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Chloridonitrosyl[*meso*-5,10,15,20-tetrakis(*p*-tolyl)porphyrinato-κ^4N,N',N'',N''']osmium(II) tetrahydrofuran tetrasolvate

Li Chen, Nan Xu,* Douglas R. Powell and George B. Richter-Addo

Department of Chemistry and Biochemistry, University of Oklahoma, 101 Stephenson Parkway, Norman, OK 73019-5251, USA
Correspondence e-mail: xunan@ou.edu

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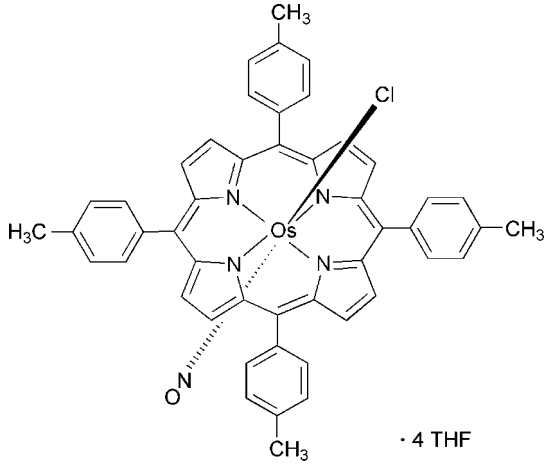
Key indicators: single-crystal X-ray study; T = 188 K; mean σ(C–C) = 0.003 Å; disorder in main residue; R factor = 0.022; wR factor = 0.058; data-to-parameter ratio = 15.3.

The title compound, $[OsCl(NO)(C_{48}H_{36}N_4)]\cdot 4C_4H_8O$, is a six-coordinate osmium(II) porphyrin complex with nitrosyl (NO) and chloride (Cl) ligands *trans* to each other in an octahedral geometry. The metal complex lies on a fourfold rotation axis that passes through the Os, N, O and Cl atoms. The NO and Cl ligands are disordered in an 0.511 (12):0.486 (12) ratio.

Related literature

For related osmium nitrosyl porphyrin derivatives, see: Cheng *et al.* (2001); Lee *et al.* (2001). For the synthesis, see: Cheng *et al.* (1998).



Experimental

Crystal data

$[OsCl(NO)(C_{48}H_{36}N_4)]\cdot 4C_4H_8O$
M_r = 1212.88
Tetragonal, $P4/n$
a = 16.905 (2) Å
c = 9.6220 (19) Å
V = 2749.8 (8) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 2.42 mm^{-1}
T = 188 K
0.62 × 0.58 × 0.52 mm

Data collection

Siemens P4 diffractometer
Absorption correction: ψ scan (North *et al.*, 1968)
T_{min} = 0.315, T_{max} = 0.366
8309 measured reflections
2859 independent reflections
2749 reflections with $I > 2\sigma(I)$
R_{int} = 0.024
3 standard reflections every 97 reflections
intensity decay: 6.7%

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.022
$wR(F^2)$ = 0.058
S = 0.97
2859 reflections
187 parameters
1 restraint
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.59 e Å^{-3}
$\Delta\rho_{min}$ = −1.46 e Å^{-3}

Data collection: *XSCANS* (Siemens, 1994); cell refinement: *XSCANS*; data reduction: *SHELXTL* (Sheldrick, 2008); program(s) used to solve structure: *SHELXTL*; program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: NG5100).

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S1. Comment

Six-coordinate osmium nitrosyl porphyrin complexes have been prepared as potential heme-NO structural models (Cheng *et al.* 2001 and Lee *et al*. 2001). Compared to their iron derivatives, osmium nitrosyl porphyrin compounds are more thermally stable and more easily characterized spectroscopically. In this paper, we report the structure of (chloro)(nitrosyl)(*meso*-5,10,15,20-tetrakis(*p*-tolyl)porphyrinato)osmium with four molecules of tetrahydrofuran as the solvate.

The metal complex is found to sit on a crystallographic 4 axis. The nitrosyl and chloride ligands are disordered across the porphyrin plane. The occupancies of the nitrosyl and chloride ligands refine to 0.511 (12) and 0.486 (12) for the unprimed and primed atoms, respectively. The molecular structure of (TTP)Os(NO)Cl is shown in Figure 1. The nitrosyl group binds to the osmium center through its nitrogen atom, exhibiting a linear Os—N—O conformation (180°). The average Os—N_p distance is 2.0622 (19) Å. The average Os—N(O) distance is 1.80 (3) Å and the average Os—Cl distance is 2.208 (8) Å. The average N—O distance is 1.244 (2) Å.

S2. Experimental

The titled compound was obtained as a sideproduct during the preparation of (TTP)Os(NO)(Me) from the reaction of [(TTP)Os(NO)]PF_6 with MeMgCl in THF (Cheng *et al.* 1998), and crystals were obtained by slow evaporation of a THF-hexane (1:1) solution at room temperature.

S3. Refinement

The hydrogen atoms were placed in calculated positions with C—H = 0.95 Å for aromatic carbons, 0.99 Å for methylene carbons and 0.98 Å for methyl carbons and were refined using a riding model with U_{iso} = 1.2 U_{eq}(C) for phenyl H atoms, U_{iso} = 1.5 U_{eq}(C) for methyl H atoms. The compound was made with Cl on one side of the porphyrin ring and NO on the other side of the ring. In the crystal structure, both ligands appeared to be on both sides of the ring. The Cl on one side of the ring was matched with the NO on the opposite side of the ring in the model. Because the Cl and NO groups were on a 4-fold axis, their occupancies from the two sets of ligands were set to sum to 0.25.

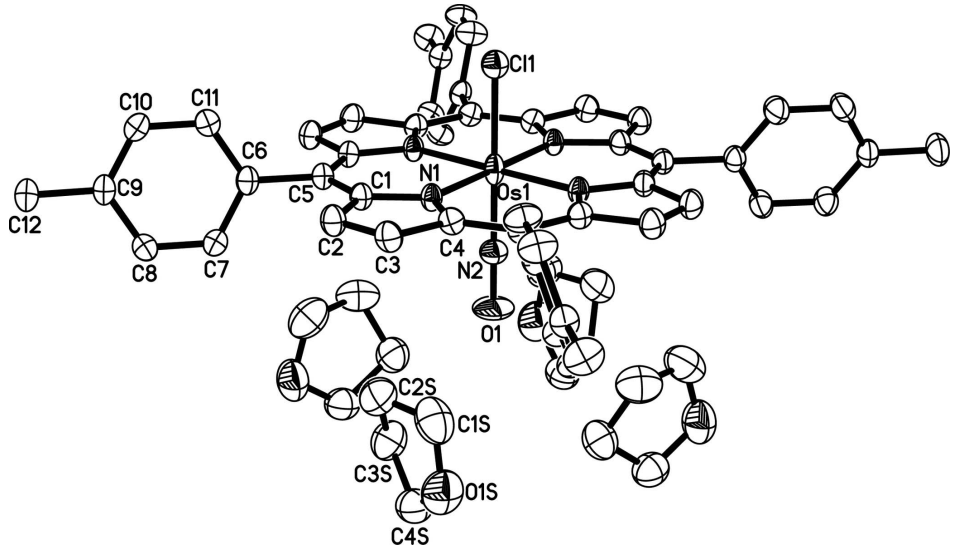

Figure 1

The molecular structure of (TTP)Os(NO)Cl·4THF. Displacement ellipsoids are drawn at the 50% probability level. H atoms are omitted for clarity.

Chloridonitrosyl[*meso*-5,10,15,20-tetrakis(*p*-tolyl)porphyrinato- κ^4N,N',N'',N''')osmium(II) tetrahydrofuran tetrasolvate

Crystal data

$[OsCl(NO)(C_{48}H_{36}N_4)]\cdot 4C_4H_8O$
$M_r = 1212.88$
Tetragonal, $P4/n$
Hall symbol: -P 4a
$a = 16.905$ (2) Å
$c = 9.6220$ (19) Å
$V = 2749.8$ (8) Å^3
$Z = 2$
$F(000) = 1240$
$D_x = 1.465$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 41 reflections
$\theta = 6.9$–$12.4°$
$\mu = 2.42$ mm^{-1}
$T = 188$ K
Block, purple
0.62 × 0.58 × 0.52 mm

Data collection

Siemens P4 diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
ω scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{min} = 0.315$, $T_{max} = 0.366$
8309 measured reflections
2859 independent reflections
2749 reflections with $I > 2\sigma(I)$
$R_{int} = 0.024$
$\theta_{max} = 26.5°$, $\theta_{min} = 2.1°$
$h = -1 \rightarrow 21$
$k = -14 \rightarrow 21$
$l = -12 \rightarrow 12$
3 standard reflections every 97 reflections
intensity decay: 6.7%

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.022$
$wR(F^2) = 0.058$
$S = 0.97$
2859 reflections
187 parameters
1 restraint
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.040P)^2 + 0.950P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.59$ e Å^{-3}
$\Delta\rho_{min} = -1.46$ e Å^{-3}
Extinction correction: *SHELXTL* (Sheldrick, 2008), $Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.00138 (16)

Special details

Refinement. Restraint: sump 0.25 0.0004 1 2 1 3 where the second and third item on the fvar instruction were occupancies of N2, O1, Cl1, and N2′, O1′, and Cl1′, respectively.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
Os1	0.2500	0.2500	0.764201 (16)	0.02581 (8)	
N1	0.35454 (11)	0.31287 (11)	0.76484 (15)	0.0223 (3)	
C1	0.42941 (13)	0.28109 (14)	0.76543 (17)	0.0245 (4)	
C2	0.48571 (14)	0.34489 (15)	0.76709 (19)	0.0298 (5)	
H2	0.5417	0.3397	0.7685	0.036*	
C3	0.44474 (14)	0.41381 (15)	0.76625 (19)	0.0294 (5)	
H3	0.4666	0.4656	0.7661	0.035*	
C4	0.36169 (14)	0.39376 (13)	0.76565 (18)	0.0245 (4)	
C5	0.44808 (13)	0.20028 (14)	0.76528 (17)	0.0246 (4)	
C6	0.53430 (14)	0.17924 (14)	0.76365 (18)	0.0254 (4)	
C7	0.57898 (12)	0.19002 (13)	0.6443 (2)	0.0308 (4)	
H7	0.5545	0.2103	0.5629	0.037*	
C8	0.65901 (12)	0.17163 (13)	0.6424 (2)	0.0318 (5)	
H8	0.6883	0.1787	0.5591	0.038*	
C9	0.69700 (14)	0.14299 (15)	0.76017 (18)	0.0279 (5)	
C10	0.65179 (13)	0.13145 (14)	0.8786 (2)	0.0361 (5)	
H10	0.6761	0.1112	0.9602	0.043*	
C11	0.57146 (12)	0.14902 (14)	0.8803 (2)	0.0350 (5)	
H11	0.5417	0.1402	0.9625	0.042*	
C12	0.78439 (16)	0.12540 (19)	0.7586 (2)	0.0390 (6)	
H12A	0.7967	0.0865	0.8309	0.058*	
H12B	0.8140	0.1742	0.7763	0.058*	
H12C	0.7993	0.1041	0.6676	0.058*	
N2	0.2500	0.2500	0.5792 (16)	0.031 (4)	0.511 (12)
O1	0.2500	0.2500	0.4507 (15)	0.057 (2)	0.511 (12)
Cl1	0.2500	0.2500	0.9929 (8)	0.031 (2)	0.511 (12)
N2′	0.2500	0.2500	0.953 (3)	0.040 (8)	:0.486 (12)
O1′	0.2500	0.2500	1.0823 (14)	0.048 (2)	0.486 (12)
Cl1′	0.2500	0.2500	0.5339 (5)	0.0303 (18)	0.486 (12)
O1S	0.39867 (19)	0.45886 (16)	0.2341 (2)	0.0674 (7)	
C1S	0.3997 (2)	0.4362 (2)	0.3748 (3)	0.0680 (9)	
H1SA	0.3451	0.4329	0.4117	0.082*	
H1SB	0.4297	0.4750	0.4308	0.082*	
C2S	0.43853 (19)	0.3572 (2)	0.3803 (3)	0.0657 (8)	
H2SA	0.4198	0.3261	0.4610	0.079*	

H2SB	0.4968	0.3622	0.3847	0.079*
C3S	0.4123 (3)	0.3206 (2)	0.2450 (3)	0.0567 (8)
H3SA	0.4515	0.2817	0.2109	0.068*
H3SB	0.3603	0.2944	0.2548	0.068*
C4S	0.40732 (18)	0.39121 (18)	0.1500 (3)	0.0550 (7)
H4SA	0.4559	0.3954	0.0931	0.066*
H4SB	0.3614	0.3859	0.0867	0.066*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Os1	0.01638 (8)	0.01638 (8)	0.04466 (12)	0.000	0.000	0.000
N1	0.0171 (8)	0.0180 (8)	0.0317 (8)	−0.0005 (7)	−0.0002 (5)	0.0002 (5)
C1	0.0190 (10)	0.0258 (11)	0.0287 (9)	−0.0003 (8)	−0.0006 (6)	−0.0003 (7)
C2	0.0227 (11)	0.0288 (12)	0.0381 (11)	−0.0019 (9)	−0.0003 (7)	−0.0016 (7)
C3	0.0249 (11)	0.0264 (11)	0.0369 (11)	−0.0050 (9)	0.0009 (7)	−0.0010 (7)
C4	0.0244 (11)	0.0202 (10)	0.0288 (9)	−0.0035 (8)	0.0008 (7)	−0.0008 (6)
C5	0.0195 (10)	0.0265 (11)	0.0278 (9)	0.0015 (8)	−0.0005 (6)	−0.0004 (7)
C6	0.0204 (10)	0.0231 (11)	0.0326 (10)	0.0001 (8)	−0.0017 (7)	−0.0027 (7)
C7	0.0261 (10)	0.0356 (11)	0.0308 (9)	0.0044 (9)	−0.0012 (7)	0.0059 (8)
C8	0.0259 (10)	0.0370 (12)	0.0324 (10)	0.0024 (9)	0.0043 (7)	0.0051 (8)
C9	0.0207 (11)	0.0267 (12)	0.0363 (11)	0.0023 (9)	−0.0014 (7)	−0.0016 (7)
C10	0.0283 (11)	0.0491 (14)	0.0309 (10)	0.0070 (10)	−0.0048 (8)	0.0054 (9)
C11	0.0259 (10)	0.0500 (14)	0.0292 (10)	0.0044 (9)	0.0020 (8)	0.0035 (9)
C12	0.0240 (12)	0.0486 (17)	0.0443 (13)	0.0071 (11)	−0.0008 (8)	0.0045 (9)
N2	0.034 (4)	0.034 (4)	0.025 (11)	0.000	0.000	0.000
O1	0.077 (5)	0.077 (5)	0.016 (5)	0.000	0.000	0.000
Cl1	0.0298 (11)	0.0298 (11)	0.032 (6)	0.000	0.000	0.000
N2′	0.039 (5)	0.039 (5)	0.04 (2)	0.000	0.000	0.000
O1′	0.065 (4)	0.065 (4)	0.015 (5)	0.000	0.000	0.000
Cl1′	0.0354 (10)	0.0354 (10)	0.020 (5)	0.000	0.000	0.000
O1S	0.0723 (18)	0.0438 (14)	0.0861 (17)	0.0008 (13)	−0.0012 (11)	0.0023 (9)
C1S	0.0578 (19)	0.077 (2)	0.0693 (19)	0.0008 (16)	0.0034 (15)	−0.0246 (17)
C2S	0.0583 (19)	0.089 (2)	0.0504 (16)	0.0095 (16)	−0.0073 (13)	0.0021 (15)
C3S	0.060 (2)	0.0456 (19)	0.0643 (19)	0.0071 (17)	−0.0055 (12)	−0.0029 (11)
C4S	0.0531 (17)	0.0637 (19)	0.0480 (14)	−0.0037 (14)	−0.0013 (12)	0.0037 (12)

Geometric parameters (Å, º)

Os1—N2	1.780 (16)	C9—C12	1.507 (3)
Os1—N2′	1.81 (3)	C10—C11	1.390 (3)
Os1—N1^{i}	2.0622 (19)	C10—H10	0.9500
Os1—N1	2.0622 (19)	C11—H11	0.9500
Os1—Cl1	2.201 (8)	C12—H12A	0.9800
Os1—Cl1′	2.216 (8)	C12—H12B	0.9800
N1—C4	1.373 (3)	C12—H12C	0.9800
N1—C1	1.375 (3)	N2—O1	1.237 (16)
C1—C5	1.402 (3)	N2′—O1′	1.25 (2)

C1—C2	1.439 (3)	O1S—C1S	1.407 (4)
C2—C3	1.355 (4)	O1S—C4S	1.408 (4)
C2—H2	0.9500	C1S—C2S	1.488 (5)
C3—C4	1.444 (3)	C1S—H1SA	0.9900
C3—H3	0.9500	C1S—H1SB	0.9900
C4—C5^{i}	1.393 (3)	C2S—C3S	1.508 (4)
C5—C6	1.500 (3)	C2S—H2SA	0.9900
C6—C11	1.384 (3)	C2S—H2SB	0.9900
C6—C7	1.386 (3)	C3S—C4S	1.506 (4)
C7—C8	1.388 (3)	C3S—H3SA	0.9900
C7—H7	0.9500	C3S—H3SB	0.9900
C8—C9	1.389 (3)	C4S—H4SA	0.9900
C8—H8	0.9500	C4S—H4SB	0.9900
C9—C10	1.386 (3)		

N2—Os1—N1	90.17 (4)	C11—C10—H10	119.4
N2′—Os1—N1	89.83 (4)	C6—C11—C10	120.9 (2)
N1—Os1—N1^{ii}	90.0	C6—C11—H11	119.6
N2′—Os1—Cl1′	180.000 (5)	C10—C11—H11	119.6
N1—Os1—Cl1′	90.17 (4)	C9—C12—H12A	109.5
C4—N1—C1	107.95 (19)	C9—C12—H12B	109.5
C4—N1—Os1	126.07 (15)	H12A—C12—H12B	109.5
C1—N1—Os1	125.98 (15)	C9—C12—H12C	109.5
N1—C1—C5	126.0 (2)	H12A—C12—H12C	109.5
N1—C1—C2	108.4 (2)	H12B—C12—H12C	109.5
C5—C1—C2	125.6 (2)	O1—N2—Os1	180.000 (2)
C3—C2—C1	107.8 (2)	O1′—N2′—Os1	180.000 (4)
C3—C2—H2	126.1	C1S—O1S—C4S	109.3 (2)
C1—C2—H2	126.1	O1S—C1S—C2S	106.5 (2)
C2—C3—C4	107.2 (2)	O1S—C1S—H1SA	110.4
C2—C3—H3	126.4	C2S—C1S—H1SA	110.4
C4—C3—H3	126.4	O1S—C1S—H1SB	110.4
N1—C4—C5^{i}	126.2 (2)	C2S—C1S—H1SB	110.4
N1—C4—C3	108.6 (2)	H1SA—C1S—H1SB	108.6
C5^{i}—C4—C3	125.2 (2)	C1S—C2S—C3S	102.0 (3)
C4^{ii}—C5—C1	125.8 (2)	C1S—C2S—H2SA	111.4
C4^{ii}—C5—C6	117.5 (2)	C3S—C2S—H2SA	111.4
C1—C5—C6	116.7 (2)	C1S—C2S—H2SB	111.4
C11—C6—C7	118.2 (2)	C3S—C2S—H2SB	111.4
C11—C6—C5	121.33 (18)	H2SA—C2S—H2SB	109.2
C7—C6—C5	120.45 (18)	C4S—C3S—C2S	102.4 (3)
C6—C7—C8	120.84 (19)	C4S—C3S—H3SA	111.3
C6—C7—H7	119.6	C2S—C3S—H3SA	111.3
C8—C7—H7	119.6	C4S—C3S—H3SB	111.3
C7—C8—C9	121.17 (19)	C2S—C3S—H3SB	111.3
C7—C8—H8	119.4	H3SA—C3S—H3SB	109.2
C9—C8—H8	119.4	O1S—C4S—C3S	107.5 (2)
C10—C9—C8	117.7 (2)	O1S—C4S—H4SA	110.2

C10—C9—C12	121.40 (18)	C3S—C4S—H4SA	110.2
C8—C9—C12	120.91 (18)	O1S—C4S—H4SB	110.2
C9—C10—C11	121.2 (2)	C3S—C4S—H4SB	110.2
C9—C10—H10	119.4	H4SA—C4S—H4SB	108.5
N2—Os1—N1—C4	90.28 (13)	C2—C3—C4—C5^{i}	179.72 (17)
N2′—Os1—N1—C4	−89.72 (13)	N1—C1—C5—C4^{ii}	−0.5 (3)
N1^{i}—Os1—N1—C4	0.11 (17)	C2—C1—C5—C4^{ii}	179.04 (17)
N1^{ii}—Os1—N1—C4	−179.55 (11)	N1—C1—C5—C6	179.03 (15)
Cl1—Os1—N1—C4	−89.72 (13)	C2—C1—C5—C6	−1.4 (3)
Cl1′—Os1—N1—C4	90.28 (13)	C4^{ii}—C5—C6—C11	−73.1 (3)
N2—Os1—N1—C1	−90.17 (13)	C1—C5—C6—C11	107.3 (2)
N2′—Os1—N1—C1	89.83 (13)	C4^{ii}—C5—C6—C7	107.2 (2)
N1^{i}—Os1—N1—C1	179.66 (10)	C1—C5—C6—C7	−72.4 (3)
N1^{ii}—Os1—N1—C1	0.00 (16)	C11—C6—C7—C8	−0.6 (3)
Cl1—Os1—N1—C1	89.83 (13)	C5—C6—C7—C8	179.2 (2)
Cl1′—Os1—N1—C1	−90.17 (13)	C6—C7—C8—C9	−0.9 (3)
C4—N1—C1—C5	179.82 (16)	C7—C8—C9—C10	1.7 (3)
Os1—N1—C1—C5	0.2 (2)	C7—C8—C9—C12	−178.2 (2)
C4—N1—C1—C2	0.18 (19)	C8—C9—C10—C11	−0.9 (3)
Os1—N1—C1—C2	−179.44 (12)	C12—C9—C10—C11	178.9 (2)
N1—C1—C2—C3	−0.5 (2)	C7—C6—C11—C10	1.3 (3)
C5—C1—C2—C3	179.82 (17)	C5—C6—C11—C10	−178.5 (2)
C1—C2—C3—C4	0.6 (2)	C9—C10—C11—C6	−0.5 (4)
C1—N1—C4—C5^{i}	179.94 (16)	C4S—O1S—C1S—C2S	20.6 (4)
Os1—N1—C4—C5^{i}	−0.4 (2)	O1S—C1S—C2S—C3S	−33.6 (4)
C1—N1—C4—C3	0.22 (19)	C1S—C2S—C3S—C4S	32.9 (4)
Os1—N1—C4—C3	179.84 (11)	C1S—O1S—C4S—C3S	1.3 (4)
C2—C3—C4—N1	−0.6 (2)	C2S—C3S—C4S—O1S	−22.0 (4)

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