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 $g_\|$, 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, $a_\|(^{14}N)$ in mT, and the quadrupole splitting constant, $P_\|$ 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 $g_\|$ 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 **1**·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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Table I. Molecular Bond Lengths (Å) and Angles (deg) for CrN(TTP) (1)

Bond Lengths

Cr-N	1.565 (6)	C54-C55	1.392 (11)	N3-C34	1.383 (9)	C42-C43	1.358 (10)
Cr-N1	2.032 (5)	C54-C5M	1.506 (11)	N3-C31	1.393 (8)	C43-C44	1.453 (9)
Cr-N3	2.039 (6)	C55-C56	1.408 (10)	C31-C32	1.427 (10)	C44-C8	1.369 (9)
Cr-N2	2.045 (6)	N2-C24	1.377 (8)	C32-C33	1.361 (10)	C8-C81	1.505 (9)
Cr-N4	2.052 (5)	N2-C21	1.381 (8)	C33-C34	1.440 (9)	C81-C86	1.365 (10)
N1-C11	1.388 (8)	C21-C22	1.434 (9)	C34-C7	1.415 (9)	C81-C82	1.389 (10)
N1-C14	1.394 (8)	C22-C23	1.347 (10)	C7-C41	1.387 (9)	C82-C83	1.389 (10)
C11-C8	1.397 (9)	C23-C24	1.435 (10)	C7-C71	1.486 (10)	C83-C84	1.375 (11)
C11-C12	1.431 (9)	C24-C6	1.390 (10)	C71-C72	1.391 (10)	C84-C85	1.359 (11)
C12-C13	1.348 (9)	C6-C31	1.395 (10)	C71-C76	1.400 (9)	C84-C8M	1.530 (10)
C13-C14	1.420 (9)	C6-C61	1.506 (9)	C72-C73	1.392 (10)	C85-C86	1.394 (11)
C14-C5	1.411 (9)	C61-C66	1.367 (11)	C73-C74	1.399 (10)	C91-C92	1.351 (13)
C5-C21	1.383 (9)	C61-C62	1.372 (11)	C74-C75	1.383 (11)	C91-C96	1.425 (13)
C5-C51	1.505 (10)	C62-C63	1.410 (11)	C74-C7M	1.511 (10)	C92-C93	1.341 (13)
C51-C56	1.384 (10)	C63-C64	1.368 (13)	C75-C76	1.379 (10)	C93-C94	1.345 (14)
C51-C52	1.398 (10)	C64-C65	1.353 (13)	N4-C41	1.393 (8)	C94-C95	1.336 (13)
C52-C53	1.393 (10)	C64-C6M	1.524 (11)	N4-C44	1.395 (8)	C95-C96	1.363 (12)
C53-C54	1.378 (11)	C65-C66	1.389 (11)	C41-C42	1.432 (9)		

Bond Angles

N-Cr-N1	102.54 (30)	C53-C52-C51	120.69 (81)	C65-C64-C63	118.89 (85)	C76-C75-C74	121.98 (77)
N-Cr-N3	104.04 (31)	C54-C53-C52	121.56 (81)	C65-C64-C6M	121.9 (10)	C75-C76-C71	121.00 (77)
N-Cr-N2	99.50 (31)	C53-C54-C55	117.92 (75)	C63-C64-C6M	119.1 (10)	C41-N4-C44	105.90 (60)
N-Cr-N4	101.53 (29)	C53-C54-C5M	121.12 (91)	C64-C65-C66	120.24 (98)	C7-C41-N4	125.11 (66)
N1-Cr-N3	153.42 (23)	C55-C54-C5M	120.93 (86)	C61-C66-C65	121.90 (90)	C7-C41-C42	124.41 (71)
N1-Cr-N2	87.25 (23)	C54-C55-C56	121.05 (78)	C34-N3-C31	106.02 (59)	N4-C41-C42	110.18 (65)
N1-Cr-N4	88.03 (23)	C51-C56-C55	120.48 (83)	N3-C31-C6	125.25 (69)	C43-C42-C41	107.35 (67)
N3-Cr-N2	88.35 (24)	C24-N2-C21	106.08 (60)	N3-C31-C32	109.25 (68)	C42-C43-C44	107.64 (64)
N3-Cr-N4	86.75 (23)	N2-C21-C5	125.57 (66)	C6-C31-C32	125.35 (69)	C8-C44-N4	125.62 (68)
N2-Cr-N4	158.97 (24)	N2-C21-C22	109.93 (62)	C33-C32-C31	108.15 (66)	C8-C44-C43	125.42 (69)
C11-N1-C14	104.97 (57)	C5-C21-C22	124.14 (69)	C32-C33-C34	106.63 (66)	N4-C44-C43	108.92 (65)
N1-C11-C8	125.08 (66)	C23-C22-C21	106.63 (67)	N3-C34-C7	126.47 (67)	C44-C8-C11	124.72 (64)
N1-C11-C12	109.40 (64)	C22-C23-C24	108.08 (66)	N3-C34-C33	109.87 (64)	C44-C8-C81	118.69 (67)
C8-C11-C12	125.51 (65)	N2-C24-C6	125.28 (69)	C7-C34-C33	123.66 (71)	C11-C8-C81	116.59 (65)
C13-C12-C11	108.01 (66)	N2-C24-C23	109.18 (68)	C41-C7-C34	122.19 (69)	C86-C81-C82	119.09 (72)
C12-C13-C14	107.04 (67)	C6-C24-C23	125.46 (68)	C41-C7-C71	120.07 (67)	C86-C81-C8	122.11 (75)
N1-C14-C5	125.09 (65)	C24-C6-C31	124.57 (67)	C34-C7-C71	117.73 (66)	C82-C81-C8	118.80 (71)
N1-C14-C13	110.39 (62)	C24-C6-C61	118.33 (68)	C72-C71-C76	117.49 (75)	C83-C82-C81	119.44 (78)
C5-C14-C13	124.53 (68)	C31-C6-C61	117.09 (69)	C72-C71-C7	119.39 (71)	C84-C83-C82	121.53 (80)
C21-C5-C14	123.10 (67)	C66-C61-C62	118.29 (75)	C76-C71-C7	123.11 (74)	C85-C84-C83	118.15 (73)
C21-C5-C51	119.85 (67)	C66-C61-C6	121.17 (80)	C71-C72-C73	121.12 (77)	C85-C84-C8M	121.68 (91)
C14-C5-C51	116.92 (66)	C62-C61-C6	120.54 (82)	C72-C73-C74	121.05 (77)	C83-C84-C8M	120.17 (92)
C56-C51-C52	118.25 (81)	C61-C62-C63	119.44 (90)	C75-C74-C73	117.33 (72)	C84-C85-C86	121.49 (82)
C56-C51-C5	120.10 (78)	C64-C63-C62	121.19 (94)	C75-C74-C7M	121.58 (85)	C81-C86-C85	120.25 (81)
C52-C51-C5	121.59 (74)			C73-C74-C7M	121.09 (87)		

one of these has been isolated and characterized as a nitridochromium(V) complex on the basis of its EPR spectrum.[10] We describe here the synthesis, characterization, and the first X-ray crystal structure of a nitrido(porphyrinato)chromium(V) complex.[11]

Experimental Section

Synthesis of Nitrido(5,10,15,20-tetra-*p*-tolylporphyrinato)chromium(V), CrN(TTP) (1). In a typical reaction, 500 mg (0.655 mmol) of azido(5,10,15,20-tetra-*p*-tolylporphyrinato)chromium(III),[12b] Cr(TTP)N_3, was dissolved in 500 mL of acid-free methylene chloride. The resulting solution was placed in a water-cooled photochemical reaction vessel and agitated vigorously with a magnetic stirrer and a nitrogen bubbler. The solution was irradiated (through a Pyrex filter with a 450-W mercury immersion lamp) for 18 h. During this time the reaction mixture turned from green to red-brown. Optimal isolated yields of **1** were obtained if the photolysis was terminated when the ratio of the Soret bands of Cr(TTP)N_3 and **1** was 1:6. The methylene chloride was removed in vacuo, and the residue was dissolved in 70 mL of benzene (distilled from potassium). This solution was eluted with benzene on basic Woelm alumina (activity 4). A rapidly moving red band was collected, concentrated, and dried in vacuo to afford 275 mg (59%) of **1** as red-purple crystals. Similar photolysis of Cr(TTP)N_3 in benzene gave an 82% yield of **1** after 2 h.

An analytical sample was prepared by a second chromatography and crystallization from benzene–pentane (diffusion technique). The resulting crystals were dried in vacuo for 6 days with occasional warming.

IR (Nujol): 1005, 1009, 1017 cm^{-1}. ^1H NMR (CD_2Cl_2): δ 8.30 (*o*-H, 8 H, br s), 7.85 (*m*-H, 4 H, br s), 7.62 (*m*-H, 4 H, br s), 2.72 (*p*-Me, 12 H, S). Mass spectrum [*m*/*e* (relative intensity)] M^+ 737 (2.9), 736 (19.4), 735 (63.0), 734 (100), 733 (1.3), 732 (2.6); $M^+ - N$ 723 (0.2), 722 (10.6), 721 (38.3), 720 (60.4), 719 (2.0), 718 (3.7). Visible spectrum [$\lambda_{max}{}^{CH_2Cl_2}$ (log ϵ)]: 400 sh, 421 nm (5.706), 475 (3.348), 502 (3.463), 542 (4.345), 578.5 (3.49). Anal. Calcd for $C_{48}H_{38}N_5Cr$ (mol wt 734.842): C, 78.46; H, 4.94; N, 9.53; Cr, 7.08. Found: C, 78.60; H, 4.96; N, 9.37; Cr, 6.92.

Nitrido[5,10,15,20-tetraphenylporphyrinato)chromium(V) (**2**) and nitrido(5,10,15,20-tetramesitylporphyrinato)chromium(V) (**3**) were prepared and isolated in an identical manner. **1**-^{15}N was prepared from Cr(TTP)$^{15}N_3$.

Solution and Refinement of CrN(TTP) (1). Crystals of CrN(TTP) (**1**) were obtained by slow diffusion of pentane into a benzene solution of **1** at room temperature. A crystal was mounted on a Syntex P2_1 automatic diffractometer, and the space group was determined to be $P2_1/c$ with $Z = 4$, $a = 17.365$ (6) Å, $b = 16.938$ (5) Å, $c = 15.736$ (8) Å, $\beta = 112.35$ (3) Å, $V = 4280$ (2) $Å^3$, and d (calcd) = 1.14 g/mL. Data were collected with use of graphite-monochromated Mo Kα radiation. The absorption coefficient was 2.95 cm^{-1}, and no absorption

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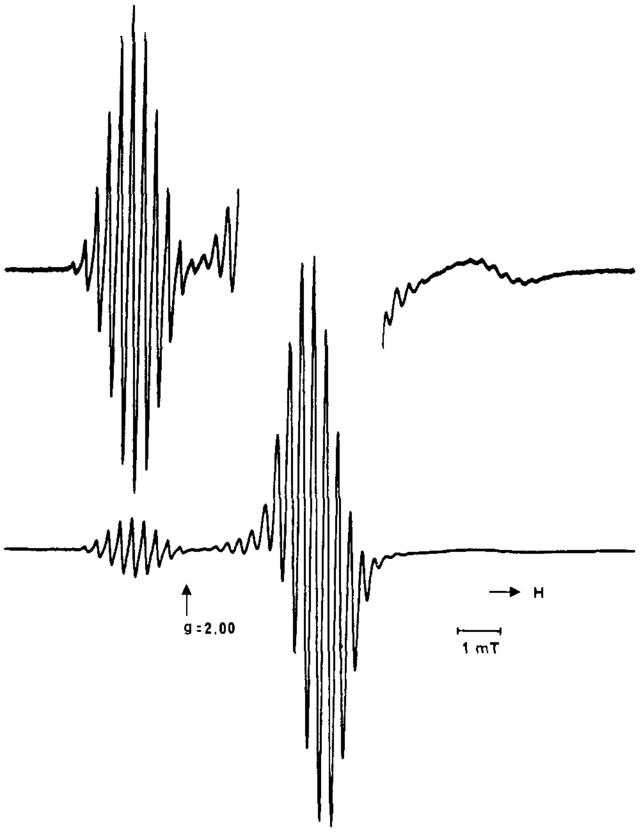

Figure 1. The ESR spectrum of CrN(TTP) (**1**) in methylene chloride at room temperature.

correction was applied. Data were reduced by methods previously described.[12a]

The structure, which was isomorphous with CrO(TTP), contained one molecule of CrN(TTP) and one molecule of benzene per asymmetric unit. Initial atomic positions were taken from CrO(TTP).[12a] Least-squares refinement based on 3296 observed data with $I > 3\sigma(I)$ and using anisotropic thermal parameters for all nonhydrogen atoms gave $R_1 = 0.089$ and $R_2 = 0.102$. Hydrogen atomic distances were calculated and added as fixed contributions to the structure factors with the assumption of a bond distance of 1.00 Å and an isotropic temperature parameter of 1.1 times the thermal parameter of the atom to which the hydrogen was attached. Refinement to convergence gave $R_1 = 0.067$ and $R_2 = 0.076$. The EPR and visible spectra of the recovered crystal dissolved in methylene chloride were identical with those obtained from bulk samples of **1**.

Results and Discussion

Photolysis of azido[5,10,15,20-tetra-*p*-tolylporphyrinato)-chromium(III) [Cr(TPP)N$_3$] in benzene for 2 h at 15 °C caused the smooth conversion of the green starting complex (λ_{max} = 450 nm) to a crimson material **1** (λ_{max} = 421, 542 nm). Similar photolyses of the tetraphenyl [Cr(TPP)N$_3$] and tetramesityl [Cr(TMP)N$_3$] derivatives afforded analogous products **2** (λ_{max} = 419, 541 nm) and **3** (λ_{max} = 420, 543 nm), respectively.[13]

Purification of **1** by alumina chromatography and crystallization from benzene–hexane gave a crystalline material with an elemental analysis consistent with a nitridochromium complex Cr(TTP)N (82% yield). Pure **1** was stable to air and moisture under ambient conditions.

Solutions of **1** showed well-resolved EPR signals at room temperature (Figure 1). The main resonance was observed at $g = 1.985$, very close to the position we have reported for oxo(porphyrinato)chromium(V) complexes.[10],[14] The pronounced ^{53}Cr satellites indicated a chromium–electron hyperfine coupling of 2.85 mT. The lowest field branch of this $I = {}^3/_2$ ^{53}Cr system was a symmetrical 11-line pattern. Thus, the four equivalent pyrrole nitrogens and the axial nitrido ligand are magnetically equivalent (a_N = 0.279 mT) in **1**.[15]

Table II. Positional Parameters for the Non-Hydrogen Atoms of CrN(TTP) (1)

atom	*x*	*y*	*z*
Cr	0.299 68 (8)	0.107 33 (7)	0.122 85 (9)
N	0.300 87 (39)	0.015 12 (34)	0.121 04 (45)
N1	0.188 69 (32)	0.130 83 (34)	0.133 18 (37)
C11	0.111 82 (43)	0.142 55 (43)	0.062 36 (50)
C12	0.050 09 (45)	0.157 77 (48)	0.099 76 (52)
C13	0.086 90 (48)	0.151 22 (47)	0.191 63 (53)
C14	0.172 19 (44)	0.133 11 (43)	0.212 83 (49)
C5	0.231 43 (43)	0.119 02 (47)	0.302 04 (48)
C51	0.199 06 (52)	0.114 06 (46)	0.377 70 (58)
C52	0.221 61 (49)	0.169 43 (50)	0.448 57 (59)
C53	0.186 33 (57)	0.167 12 (55)	0.514 27 (56)
C54	0.128 10 (48)	0.110 92 (59)	0.511 69 (55)
C55	0.107 38 (48)	0.054 21 (56)	0.442 85 (59)
C56	0.142 66 (49)	0.055 82 (52)	0.376 11 (53)
C5M	0.086 13 (55)	0.112 18 (63)	0.579 35 (59)
N2	0.354 48 (34)	0.125 35 (35)	0.261 09 (37)
C21	0.316 31 (42)	0.114 74 (50)	0.322 59 (49)
C22	0.378 25 (48)	0.107 47 (59)	0.413 68 (50)
C23	0.45289 (48)	0.117 89 (59)	0.407 39 (49)
C24	0.438 83 (46)	0.129 12 (45)	0.312 60 (51)
C6	0.500 17 (44)	0.145 23 (46)	0.278 58 (50)
C61	0.588 43 (47)	0.157 19 (58)	0.345 89 (52)
C62	0.640 03 (53)	0.093 82 (58)	0.380 73 (61)
C63	0.723 01 (55)	0.106 69 (73)	0.441 96 (62)
C64	0.753 11 (55)	0.181 24 (74)	0.466 95 (60)
C65	0.701 71 (63)	0.243 30 (69)	0.432 24 (76)
C66	0.619 37 (56)	0.231 02 (59)	0.373 52 (65)
C6M	0.844 51 (54)	0.192 18 (79)	0.529 42 (71)
N3	0.409 65 (33)	0.138 96 (34)	0.113 75 (40)
C31	0.485 67 (44)	0.152 82 (45)	0.185 85 (53)
C32	0.547 62 (45)	0.170 28 (50)	0.149 75 (57)
C33	0.511 29 (46)	0.165 83 (49)	0.056 80 (54)
C34	0.425 40 (44)	0.144 43 (43)	0.034 53 (52)
C7	0.367 34 (43)	0.131 92 (39)	−0.055 98 (49)
C71	0.400 39 (47)	0.124 76 (47)	−0.129 62 (53)
C72	0.458 90 (48)	0.066 63 (51)	−0.123 25 (51)
C73	0.492 15 (48)	0.058 66 (50)	−0.190 21 (56)
C74	0.468 85 (49)	0.109 76 (56)	−0.265 33 (49)
C75	0.409 90 (53)	0.166 74 (50)	−0.271 57 (55)
C76	0.376 73 (46)	0.175 14 (48)	−0.205 47 (57)
C7M	0.507 25 (54)	0.103 02 (62)	−0.336 25 (57)
N4	0.244 10 (33)	0.133 35 (32)	−0.014 10 (37)
C41	0.282 08 (46)	0.127 58 (42)	−0.077 22 (49)
C42	0.220 11 (48)	0.124 82 (48)	−0.168 45 (47)
C43	0.144 33 (49)	0.129 27 (50)	−0.162 08 (53)
C44	0.158 37 (45)	0.133 62 (45)	−0.065 49 (51)
C8	0.097 33 (42)	0.139 73 (43)	−0.030 87 (50)
C81	0.007 76 (46)	0.144 49 (49)	−0.096 61 (49)
C82	−0.044 09 (50)	0.080 12 (51)	−0.104 58 (56)
C83	−0.127 45 (52)	0.084 40 (53)	−0.163 28 (59)
C84	−0.160 05 (48)	0.150 96 (62)	−0.214 09 (58)
C85	−0.108 22 (57)	0.213 10 (56)	−0.205 81 (63)
C86	−0.024 04 (51)	0.209 92 (54)	−0.148 51 (59)
C8M	−0.252 35 (53)	0.153 94 (72)	−0.277 47 (69)
C91	0.118 42 (68)	0.569 96 (62)	0.344 90 (77)
C92	0.107 87 (70)	0.573 32 (60)	0.255 73 (75)
C93	0.173 25 (80)	0.577 27 (68)	0.230 36 (81)
C94	0.250 70 (77)	0.576 22 (68)	0.295 80 (88)
C95	0.263 78 (68)	0.573 04 (62)	0.384 74 (77)
C96	0.200 03 (70)	0.570 77 (61)	0.414 98 (72)

The electron–nitrido nitrogen hyperfine interaction is substantially smaller than the 0.54-mT splitting we have observed

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[13] Stable diamagnetic nitrido(porphyrinato)manganese(V) complexes may be conveniently prepared from the corresponding azidomanganese(III) precursors.

[14] Groves, J. T.; Haushalter, R. C. *J. Chem. Soc., Chem. Commun.* **1981**, 1165.

[15] The qualitative appearance of the EPR spectrum of **1** is very similar to that of the nitrosyl complex Cr(TPP)NO: Wayland, B. B.; Olson, L. W.; Siddiqui, Z. U. *J. Am. Chem. Soc.* **1976**, *98*, 94.

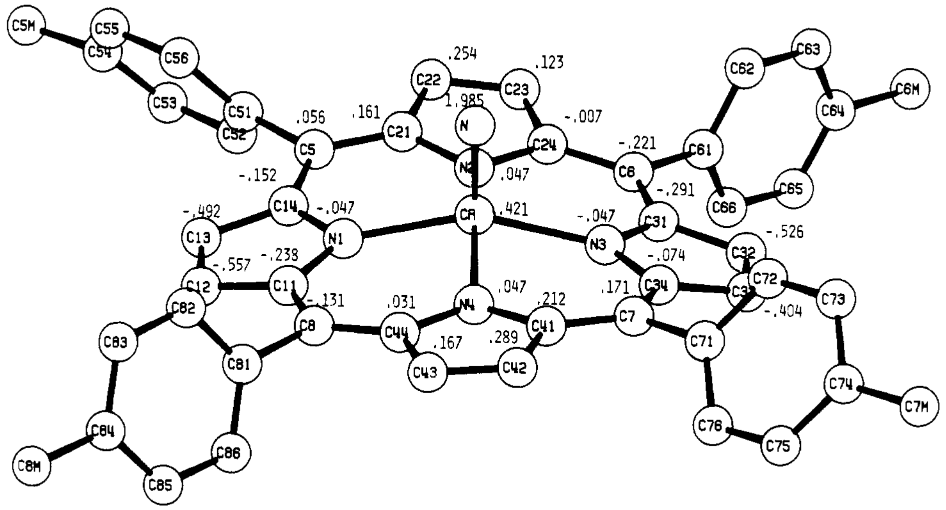

Figure 2. Structure and numbering scheme for CrN(TTP) (**1**). Superscripted numbers are deviations in Å of ring atoms from the least-squares plane of the pyrrole nitrogens.

for $Cr^{17}O(TPP)Cl$ (**4**). From the ratio of gyromagnetic ratios for ^{14}N and ^{17}O (−0.534), the calculated ^{17}O hyperfine splitting for $Cr^{17}O$ is 0.52 mT, very close to the observed value. Accordingly, the unpaired-electron density at the chromyl oxygen in **4** is similar to that of the nitridochromium(V) species (**1**).

The proton NMR spectrum of **1** showed a singlet at δ 2.72 for the *p*-methyl and other resonances at δ 7.63 (*m*-H), 7.85 (*m*-H), and 8.30 (*o*-H). The resonance due to the pyrrole β-hydrogens was not detected. The assignment of the two meta-hydrogen peaks was made on the basis of their coalescence to a single resonance (δ 7.72) at 45 °C. Similar coalescence of these resonances was observed in the corresponding oxochromium(IV) complex.[12a]

Comparison of the IR spectrum of **1** with that of $Cr(TTP)N_3$ showed several new bands near 1010 cm^{-1}. The spectrum of **1**-^{15}N showed a new band at 991 cm^{-1} and diminished intensity at 1017 cm^{-1}. The position calculated by reduced-mass considerations for this isotopic substitution was 990 cm^{-1}. Accordingly, this band has been assigned to the chromium-nitride stretching mode.[16]

The lack of any new IR band in the region of 1270 cm^{-1} supports the formulation of **1** as a chromium(V) nitride rather than a chromium(IV) porphyrin cation radical.[17] The mass spectrum of **2** showed the expected parent ion at *m*/*e* 734 and a parent−N peak at *m*/*e* 720 (see Experimental Section).

Diffusion of pentane into benzene solutions of **1** at room temperature resulted in the isolation of fragile, adequately diffracting crystals of the composition $Cr(TTP)N{\cdot}C_6H_6$. The crystal structure of **1** was isostructural with that of the oxo(5,10,15,20-tetra-*p*-tolylporphyrinato)chromium(IV) complex Cr(TTP)O (**5**), which we have recently described.[12a] The individual nitridochromium(V) units were separated by a single molecule of benzene, and no unusual interactions between porphyrin complexes were apparent. The chromium–nitrogen bond distance was very short, 1.565 Å, consistent with the formal triple bond. The porphyrin ring was distinctly saddle shaped. The chromium atom was 0.42 Å above the mean plane of the pyrrole nitrogens; two of the planar pyrrole rings were tipped away from the nitrido group so that the β-Carbons of those rings were approximately 0.40–0.56 Å below the pyrrole nitrogen plane. The other two pyrrole rings were tipped toward the nitrido group so that the β-carbons were 0.12-0.29 Å above the pyrrole plane (Figure 2).

Bond lengths and angles for **1** are presented in Table I according to the numbering scheme in Figure 2. Positional parameters for the non-hydrogen atoms of **1** are presented in Table II. The superscripted numbers are deviations in Å from the plane of the pyrrole nitrogens.

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Registry No. **1**·C_6H_6, 84174-78-7; **2**, 84174-79-8; **3**, 84192-46-1; **3**-^{15}N, 84174-80-1; **4**, 84192-58-5; $Cr(TTP)N_3$, 43145-40-0.

Supplementary Material Available: Listings of observed and calculated factor amplitudes and thermal parameters for **1** (16 pages). Ordering information is given on any current masthead page.

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[16] Griffith, W. P. *Coord. Chem. Rev.* **1972**, *8*, 369.

[17] Shimomura, E. T.; Phillippi, M. A.; Goff, H. M.; Scholz, W. F.; Reed, C. A. *J. Am. Chem. Soc.* **1981**, *103*, 6778.