tetragonal environments. We observe that the exogenous bridging ligand structurally has some effect on the overall copper coordination geometry. The exogenous bridge was found to primarily influence the copper–copper separation, the Cu–O$_{\mathrm{phenolate}}$–Cu bridging angle, and the magnetic coupling between Cu(II) ions, while a larger X bridging atom does force the coordination geometry of Cu(II) to deviate from square-based-pyramidal geometry (Table VIII). The latter is also reflected in a general shifting to lower energy of both the PhO$^-$ → Cu(II) LMCT band and the d–d envelope (Table IX) as X changes from OR$^-$ to N$_3^-$ to halide. In the proteins it is believed that the two copper atoms are separated by ca. 3.6 Å in oxy- and met-hemocyanin derivatives,[1,2,34] while in the dinuclear compounds I–V the Cu···Cu separation varies between 3.082 and 3.348 Å (Table VIII). There is an apparent preference for monoatomic bridging with shorter Cu···Cu separations (<3.4 Å), although complexes VI and VII may have bridging distances approaching 3.6 Å as solid materials.

As indicated, the spectral properties of complexes I–VII exhibit some dependence on structure, which is dependent on the bridging group X. Magnetochemical properties also vary systematically with structure. While we and others have made considerable progress in establishing structural and spectral correlations in ligand-bridged dinuclear Cu(II) compounds, further investigations are clearly required.

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Supplementary Material Available: Listings of bond lengths, bond angles, anisotropic temperature factors, and hydrogen coordinates and temperature factors for compounds III (Tables XI–XIV), IV (Tables XVI–XIX), and V (Tables XXI–XXIV) and experimental plots of μ_{eff} and χ vs. $T(k)$ for complexes I–II and V (28 pages); listings of structure factors for complexes III–V (Tables X, XV, and XX) (45 pages). Ordering information is given on any current masthead page.

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Photoirradiated and γ-Ray-Irradiated Reactions of Manganese(III, IV, V) Tetraphenylporphyrins in 2-Methyltetrahydrofuran. Reactions of Azidomanganese(III) Porphyrin

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Manganese(III, IV) tetraphenylporphyrins Mn$^{\mathrm{III}}$(TPP)X (TPP = 5,10,15,20-tetraphenylporphinato; X = I, Br, Cl, N$_3$, NCS, OAc) and Mn$^{\mathrm{IV}}$(TPP)(OCH$_3$)$_2$ in 2-methyltetrahydrofuran (MeTHF) at room temperature were reduced to yield Mn$^{\mathrm{II}}$(TPP) by photoirradiation with visible light (440–750 nm) or by γ-ray irradiation. The photoirradiation of Mn$^{\mathrm{III}}$(TPP)N$_3$ in the rigid matrix at 77 K affords Mn$^{\mathrm{V}}$(TPP)N. Photochemically stable Mn$^{\mathrm{V}}$(TPP)N was reduced to Mn$^{\mathrm{II}}$(TPP) by γ-irradiation at room temperature. γ-Irradiation of MeTHF solutions of Mn$^{\mathrm{III}}$(TPP)X at 77 K causes one-electron reduction to form the constrained complexes [Mn$^{\mathrm{II}}$(TPP)X]$^-$. Warming the matrices after γ-irradiation formed Mn$^{\mathrm{II}}$(TPP), liberating ligand X$^-$. The near-infrared bands of Mn$^{\mathrm{III}}$(TPP)X red shift along with the shifts of the bands in the visible region by varying the ligand X. The characteristic bands of the constrained complex [Mn$^{\mathrm{II}}$(TPP)X]$^-$ in the near-infrared region red shift in the order X = Cl > Br > I. The photoirradiation of Cr$^{\mathrm{III}}$(TPP)N$_3$ with visible light affords Cr$^{\mathrm{V}}$(TPP)N at room temperature and at 77 K.

Introduction

Manganese porphyrins have been of continuous interest in the last two decades because of their versatile characteristic behavior in solution: feasible formation of dioxygen complexes,[1,2] photolytic redox reactions,[3] dependency of redox potential on a coordinated monoanion ligand,[4] and electronic spectra of manganese(III) porphyrins.[5,6] Recent syntheses and/or characterization of several high-valent manganese(IV, V) porphyrins,[7,8] including nitridomanganese(V) porphyrins,[9-11] offer much information on synthetic

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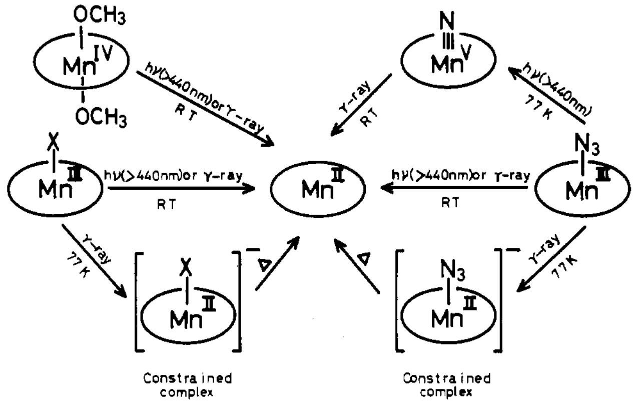
Table I. Elemental Analyses for Manganese and Chromium Porphyrins

complex	empirical formula	mol wt	% C calcd	% C found	% H calcd	% H found	% N calcd	% N found
$Mn^{III}(TPP)F$	$C_{44}H_{28}N_4FMn$	686.6	76.96	76.44	4.11	3.86	8.16	8.17
$Mn^{III}(TPP)Cl$	$C_{44}H_{28}N_4ClMn$	703.1	75.16	75.45	4.01	4.12	7.97	7.91
$Mn^{III}(TPP)Br$	$C_{44}H_{28}N_4BrMn$	747.5	70.69	70.98	3.78	3.69	7.50	7.39
$Mn^{III}(TPP)I$	$C_{44}H_{28}N_4IMn$	794.5	66.51	66.69	3.55	3.45	7.05	7.27
$Mn^{III}(TPP)N_3$	$C_{44}H_{28}N_7Mn$	709.7	74.46	74.50	3.98	3.99	13.82	13.57
$Mn^{III}(TPP)NCS$	$C_{45}H_{28}N_5SMn$	725.7	74.47	74.60	3.89	3.84	9.65	9.68
$Mn^{III}(TPP)OAc$	$C_{46}H_{31}N_4O_2Mn$	726.7	76.02	75.43	4.30	4.17	7.71	7.79
$Mn^{IV}(TPP)(OCH_3)_2$	$C_{46}H_{34}N_4O_2Mn$	729.7	75.71	75.88	4.70	4.73	7.68	7.51
$Mn^{V}(TPP)N$	$C_{44}H_{28}N_5Mn$	681.7	77.52	76.62	4.14	4.12	10.28	9.99
$Cr^{III}(TPP)N_3$	$C_{44}H_{28}N_7Cr$	706.8	74.77	74.35	3.99	3.94	13.87	13.80

catalytic reactions.[9,12] Manganese is also believed to be an essential species in green plant photosystem II (PS II).[13]

The photoreductions of $Mn^{III}(TPP)X$ (TPP = tetraphenylporphinato; X = I, Br, Cl, OAc, NCS) in 2-methyltetrahydrofuran (MeTHF) to $Mn^{II}(TPP)$ with visible light at the Soret band were preliminarily reported.[14] The quantum yield of the photoreductions depends on the ligand X in the order X = NCS > I > Br > Cl > OAc. The γ-irradiation of $Mo^{V}O(TPP)Cl$, which is the same d-type hyperporphyrin as $Mn^{III}(TPP)X$, in MeTHF at 77 K affords the constrained complex $[Mo^{IV}O(TPP)Cl]^-$, which is converted to $Mo^{IV}O(TPP)$ as the matrix is warmed.[15] The Soret bands of the electronic spectra of $[Mo^{IV}O(TPP)X]^-$ red shift in the same order, X = Br > Cl > F, as those of $Mo^{V}O(TPP)X$.[16] $Mn^{III}(TPP)Cl$ in the same solvent is also reduced to yield $[Mn^{II}(TPP)Cl]^-$ by γ-ray irradiation at 77 K.[17] The studies of photochemistry and radiation chemistry are complementary for investigating the mechanisms of the reactions and the behavior of chemical species in solution. MeTHF is a useful solvent as a glassy rigid matrix at 77 K and yields mobile electrons with γ-irradiation.[18] We report here the photochemistry and radiation chemistry of $Mn^{III}(TPP)X$, $Mn^{IV}(TPP)(OCH_3)_2$, and $Mn^{V}(TPP)N$ at room temperature and at 77 K. The electronic spectra of the complexes $Mn^{III}(TPP)X$, $[Mn^{II}(TPP)X]^-$, and $Mn^{II}(TPP)$ in the UV–near-infrared region are also discussed.

Scheme I



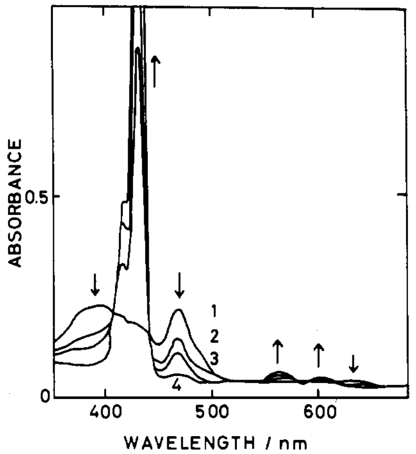


Figure 1. Spectral change of $Mn^{III}(TPP)N_3$ in MeTHF at 25 °C upon photoirradiation with 440–750-nm light for (1) 0, (2) 1, (3) 2, and (4) 5 min.

Experimental Section

Materials. Manganese(III) porphyrins $Mn^{III}(TPP)X$ (X = I, Br, Cl, N_3, NCS) were synthesized by the ligand-exchange reactions of $Mn^{III}(TPP)OAc$ with the procedure used for the corresponding iron complexes.[19] $Mn^{III}(TPP)OAc$ was synthesized by the method reported by Adler.[20] These complexes were all recrystallized from hexane–dichloromethane solutions and dried in vacuo at 150 °C for 10 h except for the fluoromanganese(III) complex. Two types of fluoromanganese(III) complex were obtained by the ligand exchange with $Mn^{III}(TPP)OAc$. The specimen of the fluoro complex that was obtained from ethanol–water and was not dried in vacuo at 150 °C dissolves easily in dichloromethane. The dried complex, confirmed to be $Mn^{III}(TPP)F$ by the elemental analysis, hardly dissolves in dichloromethane.[21] $Mn^{V}(TPP)N$[10] and $Cr^{V}(TPP)N$[24] were synthesized chemically by the method of the

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reactions of $Mn^{III}(TPP)Cl$ and $Cr^{III}(TPP)Cl$ with NaOCl in dichloromethane containing aqueous NH_3. $Mn^{IV}(TPP)(OCH_3)_2$ was obtained by the reaction of $Mn^{III}(TPP)OAc$ with NaOCl.[8] These complexes except the undried fluoromanganese(III) complex were all confirmed by the elemental analyses as shown in Table I. The pyridine adduct of $Mn^{II}(TPP)$, synthesized by the literature method[23] and stored in Ar, is unstable in air[23] and was identified to be the manganese(II) complex by the ESR and electronic spectral measurements. This adduct obtained is thought to be a five-coordinate complex, because it has been confirmed from X-ray crystallographic, magnetic, and spectral studies that manganese(II) porphyrins are either four- or five-coordinate.[2,25]

2-Methyltetrahydrofuran (MeTHF), washed with aqueous sodium hydroxide followed by drying with calcium chloride, was fractionally distilled, stored over NaK alloy in the storage vessel of the vacuum line in the dark, and again distilled immediately before use. All of the sample solutions of MeTHF were prepared in the dark and degassed by repeated freeze–pump–thaw cycles before γ-irradiation or photoirradiation. Toluene was carefully purified by the usual method[26] and stored in the vessel of the vacuum line. The MeTHF solution of $Mn^{II}(TPP)$ was prepared by the dissolution of $Mn^{II}(TPP)py$ or by the reduction of $Mn^{III}(TPP)X$ with $NaBH_4$. The reduction of manganese(III) porphyrins with $NaBH_4$ was accelerated by photoirradiation with visible light.

Measurements. The ^{60}Co γ-irradiation of sample solutions was performed in the dark at a dose rate of ca. 4 krd min^{-1}. Monochromatic light for the photoirradiation of the thermostated sample solutions was obtained by a 500-W xenon lamp with cutoff and interference filters. A 500-W high-pressure mercury lamp was used as a UV-light source. Electronic spectra in the UV–visible region and around 950 nm were recorded respectively on a Hitachi 808 spectrometer and a Hitachi EPS-3T spectrometer equipped with a PbS cell detector. ESR spectra were recorded on a JES-FE1X or JES-FE3AX spectrometer operating at 100-kHz modulation. ESR measurements for the photoreactions were carried out by the irradiation of a sample cell through the optical windows of the ESR apparatus. A Hitachi RMU-6 mass spectrometer was used to detect the gases evolved in the photooxidations of $Mn^{III}(TPP)N_3$ and $Cr^{III}(TPP)N_3$. The quantum yield was measured by employing Reinecke's salt as a standard actinometer.[27]

Results

Photoreduction. The photoirradiated and γ-irradiated reactions of manganese tetraphenylporphyrins are illustrated in Scheme I. Figure 1 shows the photoreduction of $Mn^{III}(TPP)N_3$ (λ_{max} = 473, 582, 631 nm) to $Mn^{II}(TPP)$ (λ_{max} = 430, 565, 601 nm) in MeTHF by irradiation with visible light (440–750 nm) at 25 °C:

$$Mn^{III}(TPP)X \xrightarrow[\text{MeTHF, room temp}]{h\nu\ (440-750\ \text{nm})} Mn^{II}(TPP) \qquad (1)$$

The ESR measurements indicated the formation of the manganese(II) complex, which is a d^5 high-spin complex. This photoreduction proceeded with Soret or Q-band excitation. The quantum yield with the excitation band at 468.5 nm is 2×10^{-2}, which is higher than that of the photoreduction of other $Mn^{III}(TPP)X$ complexes.[14] The order of the easiness of the photoreduction among the halogeno complexes is X = I > Br > Cl despite the reverse energy order of the photoexcitation band.[14]

The photoreduction of a $Mn^{III}(TPP)N_3$ solution containing PBN (phenyl-*N-tert*-butylnitrone) as a radical-trapping reagent at 25 °C gave an ESR signal due to the PBN radical (g = 2.007, A_N = 14.7 G, A_H = 3.3 G) aside from the signal due to $Mn^{II}(TPP)$. The UV-light irradiation (240–390 nm) of the solvent MeTHF containing only PBN also yielded the PBN radical with the same ESR parameters at room temperature. This result indicates that the PBN radical observed for the $Mn^{III}(TPP)N_3$ system is a PBN–MeTHF radical species.

Photooxidation of $Mn^{III}(TPP)N_3$. $Mn^{III}(TPP)N_3$ in the glassy rigid matrix of MeTHF at 77 K has bands at 473, 585, and 634 nm. We label these bands V, IV, and III following Boucher.[5] Figure 2 shows that these absorption peaks decrease with the appearance of new bands at 424 and 540 nm by the photoirradiation with visible light at the band V. The bands of the product agree with those of $Mn^{V}(TPP)N$ synthesized separately. The absence of an ESR signal supported the formation of an ESR-silent species, as is the case for the low-spin complex of $Mn^{V}(TPP)N$ (d^2).[28] No ESR signal due to $Mn^{II}(TPP)$ was observed. These results indicated that $Mn^{III}(TPP)N_3$ was photoreduced with visible light at room temperature and the same complex was photooxidized at 77 K, which prompted us to study the photoreaction of the analogous complex of $Cr^{III}(TPP)N_3$ in MeTHF. When the MeTHF solution of $Cr^{III}(TPP)N_3$ (λ_{max} = 396, 445, 520, 562, 592 nm) was photoirradiated with visible light (>440 nm) at room temperature, a product (λ_{max} = 419, 543 nm) was formed.[29] The product was identified as $Cr^{V}(TPP)N$ (d^1) by its characteristic ESR signal with 11 lines.[24] The photoirradiation of $Cr^{III}(TPP)N_3$ in MeTHF at 77 K also afforded $Cr^{V}(TPP)N$ (λ_{max} = 424, 547 nm at 77 K), indicating there was no difference from the photooxidation in toluene with UV–visible light.[11a,31] The liberations of nitrogen gas were confirmed by mass-spectral measurements for both the $Mn^{III}(TPP)N_3$ and the $Cr^{III}(TPP)N_3$ systems:

$$Mn^{III}(TPP)N_3 \xrightarrow[\text{MeTHF, 77 K}]{h\nu\ (440-750\ \text{nm})} Mn^{V}(TPP)N + N_2 \qquad (2)$$

$$Cr^{III}(TPP)N_3 \xrightarrow[\text{MeTHF, 77 K and room temp}]{h\nu\ (440-750\ \text{nm})} Cr^{V}(TPP)N + N_2 \qquad (3)$$

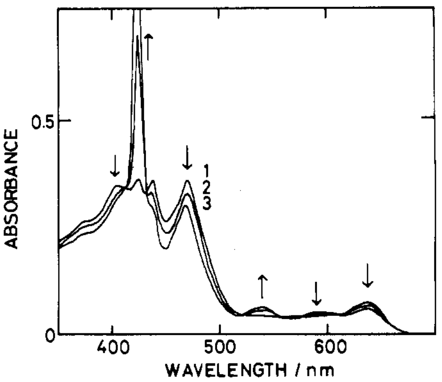

Figure 2. Spectral change of $Mn^{III}(TPP)N_3$ in MeTHF at 77 K for 60 min upon photoirradiation with 440–750-nm light.

Photolyses of $Mn^{IV}(TPP)(OCH_3)_2$ and $Mn^{V}(TPP)N$. The photoirradiation of $Mn^{IV}(TPP)(OCH_3)_2$ (λ_{max} = 420 nm) at 25 °C with the light at 424 nm afforded a complex having a band at 468 nm and $Mn^{II}(TPP)$ (λ_{max} = 430 nm). This spectral change had no isosbestic points. $Mn^{III}(TPP)OCH_3$, which has the same band at 468 nm, was also photoreduced with the light of the Soret band to $Mn^{II}(TPP)$. The photoirradiation of $Mn^{V}(TPP)N$ at room temperature with UV–visible light (350–750 nm) caused no observable change in the electronic spectrum. $Mn^{V}(TPP)N$ is stable photochemically.

Radiation Chemistry. Konishi et al. reported, by the measurements of electronic spectra in the Q-band–near-infrared region and by ESR measurements, that the γ-ray irradiation of $Mn^{III}(TPP)X$ (X = Cl,[17] Br,[17] I[32]) in MeTHF at 77 K affords the constrained complex $[Mn^{II}(TPP)X]^-$, in which the ligand X is forced to be coordinated to the central metal. The constrained complex converts to $Mn^{II}(TPP)$ by leaving the ligand X as the matrix is warmed to room temperature.[17] The reduction of manganese(III) porphyrin in methanol by γ-irradiation at 77 K was also communicated.[33] Low-temperature γ-irradiation coupled

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[29] The product could not be identified by the absorption spectral measurements because the MeTHF solutions of $Cr^{II}(TPP)$, prepared by the reaction of $Cr^{III}(TPP)Cl$ with $NaBH_4$, and of $Cr^{V}(TPP)N$ have almost the same bands at room temperature at 419, 467, and 515 nm and at 419 and 543 nm, respectively. The THF solution of $Cr^{II}(TPP)\cdot 2C_6H_5CH_3$ has bands at 421, 460, and 516 nm.[30]

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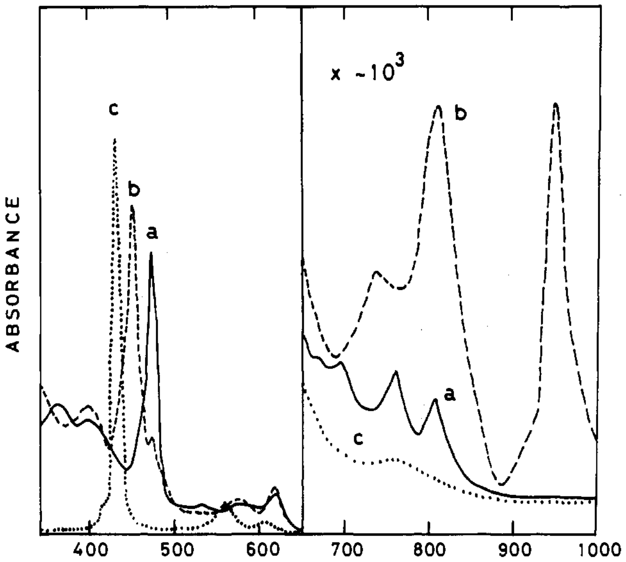

Figure 3. Change in the electronic spectra of $Mn^{III}(TPP)Cl$ in MeTHF by γ-radiolysis: (a) spectrum before γ-irradiation at 77 K; (b) spectrum after γ-irradiation for 19 h at 77 K followed by photobleaching; (c) spectrum after the matrix in (b) is warmed.

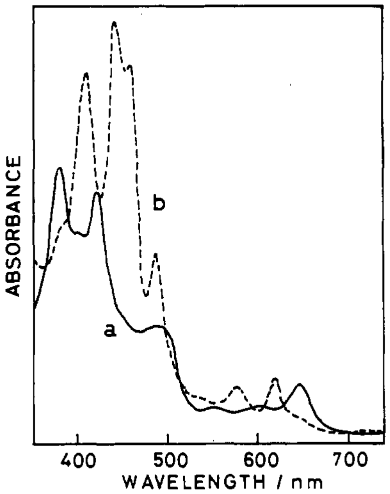

Figure 4. Change in the electronic spectra of $Mn^{III}(TPP)I$ in MeTHF by γ-radiolysis: (a) spectrum before γ-irradiation at 77 K; (b) spectrum after γ-irradiation for 19 h at 77 K followed by photobleaching.

with ESR spectroscopy was suggested to be a suitable technique for detecting manganese derivatives in biological systems because manganese(II) derivatives show characteristic ESR signals.[33] Our γ-radiolytic study aimed to clarify the following subjects: (1) the differences of the products and mechanisms between the photochemistry and radiation chemistry; (2) the reactivities of $Mn^{V}(TPP)N$ and $Mn^{IV}(TPP)(OCH_3)_2$ in the rigid matrices and at room temperature; (3) the electronic spectra of $[Mn^{II}(TPP)X]^-$, $Mn^{III}(TPP)X$, and $Mn^{II}(TPP)$ in the UV–near-infrared region.

The γ-irradiation of $Mn^{III}(TPP)X$ in MeTHF at room temperature afforded $Mn^{II}(TPP)$ (λ_{max} = 430, 565, 601 nm), which was identified by the electronic spectral and ESR measurements. When the rigid matrix of $Mn^{III}(TPP)X$ at 77 K was γ-irradiated, the constrained complex $[Mn^{II}(TPP)X]^-$ was formed (Figures 3–5). The photobleaching of the trapped electrons with visible–near-infrared light (>500 nm) at 77 K increased the amount of $[Mn^{II}(TPP)X]^-$, as observed in the $Mo^{V}O(TPP)X$ reaction systems.[15] The additional increase is due to the reduction of residual $Mn^{III}(TPP)X$ by the mobile electrons formed by the photobleaching of trapped electrons.[15]

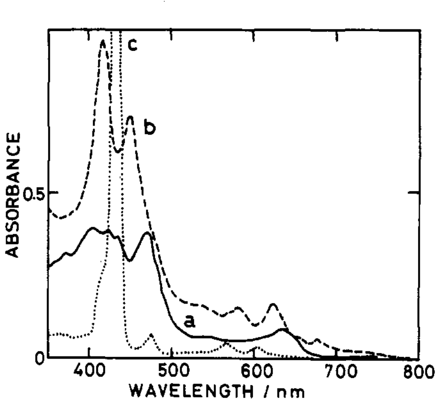

Figure 5. Change in the electronic spectra of $Mn^{III}(TPP)N_3$ in MeTHF by γ-radiolysis: (a) spectrum before γ-irradiation at 77 K; (b) spectrum after γ-irradiation for 19 h at 77 K followed by photobleaching; (c) spectrum after the matrix in (b) is warmed.

The γ-irradiation of $Mn^{IV}(TPP)(OCH_3)_2$ (λ_{max} = 423 nm) in the rigid matrix afforded a new complex (λ_{max} = 469, 580, 622 nm), which was ESR-silent. Warming the matrix yielded $Mn^{III}(TPP)OCH_3$.

The irradiation of $Mn^{V}(TPP)N$ at 77 K afforded a small amount of some new ESR-silent complex (λ_{max} = 440 nm). The reaction system, after the irradiated matrix was warmed, gave a small amount of $Mn^{II}(TPP)$. At room temperature, the reduction of $Mn^{V}(TPP)N$ to $Mn^{II}(TPP)$ with γ-rays proceeded readily.

Discussion

Photochemistry. As described above, the photolyses of $Mn^{III}(TPP)N_3$ and of $Cr^{III}(TPP)N_3$ afford $Mn^{II}(TPP)$ and $Cr^{V}(TPP)N$ at room temperature and $Mn^{V}(TPP)N$ and $Cr^{V}(TPP)N$ at 77 K, respectively. The difference in the features of the photoreactions between $Mn^{III}(TPP)N_3$ and $Cr^{III}(TPP)N_3$ suggests that the photoirradiation of these azido complexes in MeTHF at room temperature causes competitive reactions between photoreduction and photooxidation. The photoirradiation of a $Mn^{III}(TPP)N_3$ solution containing a very large amount of PBN yielded $Mn^{V}(TPP)N$ as a main product even at room temperature. The increase in the dielectric constant of the solution with the addition of a large amount of PBN may accelerate the photooxidation of $Mn^{III}(TPP)N_3$ or retard the photoreduction. Although the toluene solution of $Mn^{III}(TPP)Cl$ was slowly photoreduced with visible light to yield $Mn^{II}(TPP)$ at room temperature, the photoirradiation of the toluene solution of $Mn^{III}(TPP)N_3$ yielded mainly $Mn^{V}(TPP)N$ and a small amount of $Mn^{II}(TPP)$. The photooxidations of other azidomanganese(III) porphyrins in toluene or benzene have also been reported.[9,11a]

In the rigid matrix, $Mn^{III}(TPP)X$ (X = Cl, Br, I, NCS, OAc) was not photoreduced with visible light. The retardation of the photoreduction of $Mn^{III}(TPP)N_3$ in the rigid matrix might result in photooxidation with cleavage of the $N-N_2$ bond. The photooxidation of $Mn^{III}(TPP)N_3$ also proceeded in a solid KBr pellet. These results suggest that whether the photooxidation or the photoreduction occurs depends on the central metal, the solvent, which sometimes acts as a reactant or as a radical scavenger, and the rigidity of the solution; the photooxidations must proceed when the azido porphyrins are in the rigid matrices or are dissolved in the solvents which do not act as reducing agents. The matrix effect or cage effect may be advantageous to the photooxidation at 77 K.

Radiation Chemistry. Figure 6 and Table II show the ESR spectra and parameters of $[Mn^{II}(TPP)X]^-$ in the g = 6 region. Careful comparison suggests that the intensities of NCS, N_3, and OAc complexes are almost the same and the intensities of the halogeno complexes vary in the order Cl < Br < I. We expect that the largest and sharpest hyperfine structure of $[Mn^{II}(TPP)I]^-$ with the smallest value of $A_\perp$ may correspond to the least rhombic distortion of the complex and the least ionization of iodine ligand. On the other hand, the constrained complexes with a long ligand,

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Table II. ESR Parameters for $[Mn^{II}(TPP)X]^-$ and $Mn^{II}(TPP)py$ in MeTHF at 77 K

complex	g value		hyperfine coupling const	
	$g_\perp$	$g_\parallel$	$A_\perp/G$	$A_\parallel/G$
$[Mn^{II}(TPP)OAc]^-$	6.60	*a*	81.0	*a*
$[Mn^{II}(TPP)NCS]^-$	6.60	*a*	82.0	*a*
$[Mn^{II}(TPP)N_3]^-$	6.60	*a*	81.4	*a*
$[Mn^{II}(TPP)Cl]^-$	6.12	*a*	83.0	*a*
$[Mn^{II}(TPP)Br]^-$	6.14	*a*	80.2	*a*
$[Mn^{II}(TPP)I]^-$	6.15	*a*	77.4	*a*
$Mn^{II}(TPP)py$	6.12	2.04	76.8	83.6

[a] The signal $g_\parallel$ of manganese that should be observed in the $g = 2$ region is masked by the signals of the solvent radicals and atomic hydrogens.

OAc, NCS, or N_3, which is expected to cause large distortion from axial symmetry in the rigid matrix, showed blunt ESR signals having large $g_\perp$ parameters.

Mechanisms. The occurrence of the PBN–MeTHF radical in the photoreduction of $Mn^{III}(TPP)N_3$ at room temperature indicates that the solvent MeTHF takes part in the reaction. Two mechanisms could be possible. One of the mechanisms is photoreduction via homolytic cleavage of the Mn–N_3 bond followed by the reaction of the N_3 radical with the solvent MeTHF:

$$Mn^{III}(TPP)N_3 \xrightarrow[\text{MeTHF, room temp}]{h\nu\ (440\text{–}750\ \text{nm})} Mn^{II}(TPP) + N_3^{\bullet} \quad (4)$$

$$N_3^{\bullet} + MeTHF \rightarrow MeTHF^{\bullet} + HN_3 \quad (5)$$

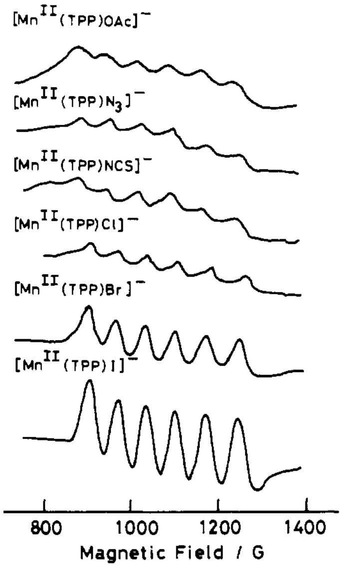

Figure 6. ESR spectra around $g = 6$ of the constrained complex $[Mn^{II}(TPP)X]^-$.

Another possible mechanism of the photoreduction is charge transfer (CT) from the porphyrin ring to the central manganese, followed by the reaction of the excited complex $[Mn(TPP)N_3]^*$ with the solvent MeTHF, as shown in reactions 6 and 7. In both

Table III. Electronic Absorption Bands of $Mn^{III}(TPP)X$ in Toluene

complex	λ_{max}/nm												
		VI					V		IV	III		II	I
At 25 °C													
$Mn^{III}(TPP)OAc$		370				395	472	520	578	614		692	755
$Mn^{III}(TPP)NCS$	333	385				405	482	525	583	619	680	705	769
$Mn^{III}(TPP)N_3$		393				418	477	535	590	630		696	755
$Mn^{III}(TPP)Cl$		373				394	478	530	584	620		698	757
$Mn^{III}(TPP)Br$		379				400	487	538	590	628		705	763
$Mn^{III}(TPP)I$		387				410	500	544	607	648		716	780
At 77 K													
$Mn^{III}(TPP)OAc$		373		400		446	468	517	575	613		*a*	*a*
$Mn^{III}(TPP)NCS$		386		407	424	450	481	520	578	615			
$Mn^{III}(TPP)N_3$		382	404	420		477	488	534	590	630			
$Mn^{III}(TPP)Cl$		373		400		445	474	523	581	618			
$Mn^{III}(TPP)Br$		378		403		451	484	525	588	623			
$Mn^{III}(TPP)I$		387		410			498	543	600	644			

[a] Absorption spectra in the near-IR region at 77 K were not measured because of the low solubility of the complexes.

Table IV. Electronic Absorption Bands of $Mn^{III}(TPP)X$ in MeTHF

complex	λ_{max}/nm at 25 °C ($\epsilon/10^4$ M^{-1} cm^{-1})								λ_{max}/nm in near-IR region at 77 K			
	VI	V	IV	III		II	I					
$Mn^{III}(TPP)OAc$	367	467 (10)	570 (0.8)	608 (0.7)		690	754		665	695	759	801
$Mn^{III}(TPP)NCS$	382	475 (8.96)	578 (0.651)	615 (0.735)	680	706	772	813	678	706	773	812
$Mn^{III}(TPP)N_3$	392	473 (2.92)	582 (0.440)	631 (0.550)			759	815		705	770	817
$Mn^{III}(TPP)Cl$	371	475 (11.58)	581 (0.952)	618 (1.10)		693	755		670	700	765	811
$Mn^{III}(TPP)Br$	377	483 (7.62)	588 (0.455)	627 (0.782)		701	766		678	709	774	820
$Mn^{III}(TPP)I$	383	498 (2.45)	601 (0.310)	649 (0.514)			783			723	792	840

Table V. Electronic Absorption Bands of $[Mn^{II}(TPP)X]^-$ in MeTHF at 77 K[a]

complex	λ_{max}/nm							
	Soret region			β	α	near-IR region		
$[Mn^{II}(TPP)OAc]^-$			446	572	609	696	797	945
$[Mn^{II}(TPP)NCS]^-$			446	575	614	708	805	936
$[Mn^{II}(TPP)N_3]^-$		418	452	580	620		798	950
$[Mn^{II}(TPP)Cl]^-$			453	580	620	737	815	950
$[Mn^{II}(TPP)Br]^-$			453	580	620	734	809	944
$[Mn^{II}(TPP)I]^-$	418	442	468	578	617	721	797	943

[a] The MeTHF solutions of $[Mn^{II}(TPP)X]^-$ were prepared by γ-radiolyses of the $Mn^{III}(TPP)X$ solutions at 77 K followed by photobleaching of trapped electrons.

$$\mathrm{Mn^{III}(TPP)N_3} \xrightarrow[\text{MeTHF, room temp}]{h\nu\ (440\text{–}750\ \text{nm})} [\mathrm{Mn(TPP)N_3}]^* \tag{6}$$

$$[\mathrm{Mn(TPP)N_3}]^* + \mathrm{MeTHF} \rightarrow \mathrm{Mn^{II}(TPP)} + \mathrm{MeTHF^{\bullet}} + \mathrm{HN_3} \tag{7}$$

these mechanisms for the photoreductions, the solvent MeTHF acts as a reducing agent. The MeTHF radical must be quenched rapidly by some successive reactions at room temperature.[34]

The generation of mobile electrons by γ-irradiation of MeTHF is well-known.[18,36] In the radiolysis of $\mathrm{Mn^{III}(TPP)N_3}$, these mobile electrons reduce the complex:

$$\mathrm{MeTHF} \overset{\gamma\text{-ray}}{\rightsquigarrow} \mathrm{MeTHF^{\bullet+}} + e^- \tag{8}$$

$$\mathrm{Mn^{III}(TPP)N_3} + e^- \rightarrow \mathrm{Mn^{II}(TPP)} + \mathrm{N_3}^- \tag{9}$$

$$\mathrm{MeTHF^{\bullet+}} + \mathrm{MeTHF} \rightarrow \mathrm{MeTHFH^+} + \mathrm{MeTHF^{\bullet}} \tag{10}$$

Comparison between visible illumination and γ-irradiation leads to the result that these two reactions are very similar; i.e., the chemical species first excited are different but the solvent MeTHF must take part in both reactions.

Electronic Spectra. The UV–near-infrared spectra of the starting materials $\mathrm{Mn^{III}(TPP)X}$ are shown in Tables III and IV for comparison with the spectra of the constrained complexes $[\mathrm{Mn^{III}(TPP)X}]^-$. Bands in the UV–visible region are assigned by Gouterman.[37] The bands V of $\mathrm{Mn^{III}(TPP)N_3}$ and $\mathrm{Mn^{III}(TPP)I}$ in MeTHF are broader than those of the other $\mathrm{Mn^{III}(TPP)X}$ complexes and the absorptivities are considerably lower than those of the complexes in toluene. We assume that the spectra of the two complexes are influenced by forming some solvated complexes with the solvent MeTHF. The red shift of the near-infrared bands I and II in the sequence I > Br > Cl was observed as well for the bands III–VI. Although the bands I and II may be assigned to a tripquartet if the bands correspond to those of the chromium(III) complex,[37,38] the CT probability could not be excluded because the shift is parallel with that of the bands III–VI. The electronic spectrum of $\mathrm{Mn^{III}(TPP)X}$ in a rigid matrix of MeTHF is essentially the same as that at room temperature except for small blue shifts of several nanometers. This shows the glassy rigid matrix of MeTHF is isotropic for these complexes.

The electronic spectral data for the solutions of the constrained complex $[\mathrm{Mn^{II}(TPP)X}]^-$ at 77 K, prepared by γ-irradiation followed by photobleaching of trapped electrons, are shown in Table V. The spectrum of $\mathrm{Mn^{II}(TPP)py}$ in benzene in the visible region is a pure $\pi \rightarrow \pi^*$ transition.[23] $[\mathrm{Mn^{II}(TPP)X}]^-$ has three main bands in the visible region, except for $[\mathrm{Mn^{II}(TPP)N_3}]^-$ and $[\mathrm{Mn^{II}(TPP)I}]^-$. The Soret, β, and α bands are located in almost the same region irrespective of ligand X, suggesting an assignment to the $\pi \rightarrow \pi^*$ transition; these bands are located around 450, 580, and 620 nm, respectively, at 77 K. The MeTHF solution of $\mathrm{Mn^{II}(TPP)}$ has absorption bands at 430, 565, and 601 nm in the visible region at room temperature and at 439, 569, and 608 nm at 77 K. The difference in wavelength of these three bands of $[\mathrm{Mn^{II}(TPP)X}]^-$ from those of $\mathrm{Mn^{II}(TPP)}$ at 77 K must be due to the rigidity of the matrix, which retains the structure of the initial complex $\mathrm{Mn^{III}(TPP)X}$. The splits of the Soret bands of $[\mathrm{Mn^{II}(TPP)N_3}]^-$ and of $[\mathrm{Mn^{II}(TPP)I}]^-$ may result from the solvation of MeTHF as suggested by the spectra of the initial complexes $\mathrm{Mn^{III}(TPP)N_3}$ and $\mathrm{Mn^{III}(TPP)I}$ at room temperature.

The near-infrared bands (700–950 nm) are characteristic for the constrained complex $[\mathrm{Mn^{II}(TPP)X}]^-$.[17] Table V shows that these bands red-shift in the order Cl > Br > I. The order is reverse to that of complexes such as $\mathrm{Mn^{III}(TPP)X}$ and $\mathrm{Mo^{V}O(TPP)X}$. The six-coordinate manganese(II) mesoporphyrin dimethyl ester in pyridine–water shows a weak band at ~700 nm at room temperature.[5a] Careful study of the near-infrared region for $\mathrm{Mn^{II}(TPP)}$ in MeTHF showed the presence of a very weak band at 740 nm at room temperature and of the two bands at 740 and 830 nm at 77 K, respectively. $\mathrm{Mn^{II}(TPP)py}$ in MeTHF has the same UV–near-infrared spectrum as that of $\mathrm{Mn^{II}(TPP)}$. The metal orbitals of $\mathrm{Mn^{II}(TPP)}$ $e_g(d_\pi)$ and $a_{1g}(d_{z^2})$, are accidentally degenerate with $a_{1u}(\pi)$ and $a_{2u}(\pi)$ of the porphyrin ligand.[39] An additional ligand raises d_{z^2} above $a_{2u}(\pi)$ and removes these degeneracy.[39] The energy levels of the d_{z^2} orbitals of $[\mathrm{Mn^{II}(TPP)X}]^-$ could be in the order Cl > Br > I. Therefore, the near-infrared bands of $[\mathrm{Mn^{II}(TPP)X}]^-$ could not be assigned to the CT bands $a_{1u}, a_{2u} \rightarrow d_{z^2}$, because the order of the red shift of the bands is Cl > Br > I, which is reverse to the order expected from the CT. Although it is not clear whether the near-infrared bands of the constrained complex $[\mathrm{Mn^{II}(TPP)X}]^-$ correspond to the very weak bands around 740 nm of $\mathrm{Mn^{II}(TPP)}$, one of the possible assignments of the near-infrared bands of $[\mathrm{Mn^{II}(TPP)X}]^-$ is CT from the central manganese(II) to the porphyrin ring, d_{z^2} or $e_g(d_\pi) \rightarrow e_g(\pi^*)$. The d_{z^2} and $e_g(d_\pi)$ levels of manganese may be raised by the ligand X in the sequence Cl > Br > I, resulting in the same order of the red shift of the near-infrared bands.

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Supplementary Material Available: Electronic absorption spectral data in the UV–near-infrared region for $\mathrm{Mn^{III}(TPP)X}$ (X = OAc, NCS, $\mathrm{N_3}$, F, Cl, Br, I) in dichloromethane at 25 °C (1 page). Ordering information is given on any current masthead page.

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(34) Photoirradiation of MeTHF with UV light at 77 K yields the MeTHF radical, which shows an ESR signal.[35] However, the MeTHF solution that was dissolved once does not show the characteristic ESR signal even at 77 K.

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