Synthesis of Early Transition Metal Porphyrin Halide Complexes: First Structural Characterization of a Vanadium(III) Porphyrin Complex

Lisa M. Berreau, J. Alan Hays, Victor G. Young, Jr., and L. Keith Woo[*,1]

Department of Chemistry, Iowa State University, Ames, Iowa 50011

Received March 19, 1993[®]

A general method for the preparation of early transition metal porphyrin halide complexes using a porphyrin dianion, $(THF)_2Li_2(POR)$ (POR = OEP, TTP; OEP = octaethylporphyrinato, TTP = *meso*-tetra-*p*-tolylporphyrinato), and the appropriate metal halide complex, MX_n (MX_n = $VCl_3(THF)_3$, $TiCl_4(THF)_2$, $TiCl_3(THF)_3$, $MoCl_4(CH_3CN)_2$, WCl_4), is described. The structure of (TTP)V^{III}Cl·THF (**2**·THF) has been determined by single-crystal X-ray diffraction analysis. Complex **2**·THF crystallizes in the centrosymmetric space group $P2_1/m$ with $a = 11.968(2)$ Å, $b = 17.072(3)$ Å, $c = 12.649(2)$ Å, $\beta = 98.62(2)°$, $V = 2555.2(8)$ Å^3, $Z = 2$, $R = 4.6\%$, and $R_w = 6.7\%$. The V–Cl bond length is 2.272(1) Å, the V–N bond lengths range from 2.040(4) to 2.050(3) Å, and the V–O bond distance is 2.141(3) Å.

Recently, there has been renewed interest in the synthesis of early transition metal porphyrin halide complexes.[2] Such compounds have led to the development of new organometallic complexes.[2a,b,d,3] Furthermore, we have shown that low-valent metalloporphyrin halides, in particular those of titanium, chromium, and manganese, serve as good oxygen or nitrogen atom acceptors in inner-sphere electron-transfer reactions.[4]

Typically, synthetic routes to the dihalogeno metalloporphyrins have involved treatment of high-valent oxo complexes, (POR)-M═O (M = Ti, V, Mo; POR = OEP, TTP, TPP, TmTP),[5] with HX (X = F, Cl, Br), SOX_2, or $(COX)_2$ to produce (POR)$M^{IV}X_2$.[6] Also, reduction of (TTP)W(O)(Cl) with Si_2Cl_6 followed by treatment with HCl(g) produced the (TTP)$W^{IV}Cl_2$ complex.[7] Lower valent compounds, such as (TPP)Ti^{III}F, have been prepared by Zn/Hg reduction of (POR)M^{IV} complexes, e.g. (TTP)$Ti^{IV}F_2$.[8] Recently, the electrochemical generation of a vanadium(III) porphyrin, X–V^{III}(TTP)(THF), by reduction of (TTP)$V^{IV}X_2$ (X = Cl, Br) was reported.[9]

Because of our interest in using metalloporphyrin halide complexes as starting materials for the synthesis of low-valent derivatives and as atom acceptor species, we have developed a more general means of preparing such vanadium, titanium, molybdenum, and tungsten compounds using a modified porphyrin dianion method first reported by Arnold.[10] In addition, the first structural characterization of a vanadium(III) porphyrin complex is reported here.

Experimental Section

General Methods. Toluene, THF, d_6-benzene, and hexanes for glovebox use were distilled from their purple sodium benzophenone ketyl solutions. $CDCl_3$ was distilled from phosphorus pentoxide. CH_3CN and CH_2Cl_2 were distilled from CaH_2. Dry solvents were subsequently degassed on a vacuum line (10^{-5} Torr) with three successive freeze–pump–thaw cycles. VCl_3, $TiCl_3$, $TiCl_4$, $MoCl_5$, and $LiN(TMS)_2$ were purchased from Aldrich and used without further purification. $VCl_3(THF)_3$,[11] $TiCl_4(THF)_2$,[11] $TiCl_3(THF)_3$,[11] $(THF)_2Li_2(TTP)$,[10] $(THF)_2Li_2(OEP)$,[10] H_2TTP,[12] $MoCl_4$-$CH_3CN)_2$,[13] and WCl_4[14] were prepared according to literature procedures.

All manipulations were performed either in a Vacuum Atmospheres glovebox equipped with a Model MO40H Dri-Train gas purifier or on a vacuum line using standard Schlenk techniques. UV–visible data were obtained using a Hewlett-Packard HP 8452A diode array spectrophotometer. ^1H NMR spectra were recorded on a Nicolet NT300 spectrometer. Room-temperature magnetic susceptibilities were measured at ambient temperature by Evans' method.[15] Elemental analyses were obtained from Desert Analytics, Tucson, AZ. The vanadium porphyrin complexes failed to give satisfactory % C analyses after several attempts with different batches.

Chloro(2,3,7,8,12,13,17,18-octaethylporphyrinato)vanadium(III). General Method. $(THF)_2Li_2(OEP)$ (87.3 mg, 0.105 mmol) was stirred with $VCl_3(THF)_3$ (45.3 mg, 0.121 mmol) in toluene (20 mL) with mild heating for 8 h. During this time the color of the solution gradually changed from claret to brown with the formation of (OEP)VCl. The solution was then filtered, concentrated to ca. 3 mL, layered with ca. 8 mL of hexane, and cooled to −20 °C for 24 h. Filtration and washing with hexanes produced a brown solid. This crude solid was then dissolved in 10 mL of CH_2Cl_2 and was filtered. The volume of CH_2Cl_2 was reduced to ca. 3 mL. The

---

[®] Abstract published in *Advance ACS Abstracts*, December 1, 1993.

(1) Presidential Young Investigator, 1990–1995; Camille and Henry Dreyfus Teacher-Scholar, 1993–1998.

(2) (a) Arnold, J.; Hoffman, C. G. *J. Am. Chem. Soc.* **1990**, *112*, 8620. (b) Brand, H.; Arnold, J. *J. Am. Chem. Soc.* **1992**, *114*, 2266. (c) Ryu, S.; Whang, D.; Kim, J.; Yeo, W.; Kim, K. *J. Chem. Soc., Dalton Trans.* **1993**, 205. (d) Kim, H. J.; Whang, D.; Kim, K.; Do, Y. *Inorg. Chem.* **1993**, *32*, 360.

(3) (a) Woo, L. K.; Hays, J. A.; Jacobson, R. A.; Day, C. L. *Organometallics* **1991**, *10*, 2102. (b) Arnold, J.; Johnson, S. E.; Knobler, C. B.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1992**, *114*, 3996.

(4) (a) Woo, L. K.; Czapla, D. J.; Goll, J. G. *Inorg. Chem.* **1990**, *29*, 3915. (b) Woo, L. K.; Hays, J. A.; Goll, J. G. *Inorg. Chem.* **1990**, *29*, 3916. (c) Woo, L. K.; Goll, J. G.; Czapla, D. J.; Hays, J. A. *J. Am. Chem. Soc.* **1991**, *113*, 8478. (d) Woo, L. K.; Goll, J. G.; Berreau, L. M.; Weaving, R. *J. Am. Chem. Soc.* **1992**, *114*, 7411.

(5) Abbreviations: OEP is the octaethylporphyrinato dianion, TTP is the *meso*-tetra-*p*-tolylporphyrinato dianion, TPP is the *meso*-tetraphenylporphyrinato dianion, and TmTP is the *meso*-tetra-*m*-tolylporphyrinato dianion.

(6) (a) Guilard, R.; Lecomte, C. *Coord. Chem. Rev.* **1985**, *65*, 87. (b) Nakajima, M.; Latour, J. M.; Marchon, J. C. *J. Chem. Soc., Chem. Commun.* **1977**, 763. (c) Richard, P.; Poncet, J. L.; Barbe, J. M.; Guilard, R.; Goulon, J.; Rinaldi, D.; Cartier, A.; Tola, P. *J. Chem. Soc., Dalton Trans.* **1982**, 1451. (d) Diebold, T.; Chevrier, B.; Weiss, R. *Inorg. Chem.* **1979**, *18*, 1193.

(7) Collman, J. P.; Garner, J. M.; Woo, L. K. *J. Am. Chem. Soc.* **1989**, *111*, 8141.

(8) Latour, J. M.; Marchon, J. C.; Nakajima, M. *J. Am. Chem. Soc.* **1979**, *101*, 3974.

(9) (a) Reeb, P.; Mugnier, Y.; Guilard, R.; Laviron, E. *Inorg. Chem.* **1987**, *26*, 209. (b) Reeb, P.; Mugnier, Y. *J. Organomet. Chem.* **1988**, *339*, 89.

(10) (a) $(THF)_2Li_2(TTP)$ was prepared according to the literature method for the preparation of $(THF)_2Li_2(OEP)$: Arnold, J. *J. Chem. Soc., Chem. Commun.* **1990**, 976. (b) Spectroscopic data for $(THF)_2Li_2(TTP)$: ^1H NMR (C_6D_6) δ 9.27 (s, 8H, β-H), 8.32 (d, 8H, $-C_6H_4CH_3$), 7.41 (d, 8H, $-C_6H_4CH_3$), 2.46 (s, 12H, $-C_6H_4CH_3$), 0.30 (br, 8H, THF), −0.25 (br, 8H, THF); UV–vis (toluene) 422 (soret), 574, 616 nm.

(11) Manzer, L. E. *Inorg. Synth.* **1982**, *21*, 135.

(12) (a) Adler, A. D.; Longo, F. R.; Finarelli, J. D.; Goldmacher, J.; Assour, J.; Korsakoff, L. *J. Org. Chem.* **1967**, *32*, 476. (b) Rousseau, K.; Dolphin, D. *Tetrahedron Lett.* **1974**, *48*, 4251.

(13) Dilworth, J. R.; Richards, R. L. *Inorg. Synth.* **1990**, *28*, 33.

(14) Schaefer, M. Ph.D. Dissertation, Iowa State University, 1971.

(15) (a) Evans, D. F. *J. Chem. Soc.* **1959**, 2003. (b) Baker, M. V.; Field, L. D.; Hambley, T. W. *Inorg. Chem.* **1988**, *27*, 2872. (c) Loliger, J.; Scheffold, R. *J. Chem. Educ.* **1972**, *49*, 646.

0020-1669/94/1333-0105$04.50/0

solution was layered with ca. 6 mL of hexanes and was cooled to –20 °C for 12 h. Filtration, washing with hexanes, and drying in vacuo produced a brown solid (30.6 mg, 47%). UV–vis (toluene): 406 (Soret), 534, 572 nm. ^{1}H NMR (C_6D_6): δ 40.26 (s, 4H, *meso*-H), 10.91 (br, 8H, $-CH_2CH_3$), 7.02 (br, 8H, $-CH_2CH_3$), 2.17 (br, 24H, $-CH_2CH_3$). ^{1}H NMR ($CDCl_3$): δ 45.18 (s, 4H, *meso*-H), 11.45 (br, 8H, $-CH_2CH_3$), 6.81 (br, 8H, $-CH_2CH_3$), 2.27 (br, 24, $-CH_2CH_3$). $\mu_{eff} = 2.51\ \mu_B$. MS{EI} calcd (found) (*m*/*e*): 618 (618), [M]$^+$; 583 (584), [M + H – Cl]$^+$. IR (KBr): $\nu_{V-Cl} = 392$ cm^{-1}. Anal. Calcd (found) for $C_{36}H_{44}N_4VCl$: C, 69.87 (68.60); H, 7.17 (6.51); N, 9.06 (9.91).

Chloro(5,10,15,20-tetratolylporphyrinato)vanadium(III). Using the general method outlined for preparation of (OEP)VCl, (TTP)VCl was prepared from $(THF)_2Li_2(TTP)$ (330.4 mg, 0.400 mmol) and $VCl_3(THF)_3$ (196.6 mg, 0.527 mmol) in 92% yield. UV–vis (toluene): 424 (Soret), 548 nm. ^{1}H NMR (C_6D_6): δ 8.73 (m, 8H), 7.30 (m, 8H), 5.77 (m, 8H), 2.22 (s, 12H).

Dichloro(5,10,15,20-tetratolylporphyrinato)titanium(IV). $(THF)_2Li_2(TTP)$ (128.2 mg, 0.155 mmol) and $TiCl_4(THF)_2$ (57.1 mg, 0.171 mmol) were stirred in toluene (25 mL) with mild heating for 4 h, resulting in a color change from blue-green to dark green. The solution was then allowed to cool to room temperature and was subsequently filtered. The filtrate was evaporated to dryness, the solid was redissolved in a minimum of toluene, and the resultant solution was cooled to –20 °C for 16 h. A green solid was isolated (72.9 mg, 60%). UV–vis (toluene): 320, 376 (Soret), 420, 492 nm. ^{1}H NMR(C_6D_6): δ 9.02 (s, 8H, β-H), 7.88 (d, 8H, $-C_6H_4CH_3$), 7.20 (d, 8H, $-C_6H_4CH_3$), 2.37 (s, 12H, $-C_6H_4CH_3$). Anal. Calcd (found) for $C_{48}H_{36}N_4TiCl_2$: C, 73.20 (72.26); H, 4.61 (4.38); N, 7.11 (7.30).

Chloro(5,10,15,20-tetratolylporphyrinato)titanium(III). $(THF)_2Li_2(TTP)$ (124.0 mg, 0.150 mmol) and $TiCl_3(THF)_3$ (57.0 mg, 0.154 mmol) were stirred in toluene (15 mL) with mild heating for 6 h resulting in a color change blue-green to dark purple. Following the procedure described for the isolation of $(TTP)TiCl_2$, a purple microcrystalline solid was obtained (90.5 mg, 81%). UV–vis (toluene): 428 (Soret), 552 nm. ^{1}H NMR (C_6D_6): δ 2.37 (br, $-C_6H_4CH_3$). Anal. Calcd (found) for $C_{48}H_{36}N_4TiCl$: C, 76.65 (76.08); H, 4.82 (4.73); N, 7.45 (7.51).

Dichloro(5,10,15,20-tetratolylporphyrinato)molybdenum(IV). $(THF)_2Li_2(TTP)$ (104.1 mg, 0.126 mmol) was stirred with $MoCl_4(CH_3CN)_2$ (107.0 mg, 0.334 mmol) in toluene (20 mL) with mild heating for 12 h. After the solution was allowed to cool to room temperature, it was filtered producing a purple precipitate. The solid was redissolved in CH_2Cl_2 (15 mL), and the mixture was filtered. After the filtrate was evaporated to dryness, the product was recrystallized from CH_2Cl_2/hexane (1:3) to produce a green solid (50.0 mg, 48%). UV–vis (toluene): 366, 398, 420, 496, 578 nm. ^{1}H NMR ($CDCl_3$): 17.69 (s, 8H, β-H), 10.09 (d, 8H, $-C_6H_4CH_3$), 7.71 (d, 8H, $-C_6H_4CH_3$), 2.46 (s, 12H, $-C_6H_4CH_3$). MS{EI} calcd (found) (*m*/*e*): 836 (836), [M]$^+$; 801 (801), [M – Cl]$^+$.

Dichloro(5,10,15,20-tetratolylporphyrinato)tungsten(IV). $(THF)_2Li_2(TTP)$ (131.4 mg, 0.159 mmol) was stirred with WCl_4 (88.8 mg, 0.273 mmol) in toluene (20 mL) with mild heating for 12 h. After the solution was allowed to cool to room temperature, it was filtered producing a green precipitate. The solid was redissolved in CH_2Cl_2 (15 mL), and the mixture was filtered. After the filtrate was evaporated to dryness, the product was recrystallized from CH_2Cl_2/hexane (1:2) to produce a black solid (58.6 mg, 40%). UV–vis (toluene): 336, 370, 388, 420, 466, 558 nm. ^{1}H NMR ($CDCl_3$): δ 14.39 (s, 8H, β-H), 9.12 (d, 8H, $-C_6H_4CH_3$), 8.07 (d, 8H, $-C_6H_4CH_3$), 2.85 (s, 12H, $-C_6H_4CH_3$). ^{1}H NMR (C_6D_6): δ 14.31 (s, 8H, β-H), 8.882 (d, 8H, $-C_6H_4CH_3$), 7.68 (d, 8H, $C_6H_4CH_3$), 2.49 (s, 12H, $-C_6H_4CH_3$). $\mu_{eff} = 1.75\ \mu_B$. MS{EI} calcd (found) (*m*/*e*): 924 (924), [M]$^+$. Anal. Calcd (found) for $C_{48}H_{36}N_4WCl_2$: C, 62.92 (62.44); H, 3.93 (3.77); N, 6.07 (5.85).

X-ray Crystal Structure Determination of (TTP)VCl. Crystals of (TTP)VCl·THF suitable for single-crystal X-ray diffraction were grown by layering a benzene/THF solution of (TTP)VCl with hexane. A brown platelet (0.50 × 0.45 × 0.15 mm) was attached to the tip of a glass fiber and mounted on a Siemens P4/RA diffractometer for data collection at –60 ± 1 °C using Cu Kα radiation (λ = 1.541 78 Å). Cell constants were determined from a list of reflections found by a rotation photograph. Pertinent data collection and reduction information is given in Table 1. Lorentz and polarization corrections were applied. A correction based on nonlinear decay in the standard reflections was applied to the data. An absorption correction was deemed unnecessary for this study. The agreement factor for the averaging of observed reflections was 2.9% (based on *F*).

Table 1. Crystal Data for $(TTP)VCl\cdot THF\cdot 2C_6H_6$

formula	$VClN_4OC_{52}H_{44}\cdot 2C_6H_6$
fw	983.6
space group	$P2_1/m$
a, Å	11.968(2)
b, Å	17.072(3)
c, Å	12.649(2)
β, deg	98.62(2)
V, Å^3	2555.2(8)
Z	8
d_{calc}, g/cm^3	1.345
cryst size, mm	0.50 × 0.45 × 0.15
μ(Cu Kα), mm^{-1}	2.468
data collcn instrument	Siemens P4/RA
radiation (λ, Å)	CuKα (1.541 78)
temp, K	213
scan type	$2\theta-\theta$
scan speed	constant; 11.72°/min in *x*
scan range (*x*)	0.80° plus Kα-separation
reflcns collcd	7157
independent reflcns	3580 (R_{int} = 2.86%)
obsd reflcns	2747 ($F > 6.0\sigma(F)$)
R^a	0.0460
$R_w{}^b$	0.0666
quality of fit indicator^c	1.56
largest shift/esd in final cycle	0.017
largest peak, e/Å^3	0.29

^{a} $R = \sum||F_o| - |F_c|/|F_o||$. ^{b} $R = [\sum w(|F_o| - |F_c|^2/\sum w|F_o|^2]^{1/2}$; $w = 1 - \sigma 2|F_o|$. ^{c} Quality of fit = $[\sum w(|F_o| - |F_c|)^2/N_{observns} - N_{params}]^{1/2}$.

The centric space group $P2_1/m$ was indicated initially by systematic absences and intensity statistics. The structure was solved in $P2_1$ and after completion transformed to the centrosymmetric space group. All atoms were located by a Patterson interpretation technique. All non-hydrogen atoms were refined with anisotropic thermal parameters. After the least-squares converged all hydrogen atoms were placed at calculated positions 0.96 Å from the attached atom with isotropic temperature factors set equal to the isotropic equivalent of the host atom. Two solvent molecules of benzene were found in the lattice.

The porphyrin ring is bisected by a crystallographic mirror in this space group. This requires that the THF ligand be disordered over two equivalent sites with 50% occupancy. The normal "puckering" of the THF was not found in this analysis, but rather the ligand is dynamically disordered over the two "puckered" geometries for an averaged local structure.

X-ray data collection and structure solution were carried out at the Iowa State Molecular Structure Laboratory. Refinement calculations were performed on a Digital Equipment Corp. VaxStation 3100 computer using the SHELXTL PLUS version 4.0 programs.[16]

Results

Preparation and Characterization of Vanadium(III) Porphyrins. As illustrated in eq 1, vanadium(III) porphyrin halide complexes

$$(THF)_2Li_2(POR) + MX_n \rightarrow \underset{\mathbf{1,2}}{(POR)MX_{n-2}} + 2LiCl + THF \quad (1)$$

$$\mathbf{1},\ POR = OEP \text{ and } MX_n = VCl_3(THF)_3$$

$$\mathbf{2},\ POR = TTP \text{ and } MX_n = VCl_3(THF)_3$$

were prepared using a porphyrin dianion and the appropriate metal halide complex. The vanadium complexes, (POR)V^{III}Cl (POR = OEP, TTP), were isolated as brown solids which have good solubility in toluene, benzene, THF, dichloromethane, and chloroform but have low solubility in *n*-hexane. Complexes **1** and **2** are both extremely air sensitive and are converted to the corresponding vanadyl complexes on exposure to oxygen.

The electronic absorption spectra of **1** and **2** are characteristic of porphyrin complexes with an intense Soret peak at 406 nm for

---

(16) SHELXTL PLUS, Siemens Analytical X-Ray Instruments, Inc., Madison, WI.

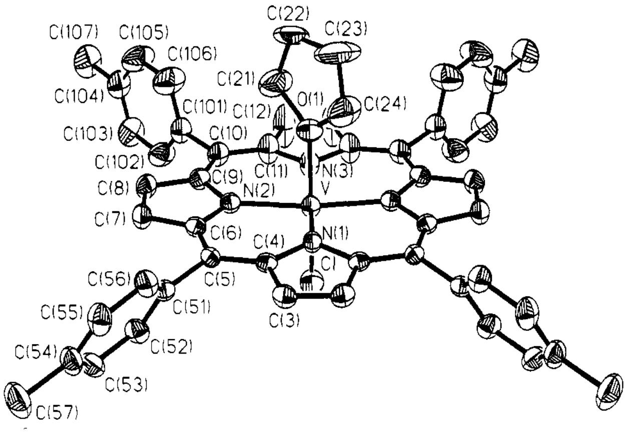

Figure 1. Molecular structure and atom-numbering scheme for (TTP)-VCl·THF (**2**). Only one of two possible orientations of the coordinated THF ligand is shown. Thermal ellipsoids are drawn at the 30% probability level.

(OEP)$V^{III}Cl$ and 426 nm for (TTP)$V^{III}Cl$ in toluene. Dilute solutions of both complexes are yellow while more concentrated solutions are brown. The absorption spectra are similar to those of vanadium(IV) porphyrins.[6c]

The ^1H NMR spectrum for (OEP)$V^{III}Cl$ in d_6-benzene shows broad resonances for the meso protons at 40.3 ppm, for the methylene protons at 10.9 and 7.0 ppm, and for the methyl protons at 2.2 ppm. The proton assignments were made on the basis of integrated intensity. The large chemical shift range is indicative of the paramagnetic character of the compound. The magnetic moment of (OEP)$V^{III}Cl$, determined at ambient temperature by Evans' method, was found to be 2.51 μ_B.[15] The TTP analogue, **2**, was also found to be paramagnetic.

X-ray Structure of (TTP)VCl·THF. The molecular structure of the TTP complex **2** was determined by single-crystal X-ray diffraction. The molecular structure and atom-numbering scheme are shown in Figure 1. Crystallographic data for the structure determination is listed in Table 1. Atomic positional parameters are given in Table 2. Table 3 presents selected bond distances and angles.

Complex **2** crystallizes in the centrosymmetric space group $P2_1/m$ with 2 molecules per unit cell. The 24 atoms of the porphyrin core are nearly coplanar, with the largest out-of-plane displacement of 0.10 Å by C(8). In addition, the vanadium ion is displaced from the mean porphyrin plane 0.15 Å toward the Cl ligand. The V–N distances range from 2.040(4) to 2.050(3) Å and are typical of those observed for other vanadium porphyrin complexes.[17] The phenyl rings form dihedral angles with the porphyrin plane of 63.4 and 85.4°.

The V–O(1) distance, 2.141(3) Å, is similar to that reported for (OEP)V(THF)$_2$ (2.174(4) Å).[17c] However, this distance is much shorter than that observed in (TPP)Fe(THF)$_2$ (Fe–O = 2.351(3) Å at room temperature and 2.288(1) Å at liquid-nitrogen temperature).[18] The iron(II) complex is high spin, $S = 2$. Similarly, the Zn–O distance of 2.380(2) Å in (TPP)Zn(THF)$_2$ suggests that the THF molecules are bound weakly to the zinc atom. In both the iron and zinc complexes, population of the d_{z^2} orbital, which is partially metal–THF antibonding, is reflected in the long metal–oxygen distance.[19] In (OEP)V(THF)$_2$ and (TTP)VCl·THF this orbital is empty and results in a stronger V–O interaction.[17c] The V–Cl bond length in **2**·THF (2.272(1) Å) is similar to that reported for other vanadium(III) macrocycles with nitrogen donor ligands. For example, a compound utilizing the dibenzotetramethyltetraaza[14]annulene ligand (tmtaa), [(tmtaa)V(Cl)]·0.5C_7H_8, has a V–Cl bond length of 2.221(5) Å.[20] Schiff base complexes have slightly longer V–Cl bond lengths, generally in the range 2.34–2.37 Å.[21]

Table 2. Atomic Coordinates (×10^5) and Equivalent Isotropic Displacement Coefficients (Å^2 × 10^4)

	x	*y*	*z*	*U*(eq)[a]
V	727(6)	25 000	25 973(6)	283(3)
Cl	10 347(9)	25 000	42 883(10)	438(4)
C(3)	–30 262(23)	21 067(17)	38 234(25)	318(10)
C(4)	–20 533(22)	18 526(16)	33 715(22)	255(9)
N(1)	–14 883(26)	25 000	30 790(26)	265(11)
C(5)	–17 096(22)	10 638(16)	33 103(22)	256(9)
C(6)	–7 621(22)	81 186(16)	28 648(21)	272(9)
C(7)	–4 824(24)	207(17)	26 818(24)	348(11)
C(8)	4 541(25)	249(18)	21 968(25)	372(11)
N(2)	202(17)	13 014(14)	25 006(17)	290(8)
C(9)	7 814(23)	8 222(17)	20 978(23)	325(10)
C(10)	17 347(24)	10 707(18)	16 798(26)	375(11)
N(3)	14 922(29)	25 000	18 835(31)	383(13)
C(11)	20 754(27)	18 540(19)	16 176(31)	470(13)
C(12)	30 642(34)	21 043(21)	12 061(43)	812(20)
C(51)	–23 405(23)	4 515(16)	38 104(23)	278(10)
C(52)	–17 820(24)	265(17)	46 671(24)	340(10)
C(53)	–23 219(26)	–5 498(18)	51 643(25)	392(11)
C(54)	–34 520(27)	–7 148(17)	48 370(28)	402(11)
C(55)	–40 172(25)	–2 846(18)	39 965(27)	401(11)
C(56)	–34 773(24)	2 828(17)	34 789(25)	349(10)
C(57)	–40 365(31)	–13 520(20)	53 752(32)	610(15)
C(101)	24 223(26)	4 614(18)	12 186(28)	402(12)
C(102)	33 145(30)	859(21)	18 202(30)	540(14)
C(103)	39 596(30)	–4 527(22)	13 647(32)	579(15)
C(104)	37 322(30)	–6 297(20)	2 938(31)	509(14)
C(105)	28 535(35)	–2 454(24)	–3 005(33)	723(17)
C(106)	22 072(33)	2 862(24)	1 548(32)	667(16)
C(107)	44 568(33)	–12 083(23)	–2 030(36)	769(18)
O(1)	–8 096(26)	25 000	9 942(24)	424(11)
C(21)	–4 984(73)	20 059(48)	922(64)	716(34)
C(22)	–11 678(120)	22 481(55)	–8 556(74)	1177(63)
C(23)	–18 500(124)	29 024(69)	–5 260(75)	1354(67)
C(24)	–16 930(66)	29 874(48)	5 780(60)	713(33)
C(1S)	–30 250(47)	21 001(29)	66 964(36)	849(20)
C(2S)	–21 343(61)	17 095(29)	64 231(37)	921(25)
C(3S)	–12 434(46)	21 014(33)	61 555(38)	990(25)
C(4S)	17 437(75)	28 877(43)	79 465(88)	1121(45)
C(5S)	26 536(58)	32 654(30)	77 418(72)	1361(43)
C(6S)	36 243(71)	28 630(38)	75 080(75)	1146(43)
C(7S)	25 786(305)	28 673(120)	87 242(166)	1475(141)
C(8S)	24 356(194)	28 292(108)	69 022(138)	1084(100)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table 3. Selected Bond Distances (Å) and Angles (deg) for **2**

V–Cl	2.272(1)	V–N(3)	2.040(4)
V–N(1)	2.050(3)	V–N(2A)	2.050(2)
V–N(2)	2.050(2)	V–O	2.141(3)
Cl–V–N(1)	94.4(1)	N(2A)–V–O(1)	86.4(1)
Cl–V–N(2)	93.6(1)	N(1)–V–N(2)	93.6(1)
Cl–V–N(4)	94.5(1)	N(1)–V–N(3)	171.1(1)
Cl–V–N(2A)	93.6(1)	N(2)–V–N(3)	89.6(1)
Cl–V–O(1)	179.1(1)	N(1)–V–N(2A)	89.8(1)
N(1)–V–O(1)	86.5(1)	N(2)–V–N(2A)	172.8(1)
N(2)–V–O(1)	86.4(1)	N(3)–V–N(2A)	89.6(1)
N(3)–V–O(1)	84.6(1)		

Preparation and Characterization of Titanium, Molybdenum, and Tungsten Porphyrin Halide Complexes. Titanium, molyb-

---

(17) (a) Poncet, J. L.; Barbe, J. M.; Guilard, R.; Oumous, H.; Lecomte, C.; Protas, J. *J. Chem. Soc., Chem. Commun.* **1982**, 1421. (b) Drew, M. G. B.; Mitchell, P. C. H.; Scott, C. E. *Inorg. Chim. Acta* **1984**, *82*, 63. (c) Poncet, J. L.; Barbe, J. M.; Guilard, R.; Oumous, H.; Lecomte, C.; Protas, J. *J. Chem. Soc., Dalton Trans.* **1984**, 2677. (d) Molinaro, F. S.; Ibers, J. A. *Inorg. Chem.* **1976**, *15*, 2278.

(18) Reed, C. A.; Mashiko, T.; Scheidt, W. R.; Spartalian, K.; Lang, G. *J. Am. Chem. Soc.* **1980**, *102*, 2302.

(19) Schauer, C. K.; Anderson, O. P.; Eaton, S. S.; Eaton, G. R. *Inorg. Chem.* **1985**, *24*, 4082.

(20) Solari, E.; De Angelis, S.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C. *Inorg. Chem.* **1992**, *31*, 96.

(21) (a) Mazzanti, M.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *Inorg. Chem.* **1986**, *25*, 4158. (b) Mazzanti, M.; Gambarotta, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *Inorg. Chem.* **1986**, *25*, 2308. (c) Solari, E.; De Angelis, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *Inorg. Chem.* **1992**, *31*, 141.

denum, and tungsten porphyrin halide complexes were also obtained by treating porphyrinato dianions with the appropriate metal halide complex (eq 2). (TTP)$Ti^{IV}Cl_2$ (**3**) and (TTP)Ti^{III}Cl (**4**) were isolated in 60% and 81% yields, respectively, after

$$(THF)_2Li_2(POR) + MX_n \rightarrow \underset{\mathbf{3-6}}{(POR)MX_{n-2}} + 2LiCl + THF \quad (2)$$

3, POR = TTP and $MX_n = TiCl_4(THF)_2$

4, POR = TTP and $MX_n = TiCl_3(THF)_3$

5, POR = TTP and $MX_n = MoCl_4(CH_3CN)_2$

6, POR = TTP and $MX_n = WCl_4$

recrystallization from toluene/hexane (1:2). Both complexes have good solubility in halogenated solvents but low solubility in *n*-hexane. In aromatic solvents, (TTP)$Ti^{IV}Cl_2$ has low solubility whereas (TTP)Ti^{III}Cl is more soluble. Spectroscopic characterization of complexes **3** and **4**, using ^{1}H NMR and UV–vis, was consistent with that previously reported for (TPP)$Ti^{IV}Cl_2$ and analogous (TPP)Ti^{III} complexes.[6b,8,22,23]

(TTP)$Mo^{IV}Cl_2$ (**5**) and (TTP)$W^{IV}Cl_2$ (**6**) were isolated after recrystallization from CH_2Cl_2/hexane (1:3). Both complexes have good solubility in dichloromethane, chloroform, and THF but limited solubility in toluene, benzene, and *n*-hexane. The ^{1}H NMR of **5** and **6** were similar to reported spectra.[6d,7]

Discussion

The synthetic method we have employed to prepare early transition metal porphyrin halide complexes of vanadium, titanium, molybdenum, and tungsten has many advantages over previously reported methods. For example, this simple route provides a convenient means of synthesizing vanadium(III) porphyrins, species previously prepared only by electrochemical methods.[9] These complexes are paramagnetic as evidenced by the large chemical shift range and broadness of the resonances in the ^{1}H NMR. The paramagnetic character of (TTP)V^{III}Cl is in sharp contrast to the diamagnetic character reported earlier.[9] (TTP)V^{III}Cl is the first vanadium(III) porphyrin to be structurally characterized. The V–O(1), V–Cl, and V–N bond lengths are similar to those in other vanadium porphyrins and vanadium-containing macrocycles.[17,20,21]

Most insertions of titanium into a porphyrin free base ultimately result in the formation of very stable oxotitanium compounds.[24] However, such complexes cannot be directly converted to low-valent titanium porphyrin compounds.[25] Previously, preparation of dihalogenotitanium(IV) porphyrins involved treatment of the oxo complexes with hydrogen halides, SOX_2, or $(COX)_2$.[6] Titanium(III) porphyrin halide complexes were synthesized by reduction of the dihalogenotitanium(IV) porphyrins using Zn/Hg.[8] The synthetic method reported here provides the titanium(IV) and titanium(III) complexes in high purity under mild conditions.

The one-pot metathesis reaction (eq 2) simplifies the preparation of (TTP)$Mo^{IV}Cl_2$ and (TTP)$W^{IV}Cl_2$, useful precursors to the low-valent chemistry of molybdenum and tungsten porphyrins. The previous route to the tungsten complex involved reduction of the W^V(POR)(O)(Cl) species with Si_2Cl_6 and resulted in a mixture of paramagnetic W^{IV}(POR)(X)(X′) complexes, where X or X′ = Cl^-, Cl_3Si^-, or Cl_3SiO^-.[7] Subsequent treatment of the mixture of products with HCl(g) produced (TTP)$W^{IV}Cl_2$.[7] In contrast to this method, synthesis of (TTP)$W^{IV}Cl_2$ using $(THF)_2Li_2$(TTP) is rather simple because of the low solubility of (TTP)$W^{IV}Cl_2$ in toluene. As the reaction proceeds, (TTP)$W^{IV}Cl_2$ precipitates out of solution. After filtration to remove the crude product from the toluene solution, the resulting solid is redissolved in CH_2Cl_2, the solution is filtered, and the product is isolated by evaporating the filtrate to dryness. Recrystallization from CH_2Cl_2/hexane provides (TTP)$W^{IV}Cl_2$ in high purity.

Acknowledgment. Support for this work was provided by the National Science Foundation, through PYI Award CHE-9057752, and the donors of the Petroleum Research Fund, administered by the American Chemical Society.

Supplementary Material Available: Listings of bond distances and bond angles (3 pages). Ordering information is given on any current masthead page.

---

(22) Marchon, J. C.; Latour, J. M.; Grand, A.; Belakhovsky, M.; Loos, M.; Goulon, J. *Inorg. Chem.* **1990**, *29*, 57.

(23) Boreham, C. J.; Buisson, G.; Duee, E.; Jordanov, J.; Latour, J. M.; Marchon, J. C. *Inorg. Chim. Acta* **1983**, *70*, 77.

(24) Fournari, P.; Guilard, R.; Fontesse, M.; Latour, J. M.; Marchon, J. C. *J. Organomet. Chem.* **1976**, *110*, 205.

(25) Malinski, T.; Chang, D.; Latour, J. M.; Marchon, J. C.; Gross, M.; Giraudeau, A.; Kadish, K. M. *Inorg. Chem.* **1984**, *23*, 3947.