Absorption Spectra of New Oxomolybdenum(V) Complexes of Tetraphenylporphyrin with Univalent Ligands

Taira Imamura,* Takayuki Numatatsu, Masashi Terui, and Masatoshi Fujimoto*
Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo 060

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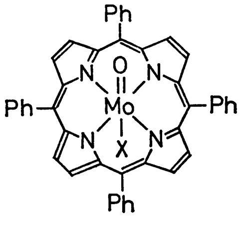
New tetraphenylporphyrin complexes, MoO(tpp)X (X=F, Br, BF_4, NCO, N_3, and NCS), are easily prepared from the complex, $MoO(tpp)OC_2H_5$, where TPP denotes *meso*-tetraphenylporphyrin. The complexes are confirmed to contain a central oxomolybdenum(V) group based on the IR and the ESR measurements. The visible absorption spectra of the complexes in dichloromethane have three main peaks, the Soret band, the α and the β bands. The degree of red shifts of the corresponding absorption maxima is found to increase in the order: $X=OC_2H_5<BF_4\simeq F<NCO<N_3<NCS<Cl<Br$, accompanied with the same order of the change in the ratio $\varepsilon_\alpha/\varepsilon_\beta$. The correlation is also observed between the red shifts of the absorption peak around 330 nm and those of the Soret band. The complexes, MoO(tpp)X, are classified to d-type hyperporphyrin.

The dependences of the absorption spectra of metalloporphyrins on the nature of the axial anionic ligands have been widely studied.[1,2] Valentine *et al.* reported that the red shift observed in the visible absorption spectra of a series of zinc(II) complexes, $Zn(tpp)X^-$, in several organic solvents is correlated with the charge and the polarizability of the axial ligand X.[2] However, the electronic spectral studies on the effect of anionic ligands in oxomolybdenum(V) porphyrin complexes were limited to a MoO(oep)X series (oep= octaethylporphyrin; X=MeO, PhO, OAc, F, NCS, and Cl).[1,3]

We easily synthesized in the present work several new oxomolybdenum(V) tetraphenylporphyrin complexes, MoO(tpp)X, and characterized the complexes based on the IR and the visible absorption spectra.



MoO(tpp)X

Experimental

Materials. All reagents are of analytical grade unless otherwise specified. Dichloromethane was distilled and passed through a column of basic alumina to remove stabilizers and impurities. The purified solvent was again distilled immediately before use. Purity of dichloromethane was checked as follows using colorations of the complex, MoO(tpp)Br, in this solvent. The complex assumes red to pink color in dichloromethane of high purity, but turns green if the solvent contains any trace of impurities. Molybdenum(V) chloride, $MoCl_5$, was stored under argon atmosphere. Potassium cyanate was recrystallized from water–ethanol mixture.[4]

Measurements. Electronic spectra were measured at 25.0±0.1 °C with a Hitachi spectrophotometer Model 808. IR spectra were measured at room temperature with a JASCO spectrometer Model IR-G. ESR spectra were measured at room temperature with a JES-ME-3X spectrometer operating at 100 kHz modulation.

Results and Discussion

Syntheses of the Complexes. The ethoxo complex, $MoO(tpp)OC_2H_5$, was synthesized as follows, according to a modified method of the literature.[5] *meso*-Tetraphenylporphyrin (2 g), molybdenum(V) chloride (5.4 g), and anhydrous sodium acetate (12 g) were dissolved in this order in decalin (300 cm^3) deoxygenated beforehand by bubbling nitrogen gas for *ca.* 1 h. The solution was refluxed for 7 h at 180—190 °C under nitrogen atmosphere, allowed to stand for 12 h at room temperature, and filtered through a glass filter. The residue was dissolved in chloroform containing 1% ethanol. The solution was filtered through a glass filter. The green filtrate was evaporated to dryness. The residue was again dissolved in chloroform containing 1% ethanol. The solution was passed through a column of alumina (Woelm, activity grade 1, neutral) and eluted with a 1:100 (v/v) mixture of ethanol and dichloromethane. After the separation of a green and a red band, the green band was selectively eluted with chloroform containing 1% ethanol. The eluate was evaporated to dryness to yield violet crystals. The crystals were recrystallized from a 1:100 (v/v) mixture of dichloromethane containing 1% ethanol and hexane (yield 23%).

The complexes, $MoO(tpp)BF_4$ and MoO(tpp)NCS, were synthesized as follows. An aqueous solution of potassium tetrafluoroborate or potassium thiocyanate was mixed in a separatory funnel with a dichloromethane solution of $MoO(tpp)OC_2H_5$. The dichloromethane layer was evaporated to dryness. The residue was dissolved in dichloromethane. The solution was filtered through a glass filter to remove potassium tetrafluoroborate or potassium thiocyanate. The filtrate was evaporated to dryness. The residue was recrystallized from a 1:10 (v/v) mixture of dichloromethane and hexane to yield green (X=NCS) or violet needles ($X=BF_4$).

The halo complexes, MoO(tpp)F, MoO(tpp)Cl, and MoO(tpp)Br, were prepared from $MoO(tpp)OC_2H_5$ in the same manner as described above, except for the addition of a small amount of a corresponding free acid, HX, to the aqueous solution of NaX or KX, in order to promote the substitution reaction. For the synthesis of the fluoro complex, a Teflon sep-

Table 1. Elemental analyses

Complex	Found (Calcd) (%) C	H	N	S
MoO(tpp)OC_2H_5	71.67 (71.78)	4.40 (4.32)	7.15 (7.28)	
MoO(tpp)F	70.06 (71.07)	3.91 (3.80)	7.15 (7.53)	
MoO(tpp)Cl	68.27 (69.53)	3.62 (3.71)	7.24 (7.37)	
MoO(tpp)Br	65.98 (65.69)	3.28 (3.51)	6.78 (6.96)	
MoO(tpp)BF_4	64.90 (65.13)	3.71 (3.48)	6.90 (6.90)	
MoO(tpp)N_3	69.02 (68.93)	3.74 (3.68)	11.31 (12.79)	
MoO(tpp)NCO	70.66 (70.50)	3.72 (3.68)	8.93 (9.14)	
MoO(tpp)NCS	68.96 (69.05)	3.92 (3.61)	8.77 (8.75)	4.02 (4.10)

aratory funnel was used. Each complex was dried *in vacuo* at 100 °C. When the complex was dried *in vacuo* at room temperature, a mixture of MoO(tpp)F and MoO(tpp)F·HF or a mixture of MoO(tpp)Cl and MoO(tpp)Cl·HCl was obtained. The synthesis of the complex, MoO(tpp)Cl, by different method was reported by Ledon *et al.*[6] The visible absorption spectra of the complex, MoO(tpp)Cl, was almost the same as that of Ledon's complex.

The complexes, MoO(tpp)N_3 and MoO(tpp)NCO, were prepared in the same manner as described for the synthesis of the halo complexes. The aqueous solution of free acids, HN_3 or HOCN, was freshly prepared by passing the aqueous solution of NaN_3 or KOCN through a column of a cation-exchange resin, Dowex 50W-X8, in the hydrogen-form. Purity of the complexes was confirmed by the elemental analyses (see Table 1).

Trials for the Syntheses of Other TPP Complexes. The synthesis of the iodo complex, MoO(tpp)I, was tried in the same manner as described in the preparation of other halo complexes; the bromo complex, MoO(tpp)Br, was used as a starting material. The IR spectra of the brown crystals thus obtained showed no evidence for the Mo=O bond. The feature of the visible absorption spectrum was different from that of the spectra of other halo complexes.

The synthesis of the perchlorato complex, MoO(tpp)ClO_4, was also tried. The visible absorption spectra in dichloromethane of the obtained compound show three peaks in the region of the α and the β bands, suggesting the formation of a complex of a different formula or a mixture containing some other complexes.

ESR Spectra. The ESR spectra of the complexes, MoO(tpp)X, always consisted of six weak lines due to ^{95,97}Mo nuclei (I=5/2) (abundance *ca.* 25%). The hyperfine structure revealed d^1 Mo(V) state of the central molybdenum atom in all the complexes synthesized. The g-values were found to be 1.967±0.005 for all complexes. 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. The ESR parameters for several complexes were already reported.[7]

IR Spectra. An intense IR absorption band ascribed to the Mo=O stretching was observed around 935—938 cm^{-1} for each complex, suggesting that synthesized complexes are all oxomolybdenum(V) complexes. The values of ν(Mo=O) are not different among F, Cl, and Br complexes (see Table 2). The BF_4, N_3, and NCO complexes have the absorption peak for the Mo=O stretching in the region of 940 cm^{-1}. The doublet IR bands ascribed to the CN stretching for the complex, MoO(tpp)NCO, were observed at 2060 and 2080 cm^{-1}. The band corresponding to the CN stretching for the complex, MoO(tpp)NCS, was observed at 2075 cm^{-1}. These results suggest that the ligands, NCO^- and NCS^-, in the complexes are coordinated to the central molybdenum atom with N atoms.

Table 2. Absorption peaks in infrared region

Complex	ν(Mo=O)/cm^{-1} (Nujol mull)
MoO(tpp)OC_2H_5	904
MoO(tpp)F	938
MoO(tpp)Cl	935
MoO(tpp)Cl[a]	937
MoO(tpp)Br	937
MoO(tpp)BF_4	940
MoO(tpp)N_3	935
MoO(tpp)NCO	940
MoO(tpp)NCS	950

a) Ref. 6.

Visible Absorption Spectra. The values of λ_{max} and ε_{max} for the electronic spectra of the complexes, MoO(tpp)Br and MoO(tpp)Cl·HCl, were previously reported by the present authors.[7] However, in the detailed characterization of the synthesized complexes, we noticed that the visible absorption spectra of these complexes, especially of MoO(tpp)Br, are very sensitive to impurities in the organic solvents applied.[8] Therefore, the absorption spectra of these complexes were remeasured and corrected. The values of λ_{max} and ε_{max} of the absorption spectra for the complexes in pure dichloromethane are listed in Table 3, suggesting that the complexes, MoO(tpp)X, belong to d-type hyperporphyrin.[1] A typical absorption spectrum is given in Fig. 1. The most intense absorption peak in the visible region, the B or the Soret band, was observed around 460—500 nm, and the other intense bands, the Q or the β and the α bands between

TABLE 3. ABSORPTION PEAKS IN UV AND VISIBLE REGIONS

Complex	λ_{max}/nm ($\varepsilon/10^4$ mol^{-1} dm^3 cm^{-1}) in CH_2Cl_2 at 25 °C					
				Soret	β	α
MoO(tpp)OC_2H_5	320(3.42)	385(sh)		454(15.8)	582(1.51)	622(1.04)
MoO(tpp)F	325(3.70)	370(sh)	390(sh)	463(9.71)	592(1.30)	635(1.04)
MoO(tpp)Cl	337(6.12)	380(sh)	417(2.90)	500(4.17)	627(0.85)	674(0.96)
MoO(tpp)Cl[a]			402(sh)	504(4.1)	632(0.84)	678(0.92)
MoO(tpp)Br	350(6.40)	375, 390(sh)	421(2.63)	508(3.45)	638(0.71)	686(0.86)
MoO(tpp)BF_4	325(4.07)	370(sh)	390(sh)	463(9.82)	591(1.35)	634(1.09)
MoO(tpp)N_3	327(4.17)	369(4.00)	412(3.37)	490(4.34)	616(0.81)	662(0.83)
MoO(tpp)NCO	333(4.76)	360(sh)	413(2.87)	488(4.66)	617(0.85)	664(0.86)
MoO(tpp)NCS	333(5.42)	370(sh)	410(sh)	493(4.55)	622(0.91)	667(0.93)

a) Ref. 6.

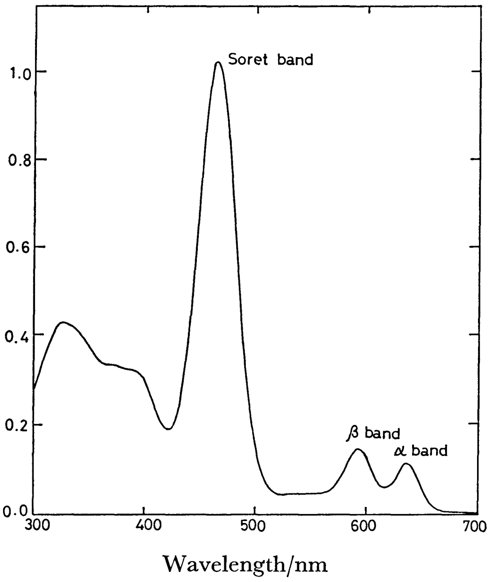


Fig. 1. Absorption spectrum of the complex, MoO(tpp)F, in CH_2Cl_2 at 25 °C. [MoO(tpp)F]$=1.08\times10^{-5}$ mol dm^{-3}.

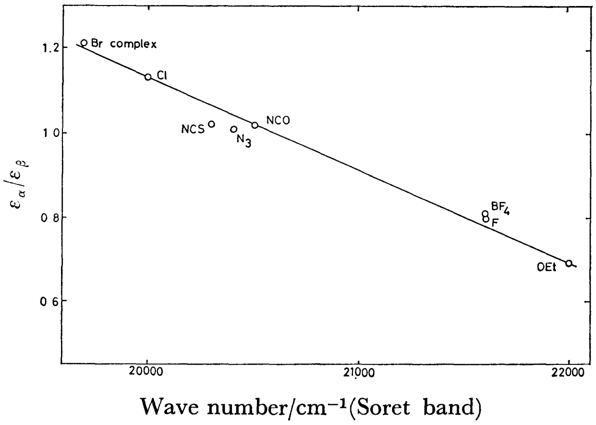


Fig. 2. The correlation between the ratios $\varepsilon_\alpha/\varepsilon_\beta$ and the wavenumbers of the Soret bands in the visible absorption spectra of the complexes, MoO(tpp)X.

550 and 700 nm, respectively. The Soret band would be assigned to charge-transfer (CT) transitions,[1,9] $a_{1u}(\pi)$, $a_{2u}(\pi)\rightarrow e_g(d,\pi)$, and/or the CT transition mixed with a $\pi\rightarrow\pi^*$ transition as assigned for the manganese(III) etioporphyrin complex.[10] The visible absorption spectra of the complexes, MoO(tpp)X, strongly depend on the anionic ligand X^-. Change in the axial ligand X, caused a red shift of the absorption peaks in the visible region relative to those of MoO(tpp)OC_2H_5; the red shift of the Soret band was accompained with the red shift of the α and the β bands. The Soret band and the β band, and the β and the α bands were separated from each other by *ca.* 125 and 40 nm, respectively. The values of the red shift are increased in the order: $X=OC_2H_5<F\simeq BF_4<NCO<N_3<NCS<Cl<Br$.

The red shifts of the visible absorption peaks are also accompanied with the change in the values of ε_{max} of these three peaks; the values of ε_{Soret}, ε_α, and ε_β decreased with increase in the red shift. A linear relationship was observed between the ratio $\varepsilon_\alpha/\varepsilon_\beta$ and the wave number of the Soret band (Fig. 2). This strong correlation between the ratio $\varepsilon_\alpha/\varepsilon_\beta$ and the wavenumber of the Soret band suggests the contribution of the configurational interaction between the transitions for the Soret band and those for the α and the β bands of the complexes, MoO(tpp)X, as suggested for the metalloporphyrins by Gouterman based on his four-orbital model.[11]

Similar red shifts were reported for the complexes, $Sn^{IV}(etio)X_2$ (etio=etioporphyrin),[12] $Mn^{III}(etio)X\cdot H_2O$,[13,14] and $Zn^{II}(tpp)X^-$.[2] The order of the red shifts is F<Cl<Br<I for the Soret bands of these complex series and also F<Cl for the complexes, MoO(oep)X.[1] The intensity ratio $\varepsilon_\alpha/\varepsilon_\beta$ also increased in the same order for Zn(tpp)X^- and in the reversed order for Sn(etio)X_2. Similar reversed relationship between the ratio $\varepsilon_\alpha/\varepsilon_\beta$ and the red shift was previously observed for a series of metalloporphyrins;[1,11] $\varepsilon_\alpha/\varepsilon_\beta$ decreases with increasing red shift of the Soret band for etioporphyrin, octaethylporphyrin, mesoporphyrin IX, and porphyrin IV complexes, but increases for TPP complexes.[2]

The orders of the red shift and of the ratio $\varepsilon_\alpha/\varepsilon_\beta$ for the complexes, MoO(tpp)X, are the same as those for the complexes Zn(tpp)X^- (see Table 4). It is interesting to note that no difference is observed in the spectral behavior between the closed-shell d^{10} zinc(II) porphyrin complexes and the open-shell d^1

Table 4. The orders of the red shift and of the ratio $\varepsilon_\alpha/\varepsilon_\beta$ in the visible absorption spectra of the halo complexes

Complex	Red shift	$\varepsilon_\alpha/\varepsilon_\beta$
Zn(tpp)X^- [a]	F < Cl < Br	F < Cl < Br
Sn(etio)X_2 [b]	F < Cl < Br	F > Cl > Br
MoO(tpp)X	F < Cl < Br	F < Cl < Br

a) Ref. 2. b) Ref. 12.

oxomolybdenum(V) porphyrin complexes. The order of the red shift for closed-shell metalloporphyrin depends largely on the electronegativity of the central metal atom[12] and on that of the axial ligand X.[2,12] In the series of the halo complexes, MoO(tpp)X (X=F, Cl, and Br), the IR band ascribed to the Mo=O stretching was observed at almost the same frequency 935—938 cm^{-1} and the *g*-values for the complexes were all observed at 1.967 ± 0.005. These data suggest the slight differences in the electronic state of the central molybdenum(V) atom (d^1) in the given complexes. Thus, decreasing electronegativity of the axial halo ligands, X=F, Cl, and Br, should primarily causes the increased electron density in the porphyrin ring *via* the central molybdenum(V) atom, resulting in the red shift and the increase in the ratio $\varepsilon_\alpha/\varepsilon_\beta$. For the NCS, NCO, and N_3 complexes, the correlation of the red shift and the electronegativity of the ligands could not be directly discussed, since the data on the electronegativity of the coordinated ligands, NCS, NCO, and N_3, are not estimated. However, from the order of the red shift, we deduce the order of the magnitude for ligand X to donate electrons to the porphyrin ring through the central moiety O=Mo–X as follows:

$$\mathrm{O{=}Mo{-}OC_2H_5 < O{=}Mo{-}BF_4 \simeq O{=}Mo{-}F < O{=}Mo{-}NCO <}$$
$$\mathrm{O{=}Mo{-}N_3 < O{=}Mo{-}NCS < O{=}Mo{-}Cl < O{=}Mo{-}Br.}$$

As in Table 3, the absorption spectra in UV and visible regions of the dichloromethane solutions of the complexes, MoO(tpp)NCS, MoO(tpp)NCO, and MoO(tpp)N_3, give almost the same values of λ_{max} and ε_{max}. This fact indicates that the thiocyanate are the cyanate anions coordinate to the central molybdenum(V) atom *via* N atom as suggested by the data of IR spectra of these complexes. Similar phenomenon was also observed for the complexes, MoO(tpp)BF_4 and MoO(tpp)F; the values of λ_{max} and ε_{max} of the absorption spectra of these complexes are alomst the same (Table 3). These results indicate that in the small ligand it is the donor atom in the ligand coordinated to the central atom that is predominantly responsible for the absorption spectra of the complex, MoO(tpp)X; the values of λ_{max} and ε_{max} in the UV and the visible absorption spectra are primarily determined by the donor atom in the axial ligand X.

Correlation of the Value of ε_{Soret} *with the Integrated Intensity of the Sored Band.* In connection with the correlation of the red shifts of λ_{max} in the visible absorption spectra of the complex, MoO(tpp)X, with the values of ε_{Soret}, ε_α, and ε_β it was observed that the degree of the broadening of the Soret band is also in the same order as that of the red shift and that the values of ε_{Soret} and the integrated intensity of the Soret band decrease with the red shifts. These facts should be explained in terms of the decrease in the magnitude of transitions in the Soret band with increase in the order of the red shift, though the Soret band becomes broader and less intense with increasing red shift. Relative integrated intensities of the Soret bands of the complexes, MoO(tpp)X, are decreased in the order: $\mathrm{F(285)\gtrsim BF_4(280)>NCS\simeq N_3\simeq NCO(200)>Cl(185)>Br(170)}$.

UV Absorption Spectra. For all complexes, MoO(tpp)X, in dichloromethane a distinct intense absorption band was observed around 330 nm (see Table 3). The order of the red shift of this band with respect to the axial ligand X was found to be the same as that of the red shift of the Soret band, except for the absorption peak of the complex MoO(tpp)N_3. The UV and the Soret bands for the complexes are separated from each other *ca.* 150 nm. The value of ε_{max} of the band, ε_{UV}, increases with the red shifts of the UV band as well as the Soret band, which is in the reversed order of ε_{Soret}; the values of ε_{UV} of the complex are increased in the following order: $\mathrm{X{=}OC_2H_5}(\varepsilon_{UV}\times10^{-4}=3.42)<\mathrm{F}(3.70)<\mathrm{BF_4}(4.01)<\mathrm{N_3}(4.17)<\mathrm{NCO}(4.76)<\mathrm{NCS}(5.42)<\mathrm{Cl}(6.12)<\mathrm{Br}(6.40)$. Thus the ratio $\varepsilon_{Soret}/\varepsilon_{UV}$ decreases in the order: $\mathrm{X{=}OC_2H_5}(\varepsilon_{Soret}/\varepsilon_{UV}=4.62)>\mathrm{F}(2.62)>\mathrm{BF_4}(2.41)>\mathrm{N_3}(1.04)>\mathrm{NCO}(0.98)>\mathrm{NCS}(0.84)>\mathrm{Cl}(0.68)>\mathrm{Br}(0.54)$. This tendency is very similar to that of the intensity ratio of the bands V and VI reported for the complexes, $\mathrm{Mn^{III}(etio)X\cdot H_2O}$, in chloroform,[13,14] and for the complexes, MoO(oep)X (X=OCH_3, F, and Cl).[1] The values of ε_{UV} for the complexes, MoO(tpp)Br, MoO(tpp)Cl, and MoO(tpp)NCS, are larger than those of ε_{Soret} for these complexes. Similar relation is observed for $\varepsilon_\alpha/\varepsilon_\beta$ (Fig. 2). These results suggest that the electronic transitions responsible for the three bands, the band around 330 nm, the B band, and the Q band, for the complexes, MoO(tpp)X, are also conjugated with each other, though the assignments of these bands for the given complexes are not yet established.

Comparison of the Visible Absorption Spectra with the IR Spectra. Based on the Raman spectral studies for the complex, $\mathrm{Mo^VO(mec)}$ (mec=2,3,17,18-tetramethyl-7,8,12,13-tetraethylcorrole), it was reported that the strong absorption band observed at 455 nm is largely due to a ligand-metal charge-transfer transition;[15] the intensity of the absorption peak observed at 950 cm^{-1} (Mo=O stretching) in the Raman spectra of MoO(mec) was enhanced to a larger extent than that expected for the core vibrations when the exciting frequency approaches the frequency of the strong band at 455 nm. The Mo=O stretching frequency is also suggested to be a sensitive probe for the surrounding.[3] Therefore it was expected that the peak ascribed to the Mo=O stretching of the complex, MoO(tpp)X, was correlated with the λ_{max} and ε_{max} of the absorption spectra in dichloromethane. However no clear correlation was observed for the complexes, MoO(tpp)X. The trans effect of an axial ligand X on the frequency of the Mo=O stretching of the complexes, MoO(tpp)X, must be small except for the complex, MoO(tpp)OC_2H_5. The Mo=O stretching for the complex, MoO(tpp)OC_2H_5, was observed at the low frequency, 904 cm^{-1}, as shown in Table 2. The M=O stretching was also observed at low frequency for other complexes, MoO(oep)OCH_3 (896 cm^{-1}) and WO(oep)OCH_3 (901 cm^{-1}).3) These phenomena could be attributed to the strong π-donor trans effect of alkoxo ligand.3)

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8) The complex assigned to MoO(tpp)O_2 in our previous report7) should be assigned to MoO(tpp)OR. The dichloromethane solution (1% v/v DMSO) of the complex, MoO(tpp)Br, containing a small excess of O_2^-, has two absorption peaks at 444 and 427 nm in the Soret band region. When the solution contains a trace amount of ethanol, the final spectrum of the reaction system agrees with that of the complex, MoO(tpp)OC_2H_5. Detailed study of the reaction of the complex, MoO(tpp)X, and O_2^- is now in progress.

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Note added in proof: When alcohol is absent in the reaction system, the complex, $Mo^{V}O$(tpp)NCS, is reduced by O_2^- to form the complex, $Mo^{IV}O$(tpp).