

thereby function as four-electron donors to the cluster. In terms of electron-counting rules, **1** is a 50-electron cluster, and thus it adopts a nido-octahedral geometry, as predicted by the skeletal electron pair theory. To our knowledge, cluster **1** represents the first example of an iron-tungsten, mixed-metal cluster triply capped by two tellurium functionalities.

Although the mechanistic features have not been established, formation of **1-3** may occur by addition of $M(\text{CO})_5$ ($M = \text{Mo}, \text{W}$) across the E-E bond of $\text{Fe}_2(\text{CO})_6(\mu\text{-E}_2)$ ($E = \text{Se}, \text{Te}$), followed by loss of one carbonyl group, cleavage of the Fe-Fe bond, and formation of two Fe-M bonds. Further studies are underway to explore the utility of **1-3** as synthons in mixed-metal cluster preparations.

Experimental Section

All reactions were performed under an atmosphere of pure argon by using standard Schlenk techniques. Solvents were purified, dried, and distilled under argon or nitrogen atmosphere prior to use. The compounds $\text{Fe}_2(\text{CO})_6(\mu\text{-Te}_2)$ ⁸ and $M(\text{CO})_5(\text{THF})$ ⁹ ($M = \text{Mo}, \text{W}$) were prepared by established procedures. Since $\text{Fe}_2(\text{CO})_6(\mu\text{-Te}_2)$ and $\text{Fe}_2(\text{CO})_6(\mu\text{-Se}_2)$ decompose in the solid state, freshly prepared solutions of these compounds were used. It is assumed that $\text{Fe}_2(\text{CO})_6(\mu\text{-E}_2)$ ($E = \text{Te}, \text{Se}$) are formed in approximately 40% yield. Infrared spectra were recorded on a Nicolet 5DXB FTIR spectrometer as solutions in NaCl cells. Mass spectra were recorded on a Shimadzu QP-1000 mass spectrometer at 70 eV for compounds **1** and **2** and 20 eV for compound **3**. Elemental analyses were performed on a Carlo-Erba automatic analyzer. Photochemical reactions were carried out in a water-cooled double-walled quartz vessel. A 125-W immersion type mercury lamp manufactured by Applied Photophysics Ltd. was used.

Preparation of $\text{Fe}_2(\text{CO})_6(\mu\text{-Se}_2)$. Solid $\text{Fe}_3(\text{CO})_9(\mu_3\text{-Se})_2$ (1.75 g, 3 mmol) was added to a solution of NaOMe (prepared by adding 0.63 g of Na, 11.6 mmol in 300 mL of MeOH), and the mixture was stirred for 12 h. The solution was diluted with hexane (200 mL) and water (200 mL) and acidified with 6 M HCl. After separation of the aqueous layer from the organic layer, the aqueous layer was further extracted with hexane (100 mL) and the combined organic extracts were washed with water (100 mL) and dried over anhydrous MgSO_4 . The organic solution was concentrated to 10 mL and chromatographed on a silica gel column, using hexane as eluant. A single purple band of $\text{Fe}_2(\text{CO})_6(\mu\text{-Se}_2)$ was obtained. IR (hexane; $\nu(\text{CO}), \text{cm}^{-1}$): 2078 (s), 2038 (s), 2002 (m).

Preparation of $[\text{Fe}_2M(\mu_3\text{-E})_2(\text{CO})_{10}]$ ($M = \text{W}, E = \text{Se}, \text{Te}; M = \text{Mo}, E = \text{Se}$). In a typical experiment, $M(\text{CO})_5(\text{THF})$ ($M = \text{Mo}, \text{W}$) (0.1 mmol) in THF solvent (100 mL) was added to a THF solution containing $\text{Fe}_2(\text{CO})_6(\mu\text{-E}_2)$ ($E = \text{Se}, \text{Te}$) (0.1 mmol), and the reaction mixture was allowed to stir at room temperature for 3 h. The solvent was removed in vacuo, and the residue was subjected to a chromatographic workup using a silica gel column. Elution with hexane afforded a violet band, identified as $\text{Fe}_2M(\text{CO})_{10}(\mu_3\text{-E})_2$ (**1**, $M = \text{W}, E = \text{Te}$; **2**, $M = \text{W}, E = \text{Se}$; **3**, $M = \text{Mo}, E = \text{Se}$).

1. Yield: 0.062 g, 75%. Mp: 156–158 °C dec. IR (hexane; $\nu(\text{CO}), \text{cm}^{-1}$): 2081 (w), 2044 (vs), 2034 (s), 2002 (s, br), 1964 (w). Mass: m/e 828 [M^+]. Anal. Calcd for $\text{C}_{10}\text{Fe}_2\text{O}_{10}\text{Te}_2\text{W}$: C, 14.45. Found: C, 14.52.

2. Yield: 0.027 g, 37%. Mp: 142–145 °C dec. IR (hexane; $\nu(\text{CO}), \text{cm}^{-1}$): 2087 (w), 2053 (vs), 2044 (vs), 2010 (s), 1969 (w). Mass: m/e 734 [M^+]. Anal. Calcd for $\text{C}_{10}\text{Fe}_2\text{O}_{10}\text{Se}_2\text{W}$: C, 16.35. Found: 15.91.

3. Yield: 0.020 g, 31%. Mp: 130 °C dec. IR (hexane; $\nu(\text{CO}), \text{cm}^{-1}$): 2090 (w), 2055 (vs), 2041 (vs), 2012 (s), 1972 (w). Mass: m/e 646 [M^+]. Anal. Calcd for $\text{C}_{10}\text{Fe}_2\text{MoO}_{10}\text{Se}_2$: C, 18.57. Found: 19.00.

X-ray Crystal Structure Determination of **1.** Crystal data are collected in Table I. The centrosymmetric triclinic space group was assigned from photographic evidence and was confirmed by the chemically rational results of refinement. ψ -scan data showed serious edge-effect aberrations for reflections with low glancing angles to the major face. Those making angles of $\leq 3^\circ$ were discarded; 242 data were eliminated. The remaining data were corrected for absorption using a laminar model, instead of the usual ellipsoidal form.

The structure was solved by direct methods. All atoms were anisotropically refined. All computations used SHELXTL (5.1) software (G. M. Sheldrick, Nicolet (Siemens), Madison, WI).

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Registry No. **1**, 138606-17-4; **2**, 138606-18-5; **3**, 138606-19-6; $\text{Fe}_2(\text{CO})_6(\mu\text{-Te}_2)$, 76185-27-8; $\text{W}(\text{CO})_5(\text{THF})$, 36477-75-5; $\text{Fe}_2(\text{CO})_6(\mu\text{-Se}_2)$, 76185-26-7; $\text{Mo}(\text{CO})_5(\text{THF})$, 53248-43-4; Fe, 7439-89-6; W, 7440-33-7; Mo, 7439-98-7.

Supplementary Material Available: Tables of crystallographic data (Table S1) and anisotropic displacement parameters (Table S2) (2 pages); a listing of structure factor amplitudes (Table S3) (8 pages). Ordering information is given on any current masthead page.

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A High-Yield One-Step Synthesis of *trans*-[Cr([14]aneN₄)Cl₂]Cl and Its Conversion to *trans*-[Cr([14]aneN₄)(H₂O)₂](CF₃SO₃)₃

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Introduction

Acid-stable macrocyclic complexes of chromium(II) are rare.^{1,2} The *trans*-Cr([14]aneN₄)(H₂O)₂²⁺ complex ([14]aneN₄ = 1,4,8,11-tetraazacyclotetradecane, hereafter L) is exceptional in this respect.¹ However, the synthetic routes to its immediate precursor, *trans*-CrL(H₂O)₂³⁺, that were available until now are laborious,³⁻⁵ and the isolation of the solid perchlorate salt is outright dangerous.

Here we report a simple, one-step synthesis of *trans*-[CrLCl₂]Cl and its safe and easy conversion to *trans*-[CrL(H₂O)₂](CF₃SO₃)₃.

Experimental Section

[14]aneN₄ (Lancaster), CrCl₃·6H₂O (Baker), dmf (Fisher), and 2,2-dimethoxypropane (Aldrich) were used without purification.

Preparation of *trans*-[CrLCl₂]Cl. A hot (nearly boiling) solution of 2.5 g (12.5 mmol) of L in dmf was added to a solution of 3 g (11.3 mmol) of CrCl₃·6H₂O in 50 mL of dmf and 10 mL of CHC(OCH₃)₂CH₃ at 100 °C. The mixture was stirred and boiled for 30 min, during which time the bluish-gray solid precipitated. After the mixture was cooled to room temperature, the product was filtered out, washed with acetone, and air-dried. Yield: 3.6 g (90%). Cr analysis: 14.3% (calcd 14.5%).

cis-[CrLCl₂]Cl was prepared in the same way, except that CrCl₃·6H₂O (3 g, 11.3 mmol) was used in excess over L (2 g, 10 mmol). Yield: 3.2 g (90%).

Preparation of *trans*-CrL(H₂O)₂³⁺. A deaerated suspension of 1 g of *trans*-[CrLCl₂]Cl in 50 mL of 0.15 M CF₃SO₃H was placed on Zn/Hg under argon. Within several seconds, the gray suspension turned into a dark-pink solution of *trans*-CrLCl(H₂O)₂²⁺. In another 5–10 min, the color changed to a cherry red (*trans*-CrL(H₂O)₂²⁺). The solution was transferred into a beaker and bubbled with a stream of O₂ for a few minutes. This was followed by ion exchange on SP-Sephadex C-25. The small amounts of dichloro and monochloro complexes were eluted with 0.1 and 0.2 M CF₃SO₃H, respectively, and the major peachy-orange band of *trans*-CrL(H₂O)₂³⁺ was eluted with 1 M CF₃SO₃H. Slow evaporation in a hood over several days yielded large red crystals of *trans*-[CrL(H₂O)₂](CF₃SO₃)₃. After filtration and recrystallization from H₂O/CF₃SO₃H, the solid was dried under vacuum. Yield: 0.70 g (34%). Cr analysis: 7.07% (calcd 7.07%).

The monochloro and dichloro complexes that had been eluted first were combined and used as a starting material in subsequent preparations.

Preparation of *trans*-[CrLCl₂]Cl from *cis*-[CrLCl₂]Cl. To a suspension of 1 g of *cis*-[CrLCl₂]Cl in boiling dmf were added 5 mL of CH₃(OC-

(8) Bogan, L. E.; Lesch, D. A.; Rauchfuss, T. B. *J. Organomet. Chem.* **1983**, *250*, 429.

(9) Schlientz, W. J.; Ruff, J. K. *Inorg. Chem.* **1972**, *11*, 2265.

(1) Bakac, A.; Espenson, J. H. *J. Chem. Soc., Chem. Commun.* **1990**, 1646.

(2) Dei, A.; Mani, F. *Inorg. Chem.* **1976**, *15*, 2574.

(3) Ferguson, J.; Tobe, M. L. *Inorg. Chim. Acta* **1970**, *4*, 109.

(4) Balachandran, U. N.; Ramasami, T.; Ramaswamy, D. *Inorg. Chem.* **1986**, *25*, 51.

(5) Kane-Maguire, N. A. P.; Wallace, K. C.; Miller, D. B. *Inorg. Chem.* **1985**, *24*, 597.

Table I. Spectral Data for *trans*-CrLCl₂⁺ and *trans*-CrL(H₂O)₂³⁺ in Acidic Aqueous Solutions^a

	λ_{\max}/nm ($\epsilon/\text{M}^{-1}\text{cm}^{-1}$)	ref
<i>trans</i> -CrLCl ₂ ⁺	572 (19.9), 407 sh (35), 365 (41)	b
	568 (22), 407 sh (33), 366 (37)	c
	567 (19.9), 404 sh (29.9), 364 (33.5)	d
	568 (20.0), 404 sh (29.0), 366 (32.8)	e
<i>trans</i> -CrL(H ₂ O) ₂ ³⁺	510 (24.0), 405 (39), 350 (53)	b
	510 (17.2), 404 (30.9), 350 (43.9)	e

^aL = [14]aneN₄. ^bReference 3. ^cReference 10. ^dReference 6. ^eThis work.

H₃)₂CH₃ and 50 mg of L. The mixture was boiled and stirred for 1 h. During that time, the color of the suspended solid changed from pink (*cis*) to bluish-gray (*trans*). Workup as above yielded 0.9 g of *trans*-[CrLCl₂]Cl (90%).

Stock solutions of *trans*-CrL(H₂O)₂²⁺ for kinetic purposes were prepared by the Zn/Hg reduction of aqueous acidic (HClO₄) solutions of *trans*-CrLCl₂⁺.

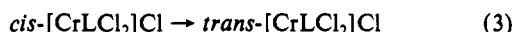
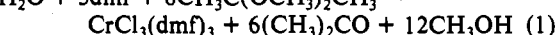
The kinetics of the Cl⁻-catalyzed oxidation of *trans*-CrL(H₂O)₂²⁺ by methyl viologen were measured by use of a Cary 219 spectrophotometer.

Results and Discussion

Literature procedures^{3,6} for the preparation of *trans*-[CrLCl₂]Cl suffer from two major problems. First, the product is a mixture of isomers containing <10% of the desired *trans* species. The isolation³ of the product is tedious, and the separation of isomers not perfect, judging by the molar extinction coefficients; see below. The conversion of the isolated *cis* isomer to the *trans* form, reported in ref 6, appears to give a purer product, but the procedure is long and involved. Also, the starting material in previous preparations,^{3,6} CrCl₃(THF)₃, is difficult to prepare and requires strictly anhydrous conditions during the preparation, storage, and use.

The most important discovery in this work is that a small excess of L changes the outcome of the preparation, which now produces high yields of *trans*-[CrLCl₂]Cl as the only product. Also, the preparation and isolation of CrCl₃(THF)₃ are not necessary. Instead, the stable (and much less expensive) CrCl₃·6H₂O is used as a starting material. This shortcut has been used earlier in the preparation of some other macrocyclic chromium complexes.^{7,8}

The chemistry involved in the preparation of *trans*-[CrLCl₂]Cl is shown in eqs 1–3. This scheme proposes the formation of



cis-[CrLCl₂]Cl as the initial product, followed by L-catalyzed isomerization to the thermodynamically more stable *trans* species. This proposal is based on the following observations. First, in the absence of excess ligand, the preparation yields the *cis* isomer almost exclusively. A suspension of the pure *cis* isomer in boiling dmf is stable, but isomerizes to the *trans* form upon addition of a small amount of the macrocyclic ligand. The catalytic effect of the free ligand derives from its basicity. The isomerization of *cis*-CrL(H₂O)₂³⁺ to the *trans* complex in homogeneous aqueous solutions is known to be base-catalyzed.^{4,6} The initial formation of the *cis* isomer, followed by isomerization to the *trans* form, was also observed for complexes of L with other transition metals.⁹

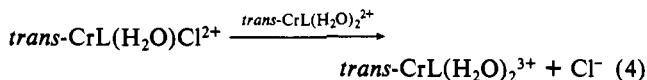
It is worth noting that the preparation of *trans*-[CrLCl₂]Cl reported in this work, as well as two previous improvements^{6,10} of the original preparation,³ resulted in the lowering of the molar absorptivities (Table I). This is probably due to a successive decrease in the contamination of the *trans* product by the more strongly absorbing *cis* isomer. A similar situation is also obtained with the diaqua derivative (Table I). The stereochemistry of both

cis- and *trans*-[CrLCl₂]Cl has been confirmed by infrared spectroscopy.⁶

When a suspension of *trans*-[CrLCl₂]Cl in acidified (CF₃SO₃H) water is placed on Zn/Hg under argon, all the solid dissolves readily, giving a pink solution. At that point, the spectrum is intermediate between those of *trans*-CrLCl₂⁺ and *trans*-CrL(H₂O)₂³⁺, as expected for *trans*-CrL(H₂O)Cl²⁺.³ This is also supported by its ion-exchange behavior, which is consistent with a 2+ charge.

Substitution reactions of transition metal complexes are well-known to be catalyzed by reduced metal ions.¹¹ This type of chemistry appears to be extremely efficient in the present system.

The next step, conversion of *trans*-CrL(H₂O)Cl²⁺ to *trans*-CrL(H₂O)₂²⁺, might take place by either direct reduction on Zn/Hg or the CrL(H₂O)₂²⁺-catalyzed dissociation of Cl⁻ from *trans*-CrL(H₂O)Cl²⁺ (eq 4), followed by Zn/Hg reduction of *trans*-CrL(H₂O)₂³⁺.



The air oxidation of solutions of *trans*-CrL(H₂O)₂²⁺ containing 3 equiv of Cl⁻ yields mainly *trans*-CrL(H₂O)₂³⁺, along with some *trans*-CrL(H₂O)Cl²⁺ and *trans*-CrLCl₂⁺. Only minor amounts of a more highly charged product (possibly a dimer) were observed during ion exchange. This is quite different from the sterically less crowded Cr²⁺(aq), which yields mainly Cr(OH)₂Cr⁴⁺ in the reaction with O₂.

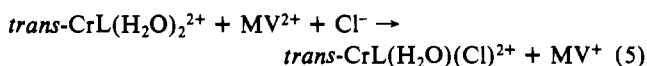
After ion exchange, the yield of *trans*-CrL(H₂O)₂³⁺ in solution is 70% based on the initial amount of *trans*-[CrLCl₂]Cl. Owing to its extreme solubility in water, the solid triflate salt is obtained in only 30–40% yield. The perchlorate salt could probably be obtained much more readily, but that was not attempted owing to the hazardous nature of the combination of the metal, L, and perchlorate. Solutions of CrL(H₂O)₂³⁺ are extremely stable and show no changes in the UV–vis spectrum for over 1 year. The isolation of the solid salts is thus unnecessary for most of the work.

The most convenient literature procedure for the preparation of *trans*-CrL(H₂O)₂³⁺ uses *trans*-CrL(CN)₂⁺ as starting material. Heating in aqueous HClO₄ for 6–8 h removes cyanide in the form of HCN and yields the diaqua product. Subsequent evaporation of H₂O then yields the solid *trans*-[CrL(H₂O)₂](ClO₄)₃. In our hands, this preparation resulted in a violent explosion of a concentrated *homogeneous solution* that was stirred at 80 °C.

The same preparation using [CrL(CN)₂]CF₃SO₃ in aqueous CF₃SO₃H succeeded in removing the CN⁻ but resulted in a mixture of products, possibly different isomers of CrL(H₂O)₂³⁺ or complexes containing a modified macrocyclic ligand. This chemistry was not pursued further.

trans-CrL(CN)₂⁺ can also be reduced to *trans*-CrL(H₂O)₂²⁺ on Zn/Hg, but this takes several hours. Subsequent oxidation with O₂ in acidic solutions yields mainly *trans*-CrL(H₂O)₂³⁺ and small amounts of the monocyano and dicyano complexes, which are easily removed by ion exchange. The protonation of the released cyanide makes the cyanide-catalyzed oxidation of CrL(H₂O)₂²⁺ by O₂ relatively unimportant, which explains the small proportion of the cyano-containing products.

CrL(H₂O)₂²⁺, formed by reduction of CrL(H₂O)₂³⁺, is stable in acidic aqueous solutions for at least several hours. Dilute solutions can be reversibly oxidized by O₂ and reduced by Zn/Hg. The spectra of both forms stay unchanged through several such cycles, indicating that no isomerization takes place. The *trans* configuration of the CrL(H₂O)₂^{2+/3+} couple was confirmed by the Cl⁻-catalyzed reaction of the reduced complex with methyl viologen (eq 5). The original kinetic study¹ of this reaction used



- (6) Poon, C. K.; Pun, K. C. *Inorg. Chem.* **1980**, *19*, 568.
 (7) Hay, R. W.; Pujari, M. P.; Bembi, R.; Jeragh, B.; Norman, P. R. *Transition Met. Chem. (London)* **1989**, *14*, 393.
 (8) Eriksen, J.; Monsted, O. *Acta Chem. Scand., Ser. A* **1984**, *38*, 775.
 (9) Poon, C. K.; Tobe, M. L. *J. Chem. Soc. A* **1968**, 1549.
 (10) Kutal, C.; Adamson, A. W. *J. Am. Chem. Soc.* **1971**, *93*, 5581.

- (11) (a) Taube, H. *Adv. Inorg. Chem. Radiochem.* **1959**, *1*, 1. (b) Sykes, A. G. *Adv. Inorg. Chem. Radiochem.* **1967**, *10*, 153.

trans-CrL(H₂O)₂²⁺, derived photochemically from *trans*-CrL(NH₃)₂³⁺, and yielded a rate constant of $(4.5 \pm 0.3) \times 10^5 \text{ M}^{-2} \text{ s}^{-1}$ in acidic D₂O at 25 °C. The reaction of the complex prepared in this work yielded $k = (5.6 \pm 0.3) \times 10^5 \text{ M}^{-2} \text{ s}^{-1}$. 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* stereochemistry³ 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*-[CrLCl₂]Cl, 27385-72-4; *cis*-[CrLCl₂]Cl, 27435-95-6; *trans*-CrL(H₂O)₂(CF₃SO₃)₃, 139040-90-7; *trans*-CrL(H₂O)₂²⁺, 139015-81-9.

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Preparation and Characterization of an A_{1u} Oxoiron(IV) Porphyrin π -Cation-Radical Complex

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Oxoiron(IV) porphyrin π -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 π -cation radical, oxoiron(IV) porphyrin π -cation radicals have been prepared in many laboratories by using *meso*-tetraarylporphyrin derivatives.³ However, most of the characterized oxoiron(IV) porphyrin π -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 π -cation-radical complexes, an a_{1u} oxoiron(IV) porphyrin π -cation-radical complex has not been prepared. The a_{1u} oxoiron(IV) porphyrin π -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 π -cation-radical complexes. We wish to report here the successful formation and characterization of an a_{1u} oxoiron(IV) porphyrin π -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. ³¹P NMR spectra were obtained on a

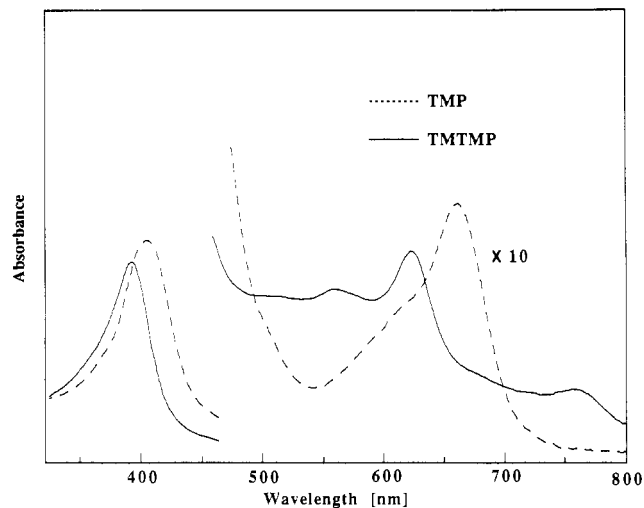


Figure 1. UV-visible absorption spectra of oxoiron(IV) porphyrin π -cation-radical complexes in dichloromethane-methanol (5:1) at -80 °C. Concentrations: TMP π cation radical, approximately $2.4 \times 10^{-5} \text{ M}$, (---); the green complex, approximately $2.6 \times 10^{-5} \text{ M}$ (—).

Varian XL-200 spectrometer. UV-vis spectra were recorded on a Hitachi U-3200 spectrophotometer. Solution magnetic measurements were performed by the NMR Evans' method¹⁰ by using tetramethylsilane as the reference substance. Diamagnetic corrections were taken from the previous report.¹¹

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 μ -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 π -cation-radical complex with a *meso*-unsubstituted porphyrin, we utilized the porphyrin substituted pyrrole β position for the mesityl group; TMTMP.

The oxidation of the TMTMP-iron(III) perchlorate complex, (TMTMP)FeClO₄, with 1.1 equiv of mCPBA in dichloromethane-methanol (5:1) at -78 °C produced a green complex,¹³

- (1) (a) Dunford, H. B.; Stillman, J. S. *Coord. Chem. Rev.* **1976**, *19*, 187-251. (b) Dunford, H. B. *Adv. Inorg. Biochem.* **1982**, *4*, 41-68.
- (2) Groves, J. T. In *Cytochrome P-450: Structure, Mechanism, and Biochemistry*; Orite de Montellano, P., Ed.; Plenum: New York, 1985; Chapter 1.
- (3) (a) Groves, J. T.; Haushalter, R. C.; Nakamura, M.; Nemo, T. E.; Evans, B. J. *J. Am. Chem. Soc.* **1981**, *103*, 2884-2886. (b) Balch, A. L.; Latos-Grazynski, L.; Renner, M. W. *J. Am. Chem. Soc.* **1985**, *107*, 2983-2985. (c) Sugimoto, H.; Tung, H.-C.; Sawyer, D. T. *J. Am. Chem. Soc.* **1988**, *110*, 2465-2470. (d) Hickman, D. L.; Nanthankumar, A.; Goff, H. M. *J. Am. Chem. Soc.* **1988**, *110*, 6384-6390. (e) Gold, A.; Jayaraj, K.; Weiss, P. D.; Chottard, G.; Bill, E.; Ding, X.; Trautwein, A. X. *J. Am. Chem. Soc.* **1988**, *110*, 5756-5761.
- (4) (a) Fajer, J.; Borg, D. C.; Forman, A.; Dolphin, D.; Felton, R. H. *J. Am. Chem. Soc.* **1970**, *93*, 3451-3459. (b) Czernuszewicz, R. S.; Macor, K. A.; Li, X.-Y.; Kincaid, J. R.; Spiro, T. G. *J. Am. Chem. Soc.* **1989**, *111*, 3860-3869.
- (5) (a) DiNello, R.; Dolphin, D. *J. Biol. Chem.* **1981**, *256*, 6903-6912. (b) Palcio, M. M.; Rutter, R.; Araiso, T.; Hager, L. P.; Dunford, H. B. *Biochem. Biophys. Res. Commun.* **1980**, *94*, 1123-1127.
- (6) (a) Su, Y. O.; Czernuszewicz, R. S.; Miller, L. A.; Spiro, T. G. *J. Am. Chem. Soc.* **1988**, *110*, 4150-4157. (b) Paeng, K.-J.; Kincaid, J. R. *J. Am. Chem. Soc.* **1988**, *110*, 7913-7915. (c) Kincaid, J. R.; Schneider, A. J.; Paeng, K.-J. *J. Am. Chem. Soc.* **1989**, *111*, 735-737.
- (7) (a) Morishima, I.; Takamuki, Y.; Shiro, Y. *J. Am. Chem. Soc.* **1984**, *106*, 7666-7672. (b) Sandusky, P. O.; Salehi, A.; Chang, C. K.; Babcock, G. T. *J. Am. Chem. Soc.* **1989**, *111*, 6437-6439.
- (8) (a) Lindsey, J. S.; Wagner, R. W. *J. Org. Chem.* **1989**, *54*, 828-836. (b) Alder, A. D.; Longo, F. R.; Finarelli, J. D.; Goldmacher, J.; Assour, J.; Korsakoff, L. *J. Org. Chem.* **1967**, *32*, 476-483.
- (9) Ono, N.; Kawamura, H.; Bougauchi, M.; Maruyama, K. *Tetrahedron* **1990**, *46*, 7483-7496.
- (10) (a) Evans, D. F. *J. Chem. Soc.* **1959**, 2003-2005. (b) Phillippi, M. A.; Goff, H. M. *J. Am. Chem. Soc.* **1982**, *104*, 6026-6034.
- (11) Eaton, S. S.; Eaton, G. R. *Inorg. Chem.* **1980**, *19*, 1095-1096.
- (12) Balch, A. L.; Chan, Y.-W.; Cheng, R.-J.; La Mar, G. N.; Latos-Grazynski, L.; Renner, M. W. *J. Am. Chem. Soc.* **1984**, *106*, 7779-7785.

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