*trans*-$CrL(H_2O)_2^{2+}$, derived photochemically from *trans*-$CrL(NH_3)_2^{3+}$, and yielded a rate constant of $(4.5 \pm 0.3) \times 10^5$ $M^{-2}$ $s^{-1}$ in acidic $D_2O$ at 25 °C. The reaction of the complex prepared in this work yielded $k = (5.6 \pm 0.3) \times 10^5$ $M^{-2}$ $s^{-1}$. The agreement between the two values is considered good, given that two different techniques were used (laser flash photolysis and conventional spectrophotometry) and that the concentration ranges of all the components had to differ by several orders of magnitude to accommodate the two techniques.

The trans stereochemistry[3] of the chromium product of reaction 5 provides additional evidence that the chromium(II) reductant is also a trans species.

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**Registry No.** *trans*-$[CrLCl_2]Cl$, 27385-72-4; *cis*-$[CrLCl_2]Cl$, 27435-95-6; *trans*-$CrL(H_2O)_2(CF_3SO_3)_3$, 139040-90-7; *trans*-$CrL(H_2O)_2^{2+}$, 139015-81-9.

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# Preparation and Characterization of an $A_{1u}$ Oxoiron(IV) Porphyrin $\pi$-Cation-Radical Complex

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Oxoiron(IV) porphyrin $\pi$-cation radicals have been thought as functional intermediates (compounds I) in the reaction cycles of peroxidases,[1] catalases,[1] and cytochrome P-450.[2] Since Groves et al.[3a] first reported that addition of *m*-chloroperoxybenzoic acid, mCPBA, to chloroiron(III) tetramesitylporphyrin, (TMP)FeCl, at −78 °C produces an oxoiron(IV)–TMP $\pi$-cation radical, oxoiron(IV) porphyrin $\pi$ cation radicals have been prepared in many laboratories by using *meso*-tetraarylporphyrin derivatives.[3] However, most of the characterized oxoiron(IV) porphyrin $\pi$-cation radical complexes were confined to the complexes which had the unpaired electron in an $a_{2u}$ orbital.[4] In contrast to $a_{2u}$ oxoiron(IV) porphyrin $\pi$-cation-radical complexes, an $a_{1u}$ oxoiron(IV) porphyrin $\pi$-cation-radical complex has not been prepared. The $a_{1u}$ oxoiron(IV) porphyrin $\pi$-cation radical is considered as the active site of compounds I of some peroxidases,[5] and recent resonance Raman studies demonstrate the notable difference in iron–oxo stretching between the oxo $a_{2u}$ radical complex and the oxo $a_{1u}$ radical complex.[6] Further, the $a_{1u}/a_{2u}$ assignments based on the ESR and absorption spectral measurements have been brought into question by several independent studies,[7] and there still remain further studies on the compounds I of peroxidases and catalases, one of which is the assignment of the orbital occupancies of compounds I based on the $a_{1u}$ and $a_{2u}$ oxoiron(IV) porphyrin $\pi$-cation-radical complexes. We wish to report here the successful formation and characterization of an $a_{1u}$ oxoiron(IV) porphyrin $\pi$-cation radical.

## Experimental Section

**Materials.** 5,10,15,20-Tetramesitylporphyrin (TMP) and its iron(III) complex were prepared according to published methods.[8] 2,7,12,17-Tetramethyl-3,8,13,18-tetramesitylporphyrin (TMTMP) was prepared by the literature method.[9] Iron was inserted in the porphyrin by refluxing a chloroform–acetic acid mixture (4:1) with ferrous chloride and sodium acetate. Iron complexes were purified by column chromatography. Cyclohexene, triphenylphosphine, and tetra-*n*-butylammonium iodide (TBAI) were purchased from Nacalai Tesque (Kyoto).

**Physical Measurements.** Proton NMR spectra were recorded on a Bruker MSL-400 spectrometer. $^{31}P$ NMR spectra were obtained on a Varian XL-200 spectrometer. UV-vis spectra were recorded on a Hitachi U-3200 spectrophotometer. Solution magnetic measurements were performed by the NMR Evans' method[10] by using tetramethylsilane as the reference substance. Diamagnetic corrections were taken from the previous report.[11]

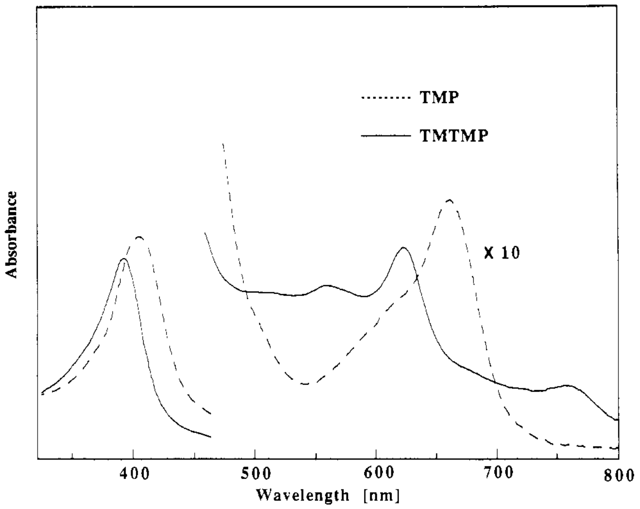

**Figure 1.** UV–visible absorption spectra of oxoiron(IV) porphyrin $\pi$-cation-radical complexes in dichloromethane–methanol (5:1) at −80 °C. Concentrations: TMP $\pi$ cation radical, approximately $2.4 \times 10^{-5}$ M, (- -); the green complex, approximately $2.6 \times 10^{-5}$ M (—).

## Results and Discussion

It has been pointed out that steric hindered substituents, such as the mesityl group, protect the active oxo ligand from the formation of the $\mu$-oxo dimer,[12] and that meso-unsubstituted porphyrins, such as protoporphyrin IX and octaethylporphyrin, appear to be more biologically relevant than tetraarylporphyrin as the models of compounds I. Thus, in order to gain a stable oxoiron(IV) porphyrin $\pi$-cation-radical complex with a meso-unsubstituted porphyrin, we utilized the porphyrin substituted pyrrole $\beta$ position for the mesityl group; TMTMP.

The oxidation of the TMTMP–iron(III) perchlorate complex, $(TMTMP)FeClO_4$, with 1.1 equiv of mCPBA in dichloromethane–methanol (5:1) at −78 °C produced a green complex,[13]

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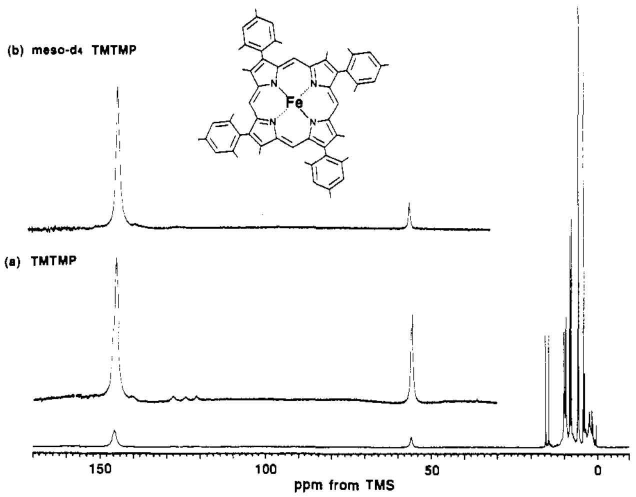

**Figure 2.** $^1$H NMR spectra of the green complex in $CD_2Cl_2$–$CD_3OD$ (5:1) at −80 °C: (a) $[(\mathrm{TMTMP})\mathrm{Fe}^{IV}{=}\mathrm{O}]^{\bullet+}$; (b) $[(\textit{meso}\text{-}\mathrm{TMTMP}\text{-}d_4)\mathrm{Fe}^{IV}{=}\mathrm{O}]^{\bullet+}$. The small peaks around 120 ppm are due to the signals for the minor component of the structural isomer of TMTMP.

**Table I.** $^1$H NMR Chemical Shifts for Ferric and Ferryl Porphyrin Complexes

| compound | $CH_3$ | *meso*-H | temp, °C | ref |
|---|---|---|---|---|
| $(\mathrm{TMTMP})\mathrm{Fe}^{III}\mathrm{ClO}_4$ | 62 | −4.5 | 22 | *a* |
| | 91 | −6 | −80 | *a* |
| $[(\mathrm{TMTMP})\mathrm{Fe}^{III}(\mathrm{CH_3OH})_2]^+$ | 68 | 44 | 22 | *a* |
| | 108 | 80.5 | −80 | *a* |
| $(\mathrm{Ethio})\mathrm{Fe}^{IV}{=}\mathrm{O}(N\text{-}\mathrm{MeIm})$ | 4 | 16 | −50 | 16 |
| $(\mathrm{TMP})\mathrm{Fe}^{IV}{=}\mathrm{O}$ | 8.4$^b$ | 6.4, 6.0$^c$ | −70 | 12 |
| $[(\mathrm{TMTMP})\mathrm{Fe}^{IV}{=}\mathrm{O}]^{\bullet+}$ | 145 | 56 | −80 | *a* |
| $[(\mathrm{TMP})\mathrm{Fe}^{IV}{=}\mathrm{O}]^{\bullet+}$ | −27$^b$ | 68$^c$ | −77 | 3a |

$^a$This study. $^b$Pyrrole proton. $^c$Meta proton.

**Table II.** Spin Density of Ferryl Porphyrin $\pi$-Cation Radicals

| compound | pyrrole $\beta$ | meso |
|---|---|---|
| $[(\mathrm{TMTMP})\mathrm{Fe}^{IV}{=}\mathrm{O}]^{\bullet+}$ | 0.029 | −0.012 |
| $[(\mathrm{TMP})\mathrm{Fe}^{IV}{=}\mathrm{O}]^{\bullet+}$ | 0.013 | |
| $a_{1u}$ orbital$^a$ | 0.026 | 0.001 |
| $a_{2u}$ orbital$^a$ | 0.013 | 0.193 |

$^a$The values from ref 19.

as observed for the oxidation of (TMP)FeCl with mCPBA.[3a] Figure 1 shows the absorption spectra of the green complex and the oxoiron(IV)–TMP $\pi$-cation radical at −80 °C. The green complex shows the broadened Soret band with a loss of intensity, a broad $\alpha,\beta$ band, and a new absorption around 600–700 nm. This spectral feature of the green complex suggests the formation of a porphyrin $\pi$-cation radical.[4a] Addition of 2.0 equiv of tetra-*n*-butylammonium iodide to the green complex reproduced the parent ferric complex, which ruled out the formation of the porphyrin ring-oxidized species such as *meso*-oxyporphyrin or isoporphyrin. It is worth noting that the spectral feature of the green complex is similar to that of horseradish peroxidase compound I, which has been assigned to an $a_{2u}$ radical, rather than that of catalase compound I, which has been assigned to an $a_{1u}$ radical.[14]

The green complex was reactive toward reducing reagents and alkenes. The absorption spectral measurements showed that treatment of the green complex with an excess amount of cyclohexene at −78 °C leads to the regeneration of ferric complexes and that the green complex reacts with *cis*-stilbene while the trans isomer is inert. These reactivities toward the olefines have been reported as characteristic of oxometalloporphyrin complexes.[15] Further, addition of 1.5 equiv of triphenylphosphine to the green complex at −78 °C produced 1.0 equiv of triphenylphosphine oxide, which was confirmed by $^{31}$P NMR spectroscopy. This result indicates that the green complex is quite reactive toward triphenylphosphine and has an active oxene ligand. All of these results suggest that the green complex is an oxoiron(IV) porphyrin $\pi$-cation-radical complex, $[(\mathrm{TMTMP})\mathrm{Fe}^{IV}{=}\mathrm{O}]^{\bullet+}$. This is the first report of the formation of the stable oxoiron(IV) porphyrin $\pi$-cation-radical complex with a meso-unsubstituted porphyrin.

More unambiguous evidence for the formation of $a_{1u}$ oxoiron(IV) porphyrin $\pi$-cation radical was obtained by $^1$H NMR measurements. Figure 2 illustrates the $^1$H NMR spectra of the reaction product of $(\mathrm{TMTMP})\mathrm{FeClO}_4$ with mCPBA, $[(\mathrm{TMTMP})\mathrm{Fe}^{IV}{=}\mathrm{O}]^{\bullet+}$, at −80 °C in $CD_2Cl_2$–$CD_3OD$. The green complex yields a well-resolved hyperfine-shifted NMR spectrum, which differs from those of the parent ferric complexes (Table I). The assignment of the signals was made by using selective deuterated samples (Figure 2b). The most downfield shifted signal at 145 ppm was assigned to the pyrrole $\beta$ methyl proton. The meso proton signal also exhibits an oxidation-induced downfield shift to 56 ppm. Observations of such large downfield shifts are unprecedented for simple paramagnetic oxoiron(IV) porphyrin complexes whose pyrrole $\beta$ methyl proton and meso proton were observed at 4 and 16 ppm, respectively.[16] The similar downfield shift of the pyrrole $\beta$ methyl proton signal was observed for the bis(imidazole) complex of a low-spin iron(III) ethioporphyrin $\pi$-cation radical.[17] Therefore, these large isotropic shifts are overall suggestive of porphyrin $\pi$-cation-radical character. The $^1$H NMR chemical shifts for $[(\mathrm{TMTMP})\mathrm{Fe}^{IV}{=}\mathrm{O}]^{\bullet+}$ and iron porphyrin complexes were summarized in Table I. The observed NMR shifts of $[(\mathrm{TMTMP})\mathrm{Fe}^{IV}{=}\mathrm{O}]^{\bullet+}$ contain shifts both by the iron(IV) paramagnetic center and the porphyrin $\pi$-cation-radical center. If any shift contribution from the iron(IV) metal center is subtracted, the NMR isotropic shift can be related to the $\pi$-spin density at the carbon to which the proton is attached.[18] The calculated and theoretical values are listed in Table II. The $\pi$-spin densities at the meso and pyrrole $\beta$ carbon are calculated [$\rho(\mathrm{meso}) = -0.012$ and $\rho(\mathrm{pyr}\text{-}\beta) = 0.029$] from the observed NMR isotropic shifts for $[(\mathrm{TMTMP})\mathrm{Fe}^{IV}{=}\mathrm{O}]^{\bullet+}$, suggesting $a_{1u}$ orbital occupancy of the unpaired electron in porphyrin.[19] The mesityl protons at the pyrrole $\beta$ position were observed at 14.7 and 14.0 ppm (*m*-H) and at 9.0 and 8.3 ppm (*o*-methyl). The splitting of the meta proton and *o*-methyl proton resonances is indicative of two different axial ligands in $[(\mathrm{TMTMP})\mathrm{Fe}^{IV}{=}\mathrm{O}]^{\bullet+}$. The small down field shift of the meta proton signal for $[(\mathrm{TMTMP})\mathrm{Fe}^{IV}{=}\mathrm{O}]^{\bullet+}$ is also consistent with the $a_{1u}$ orbital occupancy, because the spin density of the pyrrole $\beta$ carbon in the $a_{1u}$ radical orbital ($\rho = 0.029$) is smaller than that of the meso carbon in the $a_{2u}$ radical orbital ($\rho = 0.193$), which leads to the large downfield shift (68 ppm at −77 °C) of the meta proton signal for the oxoiron(IV)–TMP $\pi$-cation radical.[3a] The solution magnetic susceptibility measurement by the NMR Evans' method for $[(\mathrm{TMTMP})\mathrm{Fe}^{IV}{=}\mathrm{O}]^{\bullet+}$ yielded a value of $\mu_{\mathrm{eff}} = 3.8 \pm 0.2\ \mu_B$ at −80 °C, which is consistent with an $S = {}^3/_2$ system.

In summary, an $a_{1u}$ oxoiron(IV) porphyrin $\pi$-cation radical was successfully formed and characterized by hyperfine-shifted NMR measurements. The compound presented here provides the first opportunity to study the radical orbital occupancy of compounds

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(13) The oxidation of chloride complex, instead of perchlorate complex, did not form the corresponding green complex. However, we found that, even in the absence of methanol, addition of 1 equiv of mCPBA to the $(\mathrm{TMTMP})\mathrm{FeClO}_4$ at −80 °C also produces the green complex and that the green complex in the absence of methanol is more unstable than that in the presence of methanol.

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I of peroxidases and catalases. Studies of detailed electronic structure and reactivity of the compound are currently underway in our laboratories.

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## Preparation of Complexes of the Forms WCp*(OR)$_3$Cl, WCp*(OR)$_4$, and WCp*(X)($\eta^2$-alkyne)$_2$ (X = OR, Cl)

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### Introduction

Mono-Cp* (Cp* = $\eta^5$-C$_5$Me$_5$) tetrachloride complexes of the type MCp*Cl$_4$ (M = Mo, W) can be prepared readily by the "PCl$_5$ method".[1,2] The PCl$_5$ method has also now been used successfully to prepare a variety of other Mo and W cyclopentadienyl tetrachloride starting materials[3] and cyclopentadienyl dichloro nitrosyl complexes of molybdenum and tungsten.[4] The ready availability of tetrahalide complexes has provided an entry into a variety of mono-Cp* complexes of Mo and W in which the metal is in a relatively high oxidation state,[5-12] as well as permethyltungstenocene derivatives.[13,14] On the basis of an X-ray study of square pyramidal W($\eta^5$-C$_5$H$_4$-*i*-Pr)Cl$_4$,[3] it now seems likely that all tetrahalide species are actually monomers, even though differential vapor pressure measurements in dichloromethane suggested that W($\eta^5$-C$_5$Et$_4$-*t*-Bu)Cl$_4$ was a dimer.[15] ReCp*Cl$_4$ and a large variety and number of related compounds have now also been prepared,[16] although the PCl$_5$ method so far has not figured as prominently in Re chemistry as it has in Mo and W chemistry.

We have been interested in particular in the synthesis and use of MCp*Me$_4$ complexes (M = Mo,[8] W[7]) as a route to a variety of dinitrogen and hydrazido or hydrazine complexes containing the MCp*Me$_3$ core. WCp*Me$_4$ can be oxidized readily to yield [WCp*Me$_4$]$^+$, but the oxidation of MoCp*Me$_4$ is not reversible, and [MoCp*Me$_4$]$^+$ cannot be isolated or synthesized in situ.[8] Neither WCp*Me$_4$ nor MoCp*Me$_4$ can be reduced readily. Reduction of WCp*Me$_3$(OTf) (OTf = OSO$_2$CF$_3$) under dinitrogen yields [WCp*Me$_3$]$_2$($\mu$-N$_2$) in >90% yield.[9] Reduction of MoCp*Me$_3$(OTf) fails to yield [MoCp*Me$_3$]$_2$($\mu$-N$_2$), even though that species can be prepared by another route.[8] Recently, related chemistry of complexes that contain the ReCp*Me$_3$ core has been published in preliminary form.[17]

**Table I.** Preliminary Electrochemical Data[a]

| complex | $E_{1/2}$(red), V | $E_{pa} - E_{pc}$, mV | $E_p$(ox),[b] V |
|---|---|---|---|
| WCp*(OC$_6$H$_5$)$_3$Cl (**1a**) | −1.44 | 620 | +0.32 |
| WCp*(OC$_6$H$_5$)$_4$ (**2a**) | −1.85 | 1350 | |
| WCp*(O-3,5-C$_6$H$_3$Me$_2$)$_4$ (**2b**) | −1.55 | 620 | +0.39 |

[a] In THF vs Ag/Ag$^+$ in acetonitrile at a 200 mV s$^{-1}$ sweep rate. [b] Irreversible.

In order to further broaden the chemistry of M(V) and M(VI) mono-Cp* complexes of Mo and W, access to M(V) mono-Cp* starting materials that are less easily reduced than the MCp*Cl$_4$ species[3,15,18] is required. Dinitrogen activation by a complex containing ligands other than alkyl groups is also desirable, since alkyl groups are not likely to be stable toward protons over the long term in a catalytic dinitrogen reduction system. We report here the synthesis and characterization of a series of W(V) complexes of the types WCp*(OR)$_3$Cl and WCp*(OR)$_4$ and initial studies of the reactivity of these complexes that include the synthesis of complexes of the type WCp*(X)($\eta^2$-alkyne)$_2$ (X = OR, Cl).

### Results

The paramagnetic complexes WCp*(OR)$_3$Cl [R = C$_6$H$_5$ (**1a**), Me (**1b**)] and WCp*(OR)$_4$ [R = C$_6$H$_5$ (**2a**), 3,5-C$_6$H$_3$Me$_2$ (**2b**), 4-C$_6$H$_4$OMe (**2c**), 4-C$_6$H$_4$-*t*-Bu (**2d**), 4-C$_6$H$_4$Me (**2e**)] can be prepared at room temperature in ether or toluene in less than 1 h by adding a stoichiometric amount of alcohol and NEt$_3$ to a slurry of WCp*Cl$_4$. Adding less than 3 equiv of alcohol typically leads to mixtures of WCp*(OR)$_x$Cl$_{4-x}$ species ($x$ = 1–3). However, a chelating bis(alkoxide) complex, WCp*(OCMe$_2$CMe$_2$O)Cl$_2$ (**3**), can be prepared by adding 1 equiv of pinacol to WCp*Cl$_4$ in an analogous fashion. **1b** and **3** do not react further with excess alcohol in the presence of NEt$_3$ at room temperature, unlike analogous intermediates in reactions involving phenols. All monomeric species are presumed to possess square pyramidal structures on the basis of the structures of W($\eta^5$-C$_5$H$_4$-*i*-Pr)Cl$_4$[3] and W($\eta^5$-C$_5$Et$_3$Me$_2$)Me$_4$.[15] However, [WCp*Me$_4$]$^+$ has been shown to be a trigonal bipyramid in the solid state at −65 °C,[2] perhaps the only known example of a M(cyclopentadienyl)X$_4$ species with this geometry. For this reason, the possibility that the W(V) alkoxide species possesses a trigonal bipyramidal structure cannot be excluded.

The results of preliminary cyclic voltammetry studies on three compounds are shown in Table I. The alkoxide complexes cannot be oxidized with ferrocene to give W(VI) cations, because the oxidation potentials are too positive and the oxidations are irreversible. In contrast, square pyramidal WCp*Me$_4$ is oxidized relatively easily in dichloromethane ($E_{pa}$ = −0.305 V vs $E_{1/2}$ for ferrocene/ferrocenium), while trigonal bipyramidal [WCp*Me$_4$]$^+$ is reduced at $E_{pc}$ = −0.865 V vs $E_{1/2}$ for ferrocene/ferrocenium.[2] A reversible reduction wave is observed for all complexes in Table I between −1.2 and −1.9 V, in contrast to WCp*Me$_4$, for which no reduction wave was observed in dichloromethane. We have used phenoxide ligands to stabilize Mo(VI) centers via $\pi$ donation in complexes of the type [MoCp*Me$_3$(OAr)][PF$_6$].[8] But since there are only two orbitals capable of accepting $\pi$-electron density in square pyramidal MCp*L$_4$ complexes[19] (d$_{xy}$ and d$_{z^2}$), $\pi$ donation from two otherwise relatively electronegative phenoxide ligands

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