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PREPARATION AND CHARACTERIZATION OF OXOMOLYBDENUM(V)-PORPHYRIN COMPLEXES†

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Oxomolybdenum(V) complexes of tetraphenylporphine and octaethylporphine, Mo(O)-(OC_2H_5)(TPP) and Mo(O)(OEP)X (X = Cl or OCH_3), were prepared from the corresponding porphyrins by reaction with molybdenum pentachloride. Both ESR and electronic spectra indicate that the complexes coordinated with an alkoxide group exist in dichloromethane or chloroform as a single monomeric species, while more than one species are present in aromatic solvents for each of the complexes.

Planar complexes of transition-metal ions which belong to the second and third series have attracted much attention in reference to the preparation of linear polymeric complexes of high electric conductivity. In order to find out the means of providing mononuclear metal complexes as unit components of such polymer species, we have previously prepared and characterized oxo(2,3,17,18-tetramethyl-7,8,12,13-tetraethylcorrolato)molybdenum(V).[1] Meanwhile, porphyrin complexes of molybdenum(V) were prepared by reactions of molybdenum in a low valency state with porphyrins as reported by several authors.[2-4] Since pentavalent molybdenum has the strong affinity for oxygen, only oxo-complexes, Mo(O)(porphyrin)X, have been isolated. The axial ligands (X) in those complexes are the bridging oxo group and other oxygen donors. Fleischer *et al.*[2] prepared and characterized some oxomolybdenum(V) complexes of α,β,γ,δ-tetraphenylporphine (abbreviated as TPP) with halogen and nitrogen donors as the axial ligand. Two or more Soret bands were observed for those complexes, indicating that more than one species exist at least in some organic solvents. They also reported on spin Hamiltonian parameters without superhyperfine coupling constants which may arise from the interaction with four nitrogen donor atoms of TPP. Buchler *et al.* characterized Mo(O)(OEP)(OR) in mononuclear form by means of IR and visible spectroscopy,[3] where OEP and OR stand for 2,3,7,8,12,13,17,18-octaethylporphine and alkoxy group, respectively. We report here a new method for preparation of molybdenum(V)-porphyrin complexes, and discuss the nature of the axial coordinate bonds by means of ESR and visible spectroscopy since there remains much structural ambiguity for those complexes.

Preparation of (Ethoxo)oxo(α,β,γ,δ-tetraphenylporphinato)molybdenum(V) (**1**).——— Molybdenum pentachloride (1.8 g), TPP (340 mg), and sodium acetate (4 g) were dissolved in 120 ml of decalin, and the mixture was heated at 180-190°C under nitrogen atmosphere with stirring for 7 h. The filtrate of the reaction mixture was applied on a

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column of dry aluminum oxide (Woelm neutral, activity grade 1), and a dark green band was eluted with chloroform containing 1%(v/v) ethanol. The effluent was re-chromatographed on another fresh column of aluminum oxide with the same eluant. The dark green effluent was collected and evaporated to dryness. The solid residue of dark green luster was recrystallized from dichloromethane – hexane; yield 110 mg (25.9 %). Found: C, 71.99; H, 4.49; N, 6.93%. Calcd for $C_{46}H_{33}MoN_4O_2$: C, 71.78; H, 4.32; N, 7.28%. Preparative procedure for Mo(O)(OH)(TPP) reported by Fleischer *et al.*[2], for which molybdenum hexacarbonyl was used as a metal source, gave a metal complex of the identical composition.

Preparation of (2,3,7,8,12,13,17,18-Octaethylporphinato)oxomolybdenum(V) Complexes.——— Molybdenum pentachloride (1.5 g) underwent reaction with OEP (200 mg) in 70 ml of decalin in the presence of sodium acetate (2.7 g) under nitrogen atmosphere at 190°C for 7 h. Repeated chromatography on a column of dry aluminum oxide with dichloromethane as an eluant, followed by recrystallization from dichloromethane – hexane containing a small amount of benzene, gave green needles of metallic luster; yield 50 mg (20 %). Found: C, 63.40; H, 6.51; N, 8.06%. Calcd for $C_{36}H_{44}ClMoN_4O$ (2): C, 63.57; H, 6.52; N, 8.24%. The complex gave dark violet needles of solvolyzed species Mo(O)(OCH_3)(OEP) (3) by recrystallization from dichloromethane – methanol containing a small amount of 10% aqueous potassium hydroxide. Found: C, 64.90; H, 6.94; N, 8.19%. Calcd for $C_{37}H_{47}MoN_4O_2$: C, 65.77; H, 7.01; N, 8.29%.

Electronic Spectra.——— The electronic spectra of the present complexes are shown in Fig. 1, and the corresponding data are listed in Table 1. Each of Mo(O)-(OC_2H_5)(TPP) and Mo(O)(OCH_3)(OEP) shows one Soret band and α- and β-bands. The TPP complex in benzene, however, shows two strong bands in the 400-500 nm region and three bands in the 550-650 nm range. The former bands may be assigned to the Soret-type transition, while the latter to the α- and β-type transitions. These observations indicate that the TPP complex is present as a single species in chlorinated solvents (dichloromethane and chloroform), while as more than one species in benzene. The broadness of absorption bands for MoCl(O)(OEP) may suggests the presence of multiple number of metal complex species by solution equilibria.

ESR Spectra.——— The ESR spectra of Mo(O)(OC_2H_5)(TPP) at room temperature are shown in Figs. 2 and 3. The spectrum measured at room temperature in chloroform consists of nine intense lines at the center and six weaker bands in a wider range. The central intense lines are assigned to the superhyperfine structure due to the interaction with four nitrogen nuclei (I = 1) around Mo nucleus (^{94}Mo, ^{96}Mo, ^{98}Mo, and ^{100}Mo; I = 0). The six weaker bands are assigned to the hyperfine structure caused by the interaction with ^{95}Mo and ^{97}Mo nuclei (I = 5/2). A small difference in nuclear magnetic moment between ^{95}Mo and ^{97}Mo gives rise to the slight broadening effect on the bands. Although the TPP complex shows a similar spectral feature in benzene, eleven superhyperfine lines were observed at the center as shown in Fig. 3b. This can be attributed to one of the following effects. (i) The complex is present in benzene as a dimer species (4), so that a triplet or a double-doublet spin state is allotted to such a dimer at its ground or excited state. Each of the unpaired spins interacts with the four nitrogen nuclei to provide nine superhyperfine lines because each electron is not delocalized through Mo-O-Mo bond. Eleven lines can be observed, however, only if the two electrons have slightly different g-values from each other.

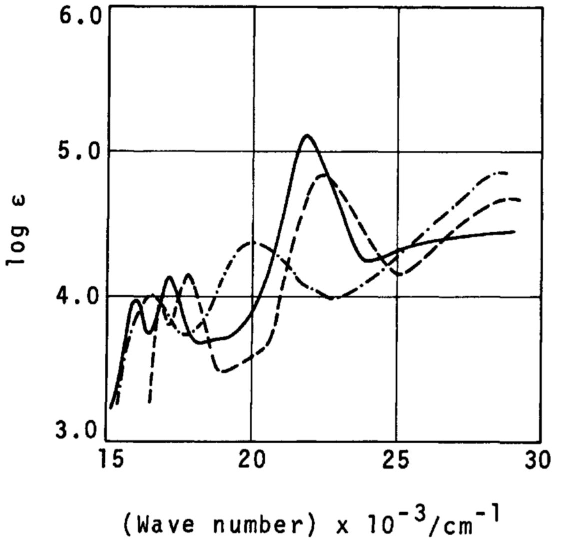
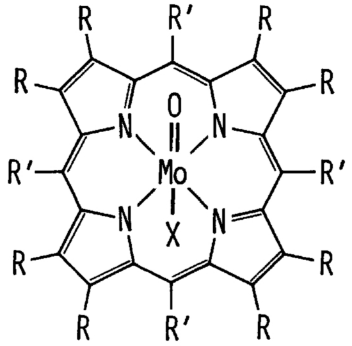


Fig. 1. Electronic absorption spectra for oxomolybdenum(V) complexes at room temperature: ——, Mo(O)(OC_2H_5)(TPP) in $CHCl_3$; —·—, MoCl(O)(OEP) in CH_2Cl_2; ----, Mo(O)(OCH_3)(OEP) in CH_2Cl_2.



1: R = H, R' = Ph, X = OC_2H_5

2: R = C_2H_5, R' = H, X = Cl

3: R = C_2H_5, R' = H, X = OCH_3

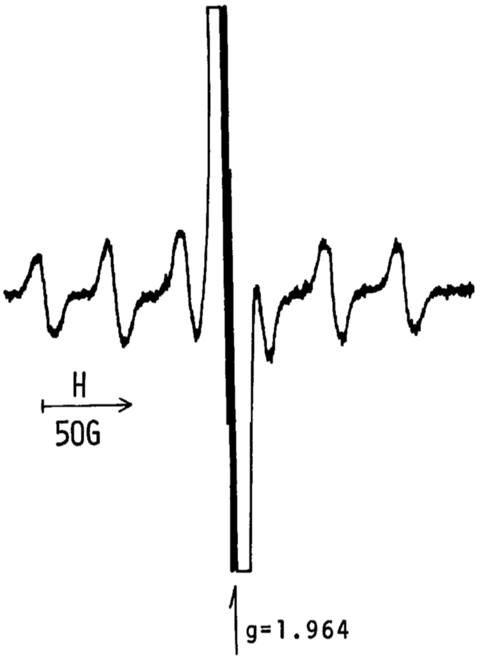


Fig. 2. ESR spectrum of Mo(O)(OC_2H_5)(TPP) in chloroform at room temperature.

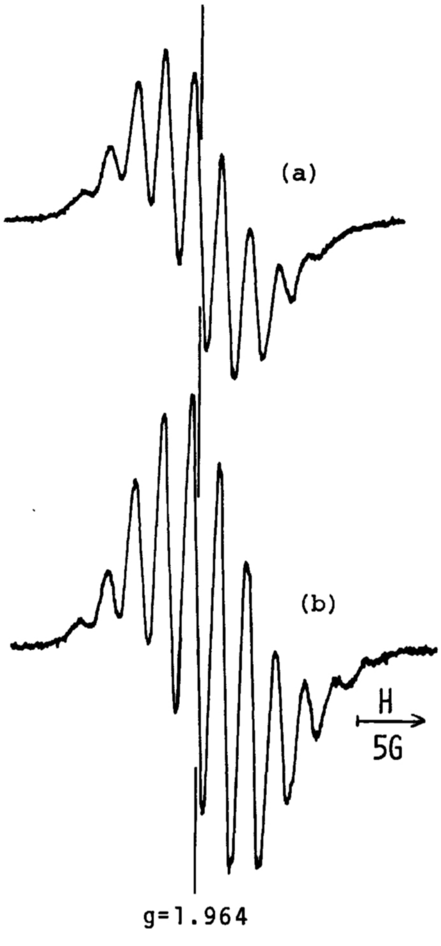


Fig. 3. Superhyperfine structures due to four nitrogen nuclei located at the center of ESR spectra of Mo(O)(OC_2H_5)(TPP): at room temperature in a) chloroform, and b) benzene.

Table 1. Electronic spectral data for visible region

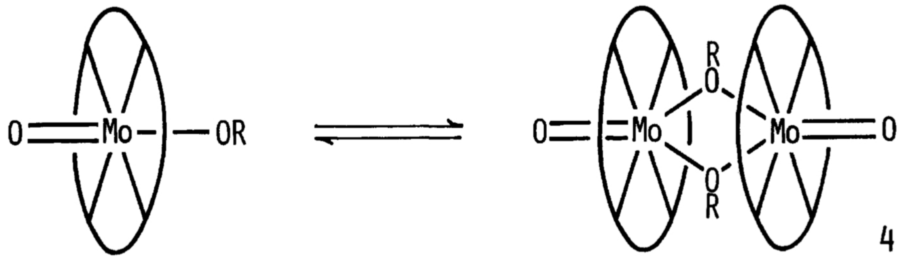
Complex	Solvent	λmax/nm ($\varepsilon \times 10^{-4}$/l mol^{-1} cm^{-1})
$Mo(O)(OC_2H_5)(TPP)$	$CHCl_3$	457 (12.8), 583 (1.42), 625 (0.95)
$MoCl(O)(OEP)$	CH_2Cl_2	497 (2.33), 607 (1.03)
$Mo(O)(OCH_3)(OEP)$	CH_2Cl_2	447 (6.72), 563 (1.44), 595 (0.90)

Table 2. Spin Hamiltonian parameters

Complex	Solvent	$\bar{g}$ *a)*	$\bar{A}_N \times 10^4$ *a)* (cm^{-1})	$\bar{A}_{Mo} \times 10^4$ *a)* (cm^{-1})	$g_\parallel$ *b)*	$g_\perp$ *b)*	$A_{Mo\parallel} \times 10^4$ *b)* (cm^{-1})	$A_{Mo\perp} \times 10^4$ *b)* (cm^{-1})
$Mo(O)(OC_2H_5)(TPP)$	$CHCl_3$	1.964	2.34	45.2	1.964	1.960	72.9	31.2
$MoCl(O)(OEP)$	CH_2Cl_2	1.962	2.39	44.0				
$Mo(O)(OCH_3)(OEP)$	CH_2Cl_2	1.962	2.34	44.0	1.964	1.960	70.8	30.4

a) Measured at room temperature. *b)* Measured at 77 K.

(ii) The complex is in monomer ⇌ dimer equilibrium in benzene solution. Both monomer and dimer show nine superhyperfine lines independently, provided that the g-value for the dimer is very close to that for the monomer. The latter effect is consistent with the corresponding electronic spectrum. The origin of eleven superhyperfine lines is, consequently, attributed to the formation of a dimer species under the following equilibrium. A similar spectral feature has been observed for MoCl(O)(OEP) as measured both in benzene and in dichloromethane, and for $Mo(O)(OCH_3)(OEP)$ as measured in benzene. The spin Hamiltonian parameters are given in Table 2.



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In conclusion, the coordinating group at the axial site *trans* to the oxo-group is bound loosely to the molybdenum so that the dimerization may occur quite readily through the double-bridge formation.

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