ESR Studies of Oxochromium(V) Porphyrin Complexes: Electronic Structure of the Cr^V=O Moiety

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ESR spectra of oxochromium(V) porphyrins were obtained to investigate the electronic structure of the Cr^V=O moiety. At room temperature, the chlorooxochromium(V) *meso*-tetramesitylporphyrin complex **1**-Cl exhibits an isotropic ESR signal, split into nine signals due to hyperfine coupling with four equivalent ^{14}N, at $g = 1.982$. A small isotropic satellite signal, split into a quartet due to hyperfine coupling by the ^{53}Cr isotope is also observed. At 77 K, **1**-Cl shows an anisotropic ESR signal with $g_{\parallel} = 1.986$ and $g_{\perp} = 1.980$ and small satellite $g_{\parallel}$ signals arising from hyperfine coupling with the ^{53}Cr isotope. The ESR parameters of **1**-Cl, obtained from ESR spectral simulation, show that the π-bonding character of the Cr^V=O bond is not as strong as that of the Cr^V≡N bond. To explore substituent effects on the bond character of the Cr^V=O moiety, ESR spectra of perchloratooxochromium(V) porphyrins having various electronegative substituents were recorded. With an increase in electronegativity of the meso-substituent, the $g_{\perp}$ value and the ^{53}Cr hyperfine coupling constant ($|a(^{53}$Cr$)|$) are increased. These changes suggest an increase in the π-bonding character of the Cr^V=O moiety with an increase in the electronegativity of the meso-substituent. Furthermore, the hyperfine coupling constant of the oxo ligand, $|a(^{17}$O$)|$, obtained from ESR spectra of ^{17}O-labeled oxochromium(V) porphyrin is increased with an increase in electronegativity of the meso-substituent. This indicates that the radical character of the oxo ligand is increased by the electronegative meso-substituent. These data suggest that the π-antibonding orbital of Cr=O is destabilized with an increase in electronegativity of the meso-substituent, which may facilitate bond breaking of the Cr=O moiety in an epoxidation reaction.

Introduction

Oxoiron porphyrin species have been implicated as intermediates in the catalytic cycles of peroxidases such as horseradish peroxidase[1] and monooxygenases such as cytochrome P-450.[2] To mimic active intermediates in enzyme systems, metalloporphyrin complexes of iron,[3] manganese,[4] and ruthenium[5] have been used as model compounds for these enzyme systems and have been shown to be capable of catalyzing oxygen transfer from oxidants such as iodosobenzene to saturated and unsaturated hydrocarbons. The reactive intermediates in these chemical reactions, as well as for the enzymatic system, are thought to be high-valent oxo metalloporphyrin complexes such as the oxoiron(IV) porphyrin π-cation radical,[6] oxomanganese(IV) porphyrin,[7] and dioxoruthenium(VI) porphyrin.[8] These complexes have been characterized spectroscopically and have been shown to be capable of the oxidation reactions. A chromium(III) porphyrin was also shown to undergo an oxygen transfer from iodosobenzene to alkene, and oxochromium(IV) and oxochromium(V) porphyrin complexes were isolated from the reaction.[9] Spectroscopic studies of these complexes demonstrated that the oxochromium(V) porphyrin is a reactive intermediate.

The discovery of catalytic oxygen atom transfer by metalloporphyrins caused considerable interest in the reaction mechanisms for both the catalytic and the enzymatic systems. On the basis of kinetic and product analysis, a metallaoxetane,[10] a π-radical cation,[11] a carbocation,[12] and a carbon radical[13] have been proposed as intermediates, as opposed to the case of a concerted oxene insertion.[14] However, since the generation of oxo metalloporphyrin species is usually the rate-limiting step

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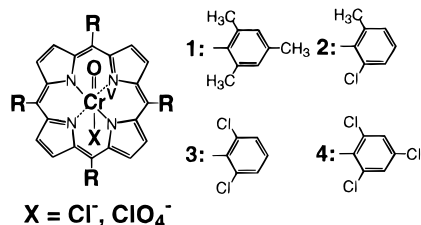
Figure 1. Structures of the oxochromium(V) porphyrins (**1**−**4**) employed in this study.

in these reactions, kinetic studies of the most significant step, oxygen atom transfer to the substrate, remain a problem. The direct observation of oxygen atom transfer by oxochromium(V) porphyrins has been reported by Bruice et al.[15] On the basis of the kinetic analysis of the reaction, they proposed that a charge transfer step is the rate-limiting process of an oxygen atom transfer from the oxo metalloporphyrin. However, as noted in their paper, it is not clear how the electrophilicity of the $Cr^V{=}O$ moiety affects the rate of the oxygen atom transfer reaction. Furthermore, only a few studies concerning the relationship between reactivity and the electronic state of the $M{=}O$ moiety of oxometal complexes have appeared.[16,17]

To further investigate the relation between reactivity and the electronic state of the $M{=}O$ moiety, we studied the ESR spectra of the oxochromium(V) porphyrins having various electronegative meso-substituents shown in Figure 1. The oxochromium(V) porphyrin has an unpaired electron in the metal center, which permits a determination of the electronic state by ESR spectroscopy. The electron−nuclear hyperfine structure resulting from the metal center and the oxo ligand reveal the electronic state of the $Cr^V{=}O$ moiety, particularly the spin densities of Cr(V) and the oxo ligand. A comparison of ESR parameters of oxochromium(V) porphyrins with those of nitridochromium(V) porphyrins clarifies the bond character of $Cr^V{=}O$. The ESR data for the oxochromium(V) porphyrins in this study reveal an electronic structural change in the $Cr^V{=}O$ moiety with an increase in electronegativity of the meso-substituent. In addition, the present result, when combined with those of previous kinetic studies,[15] allow us to gain further insight into an epoxidation mechanism.

Experimental Section

Materials. Dichloromethane and toluene were refluxed over calcium hydride for 3 h prior to distillation. *m*-Chloroperoxybenzoic acid (mCPBA) was purchased from Nacalai Tesque and used without further purification, iodosobenzene was prepared from the reaction of iodosobenzene diacetate and sodium hydroxide,[18] silver perchlorate was purchased from Aldrich, and [17]O-labeled mCPBA[19] and the *meso*-tetraarylporphyrins[20] were synthesized by previously described methods. Oxochromium(IV) porphyrins were synthesized from reactions of the

chlorochromium(III) porphyrin complexes and mCPBA, and the crude products were purified on an alumina column using benzene as the eluent.[9]

Syntheses. [Cr^V=O(P)]Cl. The chlorochromium(III) porphyrins were dissolved in dichloromethane, and iodosobenzene (solid) was added to the solutions. The reaction mixtures were then stirred for 30 min. After confirmation of chromium(V) porphyrin production by absorption spectra, the solutions were filtered through fine filter paper to remove excess iodosobenzene. UV−vis (in CH$_2$Cl$_2$; nm): **1**-Cl 418, 515, 550; **2**-Cl 419, 558; **3**-Cl 420, 558; **4**-Cl 420, 555.

[Cr^V=O(P)]ClO$_4$. These compounds were prepared via oxidations of the oxochromium(IV) porphyrins with silver perchlorate or by bulk electrolyses at constant potential. The oxochromium(IV) porphyrin complexes were dissolved in dichloromethane. Excess silver perchlorate (solid) was added, and the mixtures were then stirred for 30 min. After confirmation of the formation of the oxochromium(V) porphyrins by UV−vis absorption spectra, the solutions were filtered through fine membrane filters to remove excess silver perchlorate and silver chloride. These complexes were not further isolated because of their instability.

The complexes were also formed by reactions of chlorooxochromium(V) porphyrins with silver perchlorate. These preparations exhibited absorption spectra identical to those of the oxochromium(V) porphyrins prepared by the above method. UV−vis (in CH$_2$Cl$_2$; nm): **1**-ClO$_4$ 408, 552; **2**-ClO$_4$ 406, 556; **3**-ClO$_4$ 406, 560; **4**-ClO$_4$ 404, 570.

[Cr^V=^{17}O(P)](ClO$_4$). ^{17}O-labeled oxochromium(IV) porphyrins were prepared from reactions of the chlorochromium(III) porphyrins with [^{17}O]mCPBA. The purified complexes were further oxidized to the oxochromium(V) porphyrins, as described above. The absorption spectra of the complexes were identical with those of unlabeled complexes.

Physical Measurements. UV−vis absorption spectra were recorded on a Hitachi U-3210 spectrometer, and X-band ESR spectra were recorded on a JEOL TE-200 spectrometer. The magnetic field was calibrated using an Echo Electronics EMF-2000A NMR field meter. Theoretical ESR spectral simulations were produced using a computer program that was developed in-house.

Molecular orbital calculations of oxo- and nitridochromium(V) complexes were carried out by semiempirical INDO-type ROHF (restricted open-shell Hartree−Fock) methods.[21] CI (configuration interaction) calculations were performed for up to nine orbitals. The geometries of the chromium atoms and the axial ligands (oxo, chloride, and nitride) were based on X-ray crystallographic results for related compounds.[17,22] The chromium atom was placed 0.42 Å above the mean plane of the four nitrogen atoms for the nitride complex, and it was placed in the plane of the nitrogen atoms for the for oxo complex.

Electrochemical measurements were obtained with a three-electrode potentiostatic system. The working and counter electrodes were platinum wire. The reference electrode was Ag/AgCl separated from the bulk solution by fine glass frits. Cyclic voltammetry and differential polarography were performed on a BAS CV-50W.

ESR Samples. Each oxochromium(V) porphyrin complex was prepared immediately prior to the ESR measurements. The complex in dichloromethane was placed in an ESR tube, and the solution was degassed by the freeze−thaw method. ESR measurements were obtained at both room (25 °C) and liquid-nitrogen temperatures. For ESR measurements at liquid-nitrogen temperature, a dichloromethane−toluene mixture (1:1) was used as the solvent to form a glass. The purity of the complex was determined from its absorption spectrum after completion of the ESR measurements.

Results

Absorption Spectra. Oxochromium(V) porphyrins have been prepared from reactions of chlorochromium(III) porphyrins and iodosobenzene[23] or from one-electron oxidations of oxochromium(IV) porphyrins.[9b,15] Figure 2 shows absorption

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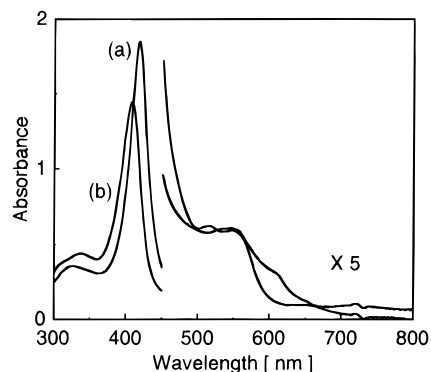(23) Groves, J. T.; Haushalter, R. C. *J. Chem. Soc., Chem. Commun.* **1981**, 1165−1166.

Figure 2. UV−vis absorption spectra of chloro- and perchloratooxochromium(V) porphyrin complexes of **1** (concentration 1.84 × 10⁻⁵ M, 1 cm path length cell) in dichloromethane: (a) **1**-Cl; (b) **1**-ClO₄.
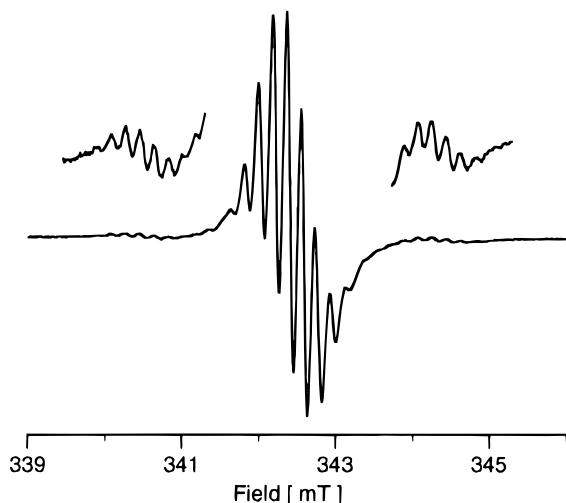

Figure 3. ESR spectrum of the chlorochromium(V) porphyrin complex of **1**, **1**-Cl, in dichloromethane at 298 K. Conditions: microwave frequency, 9.4418 GHz; microwave power, 1.00 mW; time constant, 0.1 s; gain, 4.0 × 10; modulation width, 79 μT.

spectra of oxochromium(V) tetramesitylporphyrin (TMP) complexes, **1**, prepared by the above two methods. The chlorooxochromium(V) porphyrin **1**-Cl, prepared from the reaction of the chlorochromium(III) porphyrin with iodosobenzene, shows a Soret peak at 418 nm. On the other hand, the perchloratooxochromium(V) porphyrin **1**-ClO₄, prepared from a one-electron oxidation of the oxochromium(IV) porphyrin, shows a Soret peak at 408 nm. **1**-ClO₄ was also formed when silver perchlorate was added to a solution of **1**-Cl. These findings indicate that the chloride anion binds to chromium(V) in **1**-Cl. To study the effect of the substituent, the absorption spectra of oxochromium(V) porphyrins **2**−**4** were obtained. For both the perchlorate and chloro complexes, the absorption spectra of oxochromium(V) porphyrins **2**−**4** were similar to those of **1**.

ESR Spectra. Since an oxochromium(V) complex has an unpaired electron in its 3d orbital,[23] the complex exhibits ESR signals at both room temperature and liquid-nitrogen temperature. Figure 3 shows the ESR spectrum of **1**-Cl in dichloromethane at 298 K. **1**-Cl exhibits a strong isotropic ESR signal due to the chromium isotopes with $I = 0$ (90.5%) at $g_{iso} = 1.982$. The signal is resolved in nine lines, due to electron−nuclei hyperfine interactions with four equivalent ($I = 1$) ¹⁴N nuclei. The ESR signal of **1**-Cl resulting from the less abundant chromium isotope (⁵³Cr) with $I = {}^3/_2$ (9.5%) is also observed as a satellite quartet pattern, and each of the four signals is also split into nine lines by hyperfine interactions with the nitrogen atoms. The isotropic hyperfine coupling constants of **1**-Cl were estimated to be $|a({}^{53}Cr)| = 1.97$ mT and $|a({}^{14}N)| = 0.26$ mT
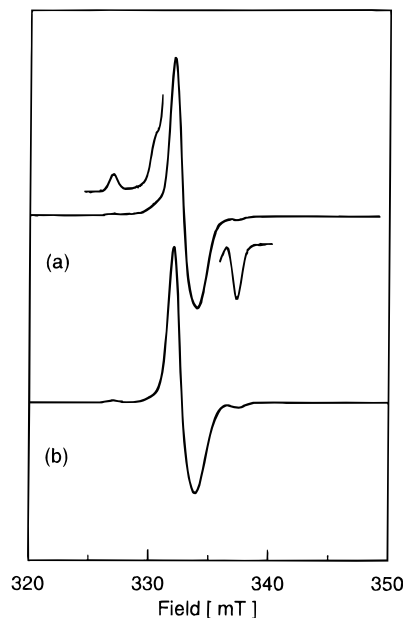

Figure 4. ESR spectra of chlorooxochromium(V) porphyrin complex of **1**, **1**-Cl. (a) Spectrum obtained in a dichloromethane−toluene (1:1) mixture at 77 K. Conditions: microwave frequency, 9.233 GHz; microwave power, 0.294 mW; time constant, 0.1 s; gain, 2.0 × 10; modulation width, 50 μT. (b) Computer simulation. $I = 0$ signal: $g_{||} = 1.986$, $g_\perp = 1.980$, $W_{||} = 0.7$ mT, $W_\perp = 2.0$ mT. $I = {}^3/_2$ signal: $g_{||} = 1.986$, $g_\perp = 1.980$, $W_{||} = 1.0$ mT, $W_\perp = 2.0$ mT, $A_{||} = 3.43$ mT, $A_\perp = 1.24$ mT.

from a computer ESR simulation. The hyperfine constants were smaller than those of chlorooxochromium(V) tetraphenylporphyrin, CrO(TPP)Cl,[23] and nitridochromium(V) octaethylporphyrin, CrN(OEP).[24]

Figure 4a shows the ESR spectrum of **1**-Cl in dichloromethane−toluene (1:1) at 77 K. An anisotropic ESR spectrum ($g_\perp = 1.9945$, $g_{||} = 1.9583$) has been reported for CrN(OEP),[24] while the ESR spectrum of **1**-Cl exhibits a less anisotropic pattern; the $g_\perp$ value is close to $g_{||}$. The nine-line pattern observed at room temperature disappears at low temperature. The quartet splitting due to ⁵³Cr can be observed only for the $g_{||}$ component with $|a_{||}({}^{53}Cr)| = 3.43$ mT. Because the $g_\perp$ component of ⁵³Cr was not observed in the spectrum, we calculated $|a_\perp({}^{53}Cr)| = 1.24$ mT with the known relation eq 1.[25] Since the $g_\perp$ value is close to $g_{||}$, we cannot determine these

$$a_{iso} = (2a_\perp + a_{||})/3 \qquad (1)$$

values from the main ESR signal. The value $g_{||} = 1.986$ was obtained from the satellite $g_{||}$ signals, and $g_\perp = 1.980$ was calculated with eq 2.[25] These g values were also supported by

$$g_{iso} = (2g_\perp + g_{||})/3 \qquad (2)$$

the ESR simulations of glassy spectra, as shown in Figure 4b. As observed for some other oxochromium(V) complexes,[26,27] the $g_\perp$ value was smaller than the $g_{||}$ value. ESR parameters for **1**-Cl are summarized in Table 1. Interestingly, the hyperfine splittings by ⁵³Cr for **1**-Cl are much smaller than those reported for CrN(OEP).[24] This may result from differences in the bond

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Table 1. ESR Parameters of Oxo- and Nitridochromium(V) Complexes

	1-Cl[a]	[CrOCl$_5$]$^{2-}$ [b]	CrN(OEP)[c]	CrN(L)[d]
g_{iso}	1.982	1.987	1.9825	1.982
$|a(^{53}Cr)|^e$	1.97		2.827	2.73
$|a(^{14}N)|^e$	0.26		0.277	0.23
$g_\parallel$	1.986	2.008	1.9583	1.956
$g_\perp$	1.980	1.977	1.9945	1.992
$a_\parallel(^{53}Cr)|^e$	3.43	3.84	4.01	4.41
$a_\perp(^{53}Cr)|^e$	1.24	1.05	2.24	2.21
P^f	−2.56	−3.26	−2.07	−2.57

^{a} This work. ^{b} Reference 26. ^{c} Reference 24. ^{d} L is *N*,*N*′-bis(pyridine-2-carbonyl)-*o*-phenylenediamine; ref 32. ^{e} mT. ^{f} Value obtained from the equation for the d$_{xy}$ orbital.
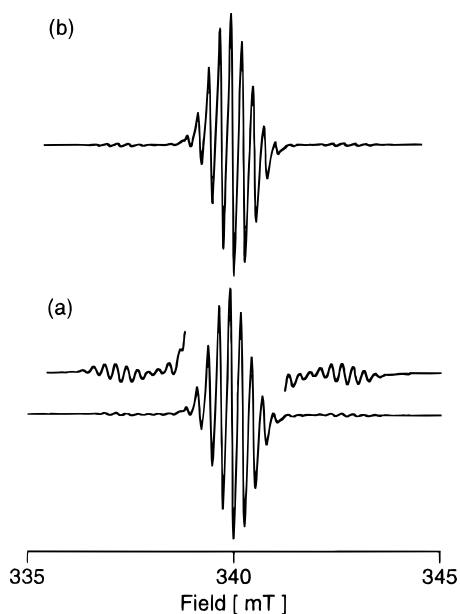

Figure 5. ESR spectrum of the perchloratooxochromium(V) porphyrin complex of **1** in dichloromethane at 298 K (a) and its computer simulation (b). (a) Conditions: microwave frequency, 9.438 GHz; microwave power, 1.00 mW; time constant, 0.1 s; gain, 7.9; modulation width, 20 μT. (b) Simulation parameters: $g_{iso} = 1.982$, $|a(^{53}Cr)| = 1.79$ mT, $|a(^{14}N)| = 0.26$ mT.

character between Cr=O and C≡N, and this is discussed, in detail, in the Discussion.

The reaction rate constants for epoxidations by perchloratooxochromium(V) porphyrins were reported previously by Bruice et al.[15] To study the relationships between reactivity and spin density of the Cr=O moiety, the ESR spectra of **1**-ClO$_4$−**4**-ClO$_4$ were obtained. Figure 5a shows the ESR spectrum of **1**-ClO$_4$ in dichloromethane at 298 K. The ESR spectrum of **1**-ClO$_4$ is better resolved than that of **1**-Cl because the hyperfine interaction ($a_{Cl} < 0.1$ mT) with the axial chloride anion has disappeared as a result of replacement by perchlorate. As shown in Figure 5b, the ESR spectrum of **1**-ClO$_4$ is well fitted by the ESR parameters $g_{iso} = 1.982$, $|a(^{53}Cr)| = 1.79$ mT, and $|a(^{14}N)| = 0.26$ mT. The hyperfine constant ^{53}Cr for **1**-ClO$_4$ was smaller than those for **1**-Cl, CrO(TPP)Cl,[23] and CrN-(OEP).[24] The ESR spectra of **2**-ClO$_4$−**4**-ClO$_4$ were all similar to that of **1**-ClO$_4$. The ESR parameters for each spectrum were obtained from a computer simulation, and the values are summarized in Table 2. The isotropic *g* value and $|a(^{14}N)|$ are constant, even when an electron-withdrawing meso-substituent is introduced. On the other hand, $|a(^{53}Cr)|$ increases with an increase in the electron-withdrawing effect of the meso-substituent.

ESR spectra of **1**-ClO$_4$−**4**-ClO$_4$ were also obtained in dichloromethane−toluene mixture (1:1) at 77 K. The ESR

Table 2. ESR Parameters of Perchloratooxochromium(V) Porphyrins

	1-ClO$_4$	**2**-ClO$_4$	**3**-ClO$_4$	**4**-ClO$_4$
g_{iso}	1.982	1.982	1.982	1.982
$|a(^{53}Cr)|^a$	1.79	1.82	1.84	1.89
$|a(^{14}N)|^a$	0.26	0.26	0.26	0.27
$|a(^{17}O)|^a$	0.36	0.38	0.38	0.39
$g_\parallel$	1.986	1.986	1.986	1.986
$g_\perp$	1.982	1.983	1.983	1.983
	1.973	1.975	1.976	1.978
$|a_\parallel(^{53}Cr)|^a$	3.48	3.53	3.55	3.64
$|a_\perp(^{53}Cr)|^{a,b}$	0.96	0.97	0.98	1.00
P	−2.94	−2.99	−3.00	−3.08
redox^c	0.76	0.86	0.93	1.00

^{a} mT. ^{b} Calculated from eq 1. ^{c} $E_{1/2}$ value (V) for Cr(IV)/Cr(V) vs Ag/AgCl.

spectra of the perchlorate complexes were more anisotropic than those of the chlorides and similar to that of CrN(OEP).[23] As observed for **1**-Cl, **1**-ClO$_4$ exhibited satellite quartet ESR signals resulting from the $g_\parallel$ component of the ^{53}Cr isotope, from which we calculated $|a_\parallel(^{53}Cr)| = 3.48$ mT. Furthermore, $g_\parallel = 1.986$ and $|a_\perp(^{53}Cr)| = 0.94$ mT were also obtained from the satellite signals and eq 1. The perpendicular components of the *g* values (1.982, 1.973) were obtained from the computer simulation of **1**-ClO$_4$ at 77 K.[28] Similarly, the ESR parameters for **2**-ClO$_4$−**4**-ClO$_4$ were calculated, and the values are summarized in Table 2. Interestingly, with an increase in the electronegativity of the meso-substituent, both the perpendicular and parallel components of the ^{53}Cr hyperfine coupling constants increase.

To further investigate the electron-withdrawing effect on the spin density of the Cr=O moiety, ESR spectra of ^{17}O-labeled oxochromium(V) porphyrins were obtained. Since the oxo ligand in an oxochromium(V) porphyrin is transferred to an alkene in epoxidation reactions, the spin density of the oxo ligand may relate to its reactivity. Figure 6a shows the ESR spectrum of ^{17}O-labeled (20% enriched) **1**-ClO$_4$ at 298 K. The ESR signals arising from hyperfine interactions with the ^{17}O nuclei are observed at the foot of the main signal. Since the hyperfine interactions with the ^{17}O atoms split the ESR spectrum of **1**-ClO$_4$ into six components due to the $I = ^5/_2$ ^{17}O nuclei, the ESR spectrum would be a superposition of the ESR spectra of 80% **1**-ClO$_4$ and 20% ^{17}O-labeled **1**-ClO$_4$. The ESR spectrum could be simulated by using the parameters $|a(^{53}Cr)| = 1.80$ mT, $|a(^{14}N)| = 0.26$ mT, and $|a(^{17}O)| = 0.36$ mT, as shown in Figure 6b.[29] On the other hand, at 77 K, hyperfine splitting due to ^{17}O nuclei was not detected. Similar ESR spectra were observed for ^{17}O-labeled **2**-ClO$_4$−**4**-ClO$_4$ at 298 K. The ESR parameters were estimated from a computer simulation, and the values are summarized in Table 2. Interestingly, $|a(^{17}O)|$ increases with an increase in the electron-withdrawing effect of the meso-substituent.

Discussion

Bond Character of Cr^V=O. The hyperfine coupling constants for oxochromium(V) porphyrins obtained herein are useful for determining their electronic ground states. The hyperfine coupling constant (*A*) can be divided into two terms: a dipolar coupling constant ($A_{dipolar}$) and an isotropic hyperfine

(28) Splitting of $g_\perp$ signals into g_x and g_y signals was observed for the perchlorate complexes, possibly due to coordination of water or the hydroxy anion at 77 K.

(29) Although the spectrum is also simulated by $|a(^{17}O)| = 0.47$ mT, which is close to the value (0.54 mT) reported for CrO(TPP)Cl, the parameters in the text gave better results.

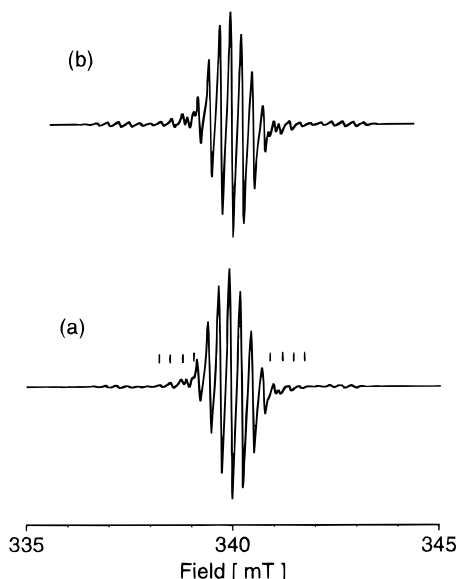**Figure 6.** ESR spectrum of the ^{17}O-labeled perchloratooxochromium(V) porphyrin complex of **1** in dichloromethane at 298 K (a) and its computer simulation (b). ESR signals for ^{17}O nuclei are indicated by solid lines. (a) Conditions: microwave frequency, 9.438 GHz; microwave power, 0.90 mW; time constant, 0.03 s; gain, 6.3; modulation width, 20 μT. (b) Simulation parameters: $g_{iso} = 1.982$, $|a(^{53}Cr)| = 1.79$ mT, $|a(^{14}N)| = 0.26$ mT, $|a(^{17}O)| = 0.36$ mT.

constant (A_{iso}); $A = A_{dipolar} + a_{iso}$.[30] The dipolar coupling constant, arising from the electron–nuclear interaction, can be treated as a tensor (A_{zz}, A_{xx}, A_{yy}), and the tensors for half-filled d orbitals are given as $4P/7$, $-2P/7$, $-2P/7$ for d_{z^2}, $2P/7$, $-P/7$, $-P/7$ for d_{yz} and d_{xz}, and $-4P/7$, $2P/7$, $2P/7$ for $d_{x^2-y^2}$ and d_{xy}. P is defined by eq 3,[31] where $\langle r^3 \rangle$ is the average value of the

$$P = g\beta g_n\beta_n/\langle r^3 \rangle \tag{3}$$

reciprocal cube of the d orbital radius. Since g_n for chromium is negative, the value for P should be negative. On the other hand, the isotropic hyperfine coupling constant due to a Fermi-contact interaction is written as eq 4.[30,31] Since an α spin in

$$a_{iso} = (8\pi/3)g\beta g_n\beta_n|\Psi_s(0)|^2 \tag{4}$$

the 3d orbital polarizes the β spin in the region near the nucleus of the inner s orbital, a_{iso} for Cr^{5+} is positive. Thus, the hyperfine coupling tensors, written as $A_{xx} = A_{yy} = A_\perp = 2P/7 + a_{iso}$ and $A_{zz} = A_{||} = -4P/7 + a_{iso}$ for half-filled $d_{x^2-y^2}$ and d_{xy} orbitals, give $P = -2.56$ mT and $a_{iso} = 1.97$ mT for **1**-Cl and $P = -2.94$ mT and $a_{iso} = 1.79$ mT for **1**-ClO$_4$. These P and a_{iso} values are reasonable when compared with the P (-5.37 mT) value for the Cr^{5+} free ion and a_{iso} obtained from ESR spectra. On the other hand, for the d_{z^2}, d_{yz}, and d_{xz} orbitals, reasonable P and a_{iso} values were not simultaneously obtained. Therefore, the present ESR spectra of chloro- and perchloratooxochromium(V) porphyrins indicate 3d$_{xy}$ ground states.

Since an unpaired electron in an oxochromium(V) porphyrin occupies the d$_{xy}$ orbital, the ESR **g** tensor can be described by eqs 5 and 6 for an octahedral field with an added tetragonal

$$g_{||} = g_{zz} = g_e - 8\lambda/\Delta E_1 \tag{5}$$

$$g_\perp = g_{xx} = g_{yy} = g_e - 2\lambda/\Delta E_2 \tag{6}$$

distortion,[25,31] where g_e is a free-spin g value (2.0023), λ is the

(30) Wertz, J. E.; Bolton, J. R. *Electron Spin Resonace*; Chapman and Hall: New York, 1986; Chapter 3.
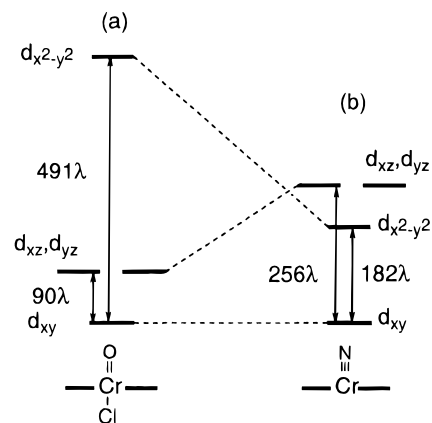

Figure 7. Diagram of the relative energy differences of the d orbitals for (a) oxo- and (b) nitridochromium(V) porphyrin complexes. The energy shown in the figure is a calculated value, based on the ESR g parameters. The energy of the d_{z^2} orbital is not shown in this diagram because the ESR results provide no information regarding its energy.

spin–orbit coupling constant, ΔE_1 is the energy gap between $d_{x^2-y^2}$ and d_{xy}, and ΔE_2 is the energy gap between d_{yz}, d_{xz}, and d_{xy}. In other words, eqs 5 and 6 show that the deviations of $g_\perp$ and $g_{||}$ from g_e indicate the magnitude of energy gaps between d_{yz}, d_{xz}, and d_{xy} and between $d_{x^2-y^2}$ and d_{xy}, respectively. Thus, ESR g values of oxochromium(V) porphyrins allow us to gain further insight into the d energy states of these complexes. Furthermore, a direct comparison of the bond characters of Cr=O and Cr≡N in oxo- and nitridochromium(V) porphyrins is possible if the assumption is made that the λ values for both complexes are similar. ΔE_1 and ΔE_2 values for **1**-Cl and CrN(OEP) were calculated, and the results are illustrated in Figure 7.

As shown in Figure 6, the dπ orbitals (d_{xz} and d_{yz}) are destabilized in going from an oxo complex to a nitrido complex, while the $d_{x^2-y^2}$ orbital is stabilized. These changes may reflect the character of Cr=O and Cr≡N bonds.[32] The stabilization of the $d_{x^2-y^2}$ orbital in the nitrido complex is explained by displacement of the chromium ion from the mean plane of porphyrin ring. The strong axial oxo and nitrido ligands displace the chromium ion above the mean porphyrin plane. The displacement of the chromium ion in the nitrido complex is much larger than that in the oxo complex because the nitrido complex has a five-coordinated structure while the oxo complex is six-coordinated. Actually, the crystal structure of a nitridochromium(V) porphyrin has shown that the chromium atom is 0.42 Å above the mean plane of pyrrole nitrogens.[22] For oxochromium(V) salen complexes, the chromium atom, which is displaced 0.53 Å above the plane in the five-coordinate structure, is pulled back to 0.26 Å by axial pyridine N-oxide ligation.[17] The large deviation from the porphyrin plane weakens the electron interaction of the $d_{x^2-y^2}$ orbital with the pyrrole nitrogen atoms, which results in the stabilization of the $d_{x^2-y^2}$ orbital. On the other hand, the destabilization of dπ orbitals in going from the oxo ligand to the nitrido ligand indicates that the π-bonding character of the nitrido ligand is much stronger than that of the oxo ligand. In other words, the nitrido complex has a stronger covalent π-bond character than the oxo complex. This is also supported by the P values for both complexes: -2.56 for **1**-Cl and -2.07 for CrN(OEP). As defined in eq 3, the magnitude of P depends on the average value of the reciprocal cube of the d orbital radius, so a smaller

(31) Atherton, N. M. *Principles of Electron Spin Resonance*; Ellis Horwood: New York, 1993; Chapters 4 and 5.
(32) Azuma, N.; Ozawa, T.; Tsuboyama, S. *J. Chem. Soc., Dalton Trans.* **1994**, 2609−2613.
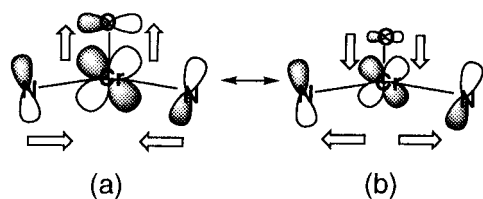
Figure 8. Idealized orbital interaction diagrams for oxygen π orbitals (p_x or p_y), the chromium d_{xz} or d_{yz} orbital, and the porphyrin e orbital: (a) electron-releasing substituent; (b) electron-withdrawing substituent.

$|P|$ value indicates a more expanded d orbital. Since the $|P|$ value for CrN(OEP) is smaller than that for **1**-Cl, an expansion of the d_{xy} orbital in CrN(OEP) is larger than that of **1**-Cl. The strong π-electron donation from the nitrido ligand to the $d\pi$ orbital leads to an expanded d_{xy} orbital, due to an electron repulsion effect. This strong π-bonding character of the nitrido complex may relate to its low reactivity toward alkenes. The strong π-electron donation from the nitrido ligand to the chromium $d\pi$ orbital results in a tight bond and a stable Cr(V) high-valent state, which is confirmed by the lower reduction potential of the nitrido complex: +0.71 V for **1**-Cl[9b] and −1.30 V for CrN(OEP).[33] The low reduction potential makes the formation of a charge transfer complex with an alkene difficult and does not lead to a nitrogen atom transfer reaction.

Relationship between Reactivity and Spin Density in the Cr═O Moiety. Oxochromium(V) porphyrins are known to be capable of oxidizing alkenes to epoxides. The mechanism of epoxidation by an oxochromium(V) porphyrin has been studied by Bruice et al.[15] They showed a linear correlation between the logarithm of the second-order rate constant for epoxidation by an oxochromium(V) porphyrin and the oxidation potential of the complex, as well as the oxidation potential of alkene. The linear relationships were interpreted such that the rate-limiting step of the epoxidation reaction is a charge transfer process. From this interpretation, it follows that the oxochromium(V) porphyrins **1**-ClO$_4$−**4**-ClO$_4$ would increase the rate constant for the epoxidation reaction in order from **1** to **4** since the oxidation potentials of the complexes increase in the same order (Table 2). However, as pointed out in ref 15, the effect of electrophilicity of the Cr═O moiety on the reaction rate constant remains unclear. In this section, the relationship between epoxidation reactivity and spin density of the Cr^V═O moiety, deduced from the present ESR study, is discussed.

As summarized in Table 2, the $g_\perp$ value increases with an increase in the electronegativity of the meso-substituent, while the $g_\parallel$ value is constant. Since the approach of the $g_\perp$ value to g_e represents the stabilization of the d_{xz} and d_{yz} orbitals as defined by eq 6, an increase in the $g_\perp$ value for a perchloratooxochromium(V) porphyrin indicates an increase in π-bonding character of the Cr^V═O moiety along with an increase in the electronegativity of the meso-substituent. As discussed above, an increase in π-bonding character is usually accompanied by a decrease in P values, due to expansion of the d_{xy} orbital. However, this is not the case. With an increase in π-bonding character of the Cr^V═O moiety, the P value is increased, suggesting a contraction of the d_{xy} orbital. This is explained by the electron-withdrawing effect of the porphyrin ring induced by an electronegative meso-substituent. Since an oxochromium(V) porphyrin has C_{4v} molecular symmetry, the d_{xz} and d_{yz} orbitals in the chromium(V) ion form bonding molecular orbitals with the e orbitals of porphyrin (Figure 8). Thus, an electron-withdrawing substituent in the porphyrin ring decreases the electron density on chromium(V). Since this electron-abstrac-

tion effect cancels the π-electron-donation effect of the oxo ligand, the electron density on the chromium(V) ion is not increased, even when the π-bonding character of Cr^V═O is increased. This leads to a contraction of the d_{xy} orbital, and results in a decrease in the P value with an increase in the electronegativity of the substituent. The contraction of the d_{xy} orbital is also reflected in $|a(^{53}Cr)|$. The contraction of the d_{xy} orbital leads to much more effective interaction with the nuclei, resulting in an increase in the isotropic hyperfine coupling constant $|a(^{53}Cr)|$.

The isotropic hyperfine coupling constant for the oxo ligand, $|a(^{17}O)|$, is also increased with an increase in the electronegativity of the meso-substituent. This result indicates that the radical character of the oxo ligand is increased by an electronegative meso-substituent. As defined in eq 3, $|a(^{17}O)|$ is determined by the spin density of the 1s and 2s orbitals at the oxo ligand nuclei. Since the spins in the 1s and 2s orbitals are induced by an exchange interaction with the spin in the d_{xy} orbital of the chromium(V) ion, an increase in $|a(^{17}O)|$ with an increase in the electronegativity of the meso-substituent suggests a strengthened Cr^V═O bond and/or a decrease in Cr═O bond length. This is consistent with an increase in π-bonding character of the Cr^V═O moiety expected from the change in the g value.

Generally speaking, an increase in the electronegativity of the meso-substituent results in the π-bonding character of the Cr^V═O moiety being strong, the spin density around the oxo ligand large, and the electron density of the Cr═O moiety small (Figure 8).

On the basis of the above discussion, we wish to make some comments on the mechanism of the oxochromium(V) porphyrin epoxidation reaction. In general, as a particular chemical bond becomes stronger, the bonding component of the involved molecular orbital becomes more energetically stabilized while the antibonding component concomitantly becomes more destabilized. Thus, the increase in π-bonding character of the Cr═O moiety observed here would suggest that the π-antibonding orbital of Cr═O is destabilized in energy with an increase in electronegativity of the meso-substituent. This implies that the Cr═O bond in an epoxidation reaction intermediate becomes weaker with an increase in electronegativity of the meso-substituent because an electron, donated from an alkene to the π-antibonding orbital, weakens the Cr═O bond. Although it is not clear how much the overall rate constant is affected by the weakening of the Cr═O bond, an increase in the oxidation potential of an oxochromium(V) porphyrin may facilitate both the charge transfer and the bond-breaking processes.

Supporting Information Available: Figure S1, showing ESR spectra of **1**-Cl−**4**-Cl in a dichloromethane−toluene mixture (1:1) at 77 K, Figure S2, showing an ESR simulation of **1**-ClO$_4$ in a dichloromethane−toluene mixture (1:1) at 77 K, Figure S3, showing ESR spectra of **1**-ClO$_4$−**4**-ClO$_4$ in a dichloromethane−toluene mixture (1:1) at 77 K, and Figure S4, presenting energy diagrams of the d orbitals for the oxo- and nitridochromium(V) porphyrin complexes obtained by semiempirical molecular orbital calculations (4 pages). Ordering information is given on any current masthead page.

(33) Bottomly, L. A.; Neely, F. L. *Inorg. Chem.* **1990**, *29*, 1860−1865.