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Tetrakis(μ-benzoato-κ²O:O′)bis[(piperidine-κN)-rhodium]

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Keywords: crystal structure; rhodium complex; benzoate; piperidine.

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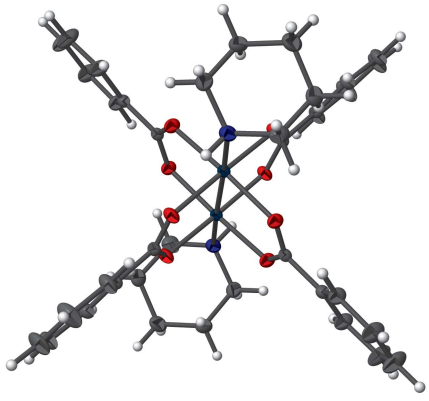
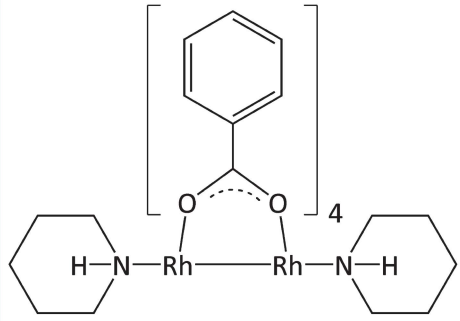
Structural data: full structural data are available from iucrdata.iucr.org

The title compound, $[Rh_2(C_7H_5O_2)_4(C_5H_{11}N)_2]$, an adduct of dimeric rhodium(II) benzoate with piperidine, was prepared. The complex lies across an inversion centre with the unique Rh^{II} ion in a slightly distorted octahedral coordination environment.

3D view



Chemical scheme



Structure description

The molecular structure lies across an inversion centre and the coordination geometry around the rhodium atoms is slightly distorted octahedral (Fig. 1). The Rh1—Rh1($-x$, $-y+2$, $-z$) distance is 2.4116 (2) Å, which is comparable to the value of 2.402 (2) Å determined for the corresponding bispyridine complex $[Rh_2(bzt)_4(py)_2]$ (Mehmet & Tocher, 1991). As a result of the sp^2-hybridized nitrogen atoms, the rhodium nitrogen distance of 2.246 (4) in the latter molecule is shorter, compared to the value of 2.3083 (13) Å found for the title compound. In $[Rh_2(bzt)_4(pip)_2]$, individual C—O distances vary within a narrow range of 0.008 (2) Å thus pointing towards an almost symmetric charge distribution within the carboxylato groups. A deviation of 0.0763 (5) Å from the plane defined by the square arrangement of the oxygen atoms was determined for the symmetry-equivalent rhodium atoms. The piperidine molecules adopt chair conformations.

Synthesis and crystallization

A procedure analogous to that for the pyridine adduct has been applied (Legzdins *et al.*, 1970). A stirred solution of rhodium trichloride trihydrate (1 g, 0.0038 mol) in methanol (125 ml) was treated with solid benzoic acid (12 g, 0.098 mol), solid sodium benzoate (5 g, 0.0035 mol) and with piperidine (8.515 g, 0.1 mol). The reaction mixture was heated to reflux for 1 h, and the formed precipitate was filtered off. The product was then washed

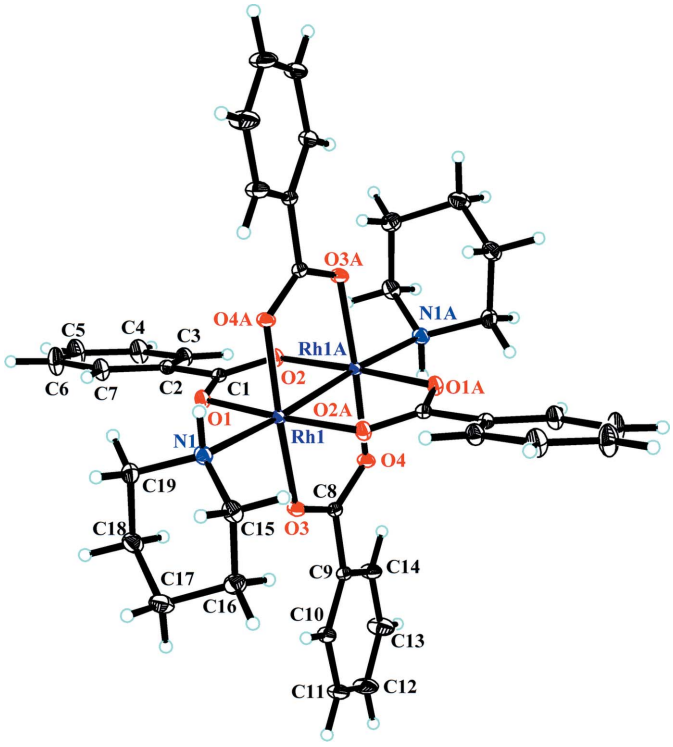


Figure 1
The molecular structure of the title compound, showing the atom labelling and displacement ellipsoids drawn at the 30% probability level [symmetry code: (A) (i) $-x, -y+2, -z$].

with methanol (2 × 5 ml) and recrystallized from chloroform/diethyl ether (2:1) to give the title compound as carmine, air-stable crystals. Yield: 0.290 g (0.340 mmol, 18%). Elemental analysis (calculated for $Rh_2C_{38}H_{42}N_2O_8$, M = 860.58 g mol^{-1}): C, 52.60 (53.04); H, 5.04 (4.92); N, 3.18 (3.26); Rh, 24.12 (23.92)%.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1.

Table 1
Experimental details.

Crystal data	
Chemical formula	$[Rh_2(C_7H_5O_2)_4(C_5H_{11}N)_2]$
M_r	860.55
Crystal system, space group	Monoclinic, $P2_1/n$
Temperature (K)	150
a, b, c (Å)	10.7224 (1), 11.1042 (2), 14.7761 (2)
β (°)	96.078 (1)
V (Å^3)	1749.41 (4)
Z	2
Radiation type	Mo $K\alpha$
μ (mm^{-1})	1.00
Crystal size (mm)	0.44 × 0.26 × 0.17
Data collection	
Diffractometer	Bruker APEXII CCD
Absorption correction	Multi-scan (*SADABS*; Bruker, 2014)
T_{min}, T_{max}	0.684, 0.746
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	35557, 5343, 4939
R_{int}	0.022
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.714
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.021, 0.055, 1.05
No. of reflections	5343
No. of parameters	230
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.81, −0.54

Computer programs: *APEX2* and *SAINT* (Bruker, 2013), *SHELXS97* (Sheldrick, 2008), *SHELXL2014* (Sheldrick, 2015), *XP* in *SHELXTL* (Sheldrick, 2008), *publCIF* (Westrip, 2010) and *PLATON* (Spek, 2009).

References

Bruker (2013). *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
Bruker (2014). *APEX2* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
Legzdins, P., Mitchell, R. W., Rempel, G. L., Ruddick, J. D. & Wilkinson, G. J. (1970). *J. Chem. Soc. A*, pp. 3322–3326.
Mehmet, N. & Tocher, D. A. (1991). *Inorg. Chim. Acta*, **188**, 71–77.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Sheldrick, G. M. (2015). *Acta Cryst.* C**71**, 3–8.
Spek, A. L. (2009). *Acta Cryst.* D**65**, 148–155.
Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.

full crystallographic data

IUCrData (2017). **2**, x170205 [https://doi.org/10.1107/S2414314617002050X]

Tetrakis(μ-benzoato-κ²*O*:*O*′)bis[(piperidine-κ*N*)rhodium]

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Tetrakis(μ-benzoato-κ²*O*:*O*′)bis[(piperidine-κ*N*)rhodium]

Crystal data

$[Rh_2(C_7H_5O_2)_4(C_5H_{11}N)_2]$
M_r = 860.55
Monoclinic, $P2_1/n$
a = 10.7224 (1) Å
b = 11.1042 (2) Å
c = 14.7761 (2) Å
β = 96.078 (1)°
V = 1749.41 (4) Å^3
Z = 2
$F(000)$ = 876
D_x = 1.634 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 9954 reflections
θ = 2.9–30.5°
μ = 1.00 mm^{-1}
T = 150 K
Prism, red
0.44 × 0.26 × 0.17 mm

Data collection

Bruker APEXII CCD diffractometer
Radiation source: fine-focus sealed tube
Detector resolution: 8.3333 pixels mm^{-1}
φ and ω scans
Absorption correction: multi-scan (SADABS; Bruker, 2014)
T_{min} = 0.684, T_{max} = 0.746
35557 measured reflections
5343 independent reflections
4939 reflections with $I > 2\sigma(I)$
R_{int} = 0.022
θ_{max} = 30.5°, θ_{min} = 2.3°
h = −15→15
k = −15→14
l = −21→20

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.021
$wR(F^2)$ = 0.055
S = 1.05
5343 reflections
230 parameters
0 restraints
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0255P)^2 + 1.4431P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.81 e Å^{-3}
$\Delta\rho_{min}$ = −0.54 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}*/U_{eq}
Rh1	0.02361 (2)	0.95634 (2)	0.07456 (2)	0.01337 (4)
O1	0.07504 (10)	0.80446 (10)	0.01222 (7)	0.01890 (19)
O2	0.03436 (10)	0.88572 (10)	−0.12799 (7)	0.0193 (2)
O3	0.19998 (9)	1.02805 (10)	0.07472 (7)	0.0185 (2)
O4	0.15364 (9)	1.10880 (10)	−0.06514 (7)	0.0190 (2)
N1	0.04978 (12)	0.85729 (12)	0.21261 (8)	0.0204 (2)
H1	−0.026 (2)	0.821 (2)	0.2074 (14)	0.030 (5)*
C1	0.06780 (12)	0.80076 (13)	−0.07406 (9)	0.0161 (2)
C2	0.10317 (12)	0.68370 (13)	−0.11396 (9)	0.0172 (2)
C3	0.12819 (16)	0.67759 (15)	−0.20431 (10)	0.0252 (3)
H3	0.1216	0.7478	−0.2413	0.030*
C4	0.1627 (2)	0.56869 (17)	−0.24021 (12)	0.0364 (4)
H4	0.1824	0.5648	−0.3013	0.044*
C5	0.1687 (2)	0.46555 (17)	−0.18722 (13)	0.0381 (4)
H5	0.1911	0.3909	−0.2124	0.046*
C6	0.1421 (2)	0.47095 (16)	−0.09732 (12)	0.0321 (4)
H6	0.1446	0.3999	−0.0613	0.039*
C7	0.11185 (15)	0.58047 (14)	−0.06047 (10)	0.0228 (3)
H7	0.0970	0.5851	0.0017	0.027*
C8	0.22654 (12)	1.08853 (13)	0.00705 (9)	0.0159 (2)
C9	0.35458 (12)	1.14222 (13)	0.01039 (9)	0.0167 (2)
C10	0.45244 (13)	1.10339 (14)	0.07328 (10)	0.0206 (3)
H10	0.4379	1.0437	0.1170	0.025*
C11	0.57143 (14)	1.15254 (16)	0.07159 (11)	0.0262 (3)
H11	0.6385	1.1258	0.1140	0.031*
C12	0.59252 (15)	1.23997 (19)	0.00863 (13)	0.0340 (4)
H12	0.6741	1.2728	0.0075	0.041*
C13	0.49488 (16)	1.2798 (2)	−0.05281 (13)	0.0364 (4)
H13	0.5090	1.3411	−0.0954	0.044*
C14	0.37677 (14)	1.23026 (16)	−0.05219 (11)	0.0251 (3)
H14	0.3102	1.2569	−0.0951	0.030*
C15	0.05381 (15)	0.93372 (16)	0.29481 (11)	0.0251 (3)
H15A	0.0422	0.8833	0.3486	0.030*
H15B	−0.0148	0.9937	0.2874	0.030*
C16	0.17947 (16)	0.99760 (16)	0.30890 (12)	0.0279 (3)
H16A	0.1831	1.0475	0.3646	0.033*
H16B	0.1881	1.0517	0.2567	0.033*
C17	0.28741 (16)	0.90793 (17)	0.31786 (13)	0.0312 (4)
H17A	0.3682	0.9518	0.3221	0.037*
H17B	0.2850	0.8602	0.3742	0.037*
C18	0.27784 (15)	0.82436 (16)	0.23619 (12)	0.0272 (3)
H18A	0.3435	0.7615	0.2456	0.033*
H18B	0.2925	0.8708	0.1811	0.033*
C19	0.14973 (16)	0.76498 (14)	0.22207 (11)	0.0249 (3)
H19A	0.1441	0.7144	0.1666	0.030*

H19B	0.1382	0.7122	0.2746	0.030*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Rh1	0.01245 (5)	0.01576 (6)	0.01178 (5)	−0.00098 (3)	0.00075 (3)	0.00050 (3)
O1	0.0226 (5)	0.0191 (5)	0.0148 (4)	0.0022 (4)	0.0014 (4)	0.0000 (4)
O2	0.0235 (5)	0.0195 (5)	0.0149 (4)	0.0023 (4)	0.0017 (4)	−0.0004 (4)
O3	0.0146 (4)	0.0238 (5)	0.0168 (5)	−0.0037 (4)	−0.0003 (3)	0.0037 (4)
O4	0.0139 (4)	0.0266 (5)	0.0163 (4)	−0.0044 (4)	0.0002 (3)	0.0036 (4)
N1	0.0206 (6)	0.0227 (6)	0.0176 (5)	−0.0028 (5)	0.0011 (4)	0.0012 (5)
C1	0.0130 (5)	0.0181 (6)	0.0171 (6)	−0.0012 (5)	0.0011 (4)	−0.0016 (5)
C2	0.0148 (5)	0.0187 (6)	0.0178 (6)	0.0010 (5)	−0.0003 (4)	−0.0021 (5)
C3	0.0344 (8)	0.0227 (7)	0.0184 (7)	0.0040 (6)	0.0029 (6)	−0.0004 (5)
C4	0.0587 (12)	0.0303 (9)	0.0209 (8)	0.0126 (8)	0.0081 (8)	−0.0032 (7)
C5	0.0615 (13)	0.0258 (9)	0.0270 (8)	0.0161 (8)	0.0047 (8)	−0.0037 (7)
C6	0.0470 (10)	0.0222 (8)	0.0268 (8)	0.0089 (7)	0.0026 (7)	0.0012 (6)
C7	0.0271 (7)	0.0215 (7)	0.0196 (6)	0.0023 (6)	0.0019 (5)	0.0002 (5)
C8	0.0137 (5)	0.0174 (6)	0.0167 (6)	−0.0007 (5)	0.0021 (4)	−0.0007 (5)
C9	0.0130 (5)	0.0201 (6)	0.0171 (6)	−0.0020 (5)	0.0021 (4)	−0.0018 (5)
C10	0.0183 (6)	0.0226 (7)	0.0205 (6)	−0.0019 (5)	−0.0004 (5)	0.0018 (5)
C11	0.0167 (6)	0.0329 (8)	0.0278 (8)	−0.0022 (6)	−0.0040 (5)	0.0027 (6)
C12	0.0168 (7)	0.0468 (11)	0.0375 (9)	−0.0113 (7)	−0.0012 (6)	0.0094 (8)
C13	0.0240 (8)	0.0479 (11)	0.0365 (9)	−0.0133 (7)	−0.0015 (7)	0.0198 (8)
C14	0.0170 (6)	0.0310 (8)	0.0265 (7)	−0.0044 (6)	−0.0014 (5)	0.0077 (6)
C15	0.0254 (7)	0.0315 (8)	0.0186 (7)	0.0033 (6)	0.0032 (5)	−0.0008 (6)
C16	0.0281 (8)	0.0270 (8)	0.0272 (8)	0.0024 (6)	−0.0038 (6)	−0.0066 (6)
C17	0.0255 (7)	0.0317 (9)	0.0342 (9)	0.0033 (6)	−0.0073 (6)	−0.0023 (7)
C18	0.0251 (7)	0.0257 (8)	0.0305 (8)	0.0060 (6)	0.0009 (6)	0.0016 (6)
C19	0.0313 (8)	0.0206 (7)	0.0220 (7)	0.0023 (6)	−0.0011 (6)	0.0016 (5)

Geometric parameters (Å, º)

Rh1—O4^{i}	2.0245 (10)	C8—C9	1.4927 (18)
Rh1—O1	2.0260 (10)	C9—C14	1.383 (2)
Rh1—O2^{i}	2.0469 (10)	C9—C10	1.3943 (19)
Rh1—O3	2.0517 (10)	C10—C11	1.390 (2)
Rh1—N1	2.3083 (12)	C10—H10	0.9500
Rh1—Rh1^{i}	2.4116 (2)	C11—C12	1.380 (2)
O1—C1	1.2696 (16)	C11—H11	0.9500
O2—C1	1.2623 (17)	C12—C13	1.384 (2)
O2—Rh1^{i}	2.0468 (10)	C12—H12	0.9500
O3—C8	1.2619 (17)	C13—C14	1.382 (2)
O4—C8	1.2740 (16)	C13—H13	0.9500
O4—Rh1^{i}	2.0244 (10)	C14—H14	0.9500
N1—C15	1.479 (2)	C15—C16	1.517 (2)
N1—C19	1.479 (2)	C15—H15A	0.9900
N1—H1	0.91 (2)	C15—H15B	0.9900

C1—C2	1.4927 (19)	C16—C17	1.522 (2)
C2—C7	1.390 (2)	C16—H16A	0.9900
C2—C3	1.391 (2)	C16—H16B	0.9900
C3—C4	1.387 (2)	C17—C18	1.517 (2)
C3—H3	0.9500	C17—H17A	0.9900
C4—C5	1.385 (3)	C17—H17B	0.9900
C4—H4	0.9500	C18—C19	1.518 (2)
C5—C6	1.389 (3)	C18—H18A	0.9900
C5—H5	0.9500	C18—H18B	0.9900
C6—C7	1.385 (2)	C19—H19A	0.9900
C6—H6	0.9500	C19—H19B	0.9900
C7—H7	0.9500		

O4^{i}—Rh1—O1	88.29 (4)	C14—C9—C10	119.57 (13)
O4^{i}—Rh1—O2^{i}	90.66 (4)	C14—C9—C8	118.87 (12)
O1—Rh1—O2^{i}	175.60 (4)	C10—C9—C8	121.54 (13)
O4^{i}—Rh1—O3	175.72 (4)	C11—C10—C9	119.60 (14)
O1—Rh1—O3	91.63 (4)	C11—C10—H10	120.2
O2^{i}—Rh1—O3	89.11 (4)	C9—C10—H10	120.2
O4^{i}—Rh1—N1	85.18 (4)	C12—C11—C10	120.30 (15)
O1—Rh1—N1	89.53 (4)	C12—C11—H11	119.9
O2^{i}—Rh1—N1	94.64 (4)	C10—C11—H11	119.9
O3—Rh1—N1	99.10 (4)	C11—C12—C13	120.05 (15)
O4^{i}—Rh1—Rh1^{i}	88.63 (3)	C11—C12—H12	120.0
O1—Rh1—Rh1^{i}	87.72 (3)	C13—C12—H12	120.0
O2^{i}—Rh1—Rh1^{i}	87.99 (3)	C14—C13—C12	119.91 (16)
O3—Rh1—Rh1^{i}	87.09 (3)	C14—C13—H13	120.0
N1—Rh1—Rh1^{i}	173.29 (3)	C12—C13—H13	120.0
C1—O1—Rh1	119.53 (9)	C13—C14—C9	120.56 (15)
C1—O2—Rh1^{i}	118.32 (9)	C13—C14—H14	119.7
C8—O3—Rh1	119.41 (9)	C9—C14—H14	119.7
C8—O4—Rh1^{i}	118.87 (9)	N1—C15—C16	109.23 (13)
C15—N1—C19	111.24 (12)	N1—C15—H15A	109.8
C15—N1—Rh1	116.27 (10)	C16—C15—H15A	109.8
C19—N1—Rh1	115.65 (9)	N1—C15—H15B	109.8
C15—N1—H1	105.9 (14)	C16—C15—H15B	109.8
C19—N1—H1	109.5 (14)	H15A—C15—H15B	108.3
Rh1—N1—H1	96.6 (14)	C15—C16—C17	111.23 (15)
O2—C1—O1	126.36 (13)	C15—C16—H16A	109.4
O2—C1—C2	117.94 (12)	C17—C16—H16A	109.4
O1—C1—C2	115.70 (12)	C15—C16—H16B	109.4
C7—C2—C3	119.83 (14)	C17—C16—H16B	109.4
C7—C2—C1	119.87 (13)	H16A—C16—H16B	108.0
C3—C2—C1	120.30 (13)	C18—C17—C16	110.14 (14)
C4—C3—C2	119.75 (15)	C18—C17—H17A	109.6
C4—C3—H3	120.1	C16—C17—H17A	109.6
C2—C3—H3	120.1	C18—C17—H17B	109.6
C5—C4—C3	120.21 (16)	C16—C17—H17B	109.6

C5—C4—H4	119.9	H17A—C17—H17B	108.1
C3—C4—H4	119.9	C17—C18—C19	111.04 (14)
C4—C5—C6	120.19 (16)	C17—C18—H18A	109.4
C4—C5—H5	119.9	C19—C18—H18A	109.4
C6—C5—H5	119.9	C17—C18—H18B	109.4
C7—C6—C5	119.62 (16)	C19—C18—H18B	109.4
C7—C6—H6	120.2	H18A—C18—H18B	108.0
C5—C6—H6	120.2	N1—C19—C18	110.38 (13)
C6—C7—C2	120.33 (14)	N1—C19—H19A	109.6
C6—C7—H7	119.8	C18—C19—H19A	109.6
C2—C7—H7	119.8	N1—C19—H19B	109.6
O3—C8—O4	125.99 (12)	C18—C19—H19B	109.6
O3—C8—C9	118.06 (12)	H19A—C19—H19B	108.1
O4—C8—C9	115.96 (12)		

Rh1^{i}—O2—C1—O1	−3.53 (19)	O3—C8—C9—C14	−165.39 (14)
Rh1^{i}—O2—C1—C2	176.69 (9)	O4—C8—C9—C14	14.5 (2)
Rh1—O1—C1—O2	2.40 (19)	O3—C8—C9—C10	16.4 (2)
Rh1—O1—C1—C2	−177.82 (8)	O4—C8—C9—C10	−163.70 (14)
O2—C1—C2—C7	−164.88 (13)	C14—C9—C10—C11	−0.8 (2)
O1—C1—C2—C7	15.32 (19)	C8—C9—C10—C11	177.43 (14)
O2—C1—C2—C3	15.5 (2)	C9—C10—C11—C12	0.6 (3)
O1—C1—C2—C3	−164.31 (14)	C10—C11—C12—C13	0.5 (3)
C7—C2—C3—C4	−0.6 (2)	C11—C12—C13—C14	−1.2 (3)
C1—C2—C3—C4	179.06 (16)	C12—C13—C14—C9	1.0 (3)
C2—C3—C4—C5	1.9 (3)	C10—C9—C14—C13	0.0 (3)
C3—C4—C5—C6	−1.0 (3)	C8—C9—C14—C13	−178.26 (17)
C4—C5—C6—C7	−1.2 (3)	C19—N1—C15—C16	60.57 (17)
C5—C6—C7—C2	2.6 (3)	Rh1—N1—C15—C16	−74.65 (14)
C3—C2—C7—C6	−1.7 (2)	N1—C15—C16—C17	−57.91 (18)
C1—C2—C7—C6	178.67 (15)	C15—C16—C17—C18	54.8 (2)
Rh1—O3—C8—O4	−1.5 (2)	C16—C17—C18—C19	−53.59 (19)
Rh1—O3—C8—C9	178.39 (9)	C15—N1—C19—C18	−60.09 (16)
Rh1^{i}—O4—C8—O3	1.6 (2)	Rh1—N1—C19—C18	75.43 (14)
Rh1^{i}—O4—C8—C9	−178.30 (9)	C17—C18—C19—N1	56.22 (17)

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