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Metal Complexes with Tetrapyrrole Ligands. 29.[1] Synthesis and Electron Spin Resonance Spectra and Electron Nuclear Double Resonance Investigations of Nitridochromium(V) Porphyrins

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Mononuclear pentacoordinated nitridochromium(V) porphyrins, nitrido(tetra-*p*-tolylporphinato)chromium(V), CrN(TTP), and nitrido(octaethylporphinato)chromium(V), CrN(OEP), are prepared by hypochlorite oxidation of the corresponding chromium(III) porphyrins, $\mathrm{CrOH(TTP)\cdot 2H_2O}$ and $\mathrm{CrOH(OEP)\cdot {}^1/_2H_2O}$, in the presence of ammonia. These remarkably stable species are identified by UV/vis, IR, and mass spectra. An investigation of these paramagnetic compounds by ESR and ENDOR spectroscopy has furnished evidence for the $\mathrm{Cr^V(d^1/d_{xy})}$ state of the central metal and the coordination of a single axial nitrogen. The X- and Q-band ESR as well as the ^{14}N ENDOR spectra are identical for both CrN(TTP) and CrN(OEP): At room temperature we find an isotropic signal at $g_0 = 1.9825$ and an isotropic ^{53}Cr hyperfine splitting $a_0(^{53}\mathrm{Cr}) = 2.83$ mT. A superhyperfine splitting $a(^{14}\mathrm{N}) = 0.27$ mT due to five apparently equivalent ^{14}N nuclei is observed. At 77 K an anisotropic ESR signal with $g_\perp = 1.9945$ and $g_\parallel = 1.9583$ and anisotropic hyperfine values of $a_\perp(^{53}\mathrm{Cr}) = 2.24$ mT and $a_\parallel(^{53}\mathrm{Cr}) = 4.01$ mT have been determined. ^{14}N ENDOR spectra measured at 3.6 K serve to discern the axial and equatorial superhyperfine splitting constants: For $\mathrm{N_{pyrrole}}$, $a_{\perp 1} = 0.36$, $a_{\perp 2} = 0.14$, and $a_\parallel = 0.31$ mT, and for $\mathrm{N_{axial}}$, $a_{\perp 1} = 0.37$, $a_{\perp 2} = 0.34$, and $a_\parallel = 0.13$ mT. The ESR and ENDOR parameters are characteristic for a d^1 system with strong spin localization in the d_{xy} orbital and nearly no spin localization in d_{z^2}, which may be the reason for the high stability of these complexes.

Introduction

Since their first description by Tsutsui in 1966,[3] chromium porphyrins have been frequently investigated. Topics of interest were novel synthetic procedures and the identification of axial ligands,[4-8] substitutionally labile chromium(III),[9] electrochemical studies of the redox states and of the axial ligand exchange,[10,11] optical emission,[12] electron spin resonance (ESR)[13] and the thermodynamics of axial ligand binding,[13] synthesis and reaction of Cr$^{\mathrm{II}}$ porphyrins with dioxygen,[14] and use of Cr$^{\mathrm{III}}$ porphyrins as catalysts for biomimetic hydrocarbon oxidations.[15-18]

Under aerobic conditions, the oxidation state of chromium in porphyrins is III. Zinc amalgam[19] or chromous acetylacetonate reduction[14] of Cr(TTP)Cl (**1A**) or Cr(OEP)Cl (**3A**) (Table I) yield Cr$^{\mathrm{II}}$ porphyrins; these are also observed as primary products of the metal insertion with chromium hexacarbonyl.[3] Cr$^{\mathrm{IV}}$ porphyrins have been first postulated from cyclic voltammograms.[10]

Recently, three groups independently succeeded in isolating oxochromium(IV) porphyrins: CrO(TPP) (**1B**),[17-19] CrO(TTP) (**2B**),[17,20] and CrO(OEP) (**3B**).[20] (**3B**).[20] Whereas we prepared the latter two complexes by oxidation of hydroxochromium(III) complexes, $\mathrm{CrOH(TTP)\cdot 2H_2O}$ (**2C**, in analogy to **1C**[5]) and $\mathrm{CrOH(OEP)\cdot {}^1/_2H_2O}$ (**3C**[21]) with hypochlorite or iodosylbenzene, Groves obtained the first Cr$^{\mathrm{V}}$ porphyrin, CrO(TPP)Cl (**1D**), from a chlorochromium(III) porphyrin, CrCl(TPP) (**1A**), by oxidation with iodosylbenzene;[15] CrO(TTP)Cl (**1D**), however, is easily reduced to CrO(TTP) (**1B**), e.g. by $\mathrm{CH_2Cl_2}$.[18] As a strong oxidant, **1D** even attacks hydrocarbons. ESR measurements of **1D** furnished evidence for a $\mathrm{Cr^V(d^1)}$ oxidation state.[18] Another Cr$^{\mathrm{V}}$ tetrapyrrole, i.e. oxo(2,3,17,18-tetramethyl-7,8,12,13-tetraethylcorrolato)chromium(V), has been also identified by ESR.[22] The ESR solution spectra of both oxochromium(V) complexes were run at 293 K and hence gave only the isotropic *g* value and hyperfine splitting constants.[18,22]

Although the related oxomanganese(V) porphyrins are even more reactive than the oxochromium(V) porphyrins,[23] we have succeeded in the preparation of very stable, diamagnetic, red nitridomanganese(V) porphyrins, i.e. MnN(TTP) (**2E**) and MnN(OEP) (**3E**), from manganese(III) porphyrins by hypochlorite oxidation in the presence of ammonia.[1] We have subjected the chromium(III) porphyrins **2C** and **3C** to the same "oxidizing nitridation" and have obtained likewise the surprisingly stable, red nitridochromium(V) porphyrins CrN-

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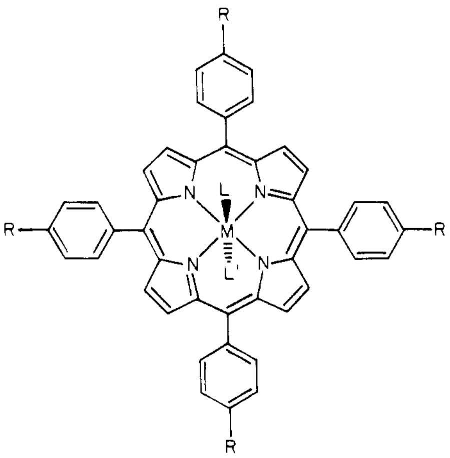
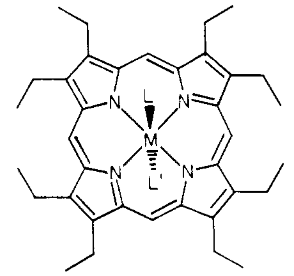
Table I. Specification of Porphyrins and Coordination Groups[a]



1, M(TPP)LL', R = H
2, M(TTP)LL', R = CH_3



3, M(OEP)LL'

	coord groups				coord groups		
	M	L	L'		M	L	L'
A	Cr	Cl		F	Cr	N	
B	Cr	O		G	Os	NH_3	NH_3
C	Cr	OH	OH_2	H	Os	N	OMe
D	Cr	O	Cl	I	Ti	O	
E	Mn	N		J	V	O	

[a] Abbreviations used: $(TPP)^{2-}$, $(TTP)^{2-}$, $(OEP)^{2-}$, and $(salen)^{2-}$ = dianions of tetraphenylporphyrin, tetra-*p*-tolylporphyrin, octaethylporphyrin, and *N,N'*-ethylenebis(salicylidenamine), respectively; Me, methyl; Et, ethyl; py, pyridine.

(TTP) (**2F**) and CrN(OEP) (**3F**).

This paper describes the synthesis and the spectroscopic characterization of **2F** and **3F**. Whereas infrared and electronic absorption spectra did not allow a doubtless identification of the chromium(V) oxidation state, ESR and ENDOR (electron nuclear double resonance) measurements in a wide range of temperature led to a characterization of the oxidation state $Cr^V(d^1/d_{xy})$. The electronic **g** tensor and, in addition, the hyperfine and quadrupole tensor components of the five nitrogen atoms provide direct information about the spin distribution in these compounds. The substitution in the porphyrin ring system is without any effect on the hyperfine coupling constants of both the pyrrole nitrogen atoms and the axial nitrogen atom, indicating a strong axial nitrogen–chromium interaction.

Experimental Section

Materials. Anhydrous chromium trichloride (Riedel de Haen), benzonitrile (Merck-Schuchardt, synthesis grade), sodium hypochlorite (aqueous solution, 13% active chlorine, BASF), and octaethylporphine [H_2(OEP), Strem Chemicals] were used as purchased. *meso*-Tetra-*p*-tolylporphine [H_2(TTP)] was synthesized and purified according to previously described procedures.[24,25] Alumina (Al_2O_3, type I, neutral) and silica gel (SiO_2, type I, neutral) were obtained from Woelm Pharmaceuticals and deactivated with water to the required grades.

Apparatus. Mass spectra were obtained with a Varian MAT 311 A instrument [electron impact (EI MS), source temperatures 200–250 °C; field ion desorption (FID MS)], infrared spectra with Perkin-Elmer 325 or 397 instruments, electronic absorption spectra (ES) with a Unicam SP 800 B spectrophotometer or an Aminco DW-2 double-wavelength spectrophotometer (Figure 1; in toluene, bathochromic shifts of 2–3 nm vs. CH_2Cl_2 are observed). X- and Q-band ESR and ENDOR spectra were measured in the temperature range 3.5–295 K with ER 420 and EN 200 spectrometers, respectively, from Bruker Analytische Messtechnik (Karlsruhe). The ESR and ENDOR spectra of **2F** and **3F** were measured in normal and perdeuterated toluene. The radiofrequency sweep range was 1–100 MHz. Low-temperature measurements were performed with an Oxford Instruments ESR 9 helium cryostat.

Elementary analyses were performed by the Alfred Bernhardt Analytische Laboratorien, D-5251 Elbach, West Germany. The samples were dried at 50 °C (10^{-3} torr).

Aquohydroxo(tetra-*p*-tolylporphinato)chromium(III) Hydrate, CrOH(TTP)$H_2O{\cdot}H_2O$ (2C). A 670-mg (1-mmol) sample of H_2(TTP) (freed from chlorin[25]) and 792 mg (5 mmol) of anhydrous $CrCl_3$ are boiled in 350 mL of benzonitrile for 24 h under reflux in a slow stream of nitrogen, which carries off the HCl formed during the reaction. After cooling and filtration from excess $CrCl_3$, the solvent is distilled off [75–80 °C (10^{-3} torr)]. The residue is dissolved in the minimum volume of CH_2Cl_2 and chromatographed on neutral alumina (grade III; column 40 × 3 cm) with CH_2Cl_2. Unreacted H_2(TTP) is eluted with CH_2Cl_2 and afterward the green Cr^{III} porphyrin with CH_2Cl_2/MeOH (9:1), 1 mL of aqueous 2 *N* NaOH added, and the solution concentrated to beginning crystallization. The yield is 658 mg of violet crystals of CrOH(TTP)$H_2O{\cdot}H_2O$ (89%).

Anal. Calcd for $C_{48}H_{41}N_4O_3Cr$ (mol wt 773.9): C, 74.50; H, 5.34; N, 7.24; O, 6.20; Cr, 6.72. Found: C, 74.76; H, 5.13; N, 7.10; O, 5.85; Cr, 7.15 (difference). ES (CH_2Cl_2), λ_{max} (log ϵ): 600 nm (4.02), 561 (4.14), 523 (3.35), 436 (5.47).

Hydroxo(octaethylporphinato)chromium(III) Hemihydrate, CrOH(OEP)$\cdot{}^1/_2H_2O$ (3C).[21] A 534-mg (1-mmol) quantity of H_2(OEP) and 960 mg (6 mmol) of $CrCl_3$ are boiled in 200 mL of benzonitrile for 6 h under reflux in a slow stream of nitrogen as mentioned above. After cooling and removal of the solvent in vacuo, the residue is dissolved in CH_2Cl_2 and the solution filtered and chromatographed on neutral alumina (grade III; column 40 × 3 cm). The small amounts of unreacted H_2(OEP) (first fraction) are discarded, and then the red main fraction eluted with CH_2Cl_2/MeOH (9:1) is collected and taken to dryness in vacuo. The residue is recrystallized from CH_2Cl_2/MeOH (1:1) and 1 mL of 10% aqueous NaOH. The yield is 548 mg of violet crystals of CrOH(OEP)$\cdot{}^1/_2H_2O$ (90%).

Anal. Calcd for $C_{36}H_{46}N_4O_{1.5}Cr$ (mol wt 610.8): C, 70.79; H, 7.59; N, 9.17; O, 3.93; Cr, 8.52. Found: C, 70.45; H, 7.40; N, 9.26; O, 4.21; Cr, 8.68 (difference). ES (CH_2Cl_2), λ_{max} (log ϵ): 646 nm (2.67), 572 (3.77), 540 (3.89), 421 (5.06), 382 (4.40), 371 (4.40), 347 (4.46). IR (KBr): 3610 (sharp, m; OH coordinated),[26] 3420

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cm^{-1} (broad; H_2O). EI MS: ~1200 [$Cr_2O(OEP)_2^+$, <<1%], 601 [$CrOH(OEP)^+$, 1%], 584 [$Cr(OEP)^+$, 100%] (data for ^{52}Cr).[21]

Nitrido(tetra-*p*-tolylporphinato)chromium(V), CrN(TTP) (2F). To a solution of 456 mg (0.6 mmol) of $CrOH(TTP)\cdot 2H_2O$ in 300 mL of $CH_2Cl_2/EtOH$ (50:1) is added 3 mL aqueous 6 N NH_3 and 150 mL of aqueous NaOCl. This two-phase mixture is stirred until the color has changed from green to red (3–4 h). The reaction mixture is washed several times with water and the organic phase separated and evaporated to dryness in vacuo. The residue is dissolved in a small amount of toluene and chromatographed on neutral silica (grade III; column 40 × 3 cm). A single red fraction is eluted with toluene, and the solution is filtered and taken to dryness in vacuo. The residue is recrystallized from benzene. The yield is 240 mg of red crystals of CrN(TTP) (55%). Green Cr^{III} porphyrins remain on the column; part of the Cr^{III} is formed during chromatography from the byproduct, CrO(TTP) (**2B**).

Anal. Calcd for $C_{48}H_{36}N_5Cr$ (mol wt 734.8): C, 78.46; H, 4.94; N, 9.53; Cr, 7.08. Found: C, 78.26; H, 5.06; N, 9.57; Cr, 7.11 (difference). ES (CH_2Cl_2), λ_{max} (log ϵ): 577 nm (3.54), 542 (4.40), 502 (3.52), 475 (3.34), 421 (5.62), 400 (4.63, sh), 379 (4.01) nm. IR (KBr): 1017 cm^{-1} (shoulder of band at 1010 cm^{-1}). FID MS: 734.

(Octaethylporphinato)nitridochromium(V), CrN(OEP) (3F). To a solution of 122 mg (0.2 mmol) of $CrOH(OEP)\cdot {}^1/_2H_2O$ in 100 mL of $CH_2Cl_2/EtOH$ (50:1) is added 1 mL of 6 N aqueous NH_3 and 25 mL of aqueous NaOCl. This two-phase mixture is stirred until the Cr^{III} visible absorption bands vanish. After thorough washing with water, the solvent is evaporated in vacuo, the residue dissolved in toluene, and the solution chromatographed on neutral silica (grade III; column 30 × 3 cm). The first red fraction is eluted with toluene, taken to dryness in vacuo, and recrystallized from benzene. The yield is 50 mg (42%) of red crystals of CrN(OEP). The Cr^{III} complexes remain on the column.

Anal. Calcd for $C_{36}H_{44}N_5Cr$ (mol wt 598.8): C, 72.21; H, 7.41; N, 11.70; Cr, 8.68. Found: C, 71.79; H, 7.23; N, 11.81; Cr, 9.17 (difference). ES (CH_2Cl_2), λ_{max} (log ϵ): 563 nm (4.46), 536 (4.12), 492 (3.29, sh), 480 (3.24, sh), 402 (5.48), 381 (3.68, sh), 331 (4.20). IR (KBr): strong porphyrin band at 1019 cm^{-1} obscures the $Cr\equiv N$ region (see **2F**). EI MS: 598 [$CrN(OEP)^+$, 100%], 584 [$Cr(OEP)^+$, 59%], 299 [$CrN(OEP)^{2+}$, 15%], 292 [$Cr(OEP)^{2+}$, 9%].

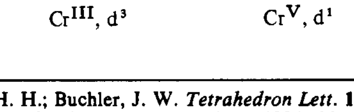
Results and Discussion

Chemistry of Nitridochromium(V) Porphyrins. Contrary to the 4d or 5d transition elements, e.g. Mo, W, Re, and Os, which display a large variety of nitrido complexes,[27] terminal nitride units of 3d-metal complexes have become known only recently, e.g. the nitridomanganese(V) unit, $Mn\equiv N^{2+}$, in MnN(TTP) (**2E**) and MnN(OEP) (**3E**),[1] and the nitridochromium(V) entity, $Cr\equiv N^{2+}$, in the ethylenebis(salicylaldimine) chelate, $CrN(salen)\cdot H_2O$,[28] which has been obtained by photolysis of an azidochromium(III) species, $CrN_3(salen)\cdot 2H_2O$.

Our synthesis is represented by the overall equation (1)

$$Cr(TTP)OH + NaOCl + NH_3 \rightarrow CrN(TTP) + NaCl + 2H_2O \quad (1)$$

Cr(TTP)Cl (**1A**) is known to bind nitrogen donors, e.g. L′ = py.[13] Therefore, in the presence of ammonia, Cr^{III} porphyrins probably take up NH_3 as at least one axial ligand, and the formation of the $Cr\equiv N$ triple bond can then be regarded as the oxidative dehydrogenation of the amminechromium entity as depicted in eq 2. This dehydrogenation of ammine complexes was first observed for the porphyrin series with a bis(ammine)osmochrome, $Os(OEP)(NH_3)_2$ (**3G**), which is attacked by a mild oxidant such as molecular oxygen and gives the nitridoosmium(VI) porphyrin OsN(OEP)OMe (**3H**) in methanol.[29]



(2)

Another remarkable feature of the nitridochromium(V) porphyrins (as well of the nitridomanganese(V) porphyrins[1]) is their stability toward reducing agents. While oxochromium(IV) or -(V) porphyrins are mild or strong oxidants (**2B** dehydrogenates alcohols;[20] **1D** attacks alkenes and alkanes[15]), the nitridochromium(V) porphyrins are conveniently purified and crystallized at room temperature by the usual techniques. The oxochromium(IV) porphyrins, which are formed as byproducts with the hypochlorite oxidation,[20] are removed during workup in the presence of alcohol by reduction to more polar Cr^{III} porphyrins. If during the synthesis of CrN(TTP) alcohol addition is omitted, several chlorine-containing nitrido species are formed besides CrN(TTP); thus, the alcohol serves to diminish the destructive power of the reaction mixture. Another reason for alcohol addition is the solubilization of $CrOH(TTP)\cdot 2H_2O$, which may form a reaction product, e.g. CrOEt(TTP)EtOH analogous to a previously described phenoxy–phenol complex, CrOPh(OEP)-PhOH.[8]

The series CrN(OEP), MnN(OEP) (d^1, d^2) is somewhat reminiscent of the similar oxometal(IV) porphyrin series TiO(OEP), VO(OEP), CrO(OEP) (**3I**, **3J**, **3B**; d^0, d^1, d^2).[6,20] All these complexes are nonpolar materials with very similar R_f values in thin-layer chromatography. Obviously, VN(OEP) (d^0) is missing; this would be the first V^V porphyrin.

Electronic Absorption, Infrared, and Mass Spectra. Apart from correct elemental analyses, the compositions of CrN(TTP) (**2F**) and CrN(OEP) (**3F**) were proved by the mass spectra. The molecular ion of **2F** was observed at a mass number 734 only in the field ion desorption mode, while **3F** could be detected by electron impact ionization at mass number 598 (see Experimental Section). This is probably due to the higher volatility of the OEP complexes as compared with the heavier, more aromatic TTP complexes.

Metal–nitrogen triple bonds absorb in the IR region between 948 and 1123 cm^{-1},[27] and $CrN(salen)\cdot H_2O$ shows a prominent band at 1012 cm^{-1}.[28] This region is obscured by strong porphyrin bands at 1010 cm^{-1} in CrN(TPP) and 1019 cm^{-1} in CrN(OEP). Isotopic replacement of ^{14}N in CrN(TTP) by ^{15}N[30] gives a new weak band at 993 cm^{-1}, a shoulder at 1017 cm^{-1} being removed from the strong porphyrin band. Hence, the $Cr\equiv N$ vibration occurs as a weak band between 1010 and 1020 cm^{-1}, similar to the weak absorption of the $Mn\equiv N$ vibration at 1049 cm^{-1} in MnN(OEP).[1]

The optical spectra of CrN(TTP) (**2F**) and CrN(OEP) (**3F**) are shown in Figure 1. They represent a weak "hypso type"; i.e., the β band in **2F** and the α band in **3F** are slightly hypsochromically shifted in comparison to "normal" porphyrin complexes, that is, derivatives of closed-shell metal ions (d^0 or d^{10}).[31,32] This hypso type spectrum is associated with metal d_π to porphyrin π^* electron donation (back-bonding). It normally occurs with d^6–d^9 ions, i.e. with electron-rich transition metal ions. In the case of **2F** and **3F**, the whole $Cr\equiv N^{2+}$ entity may be regarded as weakly electron donating, the terminal nitride ligand being a very strong σ and π donor that induces some additional electron density on the porphyrin ring

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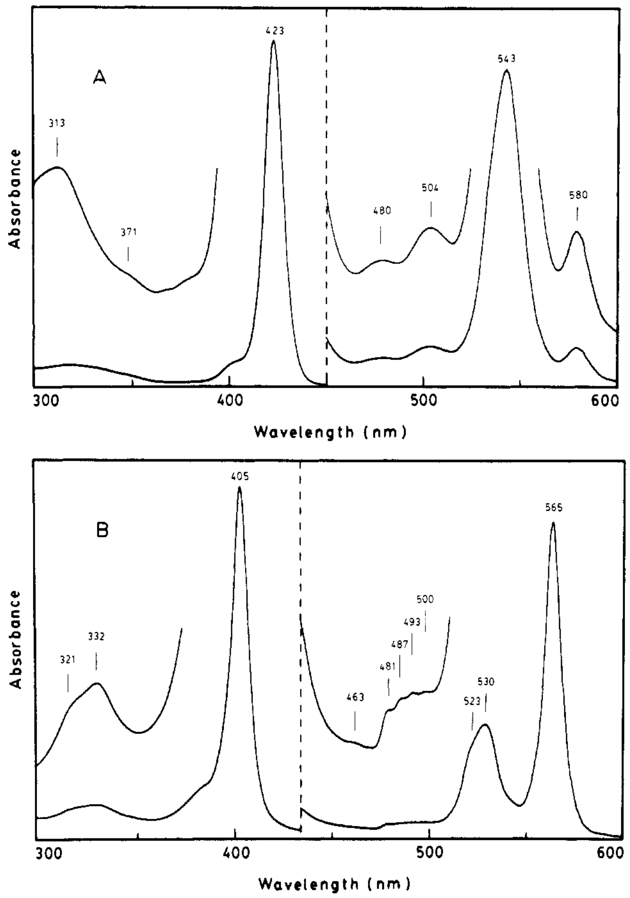

Figure 1. Electronic absorption spectra of (A) CrN(TTP) (**2F**) and (B) CrN(OEP) (**3F**) (solvent toluene; temperature 25 °C).

by $N(p_\pi)$–$Cr(d_\pi)$–porphyrin-$e_g(\pi^*)$ electronic transmission, a path discussed previously in the literature (cis effect).[32]

The view of $Cr{\equiv}N^{2+}$ being rather an electron donor than an electron acceptor can be alternatively explained by discussing the relative energy levels of the d orbitals. The nitride ligand forms a triple dative bond to the Cr^V ion involving the d_{z^2} orbital with σ bonding and the d_{xz}/d_{yz} (d_π) orbitals with π bonding. Concomitantly, these empty orbitals experience a rise in energy as compared with Cr^V ions bound to an oxide ligand, e.g. in **1D**. The $d_{x^2-y^2}$ orbital is also high because of the σ-bonding interaction with the pyrrole nitrogen atoms. Therefore, only the d_{xy} orbital is not involved in bonding, remains at a normal level, and hence should accommodate the single unpaired d electron. Strong evidence for the d_{xy} character of the unpaired electron is furnished by the ESR and ENDOR results given below. The other empty d orbitals then are all high in energy and therefore have a rather low electron affinity, which may explain the stability of the Cr^V ion in **2F** and **3F**.

The similarity of the groups CrN^{2+} (d^1)–MnN^{2+} (d^2), TiO^{2+} (d^0) and the isosteric systems VO^{2+} (d^1)–CrO^{2+} (d^2) in the porphyrin ligand is expressed by a close similarity of the optical spectra; this is illustrated in Table II by a comparison of the α bands in the OEP series and the β bands in the TTP series. Obviously, the hypso features of Cr^V porphyrins are less pronounced than those of Mn^V porphyrins; the d^2 configuration in the latter by charge repulsion causes a larger transfer of d_π-electron density to the porphyrin π^* orbitals than the d^1 configuration in the former.

The aforementioned similarity of the spectra does not allow use of these spectra as criteria for an oxidation state assignment. However, the following ESR and ENDOR investigations are conclusive of the electronic configuration of the chromium ion in **2F** and **3F**.

Table II. Comparison of the Wavelengths of the α Bands (λ_α, OEP Series) and the β Bands (λ_β, TTP Series) of Metalloporphyrins Containing the Oxometal(IV) or Nitridometal(V) Coordination Groups[1,20]

coord group	λ_α, nm	λ_β, nm
TiO^{2+}	572	546
VO^{2+}	572	549
CrO^{2+}	570	546
CrN^{2+}	563	542
MnN^{2+}	560	536

Table III. ESR g Tensor and ^{53}Cr Hyperfine Components of the Metal Ion in CrN(TTP) (**2F**)

components	g value	$a(^{53}Cr)$, mT
isotropic	1.9825 ± 0.0002	2.83 ± 0.03
⊥ direction	1.9945 ± 0.0003	2.24 ± 0.05
∥ direction	1.9583 ± 0.0005	4.01 ± 0.07

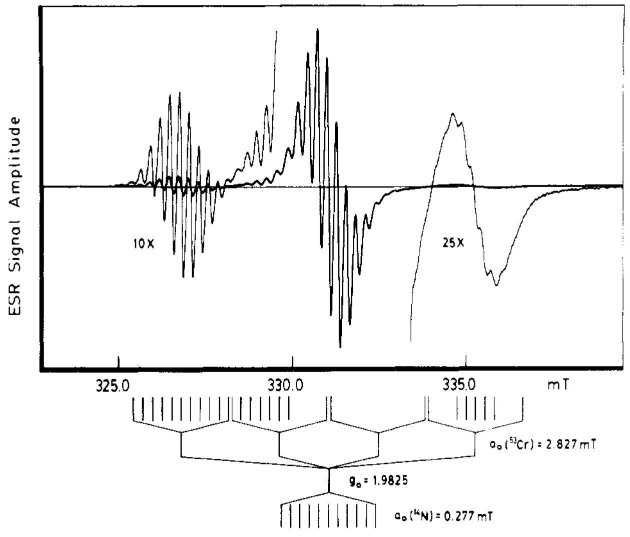

Figure 2. ESR first-derivative spectrum of CrN(OEP) (**3F**) in toluene at 295 K. The high- and low-field parts of the spectrum are amplified by factors of 25 and 10, respectively.

Electron Spin Resonance Spectra. At room temperature, the X- and Q-band ESR first-derivative spectra of CrN(TTP) (**2F**) and CrN(OEP) (**3F**) dissolved in toluene exhibit an isotropic signal at $g_0 = 1.9825$ (see Figure 2). The ESR spectra of both complexes are identical. The isotropic ESR spectrum displays a central resonance with high intensity due to the Cr isotopes with $I = 0$. In addition, a quadruplet hyperfine structure with a lower intensity of the lines due to the less abundant ^{53}Cr isotope with $I = {}^3/_2$ can be observed. The isotropic hyperfine splitting $a_0(^{53}Cr) = 2.83$ mT has been determined by X- and Q-band measurements at room temperature (see Table III).

The transition with $M_I = -{}^3/_2$ of the quadruplet shows a well-resolved superhyperfine structure with 11 lines assigned to the five nitrogen atoms. The isotropic hyperfine splitting $a_0(^{14}N) = 0.27$ mT (see Table IV) indicates that the coupling of the unpaired electron with the pyrrole and axial nitrogen nuclei is apparently equivalent. Although the central resonance shows a hyperfine structure with the same hyperfine splitting already described for the $M_I = -{}^3/_2$ transition, the number of lines cannot be determined because of the overlapping of the flanks of the central line with the $M_I = \pm{}^1/_2$ transitions of the quadruplet.

At liquid-nitrogen temperature, the ESR spectra exhibit axial symmetry with $g_\perp = 1.9945$ and $g_\parallel = 1.9583$ (see Figure 3). The deviation of $g_\perp$ from the free-spin g value is relatively small, indicating that the splitting between the d_{xy} orbital and the d_{xz}, d_{yz} orbitals is rather large. Therefore, most of the

Table IV. ^{14}N Hyperfine and Quadrupole Parameters of the Ligands of CrN(OEP) (3F)

^{14}N ligands	a_0, mT	$a_{\perp 1}$, mT	$a_{\perp 2}$, mT	$a_{\parallel}$, mT	$P_{\perp 1}$, MHz	$P_{\perp 2}$, MHz	$P_{\parallel}$, MHz
axial nitrogen	0.28^b	0.37^b	0.34^b	0.13^a	$\pm 0.88^b$	$\pm 0.73^b$	$\mp 1.61^a$
pyrrole nitrogen	0.27^b	0.36^b	0.14^a	0.31^b	$\mp 0.19^b$	$\pm 0.49^a$	$\mp 0.30^b$

[a] Calculated data (see text). [b] Experimental ESR and ENDOR data.

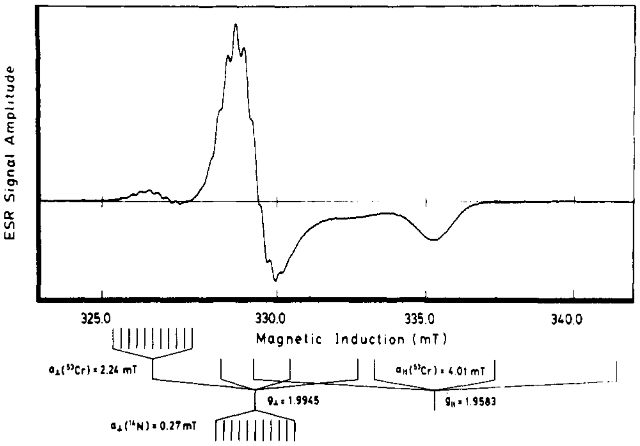

Figure 3. ESR first-derivative spectrum of CrN(OEP) (3F) in toluene at 77 K.

unpaired spin is localized in the d_{xy} ground state. However, the large high-field shift of $g_{\parallel}$ leads to the assumption that in this complex the d_{z^2} orbital approaches the ground state, resulting in a considerable coupling of both states. This result confirms the fivefold coordination (C_{4v}) of the chromium atom.

The quadruplet splitting due to ^{53}Cr can be observed only for the in-plane directions with the hyperfine splitting of $a_{\perp}$(^{53}Cr) = 2.24 mT. The quadruplet splitting coinciding with $g_{\parallel}$ cannot be observed for several reasons: (1) the small number of molecules coinciding with the magnetic field direction; (2) the low abundance of ^{53}Cr; (3) the distribution of the total intensity on four hyperfine lines. Therefore, we calculated $a_{\parallel}$(^{53}Cr) = 4.01 mT with the known relation $a_0 = (2a_{\perp} + a_{\parallel})/3$.

At low temperature (77 K), the ^{14}N superhyperfine structure appears in the central resonance and in the quadruplet resonance with $M_I = +^3/_2$ coinciding with $g_{\perp}$. Incidentally, this nitrogen hyperfine splitting of $a_{\perp}$(^{14}N) = 0.27 mT is nearly

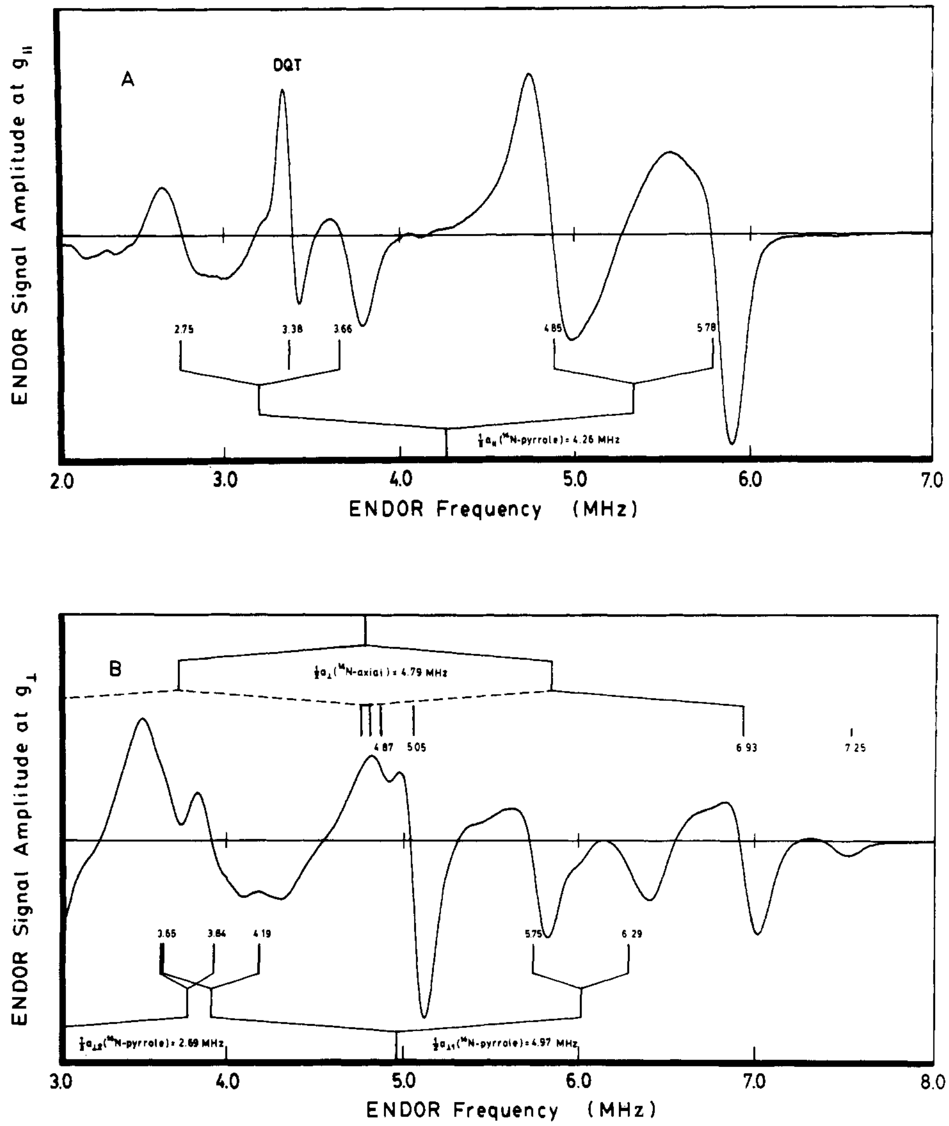

Figure 4. ^{14}N ENDOR spectrum of CrN(TTP) (2F) in toluene-d_8 at 3.6 K. Magnetic field and microwave frequency correspond to $g_{\parallel}$(A) and $g_{\perp}$(B). Free frequencies ν_0(^{14}N): 1.067 MHz (A); 1.047 MHz (B). DQT means double quantum transition.

identical with the isotropic $a_0(^{14}N)$.

^{14}N Electron Nuclear Double Resonance Spectra. The ^{14}N ENDOR measurements have been performed at 3.6 K in the frequency range 2–10 MHz in magnetic fields corresponding to the principal directions of the axial **g** tensor.

Coinciding with $g_{\parallel}$, four ^{14}N ENDOR transitions at 5.78, 4.85, 3.66, and 2.75 MHz can be attributed to the pyrrole nitrogen atoms (see Figure 4A) centered around the hyperfine value and split by the nuclear Zeeman and the quadrupole interaction for $I = 1$ according to $\nu(\text{ENDOR}) = |A/2 \pm \nu_0 \pm 3P/2|$. The hyperfine splitting constant, $a_{\parallel}(^{14}N)$ in mT, and the quadrupole splitting constant, $P_{\parallel}$ in MHz, are compiled in Table IV. An additional relatively narrow resonance at 3.38 MHz (DQT) is probably due to a double quantum transition.

In the direction of $g_{\perp}$ we observe a much more complex pattern of ENDOR transitions (see Figure 4B). The resonances at 6.29, 5.75, 4.19, 3.84, 3.65, and 3.64 MHz have been attributed to the four magnetically and geometrically equivalent pyrrole nitrogens.[33] This assignment is based on the comparison of the spectrum with the corresponding ^{14}N ENDOR spectrum of the isoelectronic VO(TTP).[34] The $a_{\perp 1,2}$ and $P_{\perp 1,2}$ values for the pyrrole N are shown in Table IV. Moreover, this assignment has been confirmed by the isotopic replacement of the axial nitrogen for ^{15}N, which leaves these resonances unchanged.[30] The additional resonances at 7.25, 6.93, 5.05, and 4.87 MHz have then been assigned to the axial nitrogen (see Figure 4B). However, the correct assignment of the resonances of the axial N could only be performed on the basis of isotopic replacement of the axial nitrogen. With the hyperfine constants for axial ^{15}N and by use of the magnetogyric ratio, the hyperfine constants for axial ^{14}N $a_{\perp 1,2}$ have been calculated. Now, on the basis of these $a_{\perp}$ values of axial ^{14}N (Table IV), we obtained a very large in-plane quadrupole splitting, $P_{\perp 1,2} = \pm 0.7$ to ± 0.9 MHz, which is of the same order of magnitude as the nuclear Zeeman splitting. Furthermore, we assume that, from the above-mentioned four resonances, one, namely that at 7.25 MHz, has to be attributed to a hyperfine splitting $a_{\perp 2}$ for the axial nitrogen.

Another broad line at 9.9 MHz not shown in Figure 4B is assumed to be a transition with $|\Delta M_I| = 2$. As already stated on the basis of ESR data, the relatively small hyperfine coupling for the axial ^{14}N atom indicates a very small delocalization of the unpaired spin into the d_{z^2} orbital. Thus, nitridochromium(V) porphyrins are $S = {}^1/_2$ systems without any organic radical character. Therefore, the high-field shift of $g_{\parallel}$ together with the small hyperfine coupling of the axial nitrogen due to the empty d_{z^2} orbital reasonably explains the large stability of these complexes.

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Registry No. **2C**, 84174-27-6; **3C**, 50733-41-0; **2F**, 84174-28-7; **3F**, 84174-29-8; NH_3, 7664-41-7.

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Synthesis and Molecular Structure of a Nitrido(porphyrinato)chromium(V) Complex

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Irradiation of solutions of azido(5,10,15,20-tetra-*p*-tolylporphyrinato)chromium(III) in methylene chloride or benzene gave nitrido(5,10,15,20-tetra-*p*-tolylporphyrinato)chromium(V) (**1**) in yields of 59% and 82%, respectively. Solutions of **1** showed well-resolved EPR spectra at room temperature ($g = 1.985$, $A_{^{53}Cr} = 2.85$ mT, $A_N = 0.279$ mT). The IR spectra of nitrido(5,10,15,20-tetra-*p*-tolylporphyrinato)chromium(V) (**1**) and **1**-^{15}N showed bands at 1017 and 991 cm^{-1}, which were assigned to $\nu_{Cr\equiv^{14}N}$ and $\nu_{Cr\equiv^{15}N}$, respectively. The molecular structure of $\mathbf{1}\cdot C_6H_6$ indicated a chromium–nitrogen distance of 1.565 Å, with the chromium 0.42 Å above the mean plane of the pyrrole nitrogens. The periphery of the porphyrin ring was saddle-shaped with excursions 0.56 Å below and 0.29 Å above the plane of the pyrrole nitrogens.

The importance of metal oxides and metal carbenes in homogeneous and heterogeneous atom-transfer reactions is now well recognized.[1] By comparison metal nitrides and imides have received little attention,[2] particularly with respect to the reactivity of such complexes with organic compounds. Imido-[3] and nitridoosmium[4] complexes are known and have been structurally characterized. Further, complexes of the type $OsO_3(NR)$ and $OsO_2(NR)_2$ have been shown to undergo addition reactions with alkenes.[5] Since high-valent, first-row transition-metal oxides in controlled ligand environments have been shown to be effective oxygen-transfer agents in stoichiometric and catalytic reactions,[6-8] we have sought a convenient synthetic entry to the corresponding nitrides and imides.

The photolysis of chromium(III) azides has been reported to produce "coordinated nitrene" complexes.[9] Very recently,

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