The energy requirement for the rearrangement probably constitutes nearly all of the difference in free energy barriers for recombinations of $Mn(CO)_5\cdot$ and $Mn(CO)_4PR_3\cdot$ radicals. This energy requirement is not very large; for the bulkiest ligand, $P(i\text{-}Pr)_3$, the difference in ΔG^* for recombination of the $Mn(CO)_4P(i\text{-}Pr)_3\cdot$ and $Mn(CO)_5\cdot$ radicals amounts to only 14 kJ/mol (3.3 kcal/mol). Recombination to yield the diaxial product is highly selective as demonstrated by the observation that when a solution of the diaxially substituted $Mn_2(CO)_8L_2$ compound in an IR cell is repeatedly flashed with a photoflash lamp, there is no appearance of other isomers, as determined by IR. The identical experiment performed in CCl_4 has $Mn(CO)_4LCl\cdot$ as the only product, confirming that $Mn(CO)_4L\cdot$ is produced under these conditions.

One consequence of the slower rates of recombination for the $Mn(CO)_4PR_3\cdot$ radicals is that they are long-lived in solution, insofar as their lifetimes are limited by formation of the dinuclear species. This means that there will be, in general, longer time available for other chemical processes, notably substitution, atom transfer, or electron transfer, to occur. Where the steric requirements of ligands on the metal are sufficiently large, the radicals cannot assume a configuration that permits a stable metal–metal bond, so the radicals persist in solution. This occurs for the disubstituted species, $Mn(CO)_3(PR_3)_2\cdot$. In this limiting case it is possible to directly measure the rates of substitution[10] or atom transfer.[9] The results to date show that the disubstituted species are much less labile toward substitution than $Mn(CO)_5\cdot$ and that substitution proceeds by an associative route. That this is the case, even with bulky phosphines on the metal, indicates that dissociative loss of ligands from $Mn(CO)_3(PR_3)_2\cdot$ radicals is slow. There is reason also to believe that monosubstituted radicals, $Mn(CO)_4PR_3\cdot$, are less labile than $Mn(CO)_5\cdot$. We are currently examining the reactivities of the $Mn(CO)_4PR_3\cdot$ radicals toward atom-transfer agents. We have also recently completed a study of the formation of $Mn_2(CO)_7L_2$ by flash photolysis and measured the rates of back-reaction with CO.[24]

Registry No. $Mn_2(CO)_{10}$, 10170-69-1; $Mn_2(CO)_8(P(n\text{-}Bu)_3)_2$, 15609-33-3; $Mn_2(CO)_8(P(i\text{-}Bu)_3)_2$, 83634-21-3; $Mn_2(CO)_8(P(i\text{-}Pr)_3)_2$, 75847-41-5; $Mn_2(CO)_8(PPh_3)_2$, 15279-67-1; $Mn_2(CO)_8(P(OPh)_3)_2$, 15228-70-3; $Mn_2(CO)_8(dppe)$, 75847-46-0; $Mn(CO)_5\cdot$, 54832-42-7; $Mn(CO)_4P(n\text{-}Bu)_3\cdot$, 45264-38-8; $Mn(CO)_4P(i\text{-}Bu)_3\cdot$, 92186-52-2; $Mn(CO)_4P(i\text{-}Pr)_3\cdot$, 92186-53-3; $Mn(CO)_4P(OPh)_3\cdot$, 47670-58-6; $Mn(CO)_4PPh_3\cdot$, 14971-47-2.

---

(24) Herrick, R. S.; Brown, T. L. *Inorg. Chem.*, in press.

Contribution from the Department of Chemistry, Faculty of Science, and Department of Nuclear Engineering,
Faculty of Engineering, Hokkaido University, Sapporo 060, Japan

Optical and ESR Studies for the Reaction of Molybdenum Tetraphenylporphyrins in γ-Ray-Irradiated 2-Methyltetrahydrofuran

TAIRA IMAMURA,* MASAYUKI TAKAHASHI, TETSUYA TANAKA, TAKASHI JIN,
MASATOSHI FUJIMOTO,* SADASHI SAWAMURA, and MEISEKI KATAYAMA

Received September 7, 1983

The molybdenum(V) tetraphenylporphyrins, $Mo^VO(TPP)X$ (X = NCS, F, Cl, Br), in the glassy matrix of 2-methyltetrahydrofuran (MeTHF) at 77 K are reduced by γ-ray irradiation to form the constrained complexes, $[Mo^{IV}O(TPP)X]^-$, in which the ligand X is forced to be coordinated to the central molybdenum. When the solution is warmed, $Mo^{IV}O(TPP)$ is formed by release of the ligand X. The bands of the visible absorption spectra of $[Mo^{IV}O(TPP)X]^-$ formed in the rigid matrix depend on the ligand X and shift to longer wavelengths in the order of X = F < NCS < Cl < Br. The formation of the complex of MeTHF, $Mo^{IV}O(TPP)MeTHF$, was also detected as the temperature of the solution of $Mo^{IV}O(TPP)$ was lowered to −72 °C. The velocity of the backward reaction of $Mo^{IV}O(TPP)$ to form $Mo^VO(TPP)X$ is dependent on the ligand X.

Introduction

Molybdenum porphyrin complexes have been widely studied in the last several years because of the versatility of their reactions in organic solvents. The molybdenum(V) tetraphenylporphyrin complexes, $Mo^VO(TPP)X$ (X = NCS, Br), are reduced by superoxide ion to form the molybdenum(IV) tetraphenylporphyrin complex, $Mo^{IV}O(TPP)$, via an intermediate that is suggested to be the dioxygen complex.[1] The methoxo complex, $Mo^VO(TPP)OCH_3$, is also reduced photochemically to the Mo(IV) complex in benzene solution.[2] In the course of the photochemical reaction of the *trans*-diperoxo complex, $Mo^{VI}(O_2)_2(TTP)$ (TTP = tetra-*p*-tolylporphinato), to form *cis*-dioxo complex, $Mo^{VI}(O)_2(TTP)$, a change in the oxidation state of the central molybdenum of the complexes was suggested.[3,4] Thus, these reaction processes may include transient reaction intermediates in which the oxidation state of the central molybdenum is different from that of the starting materials. Detection and characterization of the intermediates have significance for the elucidation of the mechanisms of electron-transfer and photochemical reactions, so we were motivated to study the reaction of $Mo^VO(TPP)X$ by γ-irradiation, which is considered to cause simple oxidation–reduction reactions of the complex.

The Soret bands, the α bands, and the β bands of the spectra of these complexes, $Mo^VO(TPP)X$, shift to longer wavelength in the order X = F < Cl < Br, which was ascribed to the electronegativity of the ligand X.[5] Thus, we were also interested in a spectroscopic study of the intermediate, which might be observed as a constrained complex in which the ligand X was forced to be coordinated to the central molybdenum, owing to the rigidity of the solvent matrix at 77 K.[6]

---

* To whom correspondence should be addressed at the Department of Chemistry.

(1) Imamura, T.; Hasegawa, K.; Fujimoto, M. *Chem. Lett.* **1983**, 705.
(2) Ledon, H. J.; Bonnet, M. *J. Am. Chem. Soc.* **1981**, *103*, 6209.
(3) Ledon, H.; Bonnet, M. *J. Chem. Soc., Chem. Commun.* **1979**, 702.
(4) Mentzen, B. F.; Bonnet, M. C.; Ledon, H. J. *Inorg. Chem.* **1980**, *19*, 2061.
(5) Imamura, T.; Numatatsu, T.; Terui, M.; Fujimoto, M. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 170.
(6) The complex in this situation was termed a constrained complex: Konishi, S.; Hoshino, M.; Yamamoto, K.; Imamura, M. *Chem. Phys. Lett.* **1980**, 72, 459.

0020-1669/84/1323-3752$01.50/0

2-Methyltetrahydrofuran was chosen as a solvent because it easily forms a glass at 77 K and because much information is available on trapped electrons,[7-14] cation and neutral radicals,[15-17] trapped intermediates,[18,19] photobleaching,[20-23] electrical conductivity,[24] and chemical reactions.[25-28]

Experimental Section

Molybdenum(V) tetraphenylporphyrin complexes, $Mo^VO(TPP)X$ (X = F, Cl, Br, NCS), and molybdenum(IV) tetraphenylporphyrin complex, $Mo^{IV}O(TPP)$, were synthesized according to the previously described methods.[1,5] 2-Methyltetrahydrofuran, washed with aqueous sodium hydroxide and dried with calcium chloride, was purified by fractional distillation, stored on Na–K alloy, and again distilled in vacuo immediately before use.[8] Sample solutions were all deaerated by repeated freeze–thaw cycles before γ-irradiation. γ-Ray from a 1.8-kCi ^{60}Co source at the dose rate of 2.3 krd min^{-1} were used to irradiate sample solutions in a sealed quartz cell at room temperature or in a sample cell in a Dewar vessel containing liquid nitrogen. The optical path length of the cell was 2 mm.

The spectrum at 77 K was measured with the optical cell in a liquid-nitrogen Dewar vessel with two optical windows. Electronic spectra were recorded on a Hitachi 808 spectrophotometer. A JEOL JES-FEIX spectrometer operating at 100-kHz modulation in the X band was used for ESR. Glass tubes for ESR measurements were double-walled vessels that insulated the sample from temperature changes during transfer from Dewar to spectrometer. A 600-W tungsten lamp was used to photobleach (>350 nm) the absorption due to trapped electrons in the solvent matrices.

Results and Discussion

Electronic Spectra. The electronic spectrum of $Mo^VO(TPP)NCS$ in MeTHF has absorption maxima at 492, 621, and 667 nm at room temperature. Under γ-irradiation, these absorption peaks decrease with concomitant growth of an absorption maximum at 427 nm. The spectrum having the band at 427 nm coincides with that of $Mo^{IV}O(TPP)$, synthesized independently.[1] The reaction is complete after 3-min γ-irradiation. Additional γ-irradiation causes decomposition of the complex, indicated by complete disappearance of the absorbance in the whole visible region. The Soret band of the electronic spectrum of $Mo^VO(TPP)NCS$ splits into two bands at 496 and 512 nm in the rigid matrix of MeTHF at 77 K, and the absorbances of these bands are decreased by γ-irradiation for 17 h, with the appearance of a new band at 448 nm. The molar absorption coefficient at 448 nm of the complex was estimated to be $\epsilon = 10.8 \times 10^5$ M^{-1} cm^{-1}. γ-Irradiation of solutions of the other complexes, $Mo^VO(TPP)X$ (X = F, Cl, Br), gave almost the same spectral change as that of the $Mo^VO(TPP)NCS$ system at room temperature and at 77 K. Warming the rigid matrix of the irradiated sample to room temperature caused the 427-nm band of the $Mo^{IV}O(TPP)$ spectrum to appear, indicating that the complex at 448 nm formed at 77 K is a constrained complex. Figure 1 shows these spectral changes. The broad absorption in the visible–near-infrared region (>550 nm) is due to the trapped electron in the MeTHF glass matrix.[7] The absorption in the region of 500 nm in Figure 1c is due to the residual $Mo^VO(TPP)NCS$, indicating ca. 80% completion of the reaction after photobleaching. The absorption band at 427 nm of $Mo^{IV}O(TPP)$ reversibly shifts to 442 nm as the solution is cooled to 77 K

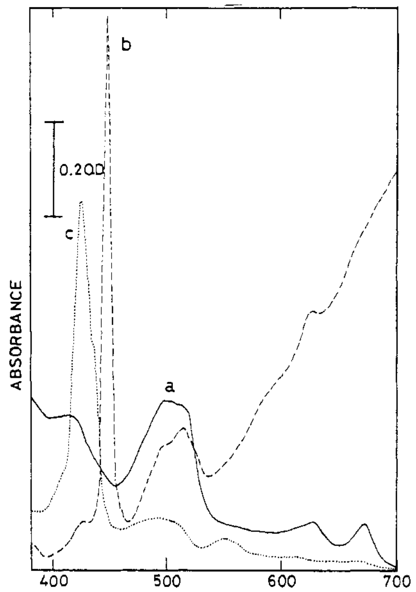


Figure 1. Change in the electronic spectra of $Mo^VO(TPP)NCS$ in MeTHF by γ-radiolysis at $[Mo^VO(TPP)NCS]_0 = 2 \times 10^{-5}$ M. Solid (a), broken (b), and dotted lines (c) show respectively the spectrum before γ-irradiation at 77 K, after γ-irradiation for 17 h at 77 K, and after warming the matrix (b) (path length 2 mm).

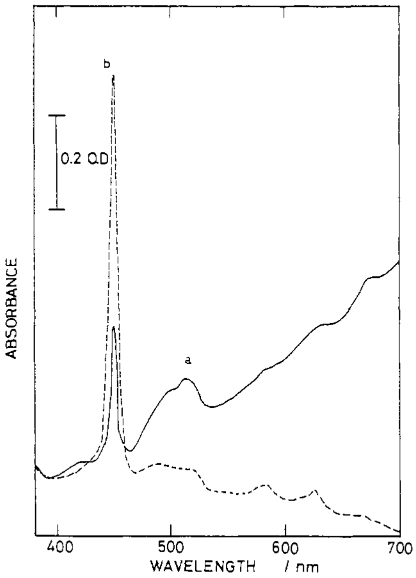


Figure 2. Successive formation of the constrained complex, $[Mo^{IV}O(TPP)NCS]^-$, by photobleaching. Solid and broken lines show respectively the electronic spectrum of the solution γ-irradiated for 8 h at 77 K and photobleached for 2 min after γ-irradiation.

---

(7) Ronayne, M. R.; Guarino, J. P.; Hamill, W. H. *J. Am. Chem. Soc.* **1962**, *84*, 4230.

(8) Dainton, F. S.; Salmon, G. A. *Proc. R. Soc. London, Ser. A* **1965**, *285*, 319.

(9) Smith, D. R.; Pieroni, J. J. *Can. J. Chem.* **1965**, *43*, 876.

(10) Smith, D. R.; Pieroni, J. J. *Can. J. Chem.* **1965**, *43*, 2141.

(11) Willard, J. E. *J. Phys. Chem.* **1975**, *79*, 2966.

(12) Ichikawa, T.; Yoshida, H.; Hayashi, K. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 2685.

(13) Ito, T.; Fueki, K.; Kuri, Z. *J. Phys. Chem.* **1975**, *79*, 1513.

(14) Kira, A., Imamura, M. *Chem. Phys. Lett.* **1978**, *60*, 44.

(15) Murabayashi, S.; Shiotani, M.; Sohma, J. *Chem. Phys. Lett.* **1977**, *48*, 80.

(16) Murabayashi, S.; Shiotani, M.; Sohma, J. *Chem. Phys. Lett.* **1977**, *51*, 568.

(17) Kubodera, H.; Shida, T.; Shimokoshi, K. *J. Phys. Chem.* **1981**, *85*, 2583.

(18) Hamill, W. H. "Radical Ions"; Kaiser, E. T., Kevan, L., Eds.; Wiley: New York, 1968; p 321.

(19) Kevan, L. *Actions Chim. Biol. Radiat.* **1979**, *15*, 81.

(20) Dyne, P. J.; Miller, O. A. *Can. J. Chem.* **1965**, *43*, 2696.

(21) Dismukes, G. C.; Hager, S. L.; Morine, G. H.; Willard, J. E. *J. Chem. Phys.* **1974**, *61*, 426.

(22) Hager, S. L.; Willard, J. E. *J. Chem. Phys.* **1974**, *61*, 3244.

(23) Thissen, H. P. H.; Völker, S.; Schmidt, M.; Port, H. *Chem. Phys. Lett.* **1983**, *94*, 537.

(24) Ling, A. C.; Willard, J. E. *J. Phys. Chem.* **1969**, *73*, 2408.

(25) Shida, T.; Kira, A. *J. Phys. Chem.* **1969**, *73*, 4315.

(26) Konishi, S.; Hoshino, M.; Yamamoto, K.; Imamura, M. *Chem. Phys. Lett.* **1980**, *72*, 459.

(27) Konishi, S.; Hoshino, M.; Imamura, M. *J. Phys. Chem.* **1980**, *84*, 3437.

(28) Hoshino, M.; Konishi, S.; Terai, Y.; Imamura, M. *Inorg. Chem.* **1982**, *21*, 89.

from room temperature. The appearance of the band at 442 nm at 77 K indicated the formation of a new complex that was finally ascribed to $Mo^{IV}O(TPP)MeTHF$ by the optical and ESR studies of the behavior of $Mo^{IV}O(TPP)$ in MeTHF.

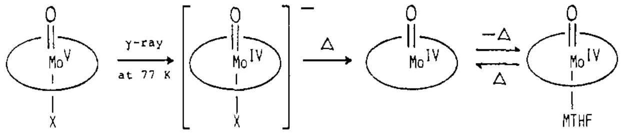
The intensity of the 427-nm absorption band of the $Mo^{IV}O(TPP)$ synthesized independently was decreased, with an increase in the absorption at 437 nm as the temperature of the MeTHF solution was lowered from 20 to −72 °C. The spectral change was reversible in this temperature range and has isosbestic points. The ratio of the absorbances at 427 and 437 nm of the MeTHF solution of $Mo^{IV}O(TPP)$ does not depend on the initial concentration of $Mo^{IV}O(TPP)$ at constant temperature, indicating that the band at 437 nm is not attributable to the polymerized species of $Mo^{IV}O(TPP)$. The ESR study indicated that the complex having the absorption band at 437 nm was diamagnetic, i.e., the oxidation state of the molybdenum was still Mo(IV) (d^2). The absorption band at 437 nm was finally ascribed to that of the new complex, $Mo^{IV}O(TPP)MeTHF$. The spectrum of $Mo^{IV}O(TPP)MeTHF$ in rigid matrix at 77 K has the absorption band at 442 nm.

Photobleaching. The trapped electron of the sample solution irradiated with γ-radiation at 77 K has absorption in the visible–near-infrared region.[7] The absorption of the constrained complex at 448 nm was increased by photobleaching for 2 min with the decrease of the absorption of the trapped electron, which indicated that free electron formed by the photobleaching reduces the residual $Mo^{V}O(TPP)X$ complex in the rigid matrix (Figure 2). The trapped electron band is known to be photosensitive, being bleached by visible and near-infrared light.[20] If solutes with high electron affinity such as biphenyl,[7] iron(III) chloride,[8] and tetraphenylhydrazine[25] are present in the matrices, the intensity of the radical anion bands of these solutes increases as the intensity of the electron band decreases. A direct photoirradiation of $Mo^{V}O(TPP)NCS$ solution at 77 K, which is not γ-irradiated beforehand, affords no formation of the constrained complex.

ESR Measurements. The oxidation state of the central molybdenum of $Mo^{V}O(TPP)X$ is 5+, and paramagnetism results. The ESR spectrum of the MeTHF solution of $Mo^{V}O(TPP)NCS$ consists of a strong central line ($\bar{g} = 1.967$) due to $^{94,96,98,100}Mo$ nuclei ($I = 0$; natural abundance ca. 75%), which is split to nine lines by four coordinated nitrogens of the TPP^{2-} ligand.[29] γ-Irradiation of the sample solution at room temperature caused the ESR signal due to Mo^{V} (d^1) to diminish, owing to the formation of $Mo^{IV}O(TPP)$, which is ESR silent. The ESR spectrum of the complex, $Mo^{V}O(TPP)NCS$, in the rigid matrix at 77 K has a perpendicular component at $g_{\perp} = 1.963$. The parallel component, $g_{\parallel}$, was not obtained because of the ambiguity of the signal. The intense $g_{\perp}$ signal of Mo(V) is decreased by γ-irradiation at 77 K and is still further decreased by photobleaching. The decrease is due to the formation reaction of the constrained complex. The results indicate that the oxidation state of the central molybdenum of the constrained complex is Mo^{IV} (d^2). Signals at $g = 2.003$ and 1.871 produced by γ-irradiation were ascribed to a solvent-trapped electron[9] and some radicals formed in the ESR glass tube, respectively. The signal at $g = 2.003$ diminished and the height of the signal at $g = 1.871$ increased by photobleaching pure MeTHF that had been γ-irradiated at 77 K. When the sample solution is warmed, $Mo^{IV}O(TPP)$ is formed and is naturally ESR silent. The ESR study indicated that the central molybdenum of the $Mo^{V}O(TPP)NCS$ was reduced by getting one electron, and the ligand TPP^{2-} was not reduced.

Mechanisms of the Reaction. The optical and the ESR studies indicate that γ-irradiation of the MeTHF solution of

Scheme I



$Mo^{V}O(TPP)X$ at 77 K causes one-electron reduction of $Mo^{V}O(TPP)X$ to form the constrained complex, which is thought to be a reaction intermediate. Warming the matrices to room temperature causes formation of $Mo^{IV}O(TPP)$ by release of the ligand X, where no change in the oxidation state of the central molybdenum occurs. When the solution of $Mo^{IV}O(TPP)$ is brought back to low temperature, MeTHF coordinates to the molybdenum of $Mo^{IV}O(TPP)$ (Scheme I).

As for the radiation chemistry of organic solvents, the mechanism of the reactions has been widely studied.[18,19] The mechanism of the generation of electrons from MeTHF proposed by Kevan[19] is summarized as shown in eq 1–4, and the first step in the photobleaching process is proposed as eq 5.

$$\mathrm{MeTHF} \rightsquigarrow \mathrm{MeTHF}^{+\cdot} + e_m^- \qquad (1)$$

$$e_m^- \rightarrow e_t^- \qquad (2)$$

$$e_m^- + S \rightarrow S^- \qquad (3)$$

$$\mathrm{MeTHF}^{+\cdot} + \mathrm{MeTHF} \rightarrow \mathrm{MeTHF}\cdot + \mathrm{MeTHFH}^+ \qquad (4)$$

$$e_t^- \xrightarrow{h\nu} e_m^- \qquad (5)$$

e_m^-, e_t^-, and S represent mobile electrons, trapped electrons, and a solute with high electron affinity, respectively. The mobile electron, e_m^-, acts as a reducing agent to the $Mo^{V}O(TPP)X$ complex to form the constrained complex. The formation of the constrained complexes, $[Co^{II}(TPP)Cl]^-$ [6] and alkylcobaloximes,[28] has been reported, and their electronic states were investigated by ESR spectroscopy. Unfortunately, the response of the electronic ground state of the central molybdenum of the constrained complexes to variation of the ligand X could not be studied in the present work, because the Mo(IV) is ESR silent. However, the effect of the ligand X on the electronic spectra was clearly observed.

Spectral Data. The absorption bands and the molar absorption coefficients of the complexes observed in this work in UV–visible region are summarized in Table I. The spectrum of $Mo^{V}O(TPP)X$ in MeTHF at room temperature has the Soret band with an unsymmetric shape. The unsymmetry of the Soret bands may be due to the presence of some solvated $Mo^{V}O(TPP)X$ in MeTHF. The Soret band of $Mo^{V}O(TPP)X$ splits into two bands in the rigid matrix at 77 K as shown in Table I. The major bands above 400 nm, i.e., Soret, α, and β bands of the complexes at 25 °C and 77 K, cause a red shift in the order X = F < NCS < Cl < Br, which is the same order as that of the increasing softness of the ligands. The red shift is accompanied by the decrease in the molar absorption coefficients. ESR study indicated that the differences of the electronic states of the central molybdenum between these molybdenum(V) complexes were slight.[5]

In the series of constrained complexes, $[Mo^{IV}O(TPP)X]^-$, the Soret bands at 77 K were located around 450 nm and also showed a red shift in the same order, X = F < NCS < Cl < Br. The difference of the energy of the Soret bands between $Mo^{V}O(TPP)F$ and $Mo^{V}O(TPP)Br$ (1910 cm^{-1}) is larger than that of the Soret bands between $[Mo^{IV}O(TPP)F]^-$ and $[Mo^{IV}O(TPP)Br]^-$ (820 cm^{-1}), suggesting the smaller effect of the difference of the coordinating ligands X on the $Mo^{IV}O(TPP)$ moiety. This result can be attributed first to the difference of the oxidation state of the molybdenum and second to the rigidity of the matrix, which affects the degree to which the ligand X and the central molybdenum of the constrained

---

(29) Imamura, T.; Terui, M.; Takahashi, Y.; Numatatsu, T.; Fujimoto, M. *Chem. Lett.* **1980**, *89*.

Table I. Absorption Bands in UV-Visible Region

complex	λ_{max}/nm in MeTHF ($\epsilon/10^4$ M^{-1} cm^{-1})							temp, °C
				Soret		β	α	
$Mo^VO(TPP)F$	326 (2.95)	368 (sh)	387 (sh)	463 (9.55)		587 (1.21)	627 (0.99)	25
$Mo^VO(TPP)NCS$	333 (4.81)	370 (sh)	415 (3.32)	492 (4.76)		621 (0.94)	667 (0.98)	
$Mo^VO(TPP)Cl$	340 (5.11)		418 (2.86)	493 (4.03)		623 (0.83)	670 (0.93)	
$Mo^VO(TPP)Br$	352 (5.52)		423 (2.62)	508 (3.27)		635 (0.67)	688 (0.86)	
$Mo^VO(TPP)F$		370 (2.7)	390 (sh)	460 (9.5)	475 (11)	591 (1.7)	633 (2.1)	−196
$Mo^VO(TPP)NCS$		370 (4.1)	418 (3.5)	496 (5.1)	512 (5.0)	625 (1.1)	671 (1.6)	
$Mo^VO(TPP)Cl$			420 (3.8)	499 (4.2)	516 (4.3)	630 (1.0)	675 (1.6)	
$Mo^VO(TPP)Br$	356 (6.8)		425 (2.8)	507 (3.6)	527 (3.7)	642 (0.86)	689 (1.4)	
$[Mo^{IV}O(TPP)F]^-$				447 (67)		577 (1.9)	617 (1.6)	−196
$[Mo^{IV}O(TPP)NCS]^-$				448 (108)		583 (2.1)	625 (1.8)	
$[Mo^{IV}O(TPP)Cl]^-$				456 (35)		588 (2.2)	631 (2.1)	
$[Mo^{IV}O(TPP)Br]^-$				464 (23)		592 (1.8)	638 (2.2)	
$Mo^{IV}O(TPP)MeTHF$				442 (59)		572 (4.1)	610 (4.0)	−196
$Mo^{IV}O(TPP)MeTHF$				437 (41)		566 (2.0)	606 (1.1)	−72
$Mo^{IV}O(TPP)$				427 (36)		555 (2.3)	588 (0.58)	25

complexes separate. The Soret bands of these constrained complexes have relatively high molar absorption coefficients that decrease with the red shift of the Soret bands except in the constrained complex of $[Mo^VO(TPP)NCS]^-$. The extraordinary high molar absorption coefficient and the sharpness of the Soret band at 448 nm of $[Mo^{IV}O(TPP)NCS]^-$ may reflect the rigidity of the matrices that constrains the structure of the core vibration of the complex. We presume that a long ligand as NCS^- is forced to strongly coordinate to the central molybdenum of the constrained complex by the rigidity of the solvent to cause a high molar absorption coefficient. From the spectral data the following conclusions are drawn: (1) The shift of the Soret band is accompanied by shifts of the α and β bands in the $Mo^VO(TPP)X$ series at 25 °C and also for the constrained complex $[Mo^{IV}O(TPP)X]^-$ series at 77 K. (2) The red shift of the major bands in the complexes having the same oxidation state of molybdenum depends on the electronegativity of the coordinating ligand X. (3) The Soret band moves toward the UV region as the oxidation state of the central molybdenum of the six-coordinated complexes changes from 5+ to 4+. The Soret bands in dichloromethane of $Mo^VO(TPP)\cdot Me_2SO\cdot X$ and $Mo^{IV}O(TPP)\cdot Me_2SO$, which are not constrained complexes, are located at 480 and 444 nm, respectively, indicating the same trend.[30] (4) The Soret band of the five-coordinated complex $Mo^{IV}O(TPP)$, which is formed by releasing the ligand X, is more blue shifted and is at 427 nm.

Backward Reaction. If the solution of $Mo^{IV}O(TPP)$ formed by γ-irradiation was allowed to stand at room temperature, the reaction would proceed backward to form the initial complex $Mo^VO(TPP)X$, except for the reaction system of $Mo^VO(TPP)Br$ in which the spectrum of the Mo(V) complex formed by the backward reaction of $Mo^{IV}O(TPP)$ is different from that of $Mo^VO(TPP)Br$. Thus, the tendency for the initial complex, $Mo^VO(TPP)X$, to be regained by the backward reaction depends on the coordinating strength of the ligand X to the central molybdenum. Oxidizing agents for the backward reaction must be the residual cation radicals formed by the reaction (1). The order of the magnitude of the formation constants, K_x, for the substitution reaction of $Mo^VO(TPP)X$ with dimethyl sulfoxide in dichloromethane is $K_F < K_{NCS} \approx K_{Cl} \ll K_{Br}$ and indicates that F^- is most strongly coordinating to molybdenum,[30] which is reflected in the velocity of the backward reaction described above. With the initial concentration of $[Mo^VO(TPP)X]_0$ (X = F, NCS) $\approx 10^{-5}$ M, it takes over 12 h and less than 30 min, respectively, to complete the backward reaction at 25 °C to reproduce the initial complexes, $Mo^VO(TPP)NCS$ and $Mo^VO(TPP)F$, from their $Mo^{IV}O(TPP)$ complexes. Thus, the backward reaction from $Mo^{IV}O(TPP)$ formed by γ-irradiation may depend on the affinity between the ligand X and the central molybdenum of $Mo^{IV}O(TPP)$.

Registry No. MeTHF, 96-47-9; $Mo^VO(TPP)F$, 76771-79-4; $Mo^VO(TPP)NCS$, 73515-84-1; $Mo^VO(TPP)Cl$, 68070-21-3; $Mo^VO(TPP)Br$, 73515-72-7; $[Mo^{IV}O(TPP)F]^-$, 92186-23-7; $[Mo^{IV}O(TPP)NCS]^-$, 92186-24-8; $[Mo^{IV}O(TPP)Cl]^-$, 92186-25-9; $[Mo^{IV}O(TPP)Br]^-$, 92186-26-0; $Mo^{IV}O(TPP)MeTHF$, 92186-27-1; $Mo^{IV}O(TPP)$, 33519-60-7.

---

[30] Unpublished results: Tanaka, T. M.S. Thesis, Hokkaido University, 1983.