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The Crystal and Molecular Structure of Quadrivalent Osmium Porphyrin; μ-Oxo-bis[methoxo(octaethylporphinato)osmium(IV)]

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The crystal structure of the title complex has been determined by the X-ray method. The complex crystallizes in the monoclinic space group P2/c with a=24.171(9), b=14.037(3), c=24.401(9) Å, β=119.68(9)°, and Z=4. The structure was solved by the heavy-atom method and refined to R=0.094 for 3838 reflections. Two independent dimers exist with a crystallographically imposed two-fold axis in the unit cell. The two dimers are in an approximately orthogonal arrangement, and they take very similar conformations. The noticeable structural parameters are the average distances of 2.033(28) Å for Os^{IV}-N, 1.808(3) Å for Os^{IV}-O^{2-}, and 1.997(29) Å for Os^{IV}-OCH_3. The two porphinato cores bridged by a μ-oxo oxygen atom rotate around the approximately linear Os-O-Os bond (the average valence angle=178°) by 23(1)° from the eclipsed form. The porphine ring is planar within 0.10 Å, and deviation of the Os atom from the porphinato plane of the four nitrogen atoms is 0.06 Å. These results were compared, in the relation of the specific physicochemical properties in solution, with those of the corresponding Ru^{IV} complexes reported previously.

We have recently been studying the molecular and crystal structures of ruthenium(IV) porphyrins[1] as a model of quadrivalent iron porphyrins, which have received attention in relation to the structure of catalases, horseradish peroxidases, and cytochrome c peroxidases in the redox process.[2] In the recently established structures of the ruthenium(IV) porphyrins, the quadrivalent state of the metal ion was observed to be stabilized by the strong O^{2-} ligand in the axial direction, and such a structural aspect around the ruthenium(IV) ion gave a good assumption for the undetermined axial ligands around the iron(IV) ion in peroxidases. The quadrivalent osmium ion has the same number of outer-shell (d+s) electrons as the ruthenium(IV) ion, and it also forms iron(IV) porphyrin analogues. Several osmium(IV) porphyrin complexes have been obtained so far in similar reactions aimed at getting the ruthenium(IV) complexes;[1,3c] in those complexes the bivalent osmium porphyrins were oxidized to the quadrivalent state at the same time that the indole derivatives were oxidized by the molecular oxygen with the bivalent osmium porphyrins.[3] The physicochemical properties of the title complex in solution are very similar to those of the corresponding ruthenium(IV) complexes. The ^{1}H-NMR, absorption spectra, and cyclic voltammetry suggested that the osmium(IV) porphyrins formed a linear μ-oxo dimer structure as well as the ruthenium(IV) complexes. However, the osmium(IV) complex in an acid solution showed a slightly different behavior from the ruthenium(IV) complex. The μ-oxo oxygen atom had a high affinity for protons in the presence of a 1% acid such as CF_3COOH, HCl, and $HClO_4$.[3c] The cause of the high proton affinity might lie in the μ-oxo bridge structure of the osmium(IV) porphyrin dimer. A detailed comparison of the structure of the dimer with that of the ruthenium(IV) complex was of interest.

Experimental

Dark-violet plate-like crystals of the μ-oxo-bis[methoxo(octaethylporphinato)osmium(IV)] complex, $[Os^{IV}(oep)(OCH_3)]_2O$, obtained by the 2,3-dimethylindole treatment of $[Os^{II}(oep)(CO)(CH_3OH)]$ in dichloromethane,[3c] were subjected to X-ray experiments.

Crystal Data. $C_{74}H_{94}N_8O_3Os_2$, M=1522, monoclinic, space group P2/c, a=24.171(9), b=14.037(3), c=24.401(9) Å, β=119.68(9)°, U=7192(5) Å^3, Z=4, D_c=1.407 g cm^{-3}, D_m=1.40 g cm^{-3}, $F(000)$=3048, λ=0.71073 Å, μ(Mo $K\alpha$)=38.27 cm^{-1}.

The diffraction intensities were measured on a Rigaku AFC-5 diffractometer with graphite-monochromated Mo $K\alpha$ radiation. The intensity data of 4056 reflections in the $2\theta<50°$ range were collected in the ω–2θ scan mode with a scan rate of 5° min^{-1} and using a crystal with dimensions of 0.5×0.5×0.3 mm. During the course of the data collection, three reflections were monitored every 60 reflections. The intensity data were converted to the F_o data in the usual manner. Absorption correction was applied in the spherical approximation. The standard deviations $\sigma(F_o)$ were estimated by means of the counting statistics. A total of 3838 independent reflections with $F_o>3\sigma(F_o)$ were retained as observed, and used in solving and refining the structure.

The structure was solved by the heavy-atom method. The four osmium atoms were located by a sharpened Patterson synthesis. Although the systematic absences of $h0l$ for $l=2n+1$ led to two possible space groups, Pc and P2/c, the configuration was tentatively assumed to be the space group P2/c; the successive Fourier syntheses revealed the approximate structure. The block-diagonal least-squares refinement to examine the two possible space groups, P2/c and Pc, resulted in the rejection of the latter space group Pc, because it gave several abnormal bond distances and angles, and also gave non-positive temperature factors for some light atoms. Thus, a trial structure based on the space group P2/c was chosen for the further refinement. Several cycles of the block-diagonal least-squares refinement including the anisotropic thermal parameters were carried out with the weighting scheme of $w^{-1}=(\sigma^2(F_o)+(0.023F_o)^2)$. The atomic scattering factors[4a] and the anomalous dispersion terms[4b] were taken from the International Tables for X-Ray Crystallography, IV. The hydrogen atoms were included as a fixed contribution in the last cycle; their positions were assumed to be in accord with the idealized geometry (C–H=1.00 Å), and their temperature factors were assumed to be isotropic (B=8.00 Å^2). The final R value was 0.094. The final difference Fourier map showed no peak greater than 0.6 e/Å^3; most of the largest peaks were around the osmium atoms. All the computations

were performed on a FACOM M-200 computer at the Data Processing Center of Kyoto University by using the program system KPAX. The positional parameters of the non-hydrogen atoms are given in Table 1.[5]

Results and Discussion

The unit cell is comprised of four discrete μ-oxo dimers of $[Os^{IV}(oep)(OCH_3)]_2O$ (see Fig. 1). There are two independent dimers, A and B, which take an

Table 1. Fractional coordinates ($\times 10^4$) and isotropic thermal parameters, with estimated standard deviations in parentheses

Atom[a]	x	y	z	B_{eq}/Å^2 [b]	Atom[a]	x	y	z	B_{eq}/Å^2 [b]
Os(A)	569(1)	440(1)	2224(1)	5.39	C(31A)	−8(26)	−3445(40)	1480(21)	16.5
Os(B)	4402(1)	3807(1)	1673(1)	4.92	C(32A)	258(28)	−3687(40)	1071(29)	17.1
N(1A)	965(12)	1627(19)	2729(12)	5.43	C(33A)	1963(20)	−2687(29)	3803(22)	9.84
N(2A)	−21(11)	1280(20)	1462(11)	5.47	C(34A)	2399(21)	−3011(33)	3544(25)	11.4
N(3A)	204(14)	−690(19)	1695(15)	7.31	C(35A)	2496(26)	−760(31)	4680(26)	13.1
N(4A)	1177(11)	−336(17)	2948(13)	4.57	C(36A)	3123(27)	−600(47)	4646(30)	18.5
N(1B)	3797(13)	3074(20)	1806(14)	6.34	C(37A)	1119(25)	647(40)	1355(30)	15.7
N(2B)	4799(11)	2592(18)	1548(11)	4.33	C(1B)	3345(15)	3378(23)	1977(15)	4.89
N(3B)	5006(11)	4551(19)	1439(12)	5.12	C(2B)	2986(18)	2563(27)	2070(19)	7.78
N(4B)	3938(13)	5068(20)	1769(16)	7.43	C(3B)	3243(18)	1807(27)	1974(19)	7.43
O(1A)	0	411(20)	2500	5.73	C(4B)	3785(14)	2005(25)	1858(15)	5.25
O(1B)	5000	3801(25)	2500	7.48	C(5B)	4120(17)	1422(32)	1730(21)	8.90
O(2A)	1241(14)	437(20)	1964(12)	9.06	C(6B)	4603(18)	1653(28)	1577(17)	7.40
O(2B)	3723(11)	3853(19)	778(10)	6.90	C(7B)	4967(20)	1035(25)	1457(20)	7.64
C(1A)	1507(19)	1606(22)	3356(17)	6.17	C(8B)	5379(20)	1504(28)	1356(24)	9.56
C(2A)	1607(18)	2647(28)	3505(18)	7.10	C(9B)	5252(18)	2530(26)	1382(17)	7.13
C(3A)	1200(18)	3260(28)	3013(17)	7.18	C(10B)	5575(19)	3299(24)	1281(18)	6.63
C(4A)	790(15)	2505(31)	2509(17)	7.83	C(11B)	5450(14)	4223(21)	1307(14)	3.75
C(5A)	309(14)	2839(26)	1917(16)	5.35	C(12B)	5809(19)	5020(26)	1232(21)	8.55
C(6A)	−60(16)	2281(22)	1446(15)	5.42	C(13B)	5477(16)	5819(24)	1270(19)	6.11
C(7A)	−545(17)	2584(28)	803(18)	6.98	C(14B)	4998(19)	5596(26)	1438(18)	7.74
C(8A)	−852(19)	1788(29)	470(20)	8.66	C(15B)	4635(19)	6179(27)	1563(18)	7.21
C(9A)	−489(18)	995(28)	885(17)	7.29	C(16B)	4195(13)	5926(22)	1709(14)	4.46
C(10A)	−618(20)	4(32)	757(19)	10.0	C(17B)	3741(17)	6549(27)	1806(20)	7.72
C(11A)	−291(20)	−860(26)	1117(19)	8.08	C(18B)	3340(18)	6080(26)	1941(17)	7.24
C(12A)	−454(19)	−1813(31)	900(18)	8.79	C(19B)	3533(14)	5101(22)	1919(17)	4.94
C(13A)	8(15)	−2318(32)	1386(18)	9.28	C(20B)	3268(16)	4368(19)	2065(15)	4.87
C(14A)	307(17)	−1598(29)	1842(18)	8.26	C(21B)	2519(18)	2629(34)	2422(25)	11.5
C(15A)	805(16)	−1937(22)	2422(17)	5.63	C(22B)	1972(22)	2901(36)	1817(24)	11.8
C(16A)	1239(15)	−1266(28)	2999(15)	6.45	C(23B)	3080(20)	779(29)	1992(19)	8.12
C(17A)	1748(19)	−1680(27)	3580(18)	7.67	C(24B)	2629(25)	388(37)	1313(25)	12.9
C(18A)	1992(17)	−935(26)	3908(17)	6.43	C(25B)	5068(25)	−60(36)	1645(25)	12.5
C(19A)	1657(15)	−86(26)	3541(14)	5.84	C(26B)	4705(33)	−401(53)	1117(26)	19.7
C(20A)	1801(18)	853(22)	3725(17)	6.39	C(27B)	5992(26)	1171(34)	1284(21)	11.6
C(21A)	2143(17)	2965(25)	4199(17)	6.12	C(28B)	5740(27)	1136(43)	693(27)	15.8
C(22A)	2765(24)	2976(35)	4248(22)	11.8	C(29B)	6247(16)	4934(26)	1039(16)	5.91
C(23A)	1172(24)	4357(40)	3010(25)	13.2	C(30B)	5968(18)	4833(27)	332(19)	8.02
C(24A)	1510(31)	4725(37)	2702(27)	16.0	C(31B)	5754(18)	6878(31)	1355(19)	8.30
C(25A)	−736(22)	3612(30)	593(17)	9.23	C(32B)	5355(21)	7204(33)	716(24)	10.7
C(26A)	−325(28)	3993(26)	375(25)	12.4	C(33B)	3799(19)	7714(26)	1790(20)	8.31
C(27A)	−1385(21)	1689(30)	−198(19)	9.32	C(34B)	3436(22)	7988(35)	1089(27)	12.9
C(28A)	−1157(24)	1505(42)	−650(23)	15.2	C(35B)	2822(20)	6390(30)	2123(24)	10.1
C(29A)	−1002(25)	−2213(39)	265(22)	13.4	C(36B)	2209(21)	6232(37)	1573(23)	11.0
C(30A)	−686(26)	−2090(43)	−43(29)	17.3	C(37B)	3502(39)	3047(52)	361(29)	19.1

a) Symbols A and B in parentheses identify the atoms corresponding to the moieties (a) and (b) given in Fig. 2.
b) The equivalent isotropic temperature factors for non-hydrogen atoms were computed using the following expression: $B_{eq}=4/3(B_{11}a^2+B_{22}b^2+B_{33}c^2+2B_{12}ab\cos\gamma+2B_{13}ac\cos\beta+2B_{23}bc\cos\alpha)$. The B_{ij}'s are defined by: $\exp[-(h^2B_{11}+k^2B_{22}+l^2B_{33}+2hlB_{23}+2hlB_{13}+2hkB_{12})]$.

TABLE 2. BOND DISTANCES (l/Å) AND BOND ANGLES (ϕ/°), WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

(a) The coordination sphere of the osmium atom			
Os(A)-N(1A)	2.011(25)	Os(B)-N(1B)	1.942(35)
Os(A)-N(2A)	2.063(23)	Os(B)-N(2B)	2.052(27)
Os(A)-N(3A)	1.958(27)	Os(B)-N(3B)	2.091(32)
Os(A)-N(4A)	1.974(23)	Os(B)-N(4B)	2.169(33)
Os(A)-O(1A)	1.807(3)	Os(B)-O(1B)	1.809(3)
Os(A)-O(2A)	2.015(39)	Os(B)-O(2B)	1.979(19)
N(1A)-Os(A)-N(2A)	89.2(10)	N(1B)-Os(B)-N(2B)	91.8(12)
N(1A)-Os(A)-N(3A)	176.2(16)	N(1B)-Os(B)-N(3B)	174.4(11)
N(1A)-Os(A)-N(4A)	89.5(10)	N(1B)-Os(B)-N(4B)	95.2(12)
N(2A)-Os(A)-N(3A)	89.1(11)	N(2B)-Os(B)-N(3B)	86.2(11)
N(2A)-Os(A)-N(4A)	176.6(12)	N(2B)-Os(B)-N(4B)	177.2(7)
N(3A)-Os(A)-N(4A)	92.0(10)	N(3B)-Os(B)-N(4B)	95.2(12)
O(1A)-Os(A)-N(1A)	90.5(12)	O(1B)-Os(B)-N(1B)	93.6(9)
O(1A)-Os(A)-N(2A)	92.0(10)	O(1B)-Os(B)-N(2B)	89.3(10)
O(1A)-Os(A)-N(3A)	92.9(14)	O(1B)-Os(B)-N(3B)	91.5(8)
O(1A)-Os(A)-N(4A)	91.2(11)	O(1B)-Os(B)-N(4B)	93.1(12)
O(2A)-Os(A)-N(1A)	88.9(12)	O(2B)-Os(B)-N(1B)	85.4(11)
O(2A)-Os(A)-N(2A)	91.4(11)	O(2B)-Os(B)-N(2B)	93.2(10)
O(2A)-Os(A)-N(3A)	87.8(14)	O(2B)-Os(B)-N(3B)	89.5(10)
O(2A)-Os(A)-N(4A)	91.2(11)	O(2B)-Os(B)-N(4B)	84.4(11)
O(1A)-Os(A)-O(2A)	176.7(7)	O(1B)-Os(B)-O(2B)	177.3(11)
(b) The axial and equatorial ligands			
O(2A)-C(37A)	1.40(8)	O(2B)-C(37B)	1.44(7)
N(1A)-C(1A)	1.44(3)	N(1B)-C(1B)	1.42(5)
N(1A)-C(4A)	1.33(4)	N(1B)-C(4B)	1.51(4)
N(2A)-C(6A)	1.41(4)	N(2B)-C(6B)	1.41(4)
N(2A)-C(9A)	1.36(3)	N(2B)-C(9B)	1.35(6)
N(3A)-C(11A)	1.34(4)	N(3B)-C(11B)	1.35(5)
N(3A)-C(14A)	1.31(4)	N(3B)-C(14B)	1.47(4)
N(4A)-C(16A)	1.31(4)	N(4B)-C(16B)	1.40(4)
N(4A)-C(19A)	1.38(3)	N(4B)-C(19B)	1.20(6)
C(1A)-C(2A)	1.50(5)	C(1B)-C(2B)	1.52(5)
C(3A)-C(4A)	1.55(5)	C(3B)-C(4B)	1.50(6)
C(6A)-C(7A)	1.48(4)	C(6B)-C(7B)	1.37(6)
C(8A)-C(9A)	1.47(5)	C(8B)-C(9B)	1.48(5)
C(11A)-C(12A)	1.42(5)	C(11B)-C(12B)	1.48(5)
C(13A)-C(14A)	1.41(5)	C(13B)-C(14B)	1.44(7)
C(16A)-C(17A)	1.46(4)	C(16B)-C(17B)	1.51(5)
C(18A)-C(19A)	1.47(4)	C(18B)-C(19B)	1.46(5)
C(2A)-C(3A)	1.55(5)	C(2B)-C(3B)	1.31(6)
C(7A)-C(8A)	1.37(5)	C(7B)-C(8B)	1.32(7)
C(12A)-C(13A)	1.36(5)	C(12B)-C(13B)	1.41(5)
C(17A)-C(18A)	1.27(5)	C(17B)-C(18B)	1.34(6)
C(5A)-C(4A)	1.41(4)	C(5B)-C(4B)	1.29(6)
C(5A)-C(6A)	1.31(4)	C(5B)-C(6B)	1.43(7)
C(10A)-C(9A)	1.43(5)	C(10B)-C(9B)	1.42(6)
C(10A)-C(11A)	1.48(5)	C(10B)-C(11B)	1.34(4)
C(15A)-C(14A)	1.41(4)	C(15B)-C(14B)	1.34(6)
C(15A)-C(16A)	1.58(4)	C(15B)-C(16B)	1.33(6)
C(20A)-C(1A)	1.34(4)	C(20B)-C(1B)	1.43(4)
C(20A)-C(19A)	1.38(4)	C(20B)-C(19B)	1.35(5)
C(2A)-C(21A)	1.60(4)	C(2B)-C(21B)	1.73(8)
C(3A)-C(23A)	1.54(6)	C(3B)-C(23B)	1.50(5)
C(7A)-C(25A)	1.52(5)	C(7B)-C(25B)	1.59(6)
C(8A)-C(27A)	1.50(5)	C(8B)-C(27B)	1.64(8)

TABLE 2. (Continued)

C(12A)-C(29A)	1.56(5)	C(12B)-C(29B)	1.36(7)
C(13A)-C(31A)	1.60(7)	C(13B)-C(31B)	1.60(5)
C(17A)-C(33A)	1.51(5)	C(17B)-C(33B)	1.64(5)
C(18A)-C(35A)	1.68(6)	C(18B)-C(35B)	1.58(7)
C(21A)-C(22A)	1.45(7)	C(21B)-C(22B)	1.46(5)
C(23A)-C(24A)	1.45(9)	C(23B)-C(24B)	1.56(6)
C(25A)-C(26A)	1.44(9)	C(25B)-C(26B)	1.24(7)
C(27A)-C(28A)	1.48(8)	C(27B)-C(28B)	1.26(7)
C(29A)-C(30A)	1.32(9)	C(29B)-C(30B)	1.52(5)
C(31A)-C(32A)	1.47(9)	C(31B)-C(32B)	1.44(6)
C(33A)-C(34A)	1.54(8)	C(33B)-C(34B)	1.54(7)
C(35A)-C(36A)	1.57(9)	C(35B)-C(36B)	1.44(5)
Os(A)-O(1A)-Os(A)*	177.4(17)	Os(B)-O(1B)-Os(B)*	179.5(11)
Os(A)-O(2A)-C(37A)	124(2)	Os(B)-O(2B)-C(37B)	125(3)
Os(A)-N(1A)-C(1A)	123(2)	Os(B)-N(1B)-C(1B)	130(2)
Os(A)-N(1A)-C(4A)	124(2)	Os(B)-N(1B)-C(4B)	126(2)
Os(A)-N(2A)-C(6A)	127(1)	Os(B)-N(2B)-C(6B)	125(2)
Os(A)-N(2A)-C(9A)	128(2)	Os(B)-N(2B)-C(9B)	128(2)
Os(A)-N(3A)-C(11A)	135(2)	Os(B)-N(3B)-C(11B)	130(2)
Os(A)-N(3A)-C(14A)	130(2)	Os(B)-N(3B)-C(14B)	119(2)
Os(A)-N(4A)-C(16A)	129(1)	Os(B)-N(4B)-C(16B)	114(2)
Os(A)-N(4A)-C(19A)	132(2)	Os(B)-N(4B)-C(19B)	127(2)
C(1A)-N(1A)-C(4A)	113(2)	C(1B)-N(1B)-C(4B)	103(3)
C(6A)-N(2A)-C(9A)	105(2)	C(6B)-N(2B)-C(9B)	107(3)
C(11A)-N(3A)-C(14A)	94(2)	C(11B)-N(3B)-C(14B)	111(3)
C(16A)-N(4A)-C(19A)	99(2)	C(16B)-N(4B)-C(19B)	118(3)
N(1A)-C(1A)-C(2A)	101(2)	N(1B)-C(1B)-C(2B)	114(3)
N(1A)-C(4A)-C(3A)	111(2)	N(1B)-C(4B)-C(3B)	105(3)
N(2A)-C(6A)-C(7A)	109(2)	N(2B)-C(6B)-C(7B)	108(4)
N(2A)-C(9A)-C(8A)	114(3)	N(2B)-C(9B)-C(8B)	107(3)
N(3A)-C(11A)-C(12A)	110(3)	N(3B)-C(11B)-C(12B)	111(3)
N(3A)-C(14A)-C(13A)	122(3)	N(3B)-C(14B)-C(13B)	102(3)
N(4A)-C(16A)-C(17A)	119(2)	N(4B)-C(16B)-C(17B)	95(3)
N(4A)-C(19A)-C(18A)	111(2)	N(4B)-C(19B)-C(18B)	112(3)
C(1A)-C(2A)-C(3A)	115(3)	C(1B)-C(2B)-C(3B)	103(4)
C(2A)-C(3A)-C(4A)	99(3)	C(2B)-C(3B)-C(4B)	115(3)
C(6A)-C(7A)-C(8A)	108(3)	C(6B)-C(7B)-C(8B)	111(3)
C(7A)-C(8A)-C(9A)	104(2)	C(7B)-C(8B)-C(9B)	107(4)
C(11A)-C(12A)-C(13A)	102(3)	C(11B)-C(12B)-C(13B)	102(4)
C(12A)-C(13A)-C(14A)	101(3)	C(12B)-C(13B)-C(14B)	114(3)
C(16A)-C(17A)-C(18A)	101(3)	C(16B)-C(17B)-C(18B)	115(3)
C(17A)-C(18A)-C(19A)	110(2)	C(17B)-C(18B)-C(19B)	100(3)
N(1A)-C(1A)-C(20A)	129(2)	N(1B)-C(1B)-C(20B)	121(3)
N(1A)-C(4A)-C(5A)	131(3)	N(1B)-C(4B)-C(5B)	125(4)
N(2A)-C(6A)-C(5A)	124(2)	N(2B)-C(6B)-C(5B)	124(3)
N(2A)-C(9A)-C(10A)	120(3)	N(2B)-C(9B)-C(10B)	127(3)
N(3A)-C(11A)-C(10A)	115(3)	N(3B)-C(11B)-C(10B)	125(3)
N(3A)-C(14A)-C(15A)	124(3)	N(3B)-C(14B)-C(15B)	128(4)
N(4A)-C(16A)-C(15A)	121(2)	N(4B)-C(16B)-C(15B)	136(3)
N(4A)-C(19A)-C(20A)	122(2)	N(4B)-C(19B)-C(20B)	128(3)
C(20A)-C(1A)-C(2A)	130(2)	C(20B)-C(1B)-C(2B)	126(3)
C(3A)-C(4A)-C(5A)	118(3)	C(3B)-C(4B)-C(5B)	130(3)
C(5A)-C(6A)-C(7A)	127(3)	C(5B)-C(6B)-C(7B)	128(3)
C(8A)-C(9A)-C(10A)	127(3)	C(8B)-C(9B)-C(10B)	126(4)
C(10A)-C(11A)-C(12A)	126(3)	C(10B)-C(11B)-C(12B)	124(4)
C(13A)-C(14A)-C(15A)	114(3)	C(13B)-C(14B)-C(15B)	130(3)
C(15A)-C(16A)-C(17A)	120(3)	C(15B)-C(16B)-C(17B)	129(3)

TABLE 2. (Continued)

C(18A)-C(19A)-C(20A)	127(2)	C(18B)-C(19B)-C(20B)	120(4)
C(4A)-C(5A)-C(6A)	124(3)	C(4B)-C(5B)-C(6B)	128(4)
C(9A)-C(10A)-C(11A)	133(3)	C(9B)-C(10B)-C(11B)	125(4)
C(14A)-C(15A)-C(16A)	124(3)	C(14B)-C(15B)-C(16B)	127(3)
C(19A)-C(20A)-C(1A)	125(2)	C(19B)-C(20B)-C(1B)	126(4)
C(1A)-C(2A)-C(21A)	119(2)	C(1B)-C(2B)-C(21B)	127(3)
C(4A)-C(3A)-C(23A)	132(3)	C(4B)-C(3B)-C(23B)	117(3)
C(6A)-C(7A)-C(25A)	125(3)	C(6B)-C(7B)-C(25B)	125(5)
C(9A)-C(8A)-C(27A)	125(3)	C(9B)-C(8B)-C(27B)	120(4)
C(11A)-C(12A)-C(29A)	131(3)	C(11B)-C(12B)-C(29B)	125(3)
C(14A)-C(13A)-C(31A)	129(3)	C(14B)-C(13B)-C(31B)	121(3)
C(16A)-C(17A)-C(33A)	134(3)	C(16B)-C(17B)-C(33B)	120(3)
C(19A)-C(18A)-C(35A)	116(3)	C(19B)-C(18B)-C(35B)	126(3)
C(3A)-C(2A)-C(21A)	126(3)	C(3B)-C(2B)-C(21B)	128(4)
C(2A)-C(3A)-C(23A)	129(3)	C(2B)-C(3B)-C(23B)	128(4)
C(8A)-C(7A)-C(25A)	126(3)	C(8B)-C(7B)-C(25B)	121(4)
C(7A)-C(8A)-C(27A)	130(3)	C(7B)-C(8B)-C(27B)	133(3)
C(13A)-C(12A)-C(29A)	127(4)	C(13B)-C(12B)-C(29B)	131(4)
C(12A)-C(13A)-C(31A)	125(3)	C(12B)-C(13B)-C(31B)	122(3)
C(18A)-C(17A)-C(33A)	125(3)	C(18B)-C(17B)-C(33B)	125(4)
C(17A)-C(18A)-C(35A)	133(3)	C(17B)-C(18B)-C(35B)	135(3)
C(2A)-C(21A)-C(22A)	111(4)	C(2B)-C(21B)-C(22B)	90(4)
C(3A)-C(23A)-C(24A)	109(5)	C(3B)-C(23B)-C(24B)	111(3)
C(7A)-C(25A)-C(26A)	109(4)	C(7B)-C(25B)-C(26B)	98(4)
C(8A)-C(27A)-C(28A)	113(4)	C(8B)-C(27B)-C(28B)	101(4)
C(12A)-C(29A)-C(30A)	94(4)	C(12B)-C(29B)-C(30B)	115(3)
C(13A)-C(31A)-C(32A)	95(4)	C(13B)-C(31B)-C(32B)	98(3)
C(17A)-C(33A)-C(34A)	108(4)	C(17B)-C(33B)-C(34B)	106(3)
C(18A)-C(35A)-C(36A)	98(4)	C(18B)-C(35B)-C(36B)	107(4)

approximately orthogonal arrangement to each other. Each dimer has a two-fold axis through the μ-oxo oxygen atom, bisecting the line joining two osmium atoms in the dimer. Thus, the asymmetric unit consists of two $[Os^{IV}(oep)(OCH_3)]$-O- moieties. The two independent osmium porphinato moieties have similar conformations, as is illustrated in Figs. 2(a) and (b).

The numbering scheme for the carbon and nitrogen atoms in each $[Os^{IV}(oep)(OCH_3)]$-O- moiety is shown in Fig. 3. The bond distances and bond angles are listed in Table 2. The average bond distances and bond angles for chemically equivalent types of the bond in the osmium octaethylporphinato skeletons are also presented in Fig. 3. The average values agree with those of the corresponding bonds in the other metalloporphyrins,[6] within the limits of experimental error.

Figure 4 presents a perspective diagram of the environment of the osmium ion, with the average bond distances and bond angles. The porphine rings are planar within 0.10 Å, and the osmium ions are displaced by 0.06Å out of the plane defined by the four porphinato nitrogen atoms. The average Os-N distance, 2.033(28) Å,[7] is normal for the quadrivalent osmium ion, and it is comparable with the bivalent Os-N distance, 2.067(2) Å, reported in $[Os^{II}(oep)(pyridine)(CO)]$.[8] The Os^{IV}-O^{2-} distances of 1.807(3) and 1.809(3) Å are comparable with the Ru^{IV}-O^{2-} distance of 1.793(2) Å in $[Ru^{IV}(oep)Cl]_2O$,[1b] with the chloride

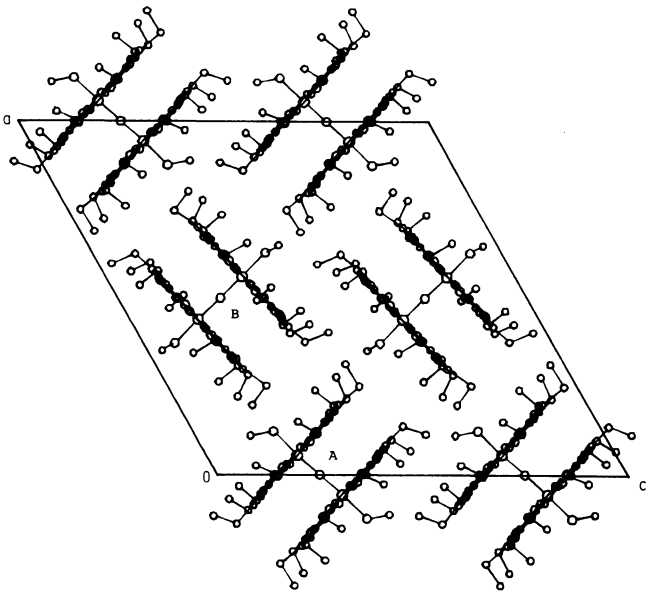

Fig. 1. Packing diagram of $[Os^{IV}(oep)(OCH_3)]_2O$ crystal as viewed parallel to *b*.

atom as the external ligand, but it seems to deviate greatly from that of 1.847(13) Å in $[Ru^{IV}(oep)(OH)]_2O$.[1a] The average Os^{IV}-OCH_3 distance of 1.997(29) Å agrees with the 5% reduction of the sum of the ionic

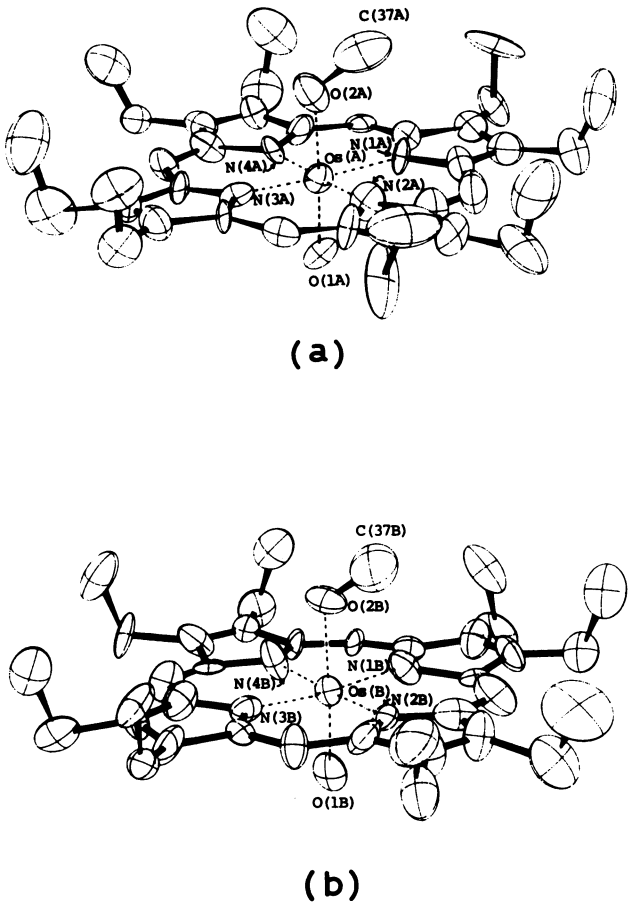

Fig. 2. Computer drawnings of the two independent osmium porphinato moieties, (a) and (b), showing 30 % probability thermal-vibration ellipsoids.

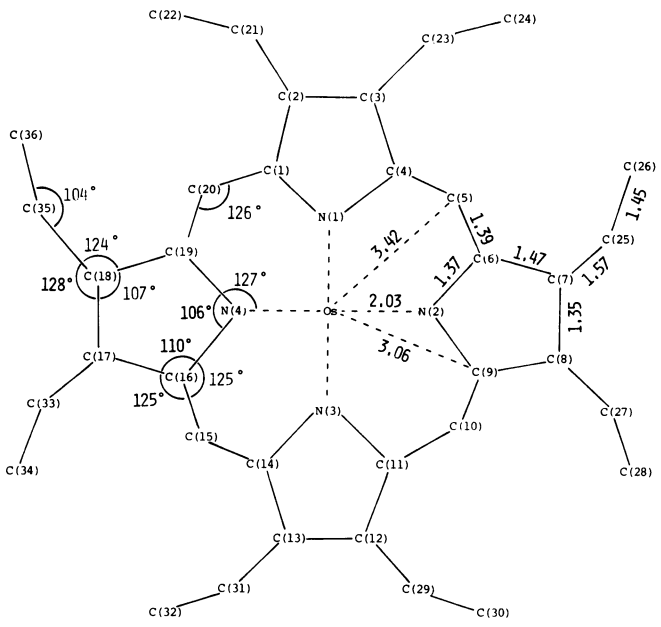

Fig. 3. Bond distances and bond angles averaged over the chemically equivalent bonds.

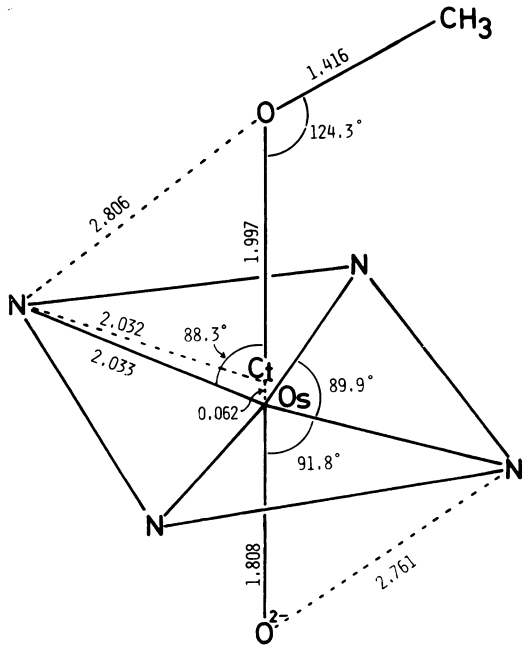

Fig. 4. Coordination sphere showing averaged bond distances and bond angles around the osmium(IV) atom in $[Os^{IV}(oep)(OCH_3)]_2O$. C_t represents the center of the porphinato skeleton.

radii,[11] 2.04 Å, due to the formation of the six-coordinate metal ion. The μ-oxo dimer consists of the two units of osmium porphyrins related by the two-fold symmetry through the O^{2-} atom. The Os-O-Os* bond has the valence angle of 178°. The two porphyrins are twisted with respect to each other so as to lie approximately midway between a staggered conformation and an eclipsed one, the N-Os-Os*-N* torsion angle being 23(1)°.[9] The average interplanar separation between the mean planes of the facing porphyrins is 3.7 Å; the closest interatomic distances are 3.60 Å for C(4A)-C(5A)* and 3.64 Å for C(11B)-C(20B)*. The binuclear porphyrin structure resembles those reported in $[Ru^{IV}(oep)(OH)]_2O$[1a] and $[Ru^{IV}(oep)Cl]_2O$,[1b] and, for the reason presented in the previous reports on the Ru^{IV} porphyrin dimers,[1] the structure is stabilized by the intramolecular π-π interactions between the face-to-face-contact porphyrins and by the $d\pi$-$p\pi$-$d\pi$ interaction in the Os^{IV}-O-Os^{IV}* bond. The diamagnetic property of this complex can also be well interpreted in terms of the π-π interactions in the Os^{IV}-O-Os^{IV}* bond system with the low-spin Os^{IV} atom.

As has been mentioned in the Introduction, the osmium-dimer complex in an acidic solution shows a high sensitivity for the protons, and the electron-donating ability of the μ-oxo bivalent anion (O^{2-}) in the Os^{IV}-O-Os^{IV} system is considerably stronger than that in the Ru^{IV}-O-Ru^{IV} system. This difference is reflected in the bond distances or bond angles around the μ-oxo oxygen. The observed Os^{IV}-O-Os^{IV} bond is almost as linear as the corresponding bonds in the ruthenium complexes,[1] in accordance with the statement of Tatsumi *et al.* that the μ-oxo dimers of d^n—d^n

($n<5$) electron systems prefer a linear M–O–M framework.[10] On the other hand, the Os^{IV}–O^{2-} distance is quite a bit smaller than the sum of the ionic radii;[11] it is also shorter than the Ru^{IV}–O^{2-} distance in $[Ru^{IV}(oep)(OH)]_2O$,[1a] although the Os^{IV}–O^{2-} distance is expected to be longer than the Ru^{IV}–O^{2-} distance from a comparison of the ionic radii of Os^{IV}(0.69 Å) and Ru^{IV}(0.65 Å) as observed in the $Os^{IV}O_2$ and $Ru^{IV}O_2$ crystals.[11,12] The short Os^{IV}–O^{2-} bond in the established structure may well account for the high sensitivity for the protons, because the shortening means a large distribution of electrons in the (Os^{IV}–O^2) π bonding orbital, and the electron-rich bonding orbital will be active for a proton.

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