Preparation and Physicochemical Properties of New Linear μ-Oxo Bridged Ruthenium(IV) and Osmium(IV) Porphyrin Dimers

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μ-Oxo-bis[(hydroxo)(octaethylporphyrinato)ruthenium(IV)] was prepared by the oxidation of (carbonyl)-(octaethylporphyrinato)ruthenium(II) with *t*-butyl hydroperoxide in good yield. Facile replacement of the hydroxyl group with various anions afforded μ-oxo dimer complexes formulated as $[\{\mathrm{Ru^{IV}(oep)X}\}_2\mathrm{O}]$ (X=Cl, Br, and $\mathrm{OCOCH_3}$). The same type of osmium complexes, $[\{\mathrm{Os^{IV}(oep)(OCH_3)}\}_2\mathrm{O}]$, $\{[\mathrm{Os^{IV}(oep)(OCH_3)}\}$-$\mathrm{O}\{\mathrm{Os^{IV}(oep)(OH)}\}]$, and $[\{\mathrm{Os^{IV}(oep)(OH)}\}_2\mathrm{O}]$ were obtained from the air oxidation product of (carbonyl)-(methanol)(octaethylporphyrinato)osmium(II) in the presence of 2,3-dimethylindole. These complexes are diamagnetic. The ^{1}H NMR data are in conformity with the linear oxo-bridged dimer structure which was proved by X-ray crystallography with $[\{\mathrm{Ru^{IV}(oep)(OH)}\}_2\mathrm{O}]$. The redox potentials were measured by the cyclic voltammetry. These complexes showed three distinct quasi-reversible redox couples assignable to metal$^{\mathrm{II}}$/metal$^{\mathrm{III}}$, metal$^{\mathrm{III}}$/metal$^{\mathrm{IV}}$, and porphyrin ligand oxidation, respectively. Significantly lower redox values and anomalous spectral features indicate a strong pπ-dπ interaction between the bridging oxygen atom and the two quadrivalent metal ions.

Higher-valent metalloporphyrins such as quadrivalent iron porphyrins have attracted the attention of chemists in relation to the structure of catalases, horseradish peroxidases, and cytochrome c peroxidases in the redox process.1) During the course of catalytic cycle of peroxidases, the reaction of the ferric enzyme with hydrogen peroxide and successive reduction with an electron generates the oxidized enzyme which was shown to involve an iron(IV) porphyrin moiety.2,3) Ruthenium and osmium which have the same number of outer shell (d+s) electrons are considered to form metalloporphyrins analogues to those of iron porphyrins. Complexes of bivalent ruthenium4) and osmium5) have been investigated as plausible models for hemoproteins and heme enzymes. For the quadrivalent complex, only one complex of osmium, $[\mathrm{Os^{IV}(oep)(OCH_3)_2}]$ has been reported by Buchler *et al.*,6) and synthesis of ruthenium(IV) porphyrins has never been reported before to our knowledge. Through an investigation of the oxidation of indole derivatives with molecular oxygen catalyzed by various metalloporphyrins, we found that bivalent ruthenium and osmium porphyrins as catalysts were oxidized to quadrivalent complexes.7,8) Our crystallographic study of the quadrivalent ruthenium complex showed a linear oxo-bridged dimer structure represented as $[\{\mathrm{Ru^{IV}(oep)(OH)}\}_2\mathrm{O}]$.9) Moreover spectral data of quadrivalent osmium complexes indicate that they have the same structure. Here we wish to report the first synthesis and physicochemical properties of ruthenium(IV) and osmium(IV) porphyrins.

Experimental

Synthesis of Complexes. *μ-Oxo-bis[(hydroxo)(octaethylporphyrinato)ruthenium(IV)], $[\{Ru^{IV}(oep)(OH)\}_2O]$ (1)*: To a benzene solution (100 cm^3) of $[\mathrm{Ru^{II}(oep)CO}]$ (100 mg)10) was added 1 cm^3 of 70% aqueous *t*-butyl hydroperoxide. The reaction mixture was stirred at room temperature until the color of the solution turned from orange red to dark brown. After removal of the solvent under reduced pressure, the residual solid was chromatographed on an alumina gel with dichloromethane as an eluent. The purple green fraction was collected and evaporated to dryness. Crystallization of the resulting solid from benzene–petroleum ether afforded slightly hygroscopic dark red crystals (90 mg) in 87% yield. Found: C, 64.59; H, 6.90; N, 8.20%. Calcd for $\mathrm{C_{72}H_{90}N_8O_3Ru_2 \cdot H_2O}$: C, 64.68; H, 6.93; N, 8.38%.

μ-Oxo-bis[(chloro)(octaethylporphyrinato)ruthenium(IV)], $[\{Ru^{IV}(oep)Cl\}_2O]$ (2): The dichloromethane solution (100 cm^3) of **1** was treated with 10% aqueous HCl. The mixture was stirred for 5 h. The solution was dried over anhydrous $\mathrm{Na_2SO_4}$ and condensed to dryness by evaporation. Crystallization of the residual solid from dichloromethane–methanol gave purple crystals (86 mg) in 80% yield. Found: C, 63.51; H, 6.51; N, 8.26%. Calcd for $\mathrm{C_{72}H_{88}N_8Cl_2ORu_2}$: C, 63.78; H, 6.54; N, 8.27%.

μ-Oxo-bis[(bromo)(octaethylporphyrinato)ruthenium(IV)], $[\{Ru^{IV}(oep)Br\}_2O]$ (3): The procedure similar to that descrived for the preparation of **2** by using aqueous HBr instead of HCl gave dark purple crystals of **3**i n 85% yield. Found: C, 59.79; H, 6.26; N, 7.71%. Calcd for $\mathrm{C_{72}H_{88}N_8Br_2ORu_2}$: C, 59.85; H, 6.14; N, 7.76%.

μ-Oxo-bis[(aceta)(tooctaethylporphyrinato)ruthenium(IV)], $[\{Ru^{IV}(oep)(OCOCH_3)\}_2O]$ (4): The mixture of **1** (100 mg) in dichloromethane (100 cm^3) and 10% acetic acid (1 cm^3) was stirred until the color of the solution changed from purple green to green. The dichloromethane solution was washed with water and dried over anhydrous $\mathrm{Na_2SO_4}$. The solution was condensed under reduced pressure to a small volume. Crystallization of the residue from dichloromethane–methanol containing trace amount of acetic acid gave purple red crystals (95 mg) in 90% yield. Found: C, 65.15; H, 7.03; N, 7.70%. Calcd for $\mathrm{C_{76}H_{94}N_8O_5Ru_2}$: C, 65.05; H, 6.75; N, 7.99%.

μ-Oxo-bis[(methoxo)(octaethylporphyrinato)osmium(IV)], $[\{Os^{IV}(oep)(OCH_3)\}_2O]$ (5), μ-Oxo-[(hydroxo)(octaethylporphyrinato)-

osmium(IV)] [(methoxo)(octaethylporphyrinatoosmium(IV)], $[\{Os^{IV}(oep)(OH)\}O\{Os^{IV}(oep)(OCH_3)\}]$, *(**6**), and μ-Oxo-bis[(hydroxo)(octaethylporphyrinato)osmium(IV)],* $[\{Os^{IV}(oep)(OH)\}_2O]$ *(**7**):* To a dichloromethane solution (100 cm^3) of (carbonyl)(methanol)(octaethylporphyrinato) osmium(II) (100 mg)[5,6,11] was added 2,3-dimethylindole (100 mg). The mixture was stirred for about 24 h in air until the color of the solution turned from orange red to brown. After removal of solvent, the residue dissolved in benzene was adsorbed on the silica gel column and first eluted with benzene–acetone (9:1 vol/vol). The dark purple effluent was collected. After removal of solvent the residual solid was recrystallized from benzene to give **5** (30 mg) as dark purple crystals. Found: C, 58.12; H, 6.16; N, 7.46%. Calcd for $C_{74}H_{94}N_8O_3Os_2$: C, 58.32; H, 6.22; N, 7.46%. The dark brown second band was eluted with benzene–acetone (8:2 vol/vol). After removal of solvent the crude crystals obtained were recrystallized from benzene–acetone (1:1 vol/vol) to give 6 (30 mg) as dark purple crystals. Found: C, 58.23; H, 6.16; N, 7.30%. Calcd for $C_{73}H_{92}N_8O_3Os_2$: C, 58.06; H, 6.14; N, 7.42%. Finally the dark brown third band was eluted with benzene–acetone (7:3 vol/vol). After removal of solvent the residual solid was recrystallized from acetone to give **7** (25 mg) as dark purple crystals. Found: C, 56.15; H, 5.91; N, 7.31%. Calcd for $C_{72}H_{90}N_8O_3Os_2\cdot H_2O$: C, 56.45; H, 6.19; N, 7.31%.

Protonated forms of μ-oxo osmium(IV) complexes, *i.e.*, μ-hydroxo complexes were obtained according to the following procedure. To a dichloromethane solution (10 cm^3) of **5** (50 mg) was added 10% aqueous acid HX (1 cm^3, X=Cl and CF_3CO_2). After removal of solvents, the residual solid was recrystallized from benzene to afford purple red crystals.

$[\{Os^{IV}(oep)Cl\}_2OH]Cl$ *(**8**):* Found: C, 55.24; H, 5.81; N, 7.10%. Calcd for $C_{72}H_{89}N_8OCl_3Os_2$: C, 55.49; H, 5.72; N, 7.14%.

$[\{Os^{IV}(oep)(OCOCF_3)\}_2OH](OCOCF_3)$ *(**9**):* Found: C, 51.89; H, 5.09; N, 6.39%. Calcd for $C_{78}H_{88}N_8O_7F_9Os_2$: C, 52.02; H, 4.93; N, 6.22%.

Molecular Weight Measurements. Molecular weights were measured at 31.5 °C in chloroform on a Knour vapor pressure osmometer.

Spectral Measurements. ^1H NMR spectra were obtained on a Varian HA-100D and JEOL HM-100 spectrometers. Infrared spectra were measured on Hitachi G-3 and JASCO DS-701G spectrophotometers. Absorption spectra were obtained on a Hitachi model 200-10 spectrophotometer.

Cyclic Voltammetry. Dichloromethane used as a solvent was dried and distilled before use. As a supporting electrolyte, tetrabutylammoium perchlorate (TBAP) was used after being subjected twice to crystallization from benzene. Cyclic voltammograms were obtained on a HA-104 potentiostat (Hokuto Denko) in combination with a HB-107A function generator. A three electrode system was used, consisting of platinum working and counter electrodes and a commercial saturated calomel electrode (SCE). The half-wave potentials were measured as that potential lying midway between the oxidation and reduction peaks for a given couple. Potentials are reported with respect to the saturated calomel electrode.

Results and Discussion

Synthesis. Oxidation of (carbonyl)(octaethylporphyrinato)ruthenium(II) by *t*-butyl hydroperoxide gave the hydroxo derivative **1** of the μ-oxo binuclear ruthenium(IV) porphyrin in a high yield, its axial hydroxyl group being readily replaced with various anions by the treatment with the respective acids. The action of the same oxidant upon (carbonyl)(methanol)(octaethylporphyrinato)osmium(II) gave sexivalent dioxo derivative, $[Os^{VI}(oep)O_2]$ as reported by Buchler *et al.*[6] On the other hand, air oxidation of (carbonyl)-(methanol)(octaethylporphyrinato)osmium(II) in the presence of 2,3-dimethylindole gave three quadrivalent complexes **5**, **6**, and **7**,[8] which could be separated by the chromatography on a silica gel. Thus a sort of peroxide derivative generated *in situ*[7] from 2,3-dimethylindole/air system oxidizes the bivalent complex only to the quadrivalent complex. The bivalent ruthenium complex was also oxidized to the quadrivalent one by this system in good yield.

$$\begin{array}{llll}
[\mathrm{Ru^{II}(oep)CO}] & \xrightarrow[\text{2,3-dimethylindole/air}]{\mathrm{(CH_3)_3COOH\ or}} & [\{\mathrm{Ru^{IV}(oep)(OH)}\}_2\mathrm{O}] & \mathbf{1}\\
\mathbf{1} & \xrightarrow{\mathrm{HX}} & [\{\mathrm{Ru^{IV}(oep)X}\}_2\mathrm{O}]\quad \mathrm{X=Cl} & \mathbf{2}\\
 & & \qquad\qquad\qquad\quad \mathrm{Br} & \mathbf{3}\\
 & & \qquad\qquad\qquad\quad \mathrm{OCOCH_3} & \mathbf{4}\\
[\mathrm{Os^{II}(oep)CO(CH_3OH)}] & \xrightarrow{\text{2,3-dimethylindole/air}} & [\{\mathrm{Os^{IV}(oep)(OCH_3)}\}_2\mathrm{O}] & \mathbf{5}\\
 & & +\ [\{\mathrm{Os^{IV}(oep)(OH)}\}\mathrm{O}\{\mathrm{Os^{IV}(oep)(OCH_3)}\}] & \mathbf{6}\\
 & & +\ [\{\mathrm{Os^{IV}(oep)(OH)}\}_2\mathrm{O}] & \mathbf{7}\\
 & \xrightarrow{\mathrm{(CH_3)_3COOH}} & [\mathrm{Os^{VI}(oep)O_2}] &
\end{array}$$

Molecular weight measurements indicate that all of the complexes of Ru(IV) and Os(IV) thus obtained contain two metalloporphyrin moieties.

Molecular weights and infrared, ^1H NMR, and absorption spectra are summarized in Table 1.

^1H NMR Spectra. All of the binuclear Ru(IV) and Os(IV) complexes obtained in this study are diamagnetic both in solid and solution states,[12] molar susceptibility of **1** in polycrystalline state being $\chi_M = -8.63\times10^{-6}$ cgs emu at 30 °C. ^1H NMR spectra of these complexes showed usual diamagnetic spectra.[13] As listed in Table 1, the characteristic features that are common to all of the complexes are the chemical shifts of the meso protons and the coupling pattern of the α-methylene protons of the pheripheral ethyl groups.

The signals for the meso protons of the binuclear ruthenium and osmium complexes appear at higher magnetic field by about 0.5—1.0 ppm than those in monomeric ruthenium(II) and osmium(II) porphy-

Table 1. Molecular weights, IR, absorption maxima and ^{1}H NMR chemical shifts of ruthenium(IV) and osmium(IV) μ-oxo bridged dimers

Compound	Molecular weight Calcd (Found)	IR ν/cm^{-1}	Absorption maxima λ_{max}/nm (log ε) in CH_2Cl_2	^{1}H NMR (δ from TMS in $CDCl_3$)			
				Meso	α-CH_2	β-CH_3	Axial ligand
1	1316(1270)	3606a)	377(5.30) 512(4.12) 580(4.32)	9.15	4.18	1.84	−4.20(OH)
2	1355(1350)		384(5.40) 500(4.10) 690(4.01)	9.29	4.18	1.88	
3	1444(1450)		387(5.41) 500(4.00) 717(4.08)	9.08	4.06	1.84	
4	1412(1430)	1659a) 1255	378(5.42) 510(4.03) 667(4.02)	9.30	4.20	1.87	−3.70($OCOCH_3$)
5	1524(1520)	2785b) 1010 525	353(4.87) 380 sh(4.77) 460 sh(3.97) 500(3.87) 610(3.79) 713(3.56)	9.22 9.42c)	4.21 4.12	1.82 1.82	−3.54(OCH_3) −4.36(OCH_3)
6	1510(1500)	2785b) 1010 3602 863 525 575	351(4.88) 380 sh(4.72) 470(3.96) 495(3.88) 597(3.77) 695(3.57)	9.02, 8.98 9.31c)	4.08 4.04	1.77 1.80	−3.52(OCH_3) −3.5(br OH) −4.48(OCH_3)
7	1496(1480)	3598b) 860 575	355(4.87) 380 sh(4.76) 470 sh(3.96) 490(3.86) 588(3.76) 680(3.56)	9.00	4.06	1.78	−3.4(br OH)
8	1801(1820)	1715 1170	363(5.07) 493 sh(3.82) 547(4.00) 600(3.87)	9.24	4.10	1.80	
9	1569(1600)		358(5.00)d) 488(3.87) 553(4.00) 599(3.88)				

a) In CCl_4. b) KBr. c) In the presence of 1% CF_3CO_2D. d) In methanol. sh; Shoulder, br; broad.

rins,[10,11] The X-ray crystallography[9] for **1** showed that it is a μ-oxo binulear porphyrinato complex of ruthenium(IV) and that the interplaner distance between the mean planes of the porphyrinato cores is 3.17 Å. The up-field shifts of the meso proton signals are, therefore, explained in terms of the mutual ring current effect in the dimeric complex. It is thus most likely suggested that ruthenium(IV) and osmium(IV) complexes **1**—**7** all have the linear μ-oxo bridged dimer structure.[9] The meso proton signals of mixed ligand complex **6** appear reasonably at 9.02 and 8.98 ppm as two singlets.

Another characteristic ^{1}H NMR feature of the present complexes that suggests the μ-oxo dimer structure is the coupling pattern of the peripheral α-methylene protons. As shown in Fig. 1, all of these complexes showed the ABX_3 coupling pattern which could be analyzed with the aid of the decoupling method. Diastereotopism of the α-methylene protons of ethyl group is due to the different magnetic circumstances above and below the porphyrinato plane. The complicated pattern of the α-methylene signals has been reported for some metalloporphyrins.[14,15] Splitting of the proton signal of α-methylene group in octaethylporphyrin is attributed to out-of-plane central ion or asymmetric axial ligation. The ruthenium atom in **1** was found to be displaced only 0.03 Å off the plane defined by the four porphyrinato nitrogen atoms.[9] The eight ethyl groups are oriented outside so as to avoid steric constraint between the peripheral ethyl groups of the two porphyrinato cores. Therefore, the hindered rotation of the ethyl group causes the nonequivalence of the α-methylene in the different magnetic atmosphere due to asymmetric ligation.

The proton of the axial ligands OH and $OCOCH_3$ for the ruthenium complexes **1** and **4** resonated at −4.20 and −3.70 ppm respectively as sharp singlets. Methoxyl protons for osmium complexes **5** and **6** appeared at −3.70 and −3.54 ppm, respectively, also as sharp singlets. These anomalous high-field shifts of the proton signal of the axial ligand can be described by a large shielding effect of the ring current in the near proximity of the metal ion. It is noteworthy that the axial hydroxyl protons for the osmium complexes **6** and **7** resonated at about −3.5 ppm as much broader signals compared with those of ruthenium complexes. Such broadening of the signals indicates a more dissociable nature of the proton of the axial hydroxyl group, and suggests lower electron density on the axial oxygen atom in the osmium complex. On the other hand, electronic and ^1H NMR spectra of these binuclear osmium(IV) complexes in the presence of acids show that their bridging oxygen atoms have certain tendency to be protonated while those of similar ruthenium(IV) complexes do not. This suggests higher electron density on the bridging oxygen of the osmium complexes. These problems will be described more fully under a separate section.

IR, VIS, and UV Absorption Spectra. Infrared spectra of **1**, **6**, and **7** showed sharp bands at 3606 (in CCl_4), 3602 (KBr), and 3598 (KBr) cm^{-1}, respectively, assignable to the stretching vibration (ν_{O-H}) of the axial hydroxyl group.[16] Two absorption peaks at 1659 and 1225 cm^{-1} for **4** are due to $\nu_{C=O}$ and ν_{C-O} of the axial acetoxyl group.[16] Three absorption bands at 2785, 1010, and 525 cm^{-1} for **5** and those at similar positions for **6** are due to the axial methoxide ligands.[6]

Data of VIS and UV absorption spectra are given in Table 1. The Soret bands of the binuclear Ru(IV) and Os(IV) complexes are observed at 373—387 and 351—355 nm, respectively, which are considerably in the shorter wave length region than those of the respective bivalent metalloporphyrins,[10] in conformity with the usual empirical rule.

The general features of the absorption spectra of these binuclear complexes at the longer wave length region are considerably different from those of usual porphyrin complexes as shown in Figs. 1 and 2. Since the absorption spectrum of monomeric quadrivalent complex, $[Os^{IV}(oep)(OCH_3)_2]$ has only normal α and β bands at 530 and 497 nm in this region,[6] the band appearing at 550—800 nm of the present osmium(IV) complexes are considered to be the characteristics of the oxo-bridged dimer structure. The same is probably true with the binuclear Ru(IV) complexes, although no mononuclear Ru(IV) porphyrins have been reported to date.

A number of chemically well defined dimeric and oligomeric halogen complexes of ruthenium[17] and osmium[18] are known having a μ-oxo bridging link between halogeno-metal moieties. These complexes exhibit anomalous light absorption mainly in the longer wave length region, which is probably of the similar nature to those of the present complexes. This, as well as other anomalous physical and chemical properties of these series of μ-oxo halogeno complexes have been successfully interpreted using an MO scheme.[17a] Such scheme presupposes a strong electronic coupling between the halogeno-metal moieties and even leads to a sort of a new chemical system. The present complexes seem to be in a more or less similar situation. The above-mentioned absorption peaks appearing at 550—800 nm that characterize such anomalous features of the spectra of these binuclear complexes are sensitive to the kind of the axial ligand. They probably have main contribution from the charge

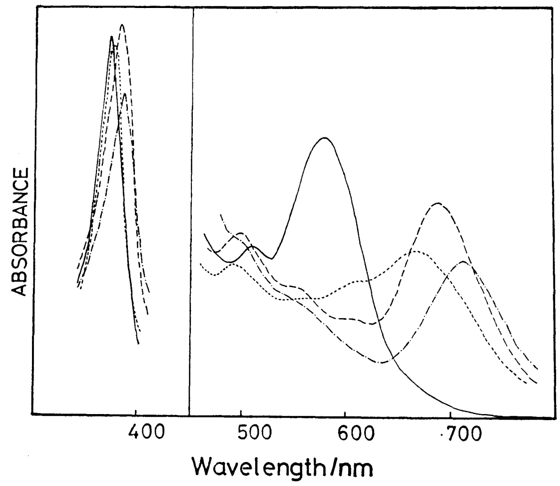


Fig. 1. Absorption spectra of the μ-oxo bridged ruthenium(IV) dimers in CH_2Cl_2.
——: $[\{Ru^{IV}(oep)(OH)\}_2O]$, ······: $[\{Ru^{IV}(oep)(OCOCH_3)\}_2O]$, — —: $[\{Ru^{IV}(oep)Cl\}_2O]$, and —·—·: $[\{Ru^{IV}(oep)Br\}_2O]$.

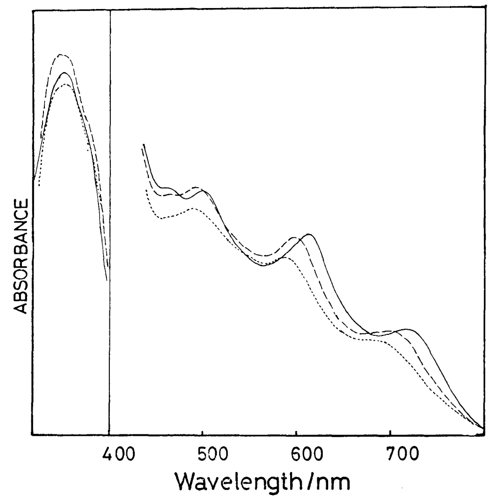


Fig. 2. Absorption spectra of the μ-oxo bridged osmium(IV) dimers in CH_2Cl_2.
——: $[\{Os^{IV}(oep)(OCH_3)\}_2O]$, — —: $[\{Os^{IV}(oep)(OH)\}O\{Os^{IV}(oep)(OCH_3)\}]$, ······: $[\{Os^{IV}(oep)(OCH_3)\}_2O]$.

transfer of the type $a_{1u},a_{2u}(p\pi)\rightarrow e_g(d_{xz},d_{yz})$. The excitation energy of the transition was in the order $\mathrm{OH} > \mathrm{OCOCH_3} > \mathrm{Cl} > \mathrm{Br}$ of the axial ligand of the ruthenium complexes, and $(\mathrm{OH})_2 > (\mathrm{OH})(\mathrm{OCH_3}) > (\mathrm{OCH_3})_2$ of those of osmium complexes. This trend seems to reflect the extent of an interaction between $p\pi$ orbitals of the axial ligand and $d\pi$ orbitals of the metal ions.

Behavior of μ-Oxo Binuclear Complexes toward Acids. As has been described previously, action of acids upon complex **1** replaces the axial hydroxyl group with the respective acid groups to give **2**, **3**, and **4**, leaving μ-oxo group unchanged. Such a change could be followed by observing the change of the absorption spectrum of **1** upon addition, *e.g.*, of aqueous HCl; no more spectral change was observed in the presence of excess amount of acids. Complexes **2**, **3**, and **4** readily regenerate **1**, *e.g.*, by simple column chromatography of them on alumina, due to reverse reaction with trace amount of water on the gel.

The behaviors of the μ-oxo bridged osmium complexes toward acids are considerably different. Treatment of these complexes with acids seems to protonate the bridged oxygen first as evidenced by electronic and ^{1}H NMR spectra. Thus, the absorption spectra of the osmium complexes vary largely with the addition of acids finally to give the same spectra *independent of* the kind of acids. The ^{1}H NMR spectrum of the osmium complex **5** in the presence of 1% $\mathrm{CF_3CO_2D}$ is illustrated in Fig. 3. By the addition of trifluoroacetic acid, the meso protons are slightly shifted toward lower magnetic field and the geminal coupling constant of the $\mathrm{ABX_3}$ pattern for α-methylene protons becomes a little smaller. It is noteworthy that the axial methoxide protons are shifted toward higher magnetic field without decrease in the intensity or broadening of the signal. These results indicate that the protonation occurs not on the axial oxygen atom but on the bridged oxygen atom, because if the protonation occured on the oxygen of the axial methoxide, the positive charge on the oxygen would be increased and the methoxyl protons should rather be shifted toward lower magnetic field. However an attempt to isolate the protonated species, $[\{\mathrm{Os^{IV}(oep)(OCH_3)}\}_2\mathrm{OH}]^+\mathrm{X}^-$ only gave the complexes $[\{\mathrm{Os^{IV}(oep)X}\}_2\mathrm{OH}]^+\mathrm{X}^-$ (X=Cl, and $\mathrm{CF_3CO_2}$), respectively, in which methoxyl group were replaced by the chloro and trifluoroacetato groups. Treatment of **8** and **9** with aqueous alkali not only deprives it of the proton from the hydroxyl bridge but also causes hydrolysis resulting

$$[\{\mathrm{Os^{IV}(oep)(OCH_3)}\}_2\mathrm{O}] \xrightarrow{\mathrm{HX}} [\{\mathrm{Os^{IV}(oep)(OCH_3)}\}_2\mathrm{OH}]^+\mathrm{X}^-$$

$$\xrightarrow{\mathrm{HX}} [\{\mathrm{Os^{IV}(oep)X}\}_2\mathrm{OH}]^+\mathrm{X}^-$$

$$\begin{array}{ll} \mathrm{X=Cl} & \mathbf{8} \\ \mathrm{CF_3CO_2} & \mathbf{9} \end{array}$$

in the replacement of the axial acid groups by the hydroxyl group. This has so far prevented the authors from obtaining oxo-bridged osmium(IV) complexes having acidic axial ligands comparable to ruthenium complexes **2**, **3**, and **4**.

As shown in Fig. 4, the Soret band for the μ-oxo osmium complexes was shifted to 359 nm and became sharp by the protonation. The charge transfer bands also were largely affected, and absorption at around 700 nm disappeared. The same spectral changes were observed in the presence of other acids such as HCl, HBr, and $\mathrm{HClO_4}$. The absorption spectra of complexes **8** and **9** also show similar spectra. This kind of spectrum is, therefore, considered to be characteristic of the species protonated at the bridging oxygen atom represented as $[\{\mathrm{Os^{IV}(oep)(OCH_3)}\}_2\mathrm{OH}]^+$. The lack of the absorption near 700 nm may be due to the decrease of the interaction between two metalloporphyrins through bridged oxygen caused by the protonation to the oxygen atom. Moreover the same characteristic absorption spectrum could be also observed in the presence of silver perchlorate instead of protons. This means that the silver ion can also react with the bridged oxygen as a Lewis acid, although the adduct of silver perchlorate could not be isolated as analytically pure crystals.

In order to understand the different behavior toward acids between ruthenium(IV) and osmium(IV) complexes in spite of having similar molecular structures, it seems helpful to consider the following canonical structures. The behavior toward acids and ^{1}H NMR data for osmium(IV) complexes indicate considerable contribution of structure (C). Canonical structure (C) points to an easy dissociation of axial hydroxyl protons

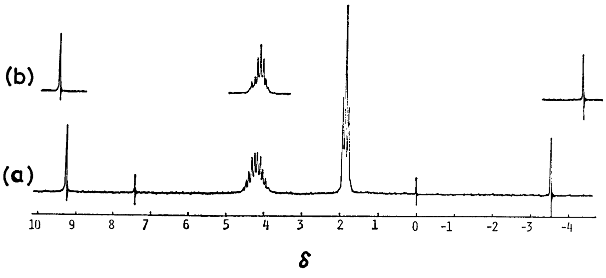


Fig. 3. The ^{1}H NMR spectra of $[\{\mathrm{Os^{IV}(oep)(OCH_3)}\}_2\mathrm{O}]$ in (a) $\mathrm{CDCl_3}$ and (b) $\mathrm{CDCl_3}$ containing 1% $\mathrm{CF_3CO_2D}$.

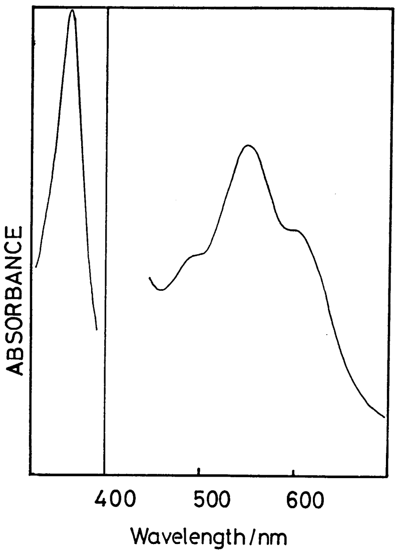
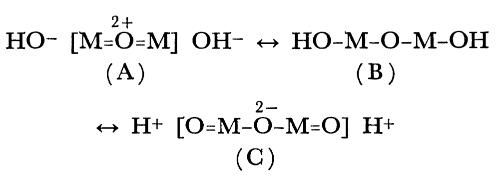


Fig. 4. Absorption spectra of $[\{\mathrm{Os^{IV}(oep)(OCH_3)}\}_2\mathrm{O}]$ in $\mathrm{CH_2Cl_2}$ containing 1% $\mathrm{CF_3CO_2H}$.



$$\underset{(\mathrm{A})}{\mathrm{HO^-}\ [\mathrm{M{=}\overset{2+}{O}{=}M}]\ \mathrm{OH^-}} \leftrightarrow \underset{(\mathrm{B})}{\mathrm{HO{-}M{-}O{-}M{-}OH}}$$

$$\leftrightarrow \underset{(\mathrm{C})}{\mathrm{H^+}\ [\mathrm{O{=}M{-}\overset{2-}{O}{-}M{=}O}]\ \mathrm{H^+}}$$

and high affinity of proton toward the bridged oxygen. On the other hand, experimental results for ruthenium(IV) complexes suggest that the more important contribution here is rather structure (A) predicting the easy replacement of axial hydroxyl group and low affinity of proton toward bridged oxygen atom. For a more detailed and quantitative discussion, a theoretical treatment involving the molecular orbital calculations seems to be indispensable.

Electrochemistry. The redox behavior of Ru(IV) and Os(IV) metalloporphyrins seems to form one of the most interesting facets of their chemistry especially from the biological point of view. Unless very accurate data are required, necessary information can be obtained simply from cyclic voltammetry. All of these complexes show three distinct quasi-reversible redox couples (Eo1, Eo2, and Eo3) as shown in Fig. 5, and half-wave potentials estimated therefrom are listed in Table 2. The number of electron concerned in each couple was determined to be about 2 by the controlled coulometry,[19] which means that two metal atoms or porphyrin ligands in a molecule are oxidized and reduced at the same time. In connection with the existing data especially of osmium porphyrins, these three redox couples of both ruthenium and osmium complexes seem to be assignable to metal$^{\mathrm{II}}$/metal$^{\mathrm{III}}$, metal$^{\mathrm{III}}$/metal$^{\mathrm{IV}}$, and to porphyrin ring oxidation, respectively.[20,21] The assignment of Eo3 to the porphyrin ring oxidation is also confirmed by the fact that the redox couple is almost insensitive to the difference of both metal and axial ligand.[20] It is noteworthy that although the redox couple Ru$^{\mathrm{II}}$/Ru$^{\mathrm{III}}$ has been confirmed electrochemically for [Ru$^{\mathrm{II}}$(porphyrin)(pyridine)$_2$],[21] the redox couple Ru$^{\mathrm{III}}$/Ru$^{\mathrm{IV}}$ has never been observed before, probably because the latter is more positive than that of porphyrin ring oxidation. Appearance of the Ru$^{\mathrm{III}}$/Ru$^{\mathrm{IV}}$ in the present complex at a potential lower than that of the ring oxidation, thus, proves the marked stabilization of Ru$^{\mathrm{IV}}$ caused by the formation of the linear Ru–O–Ru system in conformity with the successful isolation of Ru(IV) complexes only in the form of oxo-bridged dimers. Here, strong electron-donating ability of the μ-oxo (O^{2-}) ligand probably plays an important role. The Ru$^{\mathrm{III}}$/Ru$^{\mathrm{IV}}$ couple of complex **1** having axial hydroxyl groups is somewhat more negative than those of halogeno derivatives **2** and **3**. This means that the electron donation from the axial ligand, which also contributes to the lowering of the Ru$^{\mathrm{III}}$/Ru$^{\mathrm{IV}}$ couple is larger in the former.

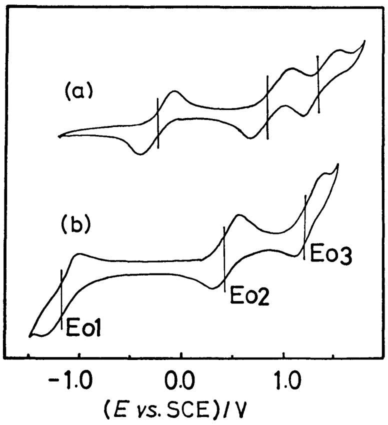


Fig. 5. Cyclic voltammograms of (a) [{Ru$^{\mathrm{IV}}$(oep)Cl}$_2$O], and (b) [{Os$^{\mathrm{IV}}$(oep)(OCH$_3$)}$_2$O] in CH_2Cl_2–TBAP.

Table 2. The half-wave potentials of ruthenium(IV) and osmium(IV) μ-oxo bridged dimer complexes (V *vs.* SCE)

Compound	Eo1	Eo2	Eo3
[{Ru$^{\mathrm{IV}}$(oep)(OH)}$_2$O]	−0.82	+0.68	+1.18
[{Ru$^{\mathrm{IV}}$(oep)Cl}$_2$O]	−0.24	+0.85	+1.32
[{Ru$^{\mathrm{IV}}$(oep)Br}$_2$O]	−0.22	+0.84	+1.30
[{Os$^{\mathrm{IV}}$(oep)(OCH$_3$)}$_2$O]	−1.18	+0.41	+1.20
[{Os$^{\mathrm{IV}}$(oep)(OH)}O-{Os$^{\mathrm{IV}}$(oep)(OCH$_3$)}]	−1.13	+0.40	+1.22
[{Os$^{\mathrm{IV}}$(oep)(OH)}$_2$O]	−1.12	+0.37	+1.23

Formation of the μ-oxo bridges, of course, lowers the redox values of Os$^{\mathrm{III}}$/Os$^{\mathrm{IV}}$ and Os$^{\mathrm{II}}$/Os$^{\mathrm{III}}$ also. Their redox values for [Os$^{\mathrm{II}}$(oep)(1-methylimidazole)$_2$] were recently reported to be 0.61 and −0.63 V, which are considerably more positive than the values of around 0.4 and −1.1 V for the present osmium dimer complexes. The influence of the protonation to the bridging oxygen on the redox values was also investigated. Figure 6 shows that in the presence of 1% CF_3CO_2H only the redox couple Eo2 was specifically shifted toward positive region by about 0.5 volt. Unfortunately the redox couple Eo1 was completely concealed by the large back ground current due to the presence of trifluoroacetic acid. These results indicate that the protonation on the bridged oxygen considerably decreases the electron donation from the bridged oxygen to the central metals. The redox values for Eo1 and Eo2 of osmium complexes are almost insensitive to the axial ligands, so that the interaction between the metals and the axial ligands acting as electron donors is considered to occur to about the same

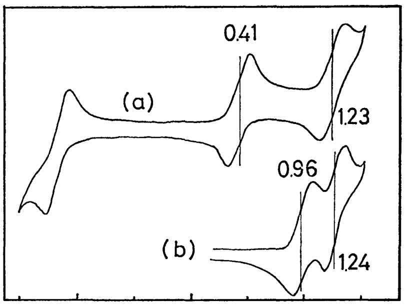


Fig. 6. Cyclic voltammograms of [{Os$^{\mathrm{IV}}$(oep)(OCH$_3$)}$_2$O] in (a) CH_2Cl_2 and (b) CH_2Cl_2 containing of 1% CF_3CO_2H.

extent.

Tervalent iron porphyrins form μ-oxo bridged dimer complexes represented as $[\{Fe^{III}(porphyrin)\}_2O]$.[22] Phillippi and Goff reported[23] that electrochemical oxidation of $[\{Fe^{III}(tetraphenylporphyrin)\}_2O]$ gave both one-electron oxidized ($[Fe^{III}–O–Fe^{IV}]^+$) and two-electron oxidized ($[Fe^{IV}–O–Fe^{IV}]^{2+}$) species at 0.79 and 1.03 V, respectively. This behavior of the iron complex is different from that of ruthenium and osmium complexes, because in ruthenium and osmium binuclear complexes two metal atoms are oxidized at the same time as discussed above. The different redox behavior of the iron complex might be explained in terms of weaker interaction between two metalloporphyrin moieties through bridged oxygen. In fact, X-ray crystallography revealed that the Fe–O–Fe group is not completely linear.[22] Moreover there is still a major question concerning oxidation of the iron complexes, that is, whether electron abstraction occurs formally from the metal (ferryl iron) or from ligand (porphyrin radical).[3c,24]

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