acoustic mode. No transition to magnetic order is expected if this ratio is smaller than 1. For $Cs_3Cr_2Cl_9$ we obtain 0.36, whereas for $Cs_3Cr_2Br_9$ it is 0.92.[8] This shows that the chloride is far from ordering magnetically whereas the bromide is only slightly undercritical. In contrast the iodide is expected to order at finite temperature if it follows the above trend with a decrease of the intradimer exchange and an increase of the interdimer exchange compared to the bromide. We are currently investigating chemical and physical properties of the iodide.

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Visible Absorption Spectral Studies of Molybdenum(V) Tetraphenylporphyrins in Organic Solvents

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Visible absorption spectra of molybdenum(V) tetraphenylporphyrin complexes, Mo^{V}O(TPP)X (X = F, Cl, Br, NCS; TPP = *meso*-tetraphenylporphinato), in organic solvents and the substitution reactions of these complexes with dimethyl sulfoxide (Me_2SO) are discussed. The measurements of molecular weight revealed that these complexes exist as monomers in dichloromethane. Organic solvents used are classified as noncoordinating and coordinating solvents for these complexes. The shift of the main absorption bands, Soret, α, and β bands, of Mo^{V}O(TPP)X in the noncoordinating solvents correlates with the function of refractive index, $(n^2 - 1)/(2n^2 + 1)$. The axial ligand X of these complexes is substituted by Me_2SO to form $[Mo^{V}O(TPP){\cdot}Me_2SO]_s{}^+X^-$ in Me_2SO–CH_2Cl_2 via the solvated complex $[Mo^{V}O(TPP)X]_s$ as an intermediate. The values of the formation constants of $[Mo^{V}O(TPP){\cdot}Me_2SO]_s{}^+X^-$ are in the order X = F $\ll$ NCS $\approx$ Cl $\ll$ Br.

Introduction

The reactions of molybdenum porphyrins in organic solvents are susceptible to influence from the impurities in solvents, air, and light. The complex Mo^{V}O(TPP)OCH_3 is formed immediately from Mo^{V}(TPP)X (X = F, Cl, Br, NCS) in dichloromethane containing a trace amount of methanol[1] and reduced photochemically to Mo^{IV}O(TPP).[2] The oxidation of Mo^{IV}O(TPP) affords Mo(V) porphyrin complexes in the presence of anions or some impurities in organic solvents. In the γ-radiolytic reaction of Mo^{V}O(TPP)X[3] and the reaction of Mo^{V}O(TPP)X with superoxide,[1,4] solvents also play a very important role. Therefore, we necessitated the study of the behavior of Mo^{V}O(TPP)X, in organic solvents.

There are many reports referring to the solvent effects on the behavior of metalloporphyrins in organic solvents.[5-15] However, the subjects of these studies are almost four-coordinated and five-coordinated metalloporphyrins with vacant sites at axial position. The present paper reports the studies of the visible absorption spectra of six-coordinated complexes Mo^{V}O(TPP)X in various organic solvents and the substitution reactions of Mo^{V}O(TPP)X with Me_2SO.

Table I. Molecular Weight of Mo^{V}O(TPP)X in Dichloromethane at 31 °C

complex	mol wt calcd	mol wt obsd
Mo^{V}O(TPP)F	743.73	759 ± 17
Mo^{V}O(TPP)Cl	760.18	771 ± 12
Mo^{V}O(TPP)Br	804.63	793 ± 14
Mo^{V}O(TPP)NCS	782.73	770 ± 14

Experimental Section

Materials. Dichloromethane, distilled, passed twice through a column of basic alumina, and dried over 4A molecular sieves overnight, was redistilled under Ar immediately before use. The purity of dichloromethane was checked spectrophotometrically by dissolving Mo^{V}O(TPP)Br. When the dichloromethane contains a trace of impurities such as alcohols, Cl^-, and some decomposed species as $CHCl_2^-$, the visible absorption spectra are changed by the formation of Mo^{V}O(TPP)Cl or Mo^{V}O(TPP)OR.[16] Dimethyl sulfoxide was kept with calcium hydride for several days, distilled at 37 °C under reduced pressure, and stored under an Ar atmosphere. Other solvents were also carefully purified by usual methods. The complex Mo^{V}O(TPP)X was synthesized by the method reported previously.[16]

Measurements. Visible absorption spectra were recorded with a Hitachi 808 spectrophotometer equipped with double-beam double monochromators at 25 ± 0.5 °C. The accuracy and reproducibility of the spectrophotometer are ±0.5 and ±0.2 nm, respectively. ESR spectra were recorded with a JEOL JES-FEIX spectrometer at 25 ± 2 °C. The molecular weight of Mo^{V}O(TPP)X in dichloromethane was measured

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Table II. Absorption Peaks of $Mo^{V}O(TPP)X$ in Noncoordinating Solvents at 25 °C

		$Mo^{V}O(TPP)NCS$ $\nu_{max}/10\ cm^{-1}$ $(\epsilon/10^4\ M^{-1}\ cm^{-1})$			$Mo^{V}O(TPP)Br$ $\nu_{max}/10\ cm^{-1}$ $(\epsilon/10^4\ M^{-1}\ cm^{-1})$		
no.[a]	solvent	Soret	β	α	Soret	β	α
1	CS_2	2001 (6.32)	1602 (1.16)	1493 (1.17)	1918 (4.46)	1558 (0.93)	1452 (1.20)
2	$C_6H_5NO_2$	2012 (4.78)	1598 (0.92)	1487 (1.01)	[b]		
3	C_6H_5Cl	2010 (5.25)	1603 (0.95)	1493 (1.01)	1947 (4.06)	1561 (0.81)	1454 (1.06)
4	C_6H_6	2010 (5.41)	1603 (1.01)	1494 (1.04)	1943 (3.96)	1559 (0.84)	1454 (1.09)
5	$C_6H_5CH_3$	2014 (5.22)	1606 (1.03)	1496 (1.06)	1946 (4.06)	1563 (0.85)	1455 (1.11)
6	CCl_4	2011 (5.34)	1613 (1.07)	1504 (1.05)	1942 (4.19)	1571 (0.85)	1463 (1.06)
7	$CHCl_3$	2006 (4.34)	1601 (0.88)	1492 (0.86)	1952 (3.49)	1563 (0.73)	1459 (0.83)
8	$C_4H_8O_2$[c]	2014 (5.02)	1604 (1.01)	1493 (1.03)	1952 (3.84)	1559 (0.81)	1454 (1.06)
9	CH_2Cl_2[d]	2015 (4.54)	1604 (0.90)	1494 (1.01)	1958 (3.59)	1565 (0.74)	1459 (0.89)
10	THF	2022 (5.05)	1607 (1.01)	1497 (1.07)	1951 (3.96)	1564 (0.84)	1457 (1.11)

[a] Order of decreasing refractive index. [b] Nitrobenzene acts as a coordinating solvent for $Mo^{V}O(TPP)Br$. [c] Dioxane. [d] The values of ν_{max} and ϵ for $Mo^{V}O(TPP)NCS$ and $Mo^{V}O(TPP)Br$ are slightly different from our former data of ref 16.

with a Hitachi molecular weight apparatus, Model 115.

Results and Discussion

Molecular Weight in Dichloromethane. The X-ray structural analysis of $Mo^{V}O(TPP)Cl$ shows that the complex exists as a monomeric form in the solid state.[17] However, X-ray structural analysis for the solid state of the complex does not always give a correct information about the structure of complexes in solution. Recently, there has been a report that the complex $Mo^{V}O(TPP)Cl$ formed by the substitution reaction of $Mo^{V}O(TPP)OCH_3$ with $(C_2H_5)_4NCl$ in dichloromethane was stably present as the dimer $[Mo^{V}O(TPP)Cl]_2$.[18] We tried to reinvestigate this reaction spectrophotometrically but could not obtain the information about the structure of the complex in pure dichloromethane because of the instability of $Mo^{V}O(TPP)OCH_3$; the absorbances of the main bands of the UV–visible absorption spectrum of $Mo^{V}O(TPP)OCH_3$ decreased gradually even in the dark. The rate of the change in the absorbance in the light is very large compared to that in the dark. This spectral behavior is mainly due to the photoreduction of $Mo^{V}O(TPP)OR$ as observed in benzene.[2]

The molecular weight of $Mo^{V}O(TPP)X$ in dichloromethane was measured at 31 °C prior to the spectrophotometric study of the complex. The measurements were repeated 5–10 times for a sample solution in the concentration range 1.1×10^{-4} to 1.6×10^{-3} M with a dichloromethane solution of H_2TPP as a standard. The results shown in Table I indicate that $Mo^{V}O(TPP)X$ is present as a monomer in dichloromethane. The presence of only one species in dichloromethane was also confirmed for $Mo^{V}O(TPP)X$ in the concentration range 1.5×10^{-7} to 3.8×10^{-5} M by obtaining the Beer's law plot. In addition, FD mass spectrum for the solid sample of $Mo^{V}O(TPP)Cl$ used in this study has main peaks at *m/e* 726 and 760; these are ascribed to the fragments $MoO(TPP)^+$ and MoO(TPP)Cl, respectively. No peaks due to the dimer $[MoO(TPP)Cl]_2$ and impurity MoO(TPP)Cl·HCl were observed. These results agree with the observation that symmetric tetraphenylporphyrin complexes usually do not form a polymerized species in organic solvents.[19]

Classification of Organic Solvents. Organic solvents are divided into two classes, coordinating solvents and noncoordinating solvents.[5,6] However, the classification is rather ambiguous and often depends on the solute species. Thus, we studied the solvent effects on the complex $Mo^{V}O(TPP)X$. Dichloromethane was used as a standard noncoordinating solvent in the classification of solvents. If, upon addition of a solvent to the dichloromethane solution of $Mo^{V}O(TPP)X$, the main three bands, Soret, α, and β bands, shift only slightly without appearance of a new peak, the solvents could be classified as the noncoordinating solvents. On the other hand, the spectra of the complex in the coordinating solvents such as alcohols, dimethyl sulfoxide, pyridine, acetonitrile, aniline, *N,N*-dimethylaniline, and dimethylformamide have new peaks, suggesting the formation of new complex species.

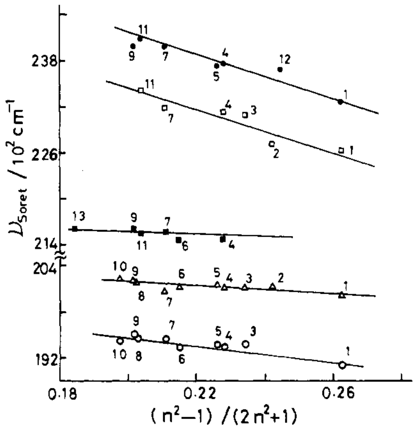

Figure 1. Plot of the wavenumber of the Soret band of $Zn^{II}(TPP)^5$ (●), (chlorophyll $a)_2{}^{22,34}$ (□), $Mn^{III}(MPIXDME)OH \cdot H_2O^7$ (■), $Mo^{V}O(TPP)NCS$ (△), and $Mo^{V}O(TPP)Br$ (○) in pure solvents vs. $(n^2 - 1)/(2n^2 + 1)$, where *n* is the refractive index of the solvents. Numbers from 1–10 refer to the organic solvents in Table II, and 11–13 indicate hexane, bromobenzene, and ethyl acetate, respectively.

Solvent Effects. Table II shows the wavelength of absorption maxima and the molar absorption coefficients of the three main bands of the complexes, $Mo^{V}O(TPP)NCS$ and $Mo^{V}O(TPP)Br$, in the noncoordinating solvents. The solvent effects for these absorption spectra may result either from the change in the difference of the energy between the ground states and the excited states, due to the change in the polarity of the solvents,[5–9] or from the change in the spin states or the oxidation states of the complexes.[10] The spectral shift of $Mo^{V}O(TPP)X$ is ascribed to the change in the polarity of the solvents, because an ESR study revealed no change in the spin state and in the oxidation state of the central molybdenum (d^1) of the complex in the noncoordinating solvents.[16] The parameters of solvent effects reported so far are dielectric constants,[11] refractive index,[5,6] which is in turn a function of dielectric constants,[20–22] donor number or acceptor number,[23] and the values of Z,[24] E_T,[25,26] Y,[27,28] χ_B,[29] Ω,[30] and F;[31] these six

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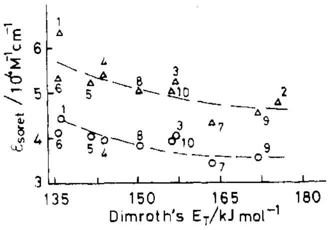

Figure 2. Plot of the molar absorption coefficient of the Soret band of $Mo^VO(TPP)NCS$ (▵) and $Mo^VO(TPP)Br$ (○) vs. Dimroth's E_T values.

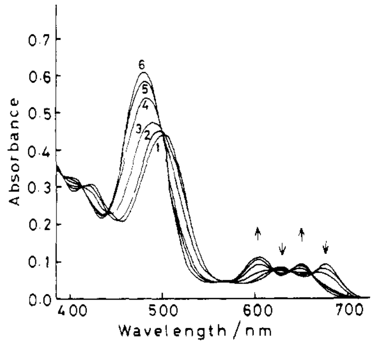

Figure 3. Visible absorption spectral changes with an increase in the Me_2SO concentration in the $Mo^VO(TPP)Cl$ dichloromethane solution. Me_2SO concentration: 0 (1); 0.056 (2); 0.282 (3); 0.705 (4); 1.410 (5); 2.538 M (6).

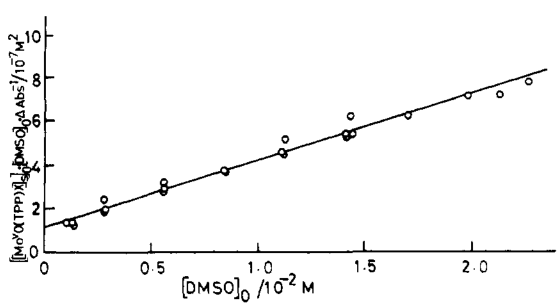

Figure 4. Benesi–Hildebrand plot for the second stage of the reaction of $Mo^VO(TPP)Br$ with Me_2SO at 25 °C. Initial concentration of the complex is (1.10–1.80) × 10^{-5} M.

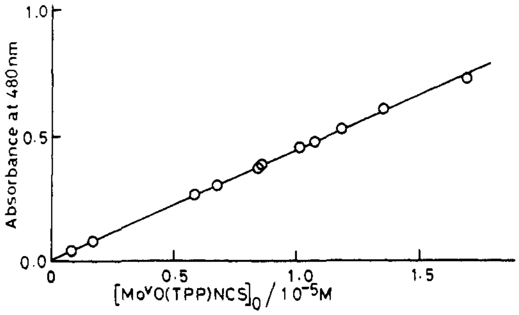

Figure 5. Plot of absorbance at 480 nm vs. initial concentration of $Mo^VO(TPP)NCS$ in 2% (v/v) (=0.28 M) $Me_2SO-CH_2Cl_2$.

values have a strong correlation.[32]

The shift of the visible absorption bands of $Mo^VO(TPP)X$ in various solvents is in good correlation with the function of the refractive index, $(n^2 - 1)/(2n^2 + 1)$. The correlation coefficients are −0.719 and −0.889 for the complexes, $Mo^VO(TPP)NCS$ and $Mo^VO(TPP)Br$, respectively.[33] The plots of the wavenumbers of the Soret bands of the complexes, $Mo^VO(TPP)NCS$, $Mo^VO(TPP)Br$, Zn(TPP),[5] chlorophyll *a*,[22] and $Mn^{III}(MPIXDME)OH{\cdot}H_2O$ (MPIXDME = mesoporphyrin dimethyl ester),[7] vs. $(n^2 - 1)/(2n^2 + 1)$ are depicted in Figure 1. Chlorophyll *a* exists as a five-coordinated dimer in noncoordinating solvents.[34] Figure 1 indicates that the higher the function of the refractive index is, the lower is the wavenumber of the Soret band of the molybdenum(V) complex. This reveals that the transition energy for the Soret band decreases with an increase in the dielectric constants of the solvents. The slopes of these plots are in the order Zn(TPP) ≈ (chlorophyll *a*)$_2$ > $Mo^VO(TPP)Br$ > $Mo^VO(TPP)NCS$ > $Mn^{III}(MPIXDME)OH{\cdot}H_2O$. This result may afford the following conclusions: (1) The visible absorption spectra of the spherical six-coordinated complexes, $Mo^VO(TPP)X$ and $Mn^{III}(MPIXDME)OH{\cdot}H_2O$, are less susceptible to the nature of the noncoordinating solvents than those of the four-coordinated complex Zn(TPP) and five-coordinated chlorophyll *a* dimer. (2) The slope for $Mo^VO(TPP)Br$ is a little steeper than that for $Mo^VO(TPP)NCS$, indicating the higher susceptibility of $Mo^VO(TPP)Br$ to the noncoordinating solvents. The complex $Mo^VO(TPP)Br$ with a soft ligand Br is also labile for the substitution reaction in the coordinating solvents as will be described in a later section.

Table II also shows that the molar absorption coefficients of the complexes, $Mo^VO(TPP)Br$ and $Mo^VO(TPP)NCS$, are strongly dependent on the noncoordinating solvents. The value of the coefficients increases with the decrease of the wavenumber of the Soret band. However, there is no correlation between the change in the molar absorption coefficients and the function of refractive index, but there is a correlation between the coefficients and the Dimroth's E_T values as shown in Figure 2. Namely, the higher the Dimroth's E_T values become, the lower are the values of the molar absorption coefficients of the Soret bands. This result indicates that the increase in the solvent polarity causes the decrease of the transition probability from the ground states to the excited states of the complex $Mo^VO(TPP)X$ at the Soret bands.

Substitution Reaction with Dimethyl Sulfoxide. The complex $Mo^VO(TPP)Cl$ in dichloromethane has visible absorption peaks at 500, 627, and 674 nm. In the presence of Me_2SO in the dichloromethane solution, the spectrum changes in two steps as the concentration of Me_2SO increases from 0 to 20% (v/v) (= 2.58 M). In the first stages of the reaction observed in the presence of a trace amount of Me_2SO, the spectrum shows a hypsochromic shift by only 1–2 nm without isosbestic points (Figure 3, curves 1 and 2). With the additional increase in the concentration of Me_2SO, new peaks appear in the second stage with isosbestic points with the final spectrum in the first stage of the reaction (Figure 3, curves 2–6). The final spectrum obtained in the second stage has absorption peaks at 478, 605, and 651 nm. The reactions of $Mo^VO(TPP)Br$ and $Mo^VO(TPP)NCS$ with Me_2SO also proceed in two steps. ESR measurements indicate no change in the oxidation state of the central molybdenum of the complexes, i.e., Mo(V) in the course of these reactions.[16]

The hypsochromic shift by 1–2 nm in the first stage of the reaction could be ascribed to the solvation of the complexes with Me_2SO and not to the change in the polarity of the mixed solvent for the following reasons: (1) The shift is observed in the region of very low concentration of Me_2SO, $<2 \times 10^{-3}$ M, for the $Mo^VO(TPP)Br$ system and in the reverse direction of the shift caused by the increase in the polarity of the noncoordinating solvents. (2) The final spectra of the first stage of the reactions of $Mo^VO(TPP)X$ are different from each other; namely, Me_2SO does not coordinate to the central molybdenum(V). The first stage of the reaction could be represented as

$$Mo^VO(TPP)X + nMe_2SO \rightleftharpoons [Mo^VO(TPP)X]_s \qquad (1)$$

where s means solvated species.

The second stage must be the substitution reaction between the ligand X in $Mo^VO(TPP)X$ and Me_2SO. The absorption bands of the final spectra in the second stage of the reaction for the systems of $Mo^VO(TPP)Br$, $Mo^VO(TPP)NCS$, and $Mo^VO(TPP)Cl$

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Table III. Formation Constants in the Second Stage of the Reactions and Absorption Peaks of $[\mathrm{Mo^VO(TPP)\cdot Me_2SO}]_s{}^+\mathrm{X}^-$ in $\mathrm{Me_2SO{-}CH_2Cl_2}$ at 25 °C

complex	K/M^{-1}	$\lambda_{\max}/\mathrm{nm}$ ($\epsilon/10^4$ $\mathrm{M^{-1}\ cm^{-1}}$)[a]		
$[\mathrm{Mo^VO(TPP)\cdot Me_2SO}]_s{}^+\mathrm{Br}^-$ [b]	180	477 (6.0)	604 (1.0)	648 (0.9)
$[\mathrm{Mo^VO(TPP)\cdot Me_2SO}]_s{}^+\mathrm{Cl}^-$ [c]	0.88	478 (7.0)	605 (1.3)	651 (0.9)
$[\mathrm{Mo^VO(TPP)\cdot Me_2SO}]_s{}^+\mathrm{NCS}^-$ [c]	0.80	477 (6.8)	604 (1.3)	651 (1.0)
$[\mathrm{Mo^VO(TPP)\cdot Me_2SO}]_s{}^+\mathrm{F}^-$	$<1 \times 10^3$			

[a] Molar absorption coefficients were evaluated from the B–H plots. [b] Concentration range of $\mathrm{Me_2SO}$ is $0 \leqslant [\mathrm{Me_2SO}] < 2.5 \times 10^{-2}$ M. [c] $0 \leqslant [\mathrm{Me_2SO}] < 2.5$ M.

are almost the same, which indicates the formation of almost the same products.

The Benesi–Hildebrand plot[35] of $[[\mathrm{Mo^VO(TPP)X}]_s]_0 \cdot [\mathrm{Me_2SO}]_0/(\Delta\mathrm{Abs}$ at 480 nm) vs. $[\mathrm{Me_2SO}]_0$ for the second stage is shown in Figure 4, where ΔAbs is the increase in the absorbance at 480 nm with the increase in the concentration of $\mathrm{Me_2SO}$.[36] The B–H plot indicates that the second stage of the reaction is of type $\mathrm{A + B \rightleftharpoons C}$ where A, B, and C correspond to $[\mathrm{Mo^VO(TPP)X}]_s$, $\mathrm{Me_2SO}$, and the product, respectively. The stoichiometry of 1:1 for the reaction was also confirmed by the linearity of the plot of the absorbance at 480 nm vs. the initial concentration of $\mathrm{Mo^VO(TPP)X}$ at the constant concentration of $\mathrm{Me_2SO}$ as shown in Figure 5. The plot of log $[(\mathrm{Abs} - \epsilon_a A_0)/(\epsilon_c A_0 - \mathrm{Abs})]$ vs. log $[\mathrm{Me_2SO}]$, where ϵ_a and ϵ_c are the molar absorption coefficients of $[\mathrm{Mo^VO(TPP)X}]_s$ and the product, respectively, and A_0 is the initial concentration of $[\mathrm{Mo^VO(TPP)X}]_s$, also shows that the type of the second stage of the reaction is $\mathrm{A + B \rightleftharpoons C}$ and the stoichiometry is 1:1 for $[\mathrm{Mo^VO(TPP)X}]_s$ to $\mathrm{Me_2SO}$. These plots all reveal that the complex C formed by the substitution reaction retains the ligands X in the vicinity of the complex under the experimental conditions.

$$[\mathrm{Mo^VO(TPP)X}]_s + \mathrm{Me_2SO} \overset{K}{\rightleftharpoons} [\mathrm{Mo^VO(TPP)\cdot Me_2SO}]_s{}^+\mathrm{X}^- \tag{2}$$

The presence of the associated $[\mathrm{Mo^VO(TPP)\cdot Me_2SO}]_s{}^+\mathrm{X}^-$ species could owe to the low dielectric constant of dichloromethane[37] and to the low tendency for the solvation of the free anions such as Br^-, Cl^-, and NCS^- in aprotic solvents[38–40] and in $\mathrm{Me_2SO}$.[41,42] The formation constant, obtained by the least-squares plot of the B–H plot and molar absorption coefficients are tabulated in Table III. The values of K obtained are in good agreement with the values obtained by the log–log plot with an experimental error of ±8%. The values of the formation constants are in the order of $\mathrm{X = F \ll NCS \approx Cl \ll Br}$, which is the same as that of the softness of these ligands and as the bathochromic shift of the Soret band of $\mathrm{Mo^VO(TPP)X}$ in dichloromethane by varying the ligand X.[16] This result indicates that the spectral shift of $\mathrm{Mo^VO(TPP)X}$ in the noncoordinating solvents reflects the order of the formation constants, i.e., the order of the strength of the bond between the ligand X and the central molybdenum(V) of the complex. The behavior of manganese[11] and iron porphyrins[43] is also dependent upon both the nature of the counterions and solvents.

The addition of the dichloromethane solution of $(\mathrm{C_2H_5})_4\mathrm{NCl}$ to the $[\mathrm{Mo^VO(TPP)\cdot Me_2SO}]_s{}^+\mathrm{Cl}^-$ solution causes the formation of the $\mathrm{Mo^VO(TPP)Cl}$ complex. The occurrence of this reaction looks like a contradiction to the equation (2), which shows the formation of the associated complex. The backward reaction of $[\mathrm{Mo^VO(TPP)\cdot Me_2SO}]_s{}^+\mathrm{X}^-$ with free ion X^- added must be promoted by the contribution of the slight dissociation of the associated complex to $[\mathrm{Mo^VO(TPP)\cdot Me_2SO}]_s{}^+$ and X^-:

$$[\mathrm{Mo^VO(TPP)\cdot Me_2SO}]_s{}^+\mathrm{X}^- \rightleftharpoons [\mathrm{Mo^VO(TPP)\cdot Me_2SO}]_s{}^+ + \mathrm{X}^- \tag{3}$$

Unfortunately, the ionic dissociation constant of the reaction (3) under the conditions of no addition of X^- could not be obtained for the following reasons: (1) The spectrum of dissociated $[\mathrm{Mo^VO(TPP)\cdot Me_2SO}]_s{}^+$ may be almost the same as that of associated $[\mathrm{Mo^VO(TPP)\cdot Me_2SO}]_s{}^+\mathrm{X}^-$. (2) Electrolytes such as $\mathrm{Bu_4NBF_4}$ and $\mathrm{Bu_4NClO_4}$ that are generally used for adjustment of ionic strength form complexes with molybdenum(V) tetraphenylporphyrins.[16] (3) The addition of electrolytes favors dissociation of the counterion.[11]

Reaction in the Solvents with High Concentration of $\mathrm{Me_2SO}$. In the high concentration of $\mathrm{Me_2SO}$ (>80% (v/v)), the Soret band around 480 nm of $[\mathrm{Mo^VO(TPP)\cdot Me_2SO}]_s{}^+$ decreased with time in the light or with photoirradiation (350–700 nm) with concomitant increase in the absorption at 445, 575, and 675 nm. The complex having the absorption bands at 445, 575, and 675 nm was confirmed to be $\mathrm{Mo^{IV}O(TPP)\cdot Me_2SO}$ by the spectrophotometric study for the reaction of $\mathrm{Me_2SO}$ with $\mathrm{Mo^{IV}O(TPP)}$ synthesized independently.[44] Two reaction paths for the photoreduction of $[\mathrm{Mo^VO(TPP)\cdot Me_2SO}]_s{}^+$ are possible: (1) through the photoreduction of $\mathrm{Mo^VO(TPP)OH}$ formed by the reaction with water contained as an impurity whose content in 100% $\mathrm{Me_2SO}$ was determined to be 1.9×10^{-3} M by the Karl Fischer method; (2) through the direct photoreduction of $[\mathrm{Mo^VO(TPP)\cdot Me_2SO}]_s{}^+$. By the addition of a small amount of water (0.02 mL) to the 10-mL $\mathrm{Me_2SO}$ solution of $[\mathrm{Mo^VO(TPP)\cdot Me_2SO}]_s{}^+$ in the dark, the absorbance around 460 nm, which is ascribed to the hydroxo complex, is increased and the photoreduction in the light is accelerated. The hydroxo complex synthesized[45] independently is also photoreduced to form $\mathrm{Mo^{IV}O(TPP)}$. The complex $[\mathrm{Mo^VO(TPP)\cdot Me_2SO}]_s{}^+$ is not photoreduced at low concentrations of $\mathrm{Me_2SO}$. These results suggest that the photoreduction of $[\mathrm{Mo^VO(TPP)\cdot Me_2SO}]_s{}^+$ in high $\mathrm{Me_2SO}$ concentration proceeds with the photoreduction of $\mathrm{Mo^VO(TPP)OH}$ formed by the reaction with water in $\mathrm{Me_2SO{-}CH_2Cl_2}$.

Registry No. $\mathrm{Mo^VO(TPP)F}$, 76771-79-4; $\mathrm{Mo^VO(TPP)Cl}$, 68070-21-3; $\mathrm{Mo^VO(TPP)Br}$, 73515-72-7; $\mathrm{Mo^VO(TPP)NCS}$, 73515-84-1; $[\mathrm{Mo^VO(TPP)\cdot Me_2SO}]^+\mathrm{Br}^-$, 86158-75-0; $[\mathrm{Mo^VO(TPP)\cdot Me_2SO}]^+\mathrm{Cl}^-$, 94782-04-4; $[\mathrm{Mo^VO(TPP)\cdot Me_2SO}]^+\mathrm{NCS}^-$, 94782-06-6; $[\mathrm{Mo^VO(TPP)\cdot Me_2SO}]^+\mathrm{F}^-$ 94782-07-7; $\mathrm{Me_2SO}$, 67-68-5.

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