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SYNTHESIS AND CHARACTERIZATION OF μ-OXO BIS(METHOXOOCTAETHYLPORPHYRINATOOSMIUM(IV))

Hiroshi SUGIMOTO* and Masayasu MORI
Department of Chemistry, Faculty of Science, Osaka City University, Osaka 558

The oxidation of octaethylporphyrinatoosmium(II)carbonyl with 2,3-dimethylindole/O_2 gave a new tetravalent osmium complex. The elemental analysis, molecular weight measurement and spectroscopic data indicate that this complex is a diamagnetic linear μ-oxo dimer of octaethylporphyrinatoosmium(IV) methoxide; $[OEPOs(IV)OCH_3]_2O$.

Osmium complexes of porphyrin are interesting from the bioinorganic point of view, because they are expected to have a homologous character with iron complexes (heme). Buchler and his coworkers synthesized many kinds of osmium(II) and (IV) complexes of octaethylporphyrin1) and widely investigated their electronic structure, electronically2) and theoretically.3) One of the most prominent character of the osmium complexes as contrasted with iron complexes is that tetravalent complexes can be easily isolated. Thus they obtained monomeric tetravalent complexes, such as $OEPOs(IV)(OCH_3)_2$ by the oxidation of the divalent complex OEPOs(II)CO.1)

In the investigation of catalytic oxidation of indole derivatives by metalloporphyrins, we have accidentally found that a catalyst OEPOs(II)CO is changed completely to a tetravalent complex.4) In this communication, we wish to report the synthesis and structure characterization of this new tetravalent osmium complex.

Octaethylporphyrinatoosmium(II)carbonyl, OEPOs(II)CO was treated with air in the presence of an excess amount of 2,3-dimethylindole in a mixture of dichloromethane-methanol until the color of the solution turned from orange red to dark purple red. After removal of solvents, the residue was chromatographed on an alumina column. The dark purple fraction was collected and the solvent was evaporated. Recrystallization of the crude materials from dichloromethane-methanol afforded purple crystals in about 70% yield.

$$\mathrm{OEPOs(II)CO} \xrightarrow[\text{in } CH_2Cl_2\text{-}CH_3OH]{\text{2,3-dimethylindole}/O_2} [\mathrm{OEPOs(IV)OCH_3}]_2\mathrm{O}$$

Anal. Calcd for $C_{74}H_{94}N_8O_3Os_2$:C,58.32; H,6.22; N,7.53. Found:C,59.15; H,6.16; N,7.46. Vis(in CH_2Cl_2)λ_{max}(logε) 353(4.87), 480(4.77), 460 (3.97), 500(3.87), 616(3.79) and 713nm(3.56). Molecular weight(in CH_2Cl_2) calcd. for $C_{74}H_{94}N_8O_3Os_2$:1524; Found 1532. Ir(KBr) 2780, 1010 cm^{-1}(axial OCH_3). Pmr(in $CDCl_3$ δ ppm from tetramethylsilane) 9.22(singlet,8H,methine), 4.21(ABX_3 multiplet, 32H,α-methylene), 1.82(triplet,48H,β-methyl) and -3.54(singlet,6H,methoxy). Pmr spectrum of the complex is illustrated in Figure 1. The magnetic susceptibility of the chloroform solution measured by Evans method showed that this complex is completely diamagnetic. The chemical shifts of α-methylene and β-methyl are in the normal range of diamagnetic metalloporphyrins, while that of methine protons is

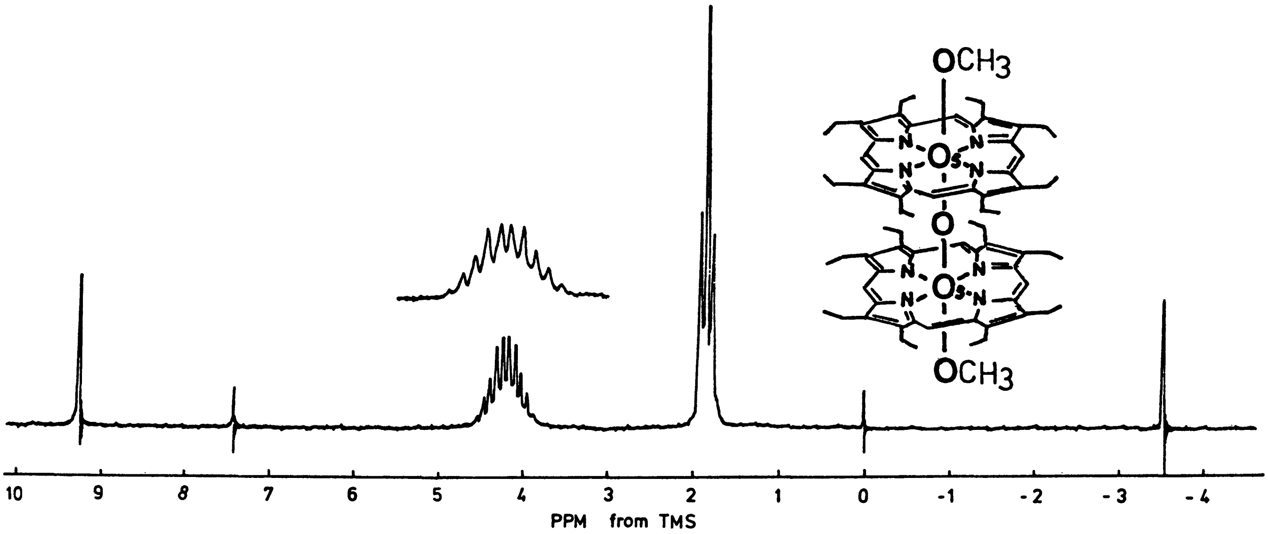

Figure 1. Pmr spectrum of $[OEPOs(IV)OCH_3]_2$.

shifted toward high magnetic field by about 1 ppm.[1] Methoxy protons resonate at -3.54 as a singlet signal. Such large up-field shift can be explained in terms of the diamagnetic ring current of porphyrin ring, if methoxy group is considered to coordinate axially to the central osmium atom. Moreover, the coupling pattern of α-methylene protons is ABX_3 multiplet which could be established by the decoupling method. This diastereotopic α-methylene may be due to the lack of equvalence in the porphyrin plane.[5] These pmr spectral features are very similar to those for the diamagnetic linear μ-oxo dimer of hydroxooctaethylporphyrinatoruthenium(IV) $[OEPRu(IV)OH]_2O$ which was recently confirmed by the X-ray crystallography.[6]

From these results, this new tetravalent osmium complex is concluded to be a diamagnetic linear μ-oxo dimer. The diamagnetism and the linear structure of the complex suggest the existence of the double bond character between metal and bridged oxygen $Osd_{xz,yz}$-$Op_{x,y}$-$Osd_{xz,yz}$, as theorized qualitatively by Orgel and Dunitz.[7]

Notes and References

1) J. W. Buchler and K. Rhobock, J. Organometal. Chem., 65, 223(1974).; J. W. Buchler and P. D. Smith, Chem. Ber., 109, 1465(1976); J. W. Buchler and P. D. Smith, Angew. Chem., 86, 378, and 820(1974).
2) G. M. Brown, F. R. Hopf, T. G. Meyer, and D. G. Whitten, J. Am. Chem. Soc., 102, 198(1975).
3) A. Antipas, J. W. Buchler, M. Gouterman and P. D. Smith, J. Am. Chem. Soc., 100, 3015(1978) and 102, 198(1980).
4) This complex could be prepared only by this method described below, although the mechanism of the oxidation is now ambigious.
5) The coupling pattern of α-methylene for other monomeric complexes such as $OEPOs(OCH_3)_2$ and $OEPOsO_2$ is reported to be A_2X_3 quartet.[1]
6) H. Masuda, T. Taga, K. Osaki, H. Sugimoto, M. Mori and H. Ogoshi, J. Am. Chem. Soc., in press.
7) J. D. Dunitz and L. E. Orgel, J. Chem Soc., 2594(1953).

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