$[AsW_8O_{30}As(OH)]^{7-}$. Polarography showed that it was the only one heteropolyanion in solution when W/As = 2[18] (Scheme I).

In conclusion, the structure of the title compound confirms the prominent role of As^{III} stereochemistry (pyramidal structure and lone pair) in the polycondensation of coordinated tungsten(VI) atoms in polyoxoanions. A type-B environment involving the three bonds of As(III) is always obtained. The stereochemistry and nature of possible α or β species in solution are consistent with Lipscomb's rule, and individual compounds can be isolated upon addition of suitable reagents.

Registry No. $K_7(AsW_8O_{30}AsOH)\cdot 12H_2O$, 95406-35-2; potassium arsenate(III), 95344-35-7; potassium tungstate, 37349-36-3.

Supplementary Material Available: Listings of structure factor amplitudes and anisotropic temperature factors of W, As, and K atoms (13 pages). Ordering information is given on any current masthead page.

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(18) The polarograms of $As_2W_8O_{31}H^{7-}$ and $AsW_9O_{33}H^{9-}$, recorded in 1 M sodium acetate/1 M acetic acid buffer, have well-defined first waves of two electrons. Half-wave potentials vs. the saturated calomel electrode are, respectively, −0.67 and −0.78 V.

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Synthesis and Characterization of Osmium Porphyrins

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During the course of our work on osmium-substituted myoglobin (osmoglobin),[2] we found that we could use $Os_3(CO)_{12}$ instead of the hazardous OsO_4[3] as a starting material for the preparation of osmium porphyrins. Here, we illustrate this method by reporting the synthesis of [Os(MIX-DME)(CO)L], where MIX-DME is mesoporphyrin IX dimethyl ester and L is either ethanol or pyridine.[4] Good yields of pure $[Os(MIX\text{-}DME)O_2]$ may be obtained from the oxidation of [Os(MIX-DME)(CO)L] complexes by *tert*-butyl hydroperoxide (TBHP). TBHP also has been used successfully as an oxidant for ruthenium porphyrins.[5]

Experimental Section

Materials. $Os_3(CO)_{12}$ and octaethylporphyrin (OEP) were purchased from Strem Co., Ltd., whereas mesoporphyrin IX dimethyl ester (MIX-DME) was obtained from Sigma Co., Ltd. All solvents used were of analytical grade. *tert*-Butyl hydroperoxide (TBHP) was supplied by Aldrich. Triphenylphosphine (Merck) was twice recrystallized from absolute ethanol before use.

Procedure for the Synthesis of [OsP(CO)L] (PH_2 = OEP, MIX-DME; L = EtOH, py). A mixture of $Os_3(CO)_{12}$ (0.1 g) and PH_2 (0.1 g) in diethylene glycol monomethyl ether ($\sim$80 mL) was refluxed under an argon atmosphere with vigorous stirring for about 8 h. The solution was cooled to room temperature. Upon addition of a saturated aqueous solution of NaCl, crude [OsP(CO)] precipitated. The product was filtered, air-dried, and then purified by chromatography using either a silica gel or an alumina column and a CH_2Cl_2/acetone mixture (3:1) as the eluent. Pure [OsP(CO)] was obtained by further chromatography using CH_2Cl_2 as the eluent (overall yeild $\sim$70%). Dissolution of [OsP(CO)] in a donor solvent L followed by the addition of excess *n*-hexane led to the precipitation of [OsP(CO)L] in nearly quantitative yield.

[Os(MIX-DME)(CO)EtOH] was prepared as a brick red solid from $Os_3(CO)_{12}$ (0.1 g), MIX-DME (0.1 g), and EtOH (1 mL). Anal. Calcd for $OsC_{39}H_{46}N_4O_6$: C, 54.9; H, 5.16; N, 6.56. Found: C, 55.0; H, 5.20; N, 6.40. ^1H NMR: Table I. IR (Nujol mull): $\nu(C{\equiv}O)$ 1902 cm^{-1}.

[Os(MIX-DME)(CO)py] was prepared as a brick red solid from $Os_3(CO)_{12}$ (0.1 g), MIX-DME (0.1 g), and py (0.5 mL). Anal. Calcd for $OsC_{42}H_{45}N_5O_5$: C, 56.7; N, 5.10; N, 7.87. Found: C, 56.6; H, 5.20; N, 7.40. ^1H NMR: Table I. IR (Nujol mull): $\nu(C{\equiv}O)$ 1902 cm^{-1}. UV–Vis spectrum in CH_2Cl_2, λ_{max}/nm (log ϵ): 392 (5.2), 508 (4.0), 538 (4.2).

[Os(OEP)(CO)L] (L = EtOH, py). These complexes were characterized as described previously.[3]

Procedure for the Synthesis of *trans*-[OsPO₂]. [OsP(CO)] (0.1 g) was stirred with TBHP (2 mL) in CH_2Cl_2/EtOH solution (1:1, $\sim$50 mL) at room temperature for 1–2 h. After evaporation of ca. two-thirds of the solvent, a violet-black crystalline solid gradually deposited. This was then purified by chromatography using either a silica gel or an alumina column and with a CH_2Cl_2/acetone mixture (10:1) as the eluent. Overall yield varied between 60% and 80%.

[Os(MIX-DME)O₂] was prepared as a black solid from [Os(MIX-DME)(CO)] (0.1 g) and TBHP (1 mL). Anal. Calcd for $OsC_{36}H_{40}N_4O_6$: C, 53.2; H, 4.67; N, 6.9. Found: C, 53.5; H, 4.38; N, 6.60. UV–Vis spectrum in CH_2Cl_2, λ_{max}/nm (log ϵ): 376 (4.87), 431(sh) (4.04), 577 (3.76). IR (Nujol mull): $\nu_{as}(OsO_2)$ 839 cm^{-1}.

[Os(OEP)O₂]. This complex was characterized as described previously.[6]

[Os(OEP)(OEt)₂]. $[Os(OEP)O_2]$ (50 mg) and PPh_3 (50 mg) were stirred in a CH_2Cl_2/EtOH mixture (1:1) at room temperature. The course of the reaction was monitored by following the UV–vis spectral changes. When the 577-nm band had completely disappeared, the solution was evaporated to dryness. IR analysis of the solid product showed that Ph_3PO formed (peaks at 712 and 1175 cm^{-1}). The osmium product was purified by chromatography using either a silica gel or an alumina column and CH_2Cl_2 as the eluent. An orange-red solid separated that was identified as *trans*-$[Os(OEP)(OEt)_2]$.[7] UV–Vis spectrum in CH_2Cl_2, λ_{max}/nm (log ϵ): 370 (4.72), 495 (3.74), 527 (3.70).

Physical Measurements. Elemental analyses were performed by the Australian National Laboratory. IR spectra of Nujol mulls were measured on a Perkin-Elmer 577 spectrometer (4000–200 cm^{-1}). Electronic absorption spectra of freshly prepared solutions were measured with a Beckman Acta CIII spectrophotometer. ^1H NMR spectra were measured with a JEOL FX90Q Fourier transform NMR spectrometer, using tetramethylsilane as an internal reference.

Results and Discussion

The preparative method developed with $Os_3(CO)_{12}$ as a starting material is applicable to many different porphyrins, including protoporphyrin IX dimethyl ester and substituted *meso*-tetraphenylporphyrins.[8] Similar metal insertions also have been observed in ethoxyethanol (boiling point $\sim$135 °C), although longer reaction times ($\sim$24 h) are usually required. The relatively low value of the CO stretching frequency in [Os(MIX-DME)(CO)py] (1902 cm^{-1}) indicates that $d\pi\ (M^{II}) \rightarrow \pi^*$ (CO) back-bonding is more extensive than in [Ru(MIX-DME)(CO)Im] ($\nu(C{\equiv}O)$ 1940 cm^{-1}).[9] Additional evidence for the strong $d\pi$ donor character of Os^{II} comes from electronic absorption spectral data: The α and β bands of [Os(MIX-DME)(CO)py] (538 and 508 nm) fall at shorter wavelengths than those of a Ru^{II} analogue (554 and 522 nm),[9] thereby indicating that $d\pi\ (M^{II}) \rightarrow \pi^*$ (porphyrin) interactions are greater in the case of the 5d central atom. These $d\pi \rightarrow \pi^*$ (ligand) effects on the electronic and vibrational spectra of ruthenium and osmium porphyrins are reasonably well understood.[10]

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(1) (a) University of Hong Kong. (b) California Institute of Technology.

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Table I. 90-MHz ^1H NMR Data[a]

	$MIX(H_2)$-DME	[Os(MIX-DME)-(CO)EtOH]	[Os(MIX-DME)-(CO)py]	$[Os(MIX\text{-}DME)O_2]$
NH	−3.94	...	...	...
$CH_2C\mathit{H}_3$	1.83	1.84	1.82	1.98
$CH_2C\mathit{H}_2CO_2$	3.24	3.20	3.24	3.43
CH_3	3.51			3.78
	3.54			3.81
	3.54	3.52 (br)	3.50 (br)	
	3.58			
$CH_2CH_2CO_2C\mathit{H}_3$	3.65	3.58	3.57	3.70
	3.66	3.60	3.60	3.72
$C\mathit{H}_2CH_3$	3.99	3.91	3.91	4.24
$C\mathit{H}_2CH_2CO_2$	4.35	4.14	4.26	4.58
methine CH	9.43	9.55	9.59	10.64

[a] Chemical shifts are in ppm referenced to Me_4Si in $CDCl_3$ solution.

Buchler and Smith reported that *trans*-$[Os(OEP)O_2]$ was formed in the reaction of [Os(OEP)(CO)py] with H_2O_2,[6] but we have had difficulties with this procedure. We suggest that a more reliable route to *trans*-$[OsPO_2]$ complexes involves the oxidation of [OsP(CO)L] with TBHP. The ^1H NMR spectrum of *trans*-$[Os(MIX\text{-}DME)O_2]$ prepared by TBHP oxidation of the corresponding Os^{II} carbonyl shows that the porphyrin ring remains intact (Table I). Os^{VI} *trans*-dioxo species containing substituted *meso*-tetraphenylporphyrins also have been prepared in this way. Recent work has shown that the ^1H NMR spectrum of *trans*-$[Os(X\text{-}TPP)O_2]$ ($X\text{-}TPPH_2$ is a substituted *meso*-tetraphenylporphyrin) displays only one set of ortho protons,[8] thereby excluding the possibility that the oxidation product is an Os^{IV} peroxo species.

Although *trans*-$[Os(OEP)O_2]$ does not react with cyclohexane or cyclohexene at room temperature, it is reduced rapidly by PPh_3 in EtOH to form *trans*-$[Os(OEP)(OEt)_2]$.[7] The pathway for this reduction, as well as other aspects of the oxidation–reduction chemistry of the *trans*-$[OsPO_2]$ complexes, are under study.

Acknowledgment. We thank Terry Collins for helpful discussions. This research was supported by National Science Foundation Grant CHE82-18502 (H.B.G.) and by the Committee on Research and Conference Grants of the University of Hong Kong (C.-M.C., C.-K.P., W.-C.C.).

Registry No. [Os(MIX-DME)(CO)], 95387-76-1; [Os(OEP)(CO)], 77244-32-7; [Os(MIX-DME)(CO)EtOH], 95387-77-2; [Os(MIX-DME)(CO)py], 95387-78-3; [Os(OEP)(CO)EtOH], 52629-19-3; [Os(OEP)(CO)py], 51286-85-2; $[Os(MIX\text{-}DME)O_2]$, 95387-79-4; $[Os(OEP)O_2]$, 51349-77-0; $[Os(OEP)(OEt)_2]$, 95406-49-8; $Os_3(CO)_{10}$, 15696-40-9.

Additions and Corrections

1984, Volume 23

Brandan A. Borgias, Stephen R. Cooper, Yun Bai Koh, and Kenneth N. Raymond*: Synthetic, Structural, and Physical Studies of Titanium Complexes of Catechol and 3,5-Di-*tert*-butylcatechol.

Page 1013. In Table VIII the *z* coordinate of atom O3 should read −0.0088 (1) and the *y* coordinates of C35 and C36 should read −0.0775 (3) and −0.1021 (3), respectively.—Brandan A. Borgias

Richard G. Finke* and Benjamin P. Hay: Thermolysis of Adenosylcobalamin: A Product, Kinetic, and Co–C5′ Bond Dissociation Energy Study.

Page 3042. In column 2, line 27, the ΔS_2^* value of 23.1 ± 1.0 eu is incorrect; it should read $\Delta S_2^* = 14.6 \pm 0.8$ eu.—Richard G. Finke