C38—H38C	0.9601
C17—C18	1.37 (2)	C39—C40	1.54 (2)
C17—C39	1.55 (2)	C39—H39A	0.9701
C18—C19	1.45 (3)	C39—H39B	0.9699
C18—C44	1.52 (3)	C40—C41	1.49 (2)
C19—C20	1.385 (18)	C40—H40A	0.9701
C20—H20	0.9299	C40—H40B	0.9699
C21—C22	1.45 (3)	C41—O7	1.21 (2)
C21—H21A	0.9699	C41—O8	1.297 (18)
C21—H21B	0.9701	C42—C43	1.48 (2)
C22—C23	1.55 (3)	C42—O8	1.48 (2)
C22—H22A	0.9700	C42—H42A	0.9700
C22—H22B	0.9700	C42—H42B	0.9699
C23—O1	1.16 (2)	C43—H43A	0.9601
C23—O2	1.36 (2)	C43—H43B	0.9599
C24—O2	1.44 (3)	C43—H43C	0.9600
C24—C25	1.50 (3)	C44—H44A	0.9600
C24—H24A	0.9700	C44—H44B	0.9600
C24—H24B	0.9700	C44—H44C	0.9600
C25—H25A	0.9601	O5—Ru1^{ii}	2.194 (11)
C25—H25B	0.9599	O9—C45	1.17 (2)

C45—Ru1—N2	95.7 (7)	H25B—C25—H25C	109.5
C45—Ru1—N4	90.2 (7)	C3—C26—H26A	109.5
N2—Ru1—N4	173.8 (5)	C3—C26—H26B	109.5
C45—Ru1—N1	95.9 (7)	H26A—C26—H26B	109.5
N2—Ru1—N1	91.7 (6)	C3—C26—H26C	109.5
N4—Ru1—N1	89.3 (5)	H26A—C26—H26C	109.5
C45—Ru1—N3	89.6 (7)	H26B—C26—H26C	109.5
N2—Ru1—N3	87.9 (6)	C7—C27—C28	111.4 (12)

N4—Ru1—N3	90.5 (5)	C7—C27—H27A	109.3
N1—Ru1—N3	174.5 (5)	C28—C27—H27A	109.3
C45—Ru1—O5^{i}	175.2 (8)	C7—C27—H27B	109.3
N2—Ru1—O5^{i}	87.0 (5)	C28—C27—H27B	109.3
N4—Ru1—O5^{i}	87.1 (5)	H27A—C27—H27B	108.0
N1—Ru1—O5^{i}	80.0 (5)	C29—C28—C27	117.0 (15)
N3—Ru1—O5^{i}	94.4 (5)	C29—C28—H28A	108.1
C1—N1—C4	104.8 (12)	C27—C28—H28A	108.0
C1—N1—Ru1	128.7 (10)	C29—C28—H28B	108.1
C4—N1—Ru1	126.3 (13)	C27—C28—H28B	108.0
C6—N2—C9	106.2 (15)	H28A—C28—H28B	107.3
C6—N2—Ru1	124.7 (14)	O3—C29—O4	117.5 (16)
C9—N2—Ru1	128.9 (9)	O3—C29—C28	121.8 (16)
C11—N3—C14	106.1 (13)	O4—C29—C28	120.6 (17)
C11—N3—Ru1	127.2 (9)	O4—C30—C31	106.7 (17)
C14—N3—Ru1	126.6 (13)	O4—C30—H30A	110.4
C16—N4—C19	107.1 (15)	C31—C30—H30A	110.4
C16—N4—Ru1	126.2 (13)	O4—C30—H30B	110.4
C19—N4—Ru1	126.6 (8)	C31—C30—H30B	110.4
N1—C1—C20	121.7 (13)	H30A—C30—H30B	108.6
N1—C1—C2	110.5 (15)	C30—C31—H31A	109.5
C20—C1—C2	127.7 (19)	C30—C31—H31B	109.5
C3—C2—C1	106.7 (17)	H31A—C31—H31B	109.5
C3—C2—C21	120.6 (13)	C30—C31—H31C	109.5
C1—C2—C21	132.8 (18)	H31A—C31—H31C	109.5
C4—C3—C2	107.7 (13)	H31B—C31—H31C	109.5
C4—C3—C26	130.7 (19)	C8—C32—H32A	109.5
C2—C3—C26	121.5 (17)	C8—C32—H32B	109.5
C5—C4—C3	128.9 (13)	H32A—C32—H32B	109.5
C5—C4—N1	120.8 (14)	C8—C32—H32C	109.5
C3—C4—N1	110.2 (17)	H32A—C32—H32C	109.4
C6—C5—C4	131.0 (13)	H32B—C32—H32C	109.4
C6—C5—H5	114.5	C12—C33—C34	120.2 (18)
C4—C5—H5	114.5	C12—C33—H33A	107.3
C5—C6—N2	125.2 (18)	C34—C33—H33A	107.3
C5—C6—C7	125.9 (13)	C12—C33—H33B	107.3
N2—C6—C7	108.9 (15)	C34—C33—H33B	107.3
C8—C7—C6	108.2 (15)	H33A—C33—H33B	106.9
C8—C7—C27	129 (2)	C33—C34—C35	109.8 (15)
C6—C7—C27	123.2 (15)	C33—C34—H34A	109.7
C7—C8—C9	107.2 (19)	C35—C34—H34A	109.7
C7—C8—C32	129.6 (16)	C33—C34—H34B	109.7
C9—C8—C32	123.2 (13)	C35—C34—H34B	109.7
C10—C9—N2	123.8 (16)	H34A—C34—H34B	108.2
C10—C9—C8	126.7 (18)	O5—C35—O6	125.9 (11)
N2—C9—C8	109.4 (13)	O5—C35—C34	118.1 (14)
C9—C10—C11	125.3 (19)	O6—C35—C34	115.4 (11)
C9—C10—H10	117.4	C37—C36—O6	107.1 (17)

C11—C10—H10	117.4	C37—C36—H36A	110.3
N3—C11—C10	126.5 (14)	O6—C36—H36A	110.3
N3—C11—C12	111.3 (14)	C37—C36—H36B	110.3
C10—C11—C12	122.1 (18)	O6—C36—H36B	110.3
C13—C12—C33	131.7 (13)	H36A—C36—H36B	108.5
C13—C12—C11	105.5 (16)	C36—C37—H37A	109.5
C33—C12—C11	122.6 (15)	C36—C37—H37B	109.5
C12—C13—C14	108.1 (13)	H37A—C37—H37B	109.5
C12—C13—C38	119.2 (17)	C36—C37—H37C	109.5
C14—C13—C38	132.5 (17)	H37A—C37—H37C	109.5
C15—C14—N3	122.1 (15)	H37B—C37—H37C	109.5
C15—C14—C13	128.9 (13)	C13—C38—H38A	109.5
N3—C14—C13	109.0 (17)	C13—C38—H38B	109.5
C14—C15—C16	129.7 (13)	H38A—C38—H38B	109.5
C14—C15—H15	115.2	C13—C38—H38C	109.5
C16—C15—H15	115.2	H38A—C38—H38C	109.5
N4—C16—C15	124.7 (18)	H38B—C38—H38C	109.5
N4—C16—C17	109.5 (15)	C40—C39—C17	108.2 (14)
C15—C16—C17	125.7 (13)	C40—C39—H39A	110.1
C18—C17—C16	107.7 (14)	C17—C39—H39A	110.1
C18—C17—C39	124.2 (19)	C40—C39—H39B	110.1
C16—C17—C39	128.0 (15)	C17—C39—H39B	110.1
C17—C18—C19	105.7 (18)	H39A—C39—H39B	108.4
C17—C18—C44	119.3 (15)	C41—C40—C39	113.1 (15)
C19—C18—C44	134.9 (13)	C41—C40—H40A	109.0
N4—C19—C20	125.4 (17)	C39—C40—H40A	109.0
N4—C19—C18	109.8 (12)	C41—C40—H40B	109.0
C20—C19—C18	124.7 (19)	C39—C40—H40B	109.0
C19—C20—C1	128.0 (19)	H40A—C40—H40B	107.8
C19—C20—H20	116.0	O7—C41—O8	119.2 (16)
C1—C20—H20	116.0	O7—C41—C40	115.9 (13)
C2—C21—C22	122.4 (11)	O8—C41—C40	124.6 (16)
C2—C21—H21A	106.7	C43—C42—O8	111.1 (17)
C22—C21—H21A	106.7	C43—C42—H42A	109.4
C2—C21—H21B	106.7	O8—C42—H42A	109.4
C22—C21—H21B	106.7	C43—C42—H42B	109.4
H21A—C21—H21B	106.6	O8—C42—H42B	109.4
C21—C22—C23	112.8 (11)	H42A—C42—H42B	108.0
C21—C22—H22A	109.0	C42—C43—H43A	109.5
C23—C22—H22A	109.0	C42—C43—H43B	109.5
C21—C22—H22B	109.0	H43A—C43—H43B	109.5
C23—C22—H22B	109.0	C42—C43—H43C	109.5
H22A—C22—H22B	107.8	H43A—C43—H43C	109.5
O1—C23—O2	124.3 (16)	H43B—C43—H43C	109.5
O1—C23—C22	119.5 (16)	C18—C44—H44A	109.5
O2—C23—C22	115.4 (16)	C18—C44—H44B	109.5
O2—C24—C25	112.9 (15)	H44A—C44—H44B	109.5
O2—C24—H24A	109.0	C18—C44—H44C	109.5

C25—C24—H24A	109.0	H44A—C44—H44C	109.5
O2—C24—H24B	109.0	H44B—C44—H44C	109.5
C25—C24—H24B	109.0	C23—O2—C24	127.3 (17)
H24A—C24—H24B	107.8	C29—O4—C30	125.7 (15)
C24—C25—H25A	109.5	C35—O5—Ru1$^{\text{ii}}$	162.6 (10)
C24—C25—H25B	109.5	C35—O6—C36	115.1 (12)
H25A—C25—H25B	109.5	C41—O8—C42	127.0 (14)
C24—C25—H25C	109.5	O9—C45—Ru1	173.9 (13)
H25A—C25—H25C	109.5		

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

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C25—H25*C*···O2$^{\text{iii}}$	0.96	2.17	3.08 (2)	157
C37—H37*C*···O9$^{\text{i}}$	0.96	2.29	2.93 (2)	123
C39—H39*A*···O7$^{\text{iv}}$	0.97	2.43	3.37 (2)	161
C39—H39*B*···O3$^{\text{v}}$	0.97	2.54	3.51 (2)	173
C43—H43*B*···O1$^{\text{vi}}$	0.96	2.19	3.00 (2)	141
C44—H44*A*···O1$^{\text{iii}}$	0.96	2.60	3.29 (2)	129

Symmetry codes: (i) $-x+3/2, y-1/2, -z+3/2$; (iii) $-x+2, y, -z+3/2$; (iv) $-x+3/2, -y+3/2, -z+1$; (v) $x, -y+1, z-1/2$; (vi) $x-1/2, -y+1/2, z-1/2$.