SUPPORTING INFORMATION

Fiber-optic Infrared Reflectance Spectroelectrochemical Studies of Osmium and Ruthenium Nitrosyl Porphyrins Containing Alkoxide and Thiolate Ligands

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1. Difference FTIR spectrum (Figure S1) showing formation of product from the first oxidation of (OEP)Ru(NO)(OEt) in CH_2Cl_2 containing 0.1 M NBu_4PF_6, with the potential held at +0.58 V vs. the $Cp_2Fe^{0/+}$ couple.

2. Low temperature (-78 °C) cyclic voltammogram of (OEP)Ru(NO)(SEt) in CH_2Cl_2 (Figure S2) containing 0.1 M NBu_4PF_6. Potentials are referenced to the $Cp_2Fe^{0/+}$ couple at $E°' = 0.00$ V). Scan rate of 200 mV/s.

3. Crystal structural information for (OEP)Os(NO)(OEt) and (OEP)Os(NO)(SEt).

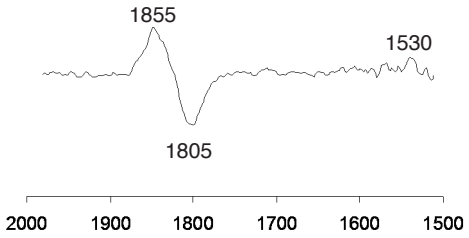

Figure S1

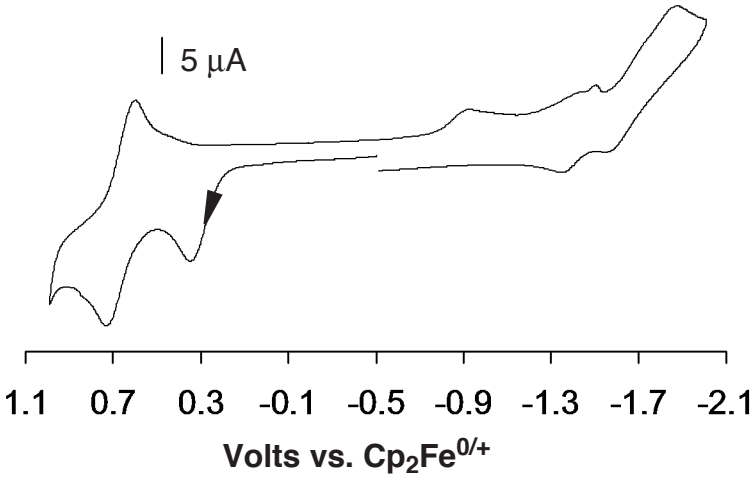

Figure S2

Table 1. Crystal data and structure refinement for (OEP)Os(NO)(OEt).

Identification code	CCDC 286639	
Empirical formula	C38 H49 N5 O2 Os	
Formula weight	798.02	
Temperature	153(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 8.6866(14) Å	□= 86.080(2)°.
	b = 10.0634(16) Å	□= 77.988(2)°.
	c = 11.0019(17) Å	□= 65.350(2)°.
Volume	854.8(2) $Å^3$	
Z	1	
Density (calculated)	1.550 Mg/m^3	
Absorption coefficient	3.771 mm^{-1}	
F(000)	404	
Crystal size	0.36 x 0.26 x 0.20 mm^3	
Theta range for data collection	2.63 to 26.50°.	
Index ranges	-10<=h<=10, -12<=k<=12, -13<=l<=13	
Reflections collected	8949	
Independent reflections	3514 [R(int) = 0.0301]	
Completeness to theta = 26.50°	99.1 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.5193 and 0.3438	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3514 / 49 / 251	
Goodness-of-fit on F^2	1.106	
Final R indices [I>2sigma(I)]	R1 = 0.0398, wR2 = 0.0966	
R indices (all data)	R1 = 0.0522, wR2 = 0.1039	
Largest diff. peak and hole	2.350 and -1.880 e.$Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for (OEP)Os(NO)(OEt). U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Os(1)	5000	5000	5000	54(1)
N(1)	3954(5)	3552(4)	5732(3)	48(1)
N(2)	3674(5)	5416(4)	3563(3)	50(1)
N(3)	2959(12)	6407(9)	5925(9)	44(2)
O(1)	1800(9)	7369(8)	6500(6)	58(2)
C(1)	4214(6)	2788(5)	6806(4)	51(1)
C(2)	3201(6)	1922(5)	6998(4)	54(1)
C(3)	2359(6)	2180(5)	6043(4)	53(1)
C(4)	2819(6)	3229(5)	5253(4)	49(1)
C(5)	2184(6)	3828(5)	4189(4)	49(1)
C(6)	2565(6)	4833(5)	3410(4)	46(1)
C(7)	1862(6)	5447(5)	2307(4)	54(1)
C(8)	2573(7)	6384(5)	1825(4)	58(1)
C(9)	3718(6)	6366(5)	2605(4)	51(1)
C(10)	4717(7)	7164(5)	2439(4)	56(1)
C(11)	3104(7)	967(6)	8103(5)	66(2)
C(12)	4635(9)	-506(7)	8008(8)	101(3)
C(13)	1234(7)	1498(6)	5766(5)	60(1)
C(14)	2218(8)	214(6)	4838(6)	72(2)
C(15)	620(7)	5033(6)	1831(5)	63(1)
C(16)	1537(8)	3665(8)	1004(7)	96(2)
C(17)	2052(13)	7312(11)	691(6)	57(3)
C(18)	3254(13)	6545(13)	-518(7)	73(3)
C(17')	2570(20)	7252(12)	621(9)	63(4)
C(18')	1608(16)	8903(10)	869(11)	73(4)
O(2)	6747(10)	3399(8)	4108(8)	44(2)
C(19)	7384(16)	3277(14)	2871(9)	71(3)
C(20)	9058(14)	1995(12)	2598(11)	64(3)

Table 3. Bond lengths [Å] and angles [°] for (OEP)Os(NO)(OEt).

Os(1)-O(2)#1	1.849(7)
Os(1)-O(2)	1.849(7)
Os(1)-N(3)#1	1.880(7)
Os(1)-N(3)	1.880(7)
Os(1)-N(1)#1	2.059(4)
Os(1)-N(1)	2.059(4)
Os(1)-N(2)	2.066(4)
Os(1)-N(2)#1	2.066(4)
N(1)-C(4)	1.364(7)
N(1)-C(1)	1.372(6)
N(2)-C(6)	1.361(7)
N(2)-C(9)	1.380(6)
N(3)-O(1)	1.165(9)
C(1)-C(10)#1	1.385(8)
C(1)-C(2)	1.454(8)
C(2)-C(3)	1.353(8)
C(2)-C(11)	1.508(7)
C(3)-C(4)	1.453(7)
C(3)-C(13)	1.494(8)
C(4)-C(5)	1.391(6)
C(5)-C(6)	1.381(7)
C(6)-C(7)	1.456(6)
C(7)-C(8)	1.354(8)
C(7)-C(15)	1.501(8)
C(8)-C(9)	1.436(8)
C(8)-C(17)	1.534(8)
C(8)-C(17')	1.535(9)
C(9)-C(10)	1.388(8)
C(10)-C(1)#1	1.385(8)
C(11)-C(12)	1.515(8)
C(13)-C(14)	1.529(7)
C(15)-C(16)	1.521(8)
C(17)-C(18)	1.532(11)
C(17')-C(18')	1.531(12)

O(2)-C(19)	1.351(12)
C(19)-C(20)	1.475(16)

O(2)#1-Os(1)-O(2)	180.000(1)
O(2)#1-Os(1)-N(3)#1	168.4(6)
O(2)-Os(1)-N(3)#1	11.6(6)
O(2)#1-Os(1)-N(3)	11.6(6)
O(2)-Os(1)-N(3)	168.4(6)
N(3)#1-Os(1)-N(3)	180.000(1)
O(2)#1-Os(1)-N(1)#1	85.2(3)
O(2)-Os(1)-N(1)#1	94.8(3)
N(3)#1-Os(1)-N(1)#1	84.1(3)
N(3)-Os(1)-N(1)#1	95.9(3)
O(2)#1-Os(1)-N(1)	94.8(3)
O(2)-Os(1)-N(1)	85.2(3)
N(3)#1-Os(1)-N(1)	95.9(3)
N(3)-Os(1)-N(1)	84.1(3)
N(1)#1-Os(1)-N(1)	180.000(1)
O(2)#1-Os(1)-N(2)	90.8(3)
O(2)-Os(1)-N(2)	89.2(3)
N(3)#1-Os(1)-N(2)	93.7(4)
N(3)-Os(1)-N(2)	86.3(4)
N(1)#1-Os(1)-N(2)	89.89(16)
N(1)-Os(1)-N(2)	90.11(16)
O(2)#1-Os(1)-N(2)#1	89.2(3)
O(2)-Os(1)-N(2)#1	90.8(3)
N(3)#1-Os(1)-N(2)#1	86.3(4)
N(3)-Os(1)-N(2)#1	93.7(4)
N(1)#1-Os(1)-N(2)#1	90.11(16)
N(1)-Os(1)-N(2)#1	89.89(16)
N(2)-Os(1)-N(2)#1	180.000(1)
C(4)-N(1)-C(1)	107.9(4)
C(4)-N(1)-Os(1)	125.6(3)
C(1)-N(1)-Os(1)	126.4(4)
C(6)-N(2)-C(9)	107.7(4)
C(6)-N(2)-Os(1)	126.2(3)

C(9)-N(2)-Os(1)	126.0(4)
O(1)-N(3)-Os(1)	172.4(10)
N(1)-C(1)-C(10)#1	125.0(5)
N(1)-C(1)-C(2)	108.5(5)
C(10)#1-C(1)-C(2)	126.6(4)
C(3)-C(2)-C(1)	107.6(4)
C(3)-C(2)-C(11)	128.0(5)
C(1)-C(2)-C(11)	124.4(5)
C(2)-C(3)-C(4)	106.8(5)
C(2)-C(3)-C(13)	128.7(5)
C(4)-C(3)-C(13)	124.4(5)
N(1)-C(4)-C(5)	125.3(4)
N(1)-C(4)-C(3)	109.2(4)
C(5)-C(4)-C(3)	125.5(5)
C(6)-C(5)-C(4)	128.0(5)
N(2)-C(6)-C(5)	124.8(4)
N(2)-C(6)-C(7)	108.7(4)
C(5)-C(6)-C(7)	126.5(5)
C(8)-C(7)-C(6)	107.1(5)
C(8)-C(7)-C(15)	129.1(5)
C(6)-C(7)-C(15)	123.8(5)
C(7)-C(8)-C(9)	107.5(4)
C(7)-C(8)-C(17)	122.0(7)
C(9)-C(8)-C(17)	130.4(7)
C(7)-C(8)-C(17')	134.8(9)
C(9)-C(8)-C(17')	117.2(9)
C(17)-C(8)-C(17')	15.8(9)
N(2)-C(9)-C(10)	124.7(5)
N(2)-C(9)-C(8)	108.9(5)
C(10)-C(9)-C(8)	126.4(4)
C(1)#1-C(10)-C(9)	127.9(4)
C(2)-C(11)-C(12)	113.9(5)
C(3)-C(13)-C(14)	112.5(4)
C(7)-C(15)-C(16)	112.2(4)
C(18)-C(17)-C(8)	111.3(6)
C(18')-C(17')-C(8)	112.0(7)

C(19)-O(2)-Os(1)	128.0(8)
O(2)-C(19)-C(20)	109.8(10)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y+1,-z+1

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for (OEP)Os(NO)(OEt). The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Os(1)	90(1)	35(1)	34(1)	11(1)	-22(1)	-21(1)
N(1)	67(2)	31(2)	31(2)	5(1)	-8(2)	-8(2)
N(2)	71(2)	34(2)	26(2)	4(1)	-6(2)	-4(2)
N(3)	64(3)	27(2)	36(2)	5(2)	-9(2)	-15(2)
O(1)	59(4)	51(4)	40(4)	2(3)	-7(3)	-1(3)
C(1)	67(3)	34(2)	31(2)	2(2)	0(2)	-6(2)
C(2)	65(3)	36(2)	40(2)	3(2)	3(2)	-6(2)
C(3)	63(3)	36(2)	40(2)	-1(2)	3(2)	-7(2)
C(4)	61(3)	30(2)	33(2)	-2(2)	2(2)	-2(2)
C(5)	59(2)	37(2)	37(2)	-3(2)	-8(2)	-9(2)
C(6)	56(2)	36(2)	32(2)	-3(2)	-6(2)	-6(2)
C(7)	61(3)	45(2)	34(2)	-1(2)	-8(2)	0(2)
C(8)	75(3)	48(3)	29(2)	3(2)	-9(2)	-6(2)
C(9)	69(3)	37(2)	31(2)	0(2)	-6(2)	-7(2)
C(10)	82(3)	38(2)	29(2)	10(2)	-9(2)	-10(2)
C(11)	70(3)	53(3)	55(3)	17(2)	2(2)	-15(2)
C(12)	84(4)	62(4)	112(6)	45(4)	15(4)	-9(3)
C(13)	67(3)	48(3)	48(3)	2(2)	5(2)	-17(2)
C(14)	84(3)	55(3)	70(4)	-9(3)	11(3)	-33(3)
C(15)	63(3)	60(3)	44(3)	3(2)	-18(2)	-2(2)
C(16)	77(3)	101(5)	88(4)	-38(4)	-47(3)	5(3)
C(17)	56(5)	68(5)	39(4)	10(4)	-14(3)	-17(4)
C(18)	76(5)	84(6)	45(5)	2(4)	-12(4)	-20(5)
C(17')	64(7)	78(6)	41(5)	30(5)	-23(4)	-22(5)
C(18')	60(6)	86(8)	61(7)	47(6)	-18(5)	-24(5)
O(2)	64(3)	27(2)	36(2)	5(2)	-9(2)	-15(2)
C(19)	88(7)	77(7)	47(6)	-6(5)	-1(5)	-39(6)
C(20)	71(6)	57(6)	58(6)	1(5)	5(5)	-30(5)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for (OEP)Os(NO)(OEt).

	x	y	z	U(eq)
H(5)	1391	3506	3970	58
H(10)	4660	7749	1720	67
H(11A)	2035	807	8197	79
H(11B)	3020	1490	8860	79
H(12A)	4522	-1040	8776	152
H(12B)	5704	-361	7883	152
H(12C)	4668	-1069	7303	152
H(13A)	266	2247	5424	71
H(13B)	737	1151	6549	71
H(14A)	1428	-194	4685	108
H(14B)	3161	-542	5180	108
H(14C)	2695	555	4056	108
H(15A)	-78	5854	1354	76
H(15B)	-179	4865	2545	76
H(16A)	680	3443	707	143
H(16B)	2199	2842	1480	143
H(16C)	2322	3829	291	143
H(17A)	849	7496	659	69
H(17B)	2096	8268	776	69
H(18A)	4458	6250	-446	109
H(18B)	2999	7216	-1210	109
H(18C)	3073	5677	-671	109
H(17C)	3783	7023	200	76
H(17D)	2026	6945	57	76
H(18D)	1432	9403	81	109
H(18E)	2288	9247	1268	109
H(18F)	485	9116	1418	109
H(19A)	7539	4173	2575	85
H(19B)	6559	3167	2429	85
H(20A)	9500	1898	1698	95

H(20B)	8902	1112	2902	95
H(20C)	9883	2123	3012	95

Table 6. Torsion angles [°] for (OEP)Os(NO)(OEt).

O(2)#1-Os(1)-N(1)-C(4)	89.9(4)
O(2)-Os(1)-N(1)-C(4)	-90.1(4)
N(3)#1-Os(1)-N(1)-C(4)	-94.7(5)
N(3)-Os(1)-N(1)-C(4)	85.3(5)
N(2)-Os(1)-N(1)-C(4)	-0.9(3)
N(2)#1-Os(1)-N(1)-C(4)	179.1(3)
O(2)#1-Os(1)-N(1)-C(1)	-87.4(4)
O(2)-Os(1)-N(1)-C(1)	92.6(4)
N(3)#1-Os(1)-N(1)-C(1)	88.1(5)
N(3)-Os(1)-N(1)-C(1)	-91.9(5)
N(2)-Os(1)-N(1)-C(1)	-178.1(3)
N(2)#1-Os(1)-N(1)-C(1)	1.9(3)
O(2)#1-Os(1)-N(2)-C(6)	-93.0(4)
O(2)-Os(1)-N(2)-C(6)	87.0(4)
N(3)#1-Os(1)-N(2)-C(6)	97.6(5)
N(3)-Os(1)-N(2)-C(6)	-82.4(5)
N(1)#1-Os(1)-N(2)-C(6)	-178.3(3)
N(1)-Os(1)-N(2)-C(6)	1.7(3)
O(2)#1-Os(1)-N(2)-C(9)	85.1(4)
O(2)-Os(1)-N(2)-C(9)	-94.9(4)
N(3)#1-Os(1)-N(2)-C(9)	-84.2(5)
N(3)-Os(1)-N(2)-C(9)	95.8(5)
N(1)#1-Os(1)-N(2)-C(9)	-0.1(3)
N(1)-Os(1)-N(2)-C(9)	179.9(3)
C(4)-N(1)-C(1)-C(10)#1	-179.8(4)
Os(1)-N(1)-C(1)-C(10)#1	-2.2(6)
C(4)-N(1)-C(1)-C(2)	0.9(5)
Os(1)-N(1)-C(1)-C(2)	178.5(3)
N(1)-C(1)-C(2)-C(3)	0.0(5)
C(10)#1-C(1)-C(2)-C(3)	-179.3(4)
N(1)-C(1)-C(2)-C(11)	-178.1(4)
C(10)#1-C(1)-C(2)-C(11)	2.6(7)
C(1)-C(2)-C(3)-C(4)	-0.9(5)
C(11)-C(2)-C(3)-C(4)	177.2(4)

C(1)-C(2)-C(3)-C(13)	176.2(4)
C(11)-C(2)-C(3)-C(13)	-5.8(8)
C(1)-N(1)-C(4)-C(5)	177.7(4)
Os(1)-N(1)-C(4)-C(5)	0.0(6)
C(1)-N(1)-C(4)-C(3)	-1.4(5)
Os(1)-N(1)-C(4)-C(3)	-179.0(3)
C(2)-C(3)-C(4)-N(1)	1.4(5)
C(13)-C(3)-C(4)-N(1)	-175.8(4)
C(2)-C(3)-C(4)-C(5)	-177.7(4)
C(13)-C(3)-C(4)-C(5)	5.1(7)
N(1)-C(4)-C(5)-C(6)	0.6(7)
C(3)-C(4)-C(5)-C(6)	179.5(4)
C(9)-N(2)-C(6)-C(5)	179.8(4)
Os(1)-N(2)-C(6)-C(5)	-1.8(6)
C(9)-N(2)-C(6)-C(7)	-0.4(5)
Os(1)-N(2)-C(6)-C(7)	178.1(3)
C(4)-C(5)-C(6)-N(2)	0.4(7)
C(4)-C(5)-C(6)-C(7)	-179.4(4)
N(2)-C(6)-C(7)-C(8)	0.1(5)
C(5)-C(6)-C(7)-C(8)	179.9(4)
N(2)-C(6)-C(7)-C(15)	178.6(4)
C(5)-C(6)-C(7)-C(15)	-1.5(7)
C(6)-C(7)-C(8)-C(9)	0.2(5)
C(15)-C(7)-C(8)-C(9)	-178.2(4)
C(6)-C(7)-C(8)-C(17)	-176.3(5)
C(15)-C(7)-C(8)-C(17)	5.2(8)
C(6)-C(7)-C(8)-C(17')	171.7(8)
C(15)-C(7)-C(8)-C(17')	-6.8(10)
C(6)-N(2)-C(9)-C(10)	-179.5(4)
Os(1)-N(2)-C(9)-C(10)	2.1(6)
C(6)-N(2)-C(9)-C(8)	0.5(5)
Os(1)-N(2)-C(9)-C(8)	-177.9(3)
C(7)-C(8)-C(9)-N(2)	-0.5(5)
C(17)-C(8)-C(9)-N(2)	175.7(5)
C(17')-C(8)-C(9)-N(2)	-173.7(6)
C(7)-C(8)-C(9)-C(10)	179.6(4)

C(17)-C(8)-C(9)-C(10)	-4.3(8)
C(17')-C(8)-C(9)-C(10)	6.4(8)
N(2)-C(9)-C(10)-C(1)#1	-2.4(8)
C(8)-C(9)-C(10)-C(1)#1	177.5(4)
C(3)-C(2)-C(11)-C(12)	102.1(7)
C(1)-C(2)-C(11)-C(12)	-80.2(8)
C(2)-C(3)-C(13)-C(14)	-95.7(6)
C(4)-C(3)-C(13)-C(14)	80.9(6)
C(8)-C(7)-C(15)-C(16)	93.4(7)
C(6)-C(7)-C(15)-C(16)	-84.8(6)
C(7)-C(8)-C(17)-C(18)	-93.2(10)
C(9)-C(8)-C(17)-C(18)	91.2(11)
C(17')-C(8)-C(17)-C(18)	54(3)
C(7)-C(8)-C(17')-C(18')	113.3(12)
C(9)-C(8)-C(17')-C(18')	-75.8(14)
C(17)-C(8)-C(17')-C(18')	73(3)
N(3)#1-Os(1)-O(2)-C(19)	-74(3)
N(3)-Os(1)-O(2)-C(19)	106(3)
N(1)#1-Os(1)-O(2)-C(19)	-51.0(11)
N(1)-Os(1)-O(2)-C(19)	129.0(11)
N(2)-Os(1)-O(2)-C(19)	38.8(11)
N(2)#1-Os(1)-O(2)-C(19)	-141.2(11)
Os(1)-O(2)-C(19)-C(20)	164.2(8)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y+1,-z+1

Table 1. Crystal data and structure refinement for (OEP)Os(NO)(SEt).0.5(CH_2Cl_2).

Empirical formula	(C_{38} H_{49} N_5 O Os S) · (C H_2 Cl_2)	
	$C_{38.5}$ H_{50} Cl N_5 O Os S	
Formula weight	856.55	
Crystal system	Monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 8.2803(10) Å	□= 90°
	b = 10.4219(13) Å	□= 91.823(3)°
	c = 22.157(3) Å	□= 90°
Volume	1911.1(4) Å^3	
Z, Z'	2, 0.5	
Density (calculated)	1.488 Mg/m^3	
Wavelength	0.71073 Å	
Temperature	100(2) K	
F(000)	866	
Absorption coefficient	3.497 mm^{-1}	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.8446 and 0.3282	
Theta range for data collection	2.60 to 30.00°	
Reflections collected	15569	
Independent reflections	5373 [R(int) = 0.0260]	
Data / restraints / parameters	5373 / 23 / 271	
wR(F^2 all data)	$wR2$ = 0.0798	
R(F obsd data)	$R1$ = 0.0370	
Goodness-of-fit on F^2	1.097	
Observed data [I > 2s(I)]	4902	
Largest and mean shift / s.u.	0.006and 0.000	
Largest diff. peak and hole	1.634 and -3.063 e/Å^3	

$wR2 = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \}^{1/2}$

$R1 = \sum ||F_o| - |F_c|| / \sum |F_o|$

Table 2. Atomic coordinates and equivalent isotropic displacement parameters for (OEP)Os(NO)(SEt).0.5(CH_2Cl_2). U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
Os(1)	0.5000	0.5000	0.5000	0.02841(6)
S(1)	0.6149(3)	0.6853(2)	0.52717(11)	0.0251(4)
N(1)	0.3444(3)	0.5175(2)	0.56956(12)	0.0227(5)
N(2)	0.3389(3)	0.5970(2)	0.44425(12)	0.0226(5)
N(3)	0.3742(13)	0.3461(9)	0.4827(5)	0.0251(4)
O(1)	0.2867(6)	0.2637(5)	0.4740(2)	0.0338(11)
C(1)	0.3687(4)	0.4714(3)	0.62684(14)	0.0214(6)
C(2)	0.2292(4)	0.4998(3)	0.66186(13)	0.0218(5)
C(3)	0.1224(4)	0.5641(3)	0.62472(14)	0.0225(6)
C(4)	0.1950(4)	0.5738(3)	0.56668(14)	0.0229(6)
C(5)	0.1250(4)	0.6296(3)	0.51551(14)	0.0245(6)
C(6)	0.1907(4)	0.6411(3)	0.45935(14)	0.0231(6)
C(7)	0.1133(4)	0.7015(3)	0.40729(14)	0.0227(6)
C(8)	0.2179(4)	0.6927(3)	0.36127(14)	0.0225(6)
C(9)	0.3602(4)	0.6260(3)	0.38477(14)	0.0224(6)
C(10)	0.4948(4)	0.5951(3)	0.35275(14)	0.0233(6)
C(11)	0.2091(4)	0.4646(3)	0.72668(14)	0.0238(6)
C(12)	0.2879(5)	0.5593(4)	0.77044(16)	0.0365(8)
C(13)	-0.0377(4)	0.6182(3)	0.63949(15)	0.0248(6)
C(14)	-0.0319(5)	0.7621(3)	0.65184(19)	0.0356(8)
C(15)	-0.0490(4)	0.7635(3)	0.40721(15)	0.0251(6)
C(16)	-0.0442(5)	0.8956(3)	0.43687(18)	0.0357(8)
C(17)	0.1948(4)	0.7423(3)	0.29837(15)	0.0261(6)
C(18)	0.2549(5)	0.8789(4)	0.29134(19)	0.0388(9)
C(19)	0.4726(12)	0.8033(10)	0.5470(7)	0.067(3)
C(20)	0.5467(16)	0.9266(13)	0.5765(7)	0.078(4)
Cl(1S)	0.408(3)	-0.069(2)	0.4926(11)	0.262(9)
C(1S)	0.493(4)	-0.028(3)	0.5617(10)	0.104(9)
Cl(2S)	0.4443(18)	-0.1346(17)	0.6174(7)	0.164(5)
Cl(1T)	0.5140(6)	0.1965(5)	0.3533(2)	0.0484(13)
C(1T)	0.586(5)	0.1044(18)	0.4127(14)	0.104(9)
Cl(2T)	0.5077(7)	-0.0482(6)	0.4168(3)	0.0609(16)

Table 3. Bond lengths [Å] and angles [°] for (OEP)Os(NO)(SEt).0.5(CH_2Cl_2).

Os(1)-N(3)	1.944(10)	C(12)-H(12C)	0.9800
Os(1)-N(1)	2.048(3)	C(13)-C(14)	1.525(5)
Os(1)-N(1)#1	2.048(3)	C(13)-H(13A)	0.9900
Os(1)-N(2)#1	2.054(2)	C(13)-H(13B)	0.9900
Os(1)-N(2)	2.054(2)	C(14)-H(14A)	0.9800
Os(1)-S(1)	2.227(2)	C(14)-H(14B)	0.9800
S(1)-C(19)	1.768(10)	C(14)-H(14C)	0.9800
N(1)-C(1)	1.366(4)	C(15)-C(16)	1.525(5)
N(1)-C(4)	1.369(4)	C(15)-H(15A)	0.9900
N(2)-C(6)	1.363(4)	C(15)-H(15B)	0.9900
N(2)-C(9)	1.369(4)	C(16)-H(16A)	0.9800
N(3)-O(1)	1.136(11)	C(16)-H(16B)	0.9800
C(1)-C(10)#1	1.389(4)	C(16)-H(16C)	0.9800
C(1)-C(2)	1.443(5)	C(17)-C(18)	1.518(5)
C(2)-C(3)	1.365(4)	C(17)-H(17A)	0.9900
C(2)-C(11)	1.497(4)	C(17)-H(17B)	0.9900
C(3)-C(4)	1.440(5)	C(18)-H(18A)	0.9800
C(3)-C(13)	1.486(5)	C(18)-H(18B)	0.9800
C(4)-C(5)	1.385(4)	C(18)-H(18C)	0.9800
C(5)-C(6)	1.379(5)	C(19)-C(20)	1.559(16)
C(5)-H(5)	0.9500	C(19)-H(19A)	0.9900
C(6)-C(7)	1.446(4)	C(19)-H(19B)	0.9900
C(7)-C(8)	1.362(5)	C(20)-H(20A)	0.9800
C(7)-C(15)	1.491(4)	C(20)-H(20B)	0.9800
C(8)-C(9)	1.451(4)	C(20)-H(20C)	0.9800
C(8)-C(17)	1.493(4)	Cl(1S)-C(1S)	1.719(3)
C(9)-C(10)	1.378(5)	C(1S)-Cl(2S)	1.720(3)
C(10)-C(1)#1	1.389(4)	C(1S)-H(1S1)	0.9900
C(10)-H(10)	0.9500	C(1S)-H(1S2)	0.9900
C(11)-C(12)	1.517(4)	Cl(1T)-C(1T)	1.721(3)
C(11)-H(11A)	0.9900	C(1T)-Cl(2T)	1.720(3)
C(11)-H(11B)	0.9900	C(1T)-H(1T1)	0.9900
C(12)-H(12A)	0.9800	C(1T)-H(1T2)	0.9900
C(12)-H(12B)	0.9800		

N(3)-Os(1)-N(1)	82.9(3)	N(1)-Os(1)-N(2)	89.82(10)
N(3)-Os(1)-N(1)#1	97.1(3)	N(1)#1-Os(1)-N(2)	90.18(10)
N(1)-Os(1)-N(1)#1	180.000(1)	N(2)#1-Os(1)-N(2)	180.00(12)
N(3)-Os(1)-N(2)#1	92.7(3)	N(3)-Os(1)-S(1)	172.0(3)
N(1)-Os(1)-N(2)#1	90.18(10)	N(1)-Os(1)-S(1)	89.58(10)
N(1)#1-Os(1)-N(2)#1	89.82(10)	N(1)#1-Os(1)-S(1)	90.42(10)
N(3)-Os(1)-N(2)	87.3(3)	N(2)#1-Os(1)-S(1)	90.02(10)

N(2)-Os(1)-S(1)	89.98(10)	C(11)-C(12)-H(12A)	109.5
C(19)-S(1)-Os(1)	112.8(4)	C(11)-C(12)-H(12B)	109.5
C(1)-N(1)-C(4)	107.5(3)	H(12A)-C(12)-H(12B)	109.5
C(1)-N(1)-Os(1)	126.2(2)	C(11)-C(12)-H(12C)	109.5
C(4)-N(1)-Os(1)	126.3(2)	H(12A)-C(12)-H(12C)	109.5
C(6)-N(2)-C(9)	107.8(3)	H(12B)-C(12)-H(12C)	109.5
C(6)-N(2)-Os(1)	126.2(2)	C(3)-C(13)-C(14)	112.9(3)
C(9)-N(2)-Os(1)	125.9(2)	C(3)-C(13)-H(13A)	109.0
O(1)-N(3)-Os(1)	172.7(8)	C(14)-C(13)-H(13A)	109.0
N(1)-C(1)-C(10)#1	124.9(3)	C(3)-C(13)-H(13B)	109.0
N(1)-C(1)-C(2)	109.3(3)	C(14)-C(13)-H(13B)	109.0
C(10)#1-C(1)-C(2)	125.8(3)	H(13A)-C(13)-H(13B)	107.8
C(3)-C(2)-C(1)	106.9(3)	C(13)-C(14)-H(14A)	109.5
C(3)-C(2)-C(11)	127.6(3)	C(13)-C(14)-H(14B)	109.5
C(1)-C(2)-C(11)	125.5(3)	H(14A)-C(14)-H(14B)	109.5
C(2)-C(3)-C(4)	106.9(3)	C(13)-C(14)-H(14C)	109.5
C(2)-C(3)-C(13)	128.2(3)	H(14A)-C(14)-H(14C)	109.5
C(4)-C(3)-C(13)	124.8(3)	H(14B)-C(14)-H(14C)	109.5
N(1)-C(4)-C(5)	124.9(3)	C(7)-C(15)-C(16)	112.3(3)
N(1)-C(4)-C(3)	109.3(3)	C(7)-C(15)-H(15A)	109.1
C(5)-C(4)-C(3)	125.7(3)	C(16)-C(15)-H(15A)	109.1
C(6)-C(5)-C(4)	127.5(3)	C(7)-C(15)-H(15B)	109.1
C(6)-C(5)-H(5)	116.3	C(16)-C(15)-H(15B)	109.1
C(4)-C(5)-H(5)	116.3	H(15A)-C(15)-H(15B)	107.9
N(2)-C(6)-C(5)	125.2(3)	C(15)-C(16)-H(16A)	109.5
N(2)-C(6)-C(7)	109.3(3)	C(15)-C(16)-H(16B)	109.4
C(5)-C(6)-C(7)	125.5(3)	H(16A)-C(16)-H(16B)	109.5
C(8)-C(7)-C(6)	107.0(3)	C(15)-C(16)-H(16C)	109.5
C(8)-C(7)-C(15)	128.5(3)	H(16A)-C(16)-H(16C)	109.5
C(6)-C(7)-C(15)	124.5(3)	H(16B)-C(16)-H(16C)	109.5
C(7)-C(8)-C(9)	107.0(3)	C(8)-C(17)-C(18)	112.8(3)
C(7)-C(8)-C(17)	127.6(3)	C(8)-C(17)-H(17A)	109.0
C(9)-C(8)-C(17)	125.4(3)	C(18)-C(17)-H(17A)	109.0
N(2)-C(9)-C(10)	125.1(3)	C(8)-C(17)-H(17B)	109.0
N(2)-C(9)-C(8)	108.9(3)	C(18)-C(17)-H(17B)	109.0
C(10)-C(9)-C(8)	126.0(3)	H(17A)-C(17)-H(17B)	107.8
C(9)-C(10)-C(1)#1	127.7(3)	C(17)-C(18)-H(18A)	109.5
C(9)-C(10)-H(10)	116.1	C(17)-C(18)-H(18B)	109.5
C(1)#1-C(10)-H(10)	116.1	H(18A)-C(18)-H(18B)	109.5
C(2)-C(11)-C(12)	113.3(3)	C(17)-C(18)-H(18C)	109.5
C(2)-C(11)-H(11A)	108.9	H(18A)-C(18)-H(18C)	109.5
C(12)-C(11)-H(11A)	108.9	H(18B)-C(18)-H(18C)	109.5
C(2)-C(11)-H(11B)	108.9	C(20)-C(19)-S(1)	114.9(8)
C(12)-C(11)-H(11B)	108.9	C(20)-C(19)-H(19A)	108.5
H(11A)-C(11)-H(11B)	107.7	S(1)-C(19)-H(19A)	108.5

C(20)-C(19)-H(19B)	108.5	Cl(2S)-C(1S)-H(1S1)	109.2
S(1)-C(19)-H(19B)	108.5	Cl(1S)-C(1S)-H(1S2)	109.2
H(19A)-C(19)-H(19B)	107.5	Cl(2S)-C(1S)-H(1S2)	109.2
C(19)-C(20)-H(20A)	111.6	H(1S1)-C(1S)-H(1S2)	107.9
C(19)-C(20)-H(20B)	107.7	Cl(2T)-C(1T)-Cl(1T)	115.7(6)
H(20A)-C(20)-H(20B)	109.5	Cl(2T)-C(1T)-H(1T1)	108.4
C(19)-C(20)-H(20C)	109.1	Cl(1T)-C(1T)-H(1T1)	108.4
H(20A)-C(20)-H(20C)	109.5	Cl(2T)-C(1T)-H(1T2)	108.3
H(20B)-C(20)-H(20C)	109.5	Cl(1T)-C(1T)-H(1T2)	108.3
Cl(1S)-C(1S)-Cl(2S)	112.2(17)	H(1T1)-C(1T)-H(1T2)	107.4
Cl(1S)-C(1S)-H(1S1)	109.2		

Symmetry transformations used to generate equivalent atoms:
#1 -x+1, -y+1, -z+1

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for (OEP)Os(NO)(SEt).0.5(CH_2Cl_2). The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Os(1)	43(1)	30(1)	12(1)	-1(1)	-4(1)	21(1)
S(1)	24(1)	28(1)	24(1)	-4(1)	-1(1)	1(1)
N(1)	32(1)	19(1)	16(1)	-1(1)	-7(1)	6(1)
N(2)	33(1)	20(1)	15(1)	-1(1)	-6(1)	4(1)
N(3)	24(1)	28(1)	24(1)	-4(1)	-1(1)	1(1)
O(1)	36(3)	32(3)	33(3)	-2(2)	-1(2)	-5(2)
C(1)	32(2)	17(1)	15(1)	-1(1)	-6(1)	-1(1)
C(2)	31(1)	18(1)	16(1)	-2(1)	-6(1)	-3(1)
C(3)	31(2)	18(1)	18(1)	-3(1)	-5(1)	1(1)
C(4)	32(2)	19(1)	18(1)	-3(1)	-5(1)	4(1)
C(5)	35(2)	21(1)	18(1)	-3(1)	-6(1)	6(1)
C(6)	35(2)	18(1)	16(1)	-1(1)	-8(1)	5(1)
C(7)	34(2)	16(1)	17(1)	0(1)	-9(1)	1(1)
C(8)	31(2)	17(1)	19(1)	1(1)	-8(1)	0(1)
C(9)	32(2)	19(1)	16(1)	1(1)	-9(1)	1(1)
C(10)	33(2)	20(1)	16(1)	2(1)	-8(1)	-1(1)
C(11)	32(2)	23(1)	17(1)	1(1)	-5(1)	-4(1)
C(12)	57(2)	33(2)	19(2)	-3(1)	-6(2)	-14(2)
C(13)	31(2)	23(1)	20(1)	0(1)	-4(1)	1(1)
C(14)	40(2)	26(2)	40(2)	-8(2)	3(2)	5(1)
C(15)	34(2)	21(1)	20(1)	0(1)	-8(1)	4(1)
C(16)	47(2)	22(2)	38(2)	-4(1)	-6(2)	8(1)
C(17)	30(2)	28(2)	21(1)	7(1)	-6(1)	1(1)
C(18)	41(2)	37(2)	39(2)	15(2)	2(2)	-6(2)
C(19)	45(5)	40(5)	117(11)	-20(6)	1(6)	1(4)
C(20)	71(7)	62(6)	99(8)	15(6)	-28(6)	-21(5)
Cl(1S)	260(13)	252(13)	277(14)	26(11)	41(10)	8(10)
Cl(2S)	138(8)	198(10)	158(9)	-32(8)	36(7)	15(8)
Cl(1T)	51(3)	49(3)	47(3)	-5(2)	7(2)	-4(2)
Cl(2T)	65(3)	69(4)	48(3)	0(3)	-7(2)	-17(3)

Table 5. Hydrogen coordinates and isotropic displacement parameters for (OEP)Os(NO)(SEt).0.5(CH_2Cl_2).

	x	y	z	U(eq)
H(5)	0.0195	0.6638	0.5196	0.029
H(10)	0.4941	0.6226	0.3119	0.028
H(11A)	0.2565	0.3786	0.7340	0.029
H(11B)	0.0923	0.4593	0.7347	0.029
H(12A)	0.2705	0.5314	0.8120	0.055
H(12B)	0.2400	0.6444	0.7641	0.055
H(12C)	0.4041	0.5634	0.7635	0.055
H(13A)	-0.0780	0.5737	0.6755	0.030
H(13B)	-0.1151	0.6015	0.6054	0.030
H(14A)	-0.1403	0.7928	0.6609	0.053
H(14B)	0.0067	0.8069	0.6162	0.053
H(14C)	0.0418	0.7791	0.6864	0.053
H(15A)	-0.1244	0.7077	0.4290	0.030
H(15B)	-0.0907	0.7721	0.3650	0.030
H(16A)	-0.1532	0.9322	0.4362	0.054
H(16B)	0.0278	0.9519	0.4147	0.054
H(16C)	-0.0039	0.8874	0.4788	0.054
H(17A)	0.0785	0.7389	0.2867	0.031
H(17B)	0.2531	0.6858	0.2705	0.031
H(18A)	0.2332	0.9078	0.2498	0.058
H(18B)	0.3714	0.8820	0.3004	0.058
H(18C)	0.1988	0.9352	0.3193	0.058
H(19A)	0.4094	0.8285	0.5102	0.081
H(19B)	0.3965	0.7647	0.5754	0.081
H(20A)	0.6576	0.9119	0.5918	0.116
H(20B)	0.4787	0.9509	0.6101	0.116
H(20C)	0.5461	0.9957	0.5465	0.116
H(1S1)	0.4544	0.0589	0.5728	0.125
H(1S2)	0.6116	-0.0240	0.5587	0.125
H(1T1)	0.7048	0.0977	0.4101	0.125
H(1T2)	0.5633	0.1497	0.4508	0.125

Table 6. Torsion angles [°] for (OEP)Os(NO)(SEt).0.5(CH_2Cl_2)

N(3)-Os(1)-S(1)-C(19)	-22(3)
N(1)-Os(1)-S(1)-C(19)	-41.9(6)
N(1)#1-Os(1)-S(1)-C(19)	138.1(6)
N(2)#1-Os(1)-S(1)-C(19)	-132.1(6)
N(2)-Os(1)-S(1)-C(19)	47.9(6)
N(3)-Os(1)-N(1)-C(1)	92.0(4)
N(1)#1-Os(1)-N(1)-C(1)	130(100)
N(2)#1-Os(1)-N(1)-C(1)	-0.7(3)
N(2)-Os(1)-N(1)-C(1)	179.3(3)
S(1)-Os(1)-N(1)-C(1)	-90.7(3)
N(3)-Os(1)-N(1)-C(4)	-85.7(4)
N(1)#1-Os(1)-N(1)-C(4)	-48(100)
N(2)#1-Os(1)-N(1)-C(4)	-178.3(3)
N(2)-Os(1)-N(1)-C(4)	1.7(3)
S(1)-Os(1)-N(1)-C(4)	91.6(3)
N(3)-Os(1)-N(2)-C(6)	81.0(4)
N(1)-Os(1)-N(2)-C(6)	-1.9(3)
N(1)#1-Os(1)-N(2)-C(6)	178.1(3)
N(2)#1-Os(1)-N(2)-C(6)	153(100)
S(1)-Os(1)-N(2)-C(6)	-91.5(3)
N(3)-Os(1)-N(2)-C(9)	-97.4(4)
N(1)-Os(1)-N(2)-C(9)	179.7(3)
N(1)#1-Os(1)-N(2)-C(9)	-0.3(3)
N(2)#1-Os(1)-N(2)-C(9)	-26(100)
S(1)-Os(1)-N(2)-C(9)	90.1(3)
N(1)-Os(1)-N(3)-O(1)	41(7)
N(1)#1-Os(1)-N(3)-O(1)	-139(7)
N(2)#1-Os(1)-N(3)-O(1)	130(7)
N(2)-Os(1)-N(3)-O(1)	-50(7)
S(1)-Os(1)-N(3)-O(1)	21(10)
C(4)-N(1)-C(1)-C(10)#1	178.4(3)
Os(1)-N(1)-C(1)-C(10)#1	0.4(4)
C(4)-N(1)-C(1)-C(2)	-0.2(3)
Os(1)-N(1)-C(1)-C(2)	-178.2(2)
N(1)-C(1)-C(2)-C(3)	-0.4(3)
C(10)#1-C(1)-C(2)-C(3)	-179.0(3)
N(1)-C(1)-C(2)-C(11)	179.8(3)
C(10)#1-C(1)-C(2)-C(11)	1.2(5)
C(1)-C(2)-C(3)-C(4)	0.8(3)
C(11)-C(2)-C(3)-C(4)	-179.4(3)
C(1)-C(2)-C(3)-C(13)	-178.0(3)
C(11)-C(2)-C(3)-C(13)	1.8(5)
C(1)-N(1)-C(4)-C(5)	-178.6(3)

Os(1)-N(1)-C(4)-C(5)	-0.6(5)
C(1)-N(1)-C(4)-C(3)	0.7(3)
Os(1)-N(1)-C(4)-C(3)	178.7(2)
C(2)-C(3)-C(4)-N(1)	-0.9(3)
C(13)-C(3)-C(4)-N(1)	177.9(3)
C(2)-C(3)-C(4)-C(5)	178.4(3)
C(13)-C(3)-C(4)-C(5)	-2.8(5)
N(1)-C(4)-C(5)-C(6)	-1.1(5)
C(3)-C(4)-C(5)-C(6)	179.7(3)
C(9)-N(2)-C(6)-C(5)	179.7(3)
Os(1)-N(2)-C(6)-C(5)	1.1(5)
C(9)-N(2)-C(6)-C(7)	-0.1(3)
Os(1)-N(2)-C(6)-C(7)	-178.7(2)
C(4)-C(5)-C(6)-N(2)	0.9(5)
C(4)-C(5)-C(6)-C(7)	-179.3(3)
N(2)-C(6)-C(7)-C(8)	-0.1(4)
C(5)-C(6)-C(7)-C(8)	-180.0(3)
N(2)-C(6)-C(7)-C(15)	-178.6(3)
C(5)-C(6)-C(7)-C(15)	1.5(5)
C(6)-C(7)-C(8)-C(9)	0.3(3)
C(15)-C(7)-C(8)-C(9)	178.7(3)
C(6)-C(7)-C(8)-C(17)	-179.1(3)
C(15)-C(7)-C(8)-C(17)	-0.7(5)
C(6)-N(2)-C(9)-C(10)	-179.1(3)
Os(1)-N(2)-C(9)-C(10)	-0.5(4)
C(6)-N(2)-C(9)-C(8)	0.3(3)
Os(1)-N(2)-C(9)-C(8)	178.9(2)
C(7)-C(8)-C(9)-N(2)	-0.4(3)
C(17)-C(8)-C(9)-N(2)	179.0(3)
C(7)-C(8)-C(9)-C(10)	179.0(3)
C(17)-C(8)-C(9)-C(10)	-1.6(5)
N(2)-C(9)-C(10)-C(1)#1	1.1(5)
C(8)-C(9)-C(10)-C(1)#1	-178.2(3)
C(3)-C(2)-C(11)-C(12)	-96.5(4)
C(1)-C(2)-C(11)-C(12)	83.3(4)
C(2)-C(3)-C(13)-C(14)	99.4(4)
C(4)-C(3)-C(13)-C(14)	-79.2(4)
C(8)-C(7)-C(15)-C(16)	-101.1(4)
C(6)-C(7)-C(15)-C(16)	77.1(4)
C(7)-C(8)-C(17)-C(18)	89.6(4)
C(9)-C(8)-C(17)-C(18)	-89.8(4)
Os(1)-S(1)-C(19)-C(20)	170.2(9)

Symmetry transformations used to generate equivalent atoms:
#1 -x+1, -y+1, -z+1