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Synthesis and Molecular Structures of the Redox Pair (Octaethylporphinato)bis(pentamethylene sulfide)osmium(II) and (Octaethylporphinato)bis(pentamethylene sulfide)osmium(III) Hexafluorophosphate

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We report the preparation, crystallization, and molecular structures of the redox pair (octaethylporphinato)bis(pentamethylene sulfide)osmium(II) and (octaethylporphinato)bis(pentamethylene sulfide)osmium(III) hexafluorophosphate. Both complexes have the osmium atom centered in the porphyrin plane with required inversion symmetry. The average $Os^{II}-N_p = 2.050(9)$ Å and the axial $Os^{II}-S$ distance is 2.352(2) Å. The average $Os^{III}-N_p$ is possibly shorter, at 2.046(2) Å, and the axial $Os^{III}-S$ distance is longer, at 2.382(2) Å. Crystal data for [Os(OEP)(PMS)$_2$]: $a = 10.540(6)$ Å, $b = 10.620(6)$ Å, $c = 11.001(4)$ Å, $\alpha = 99.21(3)°$, $\beta = 95.35(3)°$, $\gamma = 117.41(3)°$, triclinic, space group $P\bar{1}$, $V = 1059.3$ Å^3, $Z = 1$, unique observed data = 4895, $R_1 = 0.047$, $R_2 = 0.063$. Crystal data for [Os(OEP)(PMS)$_2$]PF$_6$: $a = 10.449(8)$ Å, $b = 11.161(7)$ Å, $c = 11.523(2)$ Å, $\alpha = 98.04(3)°$, $\beta = 104.63(2)°$, $\gamma = 111.93(7)°$, triclinic, space group $P\bar{1}$, $V = 1164.4$ Å^3, $Z = 1$, unique observed data = 5390, $R_1 = 0.036$, $R_2 = 0.047$.

Introduction

Our interest in the structural properties of d^5 and d^6 metalloporphyrin derivatives, coordinated by sulfur donors, was initially stimulated by the biological systems cytochrome P-450 and cytochrome *c*, where the sulfur ligand on iron is thiolate and thiaether, respectively. Our interest was further raised by the observation[2] that the Fe−S bond length in the bis-ligated thiaether derivatives of iron(II) and iron(III) porphyrinates was surprisingly insensitive to the change in oxidation state. Thus, the $Fe^{II}-S$ bond distance was 2.336(3) Å and $Fe^{III}-S$ was 2.341(16) Å. It was further noted[3] that the Fe−S bond length for all types of iron porphyrinate derivatives was surprisingly insensitive to change in the nature of the sulfur ligand or in the oxidation or spin state of iron. In this paper, we examine the structure of higher congeners of the iron thiaether derivatives, namely osmium(II) and -(III) octaethylporphyrinate derivatives.

Experimental Section

General Information. UV−vis spectra were recorded on a Perkin-Elmer Lambda 6 spectrometer. Chlorobenzene was purified by washing with sulfuric acid and then distilling over P$_2$O$_5$. Hexane was distilled from sodium/benzophenone and methylene chloride was distilled from CaH$_2$ and used immediately. Hydrazine hydrate, pentamethylene sulfide, and ammonium hexafluorophosphate were purchased from Aldrich and used without further purification.

Preparation of [Os(OEP)(PMS)$_2$].[4] All manipulations were carried out under argon using a double-manifold vacuum line, Schlenkware, and cannula techniques. [Os(OEP)(PMS)$_2$] was prepared by a slightly modified literature method.[5] To a boiling solution (~120 °C) of [Os(OEP)(O)$_2$][6] (10.0 mg, 0.013 mmol) in 10 mL of C$_6$H$_5$Cl were added a few drops of hydrazine hydrate. The color of the solution turned from olive-green to orange-red. At this point, 1.5 mL (0.145 mmol) of pentamethylene sulfide (PMS) was added. The material was dried under vacuum, and the red solid was dissolved in 5 mL of hot CH$_2$Cl$_2$. The solution was filtered, and the filtrate was layered with hexane and set aside for crystallization at room temperature. Small crystals were formed after 4−5 days. The resulting crystalline material was washed with several portions of pentane. X-ray-quality crystals were made by vapor diffusion of hexane into a methylene chloride solution of this material. Typical yields are about 70%. UV−vis in C$_6$H$_5$Cl: λ_{max} 392, 406, 588, 512 nm.

Preparation of [Os(OEP)(PMS)$_2$]PF$_6$. [Os(OEP)(PMS)$_2$] (20.0 mg, 0.022 mmol) was stirred under air for about 30 min in 10 mL of CH$_2$Cl$_2$. To this orange-red solution was added 24.6 mg (0.151 mmol) of ammonium hexafluorophosphate dissolved in the minimum amount (~1 mL) of distilled MeOH. There is only a slight color change, but the UV−vis spectrum shows an increase in the intensity of the 512 nm band. The reaction was judged complete when there was no further intensity increase in the 512 nm band (less than 1 h). The solution was layered with hexane and set aside for crystallization at room temperature. Typical yields are about 90%. X-ray-quality crystals were made by vapor diffusion of hexane into a methylene chloride solution of this preparation. UV−vis in CH$_2$Cl$_2$: λ_{max} 389, 484 (sh), 512 nm.

X-ray Diffraction Studies. Single crystals of [Os(OEP)(PMS)$_2$] and [Os(OEP)(PMS)$_2$]PF$_6$ were examined on an Enraf-Nonius FAST area detector diffractometer at the ambient laboratory temperature of 291 K. All measurements utilized graphite-monochromated Mo Kα radiation ($\bar{\lambda} = 0.710\,73$ Å). Unit cell parameters for these two derivatives are listed in Table 1. Data collection and reduction parameters were defined as before[7] and were chosen to ensure that a complete hemisphere (plus duplicates) of reciprocal space was explored. A summary of crystal data, intensity collection parameters, and refinement parameters for [Os(OEP)(PMS)$_2$] and [Os(OEP)(PMS)$_2$]PF$_6$ is reported in Table 1 and more completely in supplementary Table S1. Intensity data were corrected for absorption effects with a DIFABS correction procedure.[8]

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(4) Abbreviations used in this paper: OEP, octaethylporphyrin dianion; OEPMe$_2$, 5,15-dimethyl-2,3,7,8,13,14,17,18-octaethylporphodimethene dianion; TPP, 5,10,15,20-tetraphenylporphyrin dianion; PMS, pentamethylene sulfide; P(Ph)$_3$, triphenylphosphine; OP(Ph)$_3$, triphenylphosphine oxide; Et$_2$S, diethyl sulfide; Et$_2$SO, diethyl sulfoxide; [9]aneS$_3$, 1,4,7-trithiacyclononane; Et, ethyl; iPr, isopropyl; Ph, phenyl; N$_p$, porphinato nitrogen atom; Ct, center of the porphyrin ring.

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Table 1. Crystallographic Data for [Os(OEP)(PMS)$_2$] and [OS(OEP)(PMS)$_2$]PF$_6$

	[Os(OEP)(PMS)$_2$]	[Os(OEP)(PMS)$_2$]PF$_6$
formula	$OsS_2N_4C_{46}H_{64}$	$OsS_2PF_6N_4C_{46}H_{64}$
fw	927.37	1072.3
a, Å	10.540(6)	10.449(8)
b, Å	10.620(6)	11.161(7)
c, Å	11.001(4)	11.523(7)
α, deg	99.207(29)	98.039(28)
β, deg	95.35(3)	104.629(19)
γ, deg	117.413(26)	111.927(7)
V, Å^3	1059.3	1164.4
space group	$P\bar{1}$	$P\bar{1}$
crystal system	triclinic	triclinic
Z	1	1
μ, mm^{-1}	3.12	2.90
temp, K	291	291
R_1	4.7	3.6
R_2	6.3	4.7

The structures of the two complexes were solved in the centrosymmetric space group $P\bar{1}$ with the direct methods program MULTAN.[10] All subsequent developments of the structure solution and refinement were consistent with this centrosymmetric choice. The structure of each complex consists of a half-molecule in the asymmetric unit with the osmium atom located at an inversion center. After several cycles of least-squares refinement with isotropic temperature factors, difference Fourier syntheses led to the location of almost all hydrogen atoms. The hydrogen atom positions were idealized and included in subsequent cycles of least-squares as fixed contributors (C−H = 0.95 Å, $B(H) = B(C) \times 1.3$). Final cycles of full-matrix least-squares refinement used anisotropic temperature factors for all heavy atoms. For [Os(OEP)(PMS)$_2$] at convergence, $R_1 = 0.047$ and $R_2 = 0.063$, and the final data/variable ratio was 20.3. A final difference Fourier map was judged to be significantly free of features, with the largest peak having a height of 1.8 e/Å^3 at a distance 1.0 Å from the osmium(II) atom. Final atomic coordinates are listed in Table 2. For [Os(OEP)(PMS)$_2$]PF$_6$ the values of the unweighted and the weighted *R* factors were 0.036 and 0.047. The final data/variable ratio was 19.7. The largest electron density peak on the final difference Fourier map was 1.6 e/Å^3 at a distance 1.1 Å from the osmium(III) atom. The atomic coordinates of this complex are listed in Table 3. Anisotropic thermal parameters for all heavy atoms and the fixed hydrogen atom coordinates for both structures are available as supplementary material (Tables S2−S5).

Results

[Os(OEP)(PMS)$_2$] has been characterized by UV−vis spectroscopy and a single-crystal X-ray structure determination. The molecular structure is illustrated in Figure 1. Individual values of the bond distances and angles in the complex are given in supplementary Tables S6 and S7. Equatorial bond distances ($Os^{II}-N_p$) average to 2.050(9) Å. The axial $Os^{II}-S$ distance is 2.352(2) Å, and the values of the S−C distances of the pentamethylene sulfide (PMS) axial ligand are 1.794(8) and 1.793(10) Å. Averaged values of the bond distances and bond angles in the porphyrin core are shown in Figure 2. Also displayed in Figure 2 are the deviations (in units of 0.01 Å) of the crystallographically unique atoms from the mean plane of the 24-atom core. The deviations from planarity are unremarkable.

Table 2. Fractional Coordinates of [Os(OEP)(PMS)$_2$][a]

atom	*x*	*y*	*z*
Os	1.0000	1.0000	1.0000
S	1.20181(19)	1.04281(20)	1.14539(17)
N(1)	1.1168(6)	1.0565(6)	0.8597(5)
N(2)	1.0404(5)	1.2101(5)	1.0566(5)
C(a1)	1.1396(7)	0.9652(7)	0.7726(6)
C(a2)	1.1843(7)	1.1906(7)	0.8370(6)
C(a3)	1.1229(7)	1.3256(7)	1.0062(6)
C(a4)	0.9974(7)	1.2663(7)	1.1567(6)
C(b1)	1.2299(8)	1.0489(8)	0.6921(6)
C(b2)	1.2565(7)	1.1869(8)	0.7303(6)
C(b3)	1.1331(7)	1.4572(7)	1.0795(6)
C(b4)	1.0548(7)	1.4203(7)	1.1705(6)
C(m1)	1.1873(7)	1.3147(7)	0.9047(6)
C(m2)	0.9128(7)	1.1820(8)	1.2332(6)
C(11)	1.2768(11)	0.9868(9)	0.5842(8)
C(12)	1.1727(15)	0.9322(13)	0.4642(10)
C(21)	1.3375(9)	1.3138(8)	0.6737(7)
C(22)	1.2408(10)	1.3425(10)	0.5856(9)
C(31)	1.2183(8)	1.6073(7)	1.0564(7)
C(32)	1.3776(10)	1.6818(11)	1.1172(11)
C(41)	1.0357(9)	1.5180(8)	1.2733(7)
C(42)	1.1413(13)	1.5640(12)	1.3960(9)
C(1)	1.2905(9)	1.2268(10)	1.2369(8)
C(2)	1.4315(10)	1.2617(10)	1.3211(8)
C(3)	1.5417(9)	1.2559(11)	1.2466(9)
C(4)	1.4884(11)	1.1103(14)	1.1618(11)
C(5)	1.3494(10)	1.0605(12)	1.0677(9)

[a] The estimated standard deviations of the least significant digits are given in parentheses.

Table 3. Fractional Coordinates of [Os(OEP)(PMS)$_2$]PF$_6$[a]

atom	*x*	*y*	*z*
Os	1.0000	1.0000	1.0000
N(1)	1.0792(4)	0.8583(4)	1.0129(3)
N(2)	1.0882(4)	1.0457(4)	0.8637(3)
C(a1)	1.0632(5)	0.7758(4)	1.0925(4)
C(a2)	1.1597(5)	0.8274(5)	0.9466(4)
C(a3)	1.1689(5)	0.9907(5)	0.8186(4)
C(a4)	1.0849(5)	1.1442(5)	0.8058(4)
C(b1)	1.1375(5)	0.6927(5)	1.0758(4)
C(b2)	1.1969(5)	0.7231(5)	0.9857(4)
C(b3)	1.2191(6)	1.0576(5)	0.7295(5)
C(b4)	1.1670(5)	1.1527(5)	0.7217(5)
C(m1)	1.2000(5)	0.8884(5)	0.8562(5)
C(m2)	0.9868(5)	0.7757(5)	1.1750(5)
C(11)	1.1487(6)	0.5938(5)	1.1498(5)
C(12)	1.2723(8)	0.6599(8)	1.2737(7)
C(21)	1.2851(7)	0.6654(6)	0.9335(5)
C(22)	1.4472(8)	0.7457(10)	0.9961(8)
C(31)	1.3112(7)	1.0275(6)	0.6595(6)
C(32)	1.2237(10)	0.9341(8)	0.5335(7)
C(41)	1.1964(7)	1.2538(6)	0.6475(6)
C(42)	1.3256(9)	1.3837(7)	0.7191(8)
S	1.22427(13)	1.17321(12)	1.14034(11)
C(1)	1.1931(6)	1.2498(6)	1.2722(6)
C(2)	1.3399(7)	1.3478(6)	1.3700(6)
C(3)	1.4349(7)	1.2828(7)	1.4192(6)
C(4)	1.4723(7)	1.2117(7)	1.3204(7)
C(5)	1.3373(7)	1.1013(6)	1.2197(6)
P	1.0000	0.5000	0.5000
F(1)	0.9576(9)	0.6046(7)	0.5648(6)
F(2)	0.9972(7)	0.5644(6)	0.3865(5)
F(3)	0.8338(6)	0.4051(8)	0.4364(7)

[a] The estimated standard deviations of the least significant digits are given in parentheses.

The redox-related species [Os(OEP)(PMS)$_2$]PF$_6$ has been also characterized by UV−vis spectroscopy and a single-crystal X-ray structure determination. An ORTEP view of this complex is presented in Figure 3. Individual values of the bond distances

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(8) The process is based on an adaptation of the DIFABS[9] logic to area detector geometry by: Karaulov, A. I. Personal communication, School of Chemistry and Applied Chemistry, University of Wales, College of Cardiff, Cardiff CF1 3TB, U.K., 1993.

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(10) Programs used in this study included local modifications of Main, Hull, Lessinger, Germain, Declerq, and Woolfson's MULTAN, Jacobson's ALLS, Zalkin's FORDAP, Busing and Levy's ORFFE and ORFLS, and Johnson's ORTEP2. Atomic form factors were from: Cromer, D. T.; Mann, J. B. *Acta Crystallogr., Sect. A* **1968**, *A24*, 321. Real and imaginary corrections for anomalous dispersion in the form factor of the osmium and sulfur atoms were from: Cromer, D. T.; Liberman, D. J. *J. Chem. Phys.* **1970**, *53*, 1891. Scattering factors for hydrogen were from: Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175. All calculations were performed on VAXstation 4000−90 and VAXstation 4000-VLC computers.

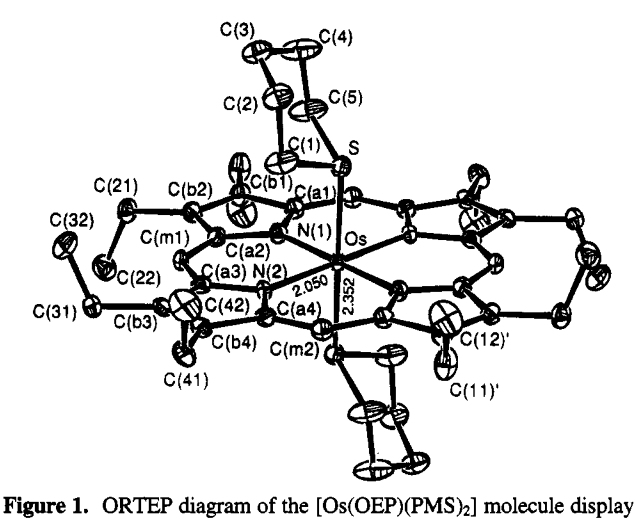

Figure 1. ORTEP diagram of the $[Os(OEP)(PMS)_2]$ molecule displaying the atom-labeling scheme used throughout the paper. Ellipsoids are contoured at the 30% probability level.

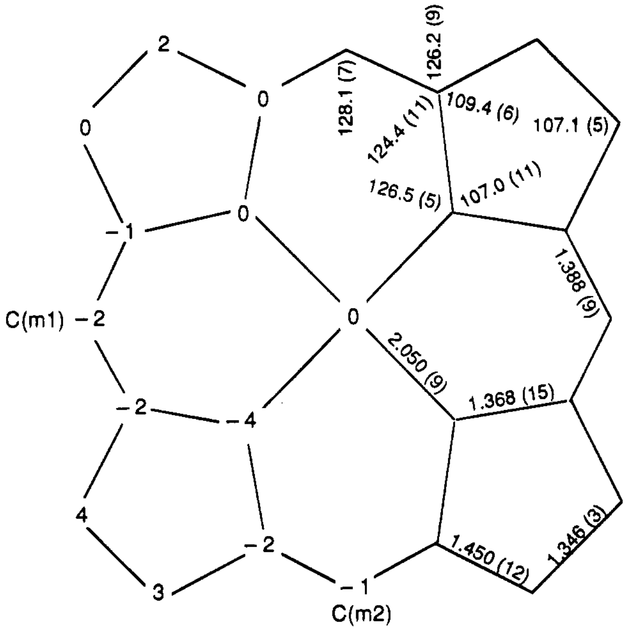

Figure 2. Formal diagram of the porphinato core in the $[Os(OEP)(PMS)_2]$ molecule displaying the displacement, in units of 0.01 Å, from the mean plane of the porphinato core. Also displayed in the figure are the average bond distances and angles for the chemically unique parameters of the core.

and angles in the complex are given in supplementary Tables S8 and S9. Equatorial bond distances ($Os^{III}-N_p$) average to 2.046(2) Å. The axial $Os^{III}-S$ distance is 2.382(2) Å, and the values of the S−C distances of the PMS axial ligand are both 1.800(6) Å. The averaged values of the bond distances and bond angles in the porphyrin core are shown in Figure 4. Also displayed in this figure are the deviations (in units of 0.01 Å) of the crystallographically unique atoms from the mean plane of the 24-atom core. Again deviations from planarity are unremarkable.

Discussion

Comparison of the averaged values of porphinato core bond distances and angles in the two $[Os(OEP)(PMS)_2]^{0/+}$ compounds that are displayed in Figures 2 and 4 shows that there is a strong congruence in the values and attests to comparable accuracy in the two determinations. Our ability to find almost all hydrogen atoms in the presence of the heavy central osmium atom also speaks to the quality of the X-ray data. It thus appears reasonable to search for differences in structural features that are concomitant with oxidation state change. It should also be noted that the structural features of both complexes are consistent with their formulation as low-spin d^5 or d^6 complexes.

There are only a limited number of osmium porphyrinate structures available for structural comparison. Most of these structures are for derivatives with osmium oxidation states higher than the osmium(II) and -(III) states dealt with herein. The average $Os^{II}-N_p$ distance of 2.050(9) Å found in $[Os(OEP)(PMS)_2]$ is similar to the corresponding distances found in $[Os(OEP)(OP(Ph)_3)_2]$ (2.029(8) Å) and $[Os(TPP)(P(Ph)_3)_2]$ (2.044(8) Å).[11] However, the corresponding distance in $[Os(OEPMe_2)(CO)(Py)]$ is possibly longer (2.067(3) Å).[12] The structure of the analogous TPP derivative, $[Os(TPP)(PMS)_2]$, has also been determined.[13] In that structure, the values $Os^{II}-N_p = 2.049(16)$ Å and $Os^{II}-S = 2.365$ Å are closely comparable to the present results.

To our knowledge, there are no reported structures for an osmium(III) porphyrin although Buchler et al.[14] have reported that osmium(II) derivatives are readily oxidized to osmium(III) compounds by dioxygen via an outer-sphere pathway. However, there are data for five osmium(IV) complexes which we quote for comparison with the parameters of $[Os^{III}(OEP)(PMS)_2]PF_6$ where the average $Os^{III}-N_p$ distance is 2.046(2) Å. The $Os^{IV}-N_p$ distance in the μ-oxo complex $[Os(OEP)(OCH_3)]_2O$ is 2.03(8) Å,[15] and the corresponding distance in $[Os(TPP)(SC_6F_4H)_2]$ is 2.049(11) Å.[16] More accurate distances are available for a series of osmium(IV) alkoxides, $[Os(TPP)(OR)_2]$: R = Et, 2.042(6) Å; R = iPr, 2.041(2) Å; R = Ph, 2.040(3) Å.[17] It is seen that, despite the large spread of $Os-N_p$ distances reported for compounds with the same oxidation state, the change in $Os-N_p$ distances follows the expected trend of decreasing distance with increasing formal oxidation state. This trend occurs for the two oxidation levels of $[Os(OEP)(PMS)_2]^{0/+}$, albeit not at a statistically significant level. The difference in the $Os^{II,III}-N_p$ bond distances would appear to be no larger than the 0.01 Å difference found for Fe(II/III) porphyrinate derivatives.[3] These $M-N_p$ bond distance differences must be primarily electrostatic in origin.

It should be noted that three osmium porphyrinates, all with formal oxidation states of +6, have longer $Os-N_p$ bond lengths that do not follow these trends. The average distances are 2.066(4) Å in $[Os(TPP)(O)_2]$,[18] 2.052(6) Å in $[Os(OEP)(O)_2]$,[6] and 2.06(2) Å in $[Os(TPP)(p\text{-}NC_6H_4NO_2)_2]$.[19] We presume that the high degree of covalency in these formally high-oxidation-state complexes leads to longer than expected $M-N_p$ distances. Such phenomena have been commented on previously in high-valent oxo and nitrido species.[20]

Unlike the sulfur-ligated iron(II/III) porphyrinates, differences do occur in the axial Os−S bond lengths with $Os^{II}-S = 2.352$-

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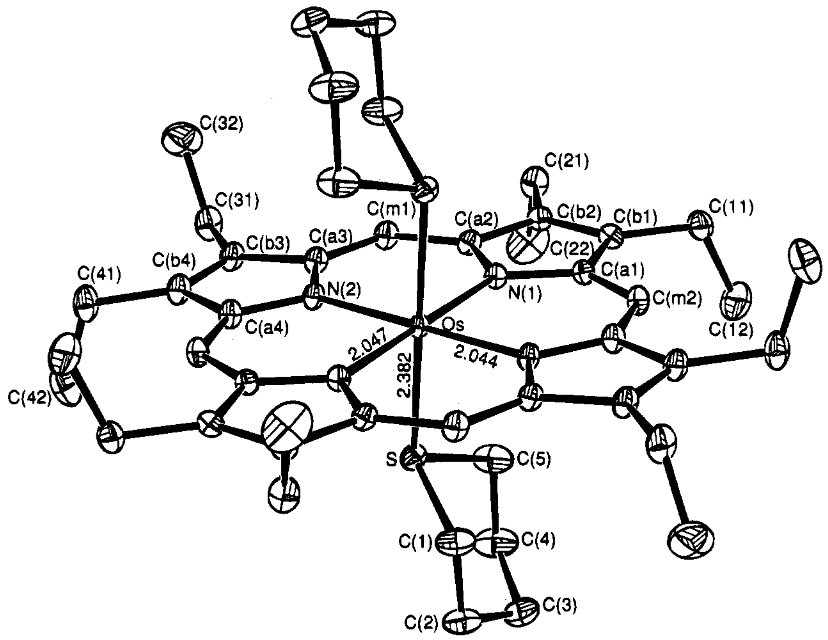

Figure 3. ORTEP diagram of the $[Os(OEP)(PMS)_2]PF_6$ molecule displaying the atom-labeling scheme used throughout the paper. Ellipsoids are contoured at the 30% probability level.

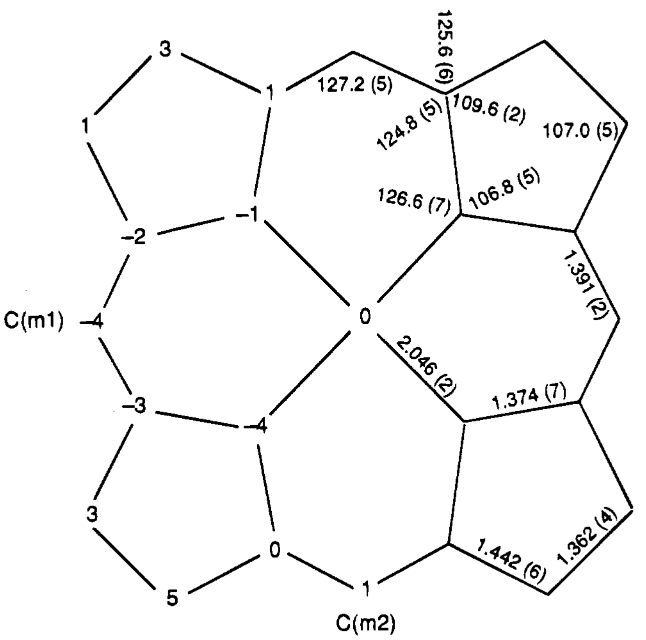

Figure 4. Formal diagram of the porphinato core in the $[Os(OEP)(PMS)_2]PF_6$ molecule displaying the displacement, in units of 0.01 Å, from the mean plane of the porphinato core. Also displayed in the figure are the average bond distances and angles for the chemically unique parameters of the core.

(2) Å and $Os^{III}-S$ = 2.382(2) Å. The 0.03 Å difference in bond lengths is a statistically significant difference. This suggests stronger π-bonding between Os^{II} and its axial ligands than occurs between Os^{III} and its axial ligands and is consistent with the greater π-donating capability of a low-spin d^6 compared to a low-spin d^5 electron configuration. Such differences in back-bonding have been previously noted in the isomeric osmium(II/III) complexes with OsS_4P_2 ligand sets,[21,22] where it was noted that π-bonding is much more important in the osmium(II) derivatives.

There are relatively few structures of osmium complexes with Os−S bonds to simple sulfur ligands. Bonds between osmium and thiolate sulfur are typically shorter[23] than the Os−thiaether sulfur distances found here. Almost all structurally characterized osmium complexes containing neutral sulfur donors are osmium(II) complexes. In these complexes the Os−S distances range from 2.321(1) Å in $[Os([9]aneS_3)_2]^{2+}$ derivatives[24] to 2.393(9) Å in $[Os(NO)Br_3(Et_2S)(Et_2SO)]$.[25] S-bound sulfoxides have also been reported;[26,27] Os−S distances are 2.324(2) and 2.351(2) Å. The variation in these Os−S distances is related, at least in part, to the presence of other π-accepting ligands in the coordination sphere.

In conclusion, structure determinations for $[Os(OEP)(PMS)_2]$ and $[Os(OEP)(PMS)_2]PF_6$ show the following structural differences that are oxidation-state-related: (i) a small (≤0.01 Å) increase in the $Os^{II}-N_p$ bond relative to $Os^{III}-N_p$; (ii) a larger (0.03 Å) difference in the axial Os−S bond with π-bonding favoring shorter Os(II) bonds relative to Os(III).

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Supplementary Material Available: Table S1, giving complete crystallographic details, Tables S2−S5, listing anisotropic temperature factors and fixed hydrogen atom coordinates, and Tables S6−S9, giving complete bond distances and angles for both complexes (9 pages). Ordering information is given on any current masthead page.

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