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NEW OXOMOLYBDENUM(V) COMPLEXES OF TETRAPHENYLPORPHINE WITH UNIVALENT LIGANDS*

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New tetraphenylporphine complexes of oxomolybdenum(V), MoO(tpp)X (X = NCS and Br), were synthesized, and characterized by means of IR, ESR, and electronic spectra. The formation of a hyperoxide complex, MoO(tpp)(O_2), in dichloromethane was confirmed.

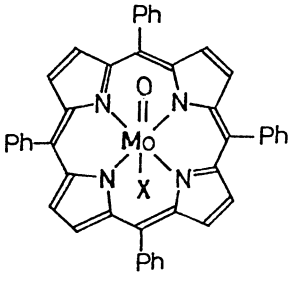
The reactions of dioxygen complexes of metalloporphyrins have been studied with current interests, especially in the biochemical redox reactions.1-5) However, only a few studies have been reported for the substitution reactions of molybdenum porphyrin complexes in solution. In the present communication, we report the preparations of a series of new molybdenum(V) complexes of meso-tetraphenylporphine (abbr. TPP) and the formation of a hyperoxide complex in dichloromethane.

Synthesis of the complexes. The starting material, ethoxo complex, MoO(tpp)(OC_2H_5), was prepared according to a modified method of the literature.6)

The thiocyanate complex, MoO(tpp)(NCS), was synthesized as follows. An aqueous solution of potassium thiocyanate was mixed with a dichloromethane solution of the ethoxo complex in a separatory funnel. The green dichloromethane solution turned gradually brown. The dichloromethane layer was evaporated to dryness. The residue was dissolved in dichloromethane. The solution was filtered through a glass filter to remove potassium thiocyanate. The filtrate was evaporated to dryness. Green needles thus obtained were recrystallized from dichloromethane-hexane (1/10 v/v).

The halo complexes, MoO(tpp)Cl·HCl and MoO(tpp)Br, were prepared in the same manner as described above, except for the addition of a small amount of free acids, HX, to the aqueous solution of NaX or KX, in order to promote the substitution reaction. The complexes were dried in vacuo (yield ca. 86%). Purity of the complexes was confirmed by the elemental analyses (see Table 1).

The absorption spectrum of the complex, MoO(tpp)Cl·HCl, prepared was almost the same as that reported for MoO(tpp)Cl by Ledon et al.7) No absorption peaks were observed at 382 and 448 nm as reported for MoO(tpp)Cl·HCl by Srivastava and Fleischer.8)



MoO(tpp)X

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The ESR spectra of all the complexes consisted of six weak lines due to ^{95,97}Mo (I = 5/2) nuclei (natural abundance ca. 25%). The hyperfine structure revealed that the central molybdenum atom is in the d^1 Mo(V) state for all the complexes shown in Table 2. A strong central line due to the molybdenum nucleus with I = 0 was split into nine lines. This superhyperfine structure was assigned to the interaction of the Mo nucleus (I = 0) with four nitrogen nuclei (I = 1) of the ligand, TPP.

An intense IR absorption band observed for each complex in the region of 904-953 cm^{-1} was ascribed to the Mo=O stretching.$^{9)}$ No definite correlation was observed between the frequencies of the Mo=O stretching and the λ_{max} of the electronic spectra (see Table 3). The Mo-Cl bond of the complex, MoO(tpp)Cl·HCl, would have an ionic character, since the absorption peaks and the IR band for Mo=O were observed in almost the same frequency range as those of MoO(tpp)Cl whose ionic character was suggested based on the structural analysis.$^{7)}$ An ionic character was also suggested for the complex, MoO(tpp)(NCS), since a band ascribed to the CN stretching of NCS of the complex in dichloromethane and Nujol mull was observed at the same frequency, 2075 cm^{-1}, as that for potassium thiocyanate in dichloromethane.

The values of λ_{max} and ε_{max} for the electronic spectra of the complexes in dichloromethane are shown in Table 3. Three absorption peaks, the Soret band, the β, and the α bands were observed. The Soret band and the β band, and the β and the α bands were separated from each other by ca. 125 and ca. 40 nm, respectively. The values of λ_{max} for the complexes were increased in the order C_2H_5O < Br < NCS < Cl. The molar absorption coefficients of the Soret band and the β band decreased in the same order accompanied by the increase in the ratio of the absorption coefficients, $\varepsilon_\alpha/\varepsilon_\beta$. The dependence of the values of λ_{max} on the univalent ligand, X, was different from that reported for the corresponding zinc complexes, Zn(tpp)X.$^{10)}$ The absorption peaks were shifted in chloroform toward longer wavelengths by 1-3 nm with a slight decrease in molar absorption coefficients.

Equilibrium of the substitution reactions in dichloromethane. Dichloromethane solutions of KX or NaX (X = NCS, Cl, Br, and C_2H_5O) were prepared by adding a small amount of dicyclohexyl-18-crown-6 or 18-crown-6 as a solubilizing agent. The presence of a small amount of crown ether does not affect spectra of the complexes. The change in the spectrum of the ethoxo complex observed by the addition of a large amount of the crown ether suggested the formation of some crown ether complex.$^{11)}$ Tetrabutylammonium chloride was also used. No difference in the spectrum was observed between potassium chloride and tetrabutylammonium chloride.

Upon mixing the dichloromethane solution of halide or thiocyanate with a dichloromethane solution of the ethoxo complex, the spectrum changed with isosbestic points, suggesting the presence of an equilibrium. The spectra in the presence of a large excess of halide or thiocyanate coincide with the spectra of the dichloromethane solution of the corresponding complex, MoO(tpp)X (X = Cl, Br, and NCS). Since the reversed change in the spectra was observed by the addition of a dichloromethane solution of sodium ethoxide, the following equilibrium was confirmed.$^{12)}$

$$\mathrm{MoO(tpp)(OC_2H_5)} + \mathrm{X^-} \rightleftharpoons \mathrm{MoO(tpp)X} + \mathrm{C_2H_5O^-}$$

Table 1. Elemental analyses

Complex	Found (Calcd) %			
	C	H	N	S
MoO(tpp)(OC$_2$H$_5$)	71.67 (71.78)	4.40 (4.32)	7.15 (7.28)	
MoO(tpp)(NCS)	68.96 (69.05)	3.92 (3.61)	8.77 (8.75)	4.02 (4.10)
MoO(tpp)Cl·HCl	67.14 (66.33)	3.81 (3.64)	7.03 (7.04)	
MoO(tpp)Br	65.98 (65.69)	3.28 (3.51)	6.78 (6.96)	

Table 2. ESR parameters a)

Complex	$\bar{g}$ d)	$\bar{A}_M$/G	$\bar{A}_N$/G
MoO(tpp)(OC$_2$H$_5$) b)	1.967	49.6	2.41
MoO(tpp)(O$_2$) c)	1.967	49.0	2.32
MoO(tpp)(NCS)	1.967	48.2	2.46
MoO(tpp)Cl·HCl	1.967	49.5	2.39
MoO(tpp)Br	1.967	48.7	2.54

a) In CH$_2$Cl$_2$ at room temperature.
b) The values of the parameters are almost the same as those reported.[6]
c) Measured with a 10%(v/v) DMSO-CH$_2$Cl$_2$ solution of MoO(tpp)(NCS) containing an excess of O$_2^-$.
d) Experimental errors are estimated to be ± 0.005.

Table 3. Absorption peaks in visible and IR regions

Complex	λ_{max}/nm (ε_{max}/10^4 mol^{-1} dm^3 cm^{-1})			ν(Mo=O)/cm^{-1}
	in CH$_2$Cl$_2$ at 25 °C			(Nujol mull)
MoO(tpp)(OC$_2$H$_5$)	454 (15.8)	582 (1.51)	622 (1.04)	904
MoO(tpp)(O$_2$) a)	453 (15.9)	578 (1.51)	618 (1.00)	
MoO(tpp)Br	481 (4.83)	602 (0.92)	648 (0.69)	937
MoO(tpp)(NCS)	496 (4.35)	623 (0.89)	668 (0.87)	953
MoO(tpp)Cl·HCl b)	499 (4.19)	626 (0.85)	673 (0.90)	935
MoO(tpp)Cl c)	504 (4.10)	632 (0.84)	678 (0.92)	937
	in CHCl$_3$ at 25 °C			
[MoO(tpp)(18-crown-6)$_n$]$^+$	477 (4.56)	612 (0.85)	657 (0.68)	

a) Measured with a 1%(v/v) DMSO-CH$_2$Cl$_2$ solution of MoO(tpp)(NCS) containing an excess of O$_2^-$. b) A shoulder was observed at 418 nm. c) Ref. 7).

Formation of a hyperoxide complex. The spectrum of the dichloromethane solution of MoO(tpp)(NCS) changed with a set of isosbestic points by the addition of a small amount of DMSO solution of potassium hyperoxide, the final composition of the solvent being kept constant. The stoichiometry of the reaction was determined to be 1 : 1 based on the results of the molar-ratio method. The final spectrum of the reaction mixture did not change by the addition of a large excess of hyperoxide under the experimental conditions. These results suggest the formation of a new complex, MoO(tpp)(O_2), in dichloromethane. The ESR parameters are almost the same as those for the complexes, MoO(tpp)X (X = Cl, Br, NCS, and C_2H_5O). This fact suggests that hyperoxide is coordinated to the molybdenum only as a ligand, having no influence on the oxidation state of the central atom.

Materials and measurements. Potassium hyperoxide (ICN Pharmaceuticals) and the crown ethers, dicyclohexyl-18-crown-6 and 18-crown-6 (Nippon Soda), were used without further purification. Potassium thiocyanate and potassium halides were dried in vacuo at 150 °C. Tetrabutylammonium chloride was dried in vacuo over P_2O_5 at room temperature. Dimethyl sulfoxide was dried with calcium hydride, distilled under reduced pressure, and stored under argon atmosphere. Chloroform and dichloromethane were passed through a column of alumina to remove ethanol or methanol added as a stabilizer, and distilled. The solutions of hygroscopic substances (KNCS, KO_2, etc.) were prepared under nitrogen atmosphere. All spectrophotometric measurements were carried out at 25 ± 0.1 °C.

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11) The composition of this complex is not clear. Apparent stability constant for 18-crown-6 was found to be larger than that for dicyclohexyl-18-crown-6. Similar tendency was reported for the zinc complex, Zn(tpp).[10)]
12) Preliminary stopped-flow measurements of the substitution reaction revealed that the pseudo-first-order rate constants evaluated in the presence of a large excess of the ligand depend on the initial concentrations of the ligand.

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