

Supporting Information

Coordination of oxovanadium(V) in an expanded porphyrin macrocycle

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Experimental

General Procedures. Prior to use, all glassware was soaked in KOH-saturated isopropyl alcohol for ca. 12 h and then rinsed with water and acetone before being thoroughly dried. Tetrahydrofuran (THF) was dried by passage through two columns of activated alumina. Methanol was dried by passage through two columns of molecular sieves. Dichloromethane, *n*-pentane and hexanes were purchased from Fisher Scientific and used as received. Deuterated dichloromethane was purchased from Cambridge Isotope Labs and used as received. 1,2-Phenylenediamine (Acros), VO(acac)₂ (Strem) and VO(Oi-Pr)₃ (Strem) were purchased commercially and used as received. Bipyrrole dialdehyde was prepared according to a previously published procedure.¹ Alumina plates for preparative thin layer chromatography (20×20 cm) were purchased from Analtech, Inc. Solutions were stirred magnetically.

Nuclear magnetic resonance (NMR) spectra were obtained on a Varian Mercury 400 MHz or on a Varian Inova 500 MHz. UV-visible spectra were recorded on a Beckman DU-640 spectrophotometer. High-resolution mass spectra were obtained at the University of Texas at Austin, Department of Chemistry and Biochemistry, Mass Spectrometry Facility. Elemental analyses were performed by Midwest Microlabs Inc., Indianapolis, IN.

Preparation of 1. Bipyrrole dialdehyde (100 mg, 0.37 mmol) was dissolved in CH₃OH (50 mL) and concentrated HNO₃ (3 drops) was added. A solution of 1,2-phenylenediamine (20 mg, 0.18 mmol) in CH₃OH (20 mL) was added dropwise (within 20 minutes) to the stirring dialdehyde solution. The reaction mixture was heated to reflux for 5 h in an argon atmosphere, allowed to cool to room temperature and filtered through a fritted funnel to remove a red solid (2+2 condensation side product). After concentrating the emerald green mother liquors to a volume of about 20 mL, triethylamine (3 drops) and water (2 mL) were added under vigorous stirring. The purple suspension obtained in this way was placed in a refrigerator (4°C) for several hours and then filtered to provide a purple solid. Recrystallization of the resulting powder from CH₂Cl₂/CH₃OH gave 61 mg of macrocycle **1** (59%).

¹H NMR (400 MHz, 296 K, CD₂Cl₂): δ 8.65 (s, 2H, iminic CHN), 7.57-7.55 (m, 2H, ArH), 7.41-7.39 (m, 2H, ArH), 7.15 (s, 1H, meso), 2.82-2.75 (m, 8H, CH₂CH₃), 2.30 (s, 6H, CH₃), 2.24 (s, 6H, CH₃), 1.29 (t, 6H, CH₂CH₃), 1.23 (t, 6H, CH₂CH₃), (pyrrolic NH not observed). ¹³C NMR (100 MHz, 296 K, CD₂Cl₂): δ 147.4, 145.7, 144.4, 143.0, 138.5, 134.0, 129.3, 126.2, 124.5, 119.4, 117.3, 115.7, 18.6, 17.8, 16.7, 16.4, 11.8, 11.5. CI-MS: (M+1)⁺ *m/z* 571; HR CI-MS: (M+1)⁺ *m/z* 571.35650 (calc. for C₃₇H₄₃N₆: 571.35437). Anal. calcd. [C₃₇H₄₂N₆](H₂O): C, 75.48; H, 7.53; N, 14.27. Found: C, 75.88; H, 7.68; N, 14.05.

Preparation of 2. Macrocycle **1** (50 mg, 0.09 mmol) was stirred with VO(acac)₂ (70 mg, 0.27 mmol) in THF (20 mL). After 2 days, no residual starting material was observed in the UV-visible absorption spectrum of the reaction mixture. The olive green mixture was then filtered through Celite and the solvent was evaporated under reduced pressure. The green solid obtained in this way was purified by means of preparative thin layer chromatography (alumina, 2% hexanes/CH₂Cl₂). The top green fraction was collected and the resulting product was recrystallized from CH₂Cl₂/*n*-pentane to yield 35 mg of complex **2** (61%).

¹H NMR (400 MHz, 296 K, CD₂Cl₂): δ 11.43 (s, 1H, pyrrolic NH), 9.80 (br d, 1H, ArNH), 9.61 (s, 1H, iminic CHN), 8.82 (d, 1H, CHNH), 8.24 (d, 1H, ArH), 8.22 (d, 1H, ArH), 7.92 (s, 1H, meso), 7.69-7.61 (m, 2H, ArH), 3.12-2.92 (m, 8H, CH₂CH₃), 2.77 (s, 3H, CH₃), 2.70 (s, 3H, CH₃), 2.50 (s, 3H, CH₃), 2.31 (s, 3H, CH₃), 1.51-1.27 (m, 12H, CH₂CH₃). ¹³C NMR (100 MHz, 296 K, CD₂Cl₂): δ 153.0, 150.0, 149.5, 149.0, 146.2, 139.6, 138.7, 138.3, 136.7, 132.3, 131.8, 130.3, 129.8, 129.4, 126.4, 125.4, 123.7, 121.3, 118.8, 117.2, 114.1, 95.2, 19.5, 19.0, 18.9, 18.3, 17.2, 17.0, 16.8, 16.5, 13.5, 12.7. ESI-MS: (M+1)⁺ *m/z* 653; HR CI-MS: (M+1)⁺ *m/z* 653.2803 (calc. for C₃₇H₄₂N₆O₂V: 653.2809). Anal. calc. [C₃₇H₄₁N₆O₂V]·(CH₂Cl₂): C, 61.87; H, 5.88; N, 11.39. Found: C, 61.77; H, 5.60; N, 11.11.

X-ray Experimental for 2 [C₃₇H₄₁N₆O₂V]·(CH₂Cl₂)₃. Crystals grew as very dark, almost black lathes from a concentrated solution of **2** in CH₂Cl₂ and CH₃OH at -20°C. The data crystal was cut from a long lathe and had approximate dimensions 0.24 x 0.23 x 0.18 mm. The data were collected on a Nonius Kappa CCD diffractometer using a graphite monochromator with MoKα radiation (λ = 0.71073 Å). A total of 511 frames of data were collected using ω-scans with a scan range of 1° and a counting time of 115 seconds per frame. The data were collected at 153 K using an Oxford Cryostream low temperature device. Details of crystal data, data collection and structure refinement are listed in Table S1. Data reduction were performed using DENZO-SMN.² The structure was solved by direct methods using SIR97³ and refined by full-matrix least-squares on F² with anisotropic displacement parameters for the non-H atoms using SHELXL-97.⁴ The hydrogen atoms on carbon were calculated in ideal positions with isotropic displacement parameters set to 1.2xU_{eq} of the attached atom (1.5xU_{eq} for methyl hydrogen atoms). The hydrogen atoms on nitrogen were observed in a ΔF map and refined with isotropic displacement parameters.

One methyl carbon, C37, on an ethyl group was found to be disordered. The disorder was modeled by assigning the variable *x* to the site occupancy for C37 and (1-*x*) to the site occupancy for the alternate orientation represented by atom, C37a. An isotropic displacement parameter was constrained to be equal for C37 and C37a while the variable *x* was refined. The bond length to C36 was restrained to be equal for C37 and C37a. The site occupancy factor refined to 85(2)% for C37. C37 was refined anisotropically while C37a was refined isotropically.

A chlorine atom on one of the methylene chloride molecules was also disordered. The solvent disorder was modeled in a similar manner to that described above. The major component of the disorder, Cl2c, had a site occupancy factor of 81(2)%, while the minor component, Cl3c, had a site occupancy factor of 19(2)%. Both atoms were refined anisotropically.

The function, $\sum w(|F_o|^2 - |F_c|^2)^2$, was minimized, where $w = 1/[(\sigma(F_o))^2 + (0.02 \cdot P)^2]$ and $P = (|F_o|^2 + 2|F_c|^2)/3$. $R_w(F^2)$ refined to 0.136, with $R(F)$ equal to 0.0703 and a goodness of fit S of 1.16. Definitions used for calculating $R(F)$, $R_w(F^2)$ and the goodness of fit, S , are given below.⁵ The data were checked for secondary extinction affects but no correction was applied. Neutral atom scattering factors and values used to calculate the linear absorption coefficient are from the International Tables for X-ray Crystallography (1992).⁶

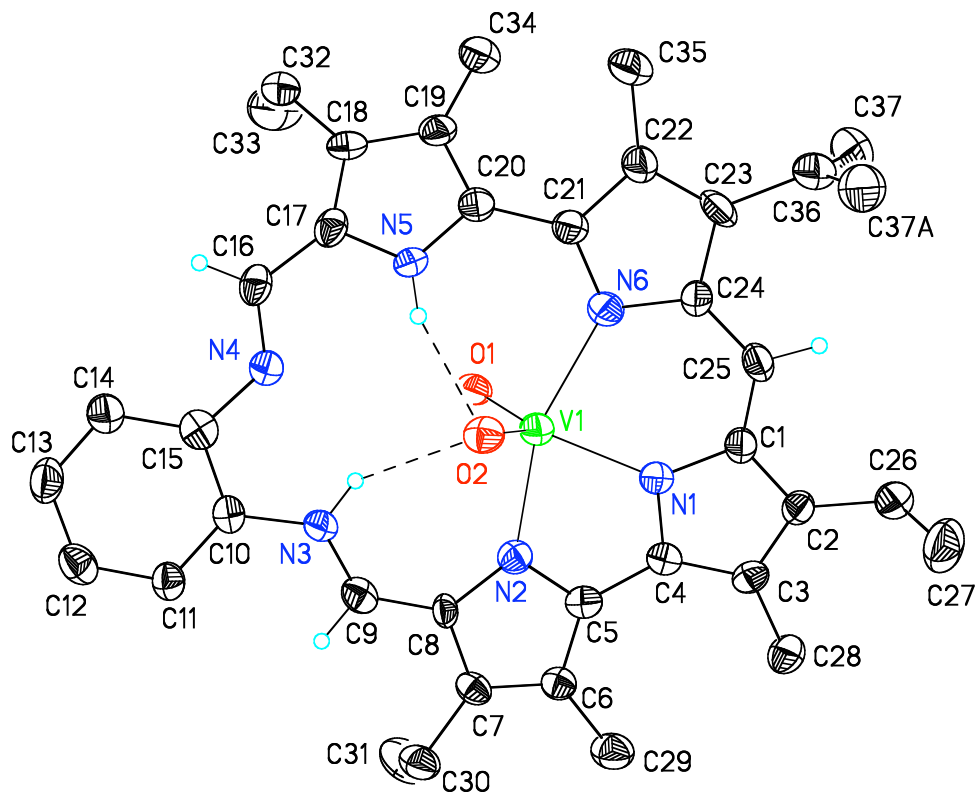


Fig. S1. View of complex 2 showing the atom labeling scheme. Displacement ellipsoids are scaled to the 50% probability level. Most hydrogen atoms have been removed for clarity. The methyl carbon on C36 is disordered about two orientations as shown. Dashed lines are indicative of H-bonding interactions. The geometries of these interactions are: N3-H3N \cdots O2, N \cdots O 3.170(5) Å, H \cdots O 2.37(5) Å, N-H \cdots O 141(4) $^\circ$; N5-H5N \cdots O2, N \cdots O 2.854(5) Å, H \cdots O 1.95(4) Å, N-H \cdots O 160(3) $^\circ$.

Table S1. Crystal data and structure refinement for 2.

Empirical formula	C ₄₀ H ₄₇ Cl ₆ N ₆ O ₂ V	
Formula weight	907.48	
Temperature	153(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 12.4914(2) Å	α = 89.426(1)°.
	b = 13.0026(3) Å	β = 88.093(1)°.
	c = 14.8379(5) Å	γ = 61.536(1)°.
Volume	2117.44(9) Å ³	
Z	2	
Density (calculated)	1.423 mg/m ³	
Absorption coefficient	0.656 mm ⁻¹	
F(000)	940	
Crystal size	0.24 x 0.23 x 0.18 mm	
Theta range for data collection	3.13 to 27.50°.	
Index ranges	-15 ≤ h ≤ 16, -16 ≤ k ≤ 16, -19 ≤ l ≤ 19	
Reflections collected	16243	
Independent reflections	9540 [R(int) = 0.1101]	
Completeness to theta = 27.50°	98.0 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	9540 / 63 / 517	
Goodness-of-fit on F ²	1.122	
Final R indices [I > 2σ(I)]	R1 = 0.0703, wR2 = 0.1106	
R indices (all data)	R1 = 0.2480, wR2 = 0.1355	
Largest diff. peak and hole	0.795 and -0.792 e.Å ⁻³	

References

- 1) (a) J. L. Sessler, M. Cyr and A. K. Burrell, *Tetrahedron*, 1992, **48**, 9661-9672; (b) R. Guilard, M. A. Aukauloo, C. Tardieux and E. Vogel, *Synthesis*, 1995, 1480-1482.
- 2) Z. Otwinowski and W. Minor, in *Methods in Enzymology*, ed. C. W. Carter, Jr. and R. M. Sweets, Academic Press, 1997, **276**, 307-326.
- 3) A. Altomare, M. C. Burla, M. Camalli, G. L. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori and R. Spagna, *J. Appl. Cryst.*, 1999, **32**, 115-119.
- 4) G. M. Sheldrick, *SHELXL97. Program for the Refinement of Crystal Structures*, 1994 University of Gottingen, Germany.
- 5) $R_w(F^2) = \left\{ \frac{\sum w(|F_o|^2 - |F_c|^2)^2}{\sum w|F_o|^4} \right\}^{1/2}$ where w is the weight given each reflection.
 $R(F) = \frac{\sum(|F_o| - |F_c|)/\sum|F_o|}{\sum|F_o|}$ for reflections with $F_o > 4(\sigma(F_o))$.
 $S = \left[\frac{\sum w(|F_o|^2 - |F_c|^2)^2}{(n - p)} \right]^{1/2}$, where n is the number of reflections and p is the number of refined parameters.
- 6) *International Tables for X-ray Crystallography* (1992). Vol. C, Tables 4.2.6.8 and 6.1.1.4, A. J. C. Wilson, editor, Boston: Kluwer Academic Press.