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Registry No. 1,8,5,6-$(\eta^5\text{-C}_5\text{H}_5)_2\text{Co}_2\text{C}_2\text{B}_5\text{H}_7$, 41636-82-2; 1,7,5,6-$(\eta^5\text{-C}_5\text{H}_5)_2\text{Co}_2\text{C}_2\text{B}_5\text{H}_7$, 53452-50-9.

Supplementary Material Available: Listing of observed and calculated structure factor amplitudes (11 pages). Ordering information is given on any current masthead page.

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Crystal and Molecular Structure of 2,3,7,8,12,13,17,18-Octaethylporphinatooxovanadium(IV)

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The structure of 2,3,7,8,12,13,17,18-octaethylporphinatooxovanadium(IV) has been determined from three-dimensional x-ray diffraction data. The complex crystallizes in the monoclinic space group $C_{2h}{}^5\text{-}P2_1/c$ with four molecules in a unit cell of dimensions $a = 14.334$ (3), $b = 23.061$ (8), $c = 9.815$ (2) Å, $\beta = 104.18$ (2)°. The structure was solved by direct methods. Least-squares refinement has led to a final value of the conventional R index (on $F_o{}^2$) of 0.084 based on 6482 reflections (including $F_o{}^2 \leq 0$). The vanadium atom is found to be 0.543 Å above the plane of the four nitrogen atoms. The average V–N bond distance is 2.102 (6) and the V–O bond length is 1.620 (2) Å. The porphyrin itself is slightly nonplanar.

Introduction

In recent years a considerable amount of interest has been devoted to synthetic models for various biological systems.[1] Although vanadyl porphyrins are not known to be involved in any biological processes, they do occur in Nature.[2] Vanadyl porphyrins have been found in oil deposits, various bitumens, and even meteorites.[3] The source of the vanadyl porphyrin in meteorites has been proposed to be some abiological synthesis.[3] Vanadium has been found in blood cells of certain ascidians, but the mode of bonding to the protein is not understood.[4] The degradation of chlorophyll and other biologically active porphyrins is thought to be the source of vanadyl porphyrins in petroleum.[3,5] The porphyrin which is commonly found in petroleum has been identified as an analogue of etioporphyrin I (Figure 1). Since 2,3,7,8,12,13,17,18-octaethylporphyrin (OEP) is a close synthetic model for these natural porphyrins, the structure of VO(OEP) has been determined and is reported here. The structure is compared with that of vanadyl deoxophylloerythroetioporphyrin, which is a model for chlorophyll. This is the only other vanadyl porphyrin whose structure has been determined.

Experimental Section

A sample of VO(OEP) was kindly supplied by Professor H. H. Inhoffen. Suitable crystals, deep red in color, were obtained by slow evaporation from a chloroform–toluene solution. Preliminary Weissenberg photographs, showed monoclinic symmetry and systematic absences ($0k0$, $k \neq 2n$; $h0l$, $l \neq 2n$) consistent with space group $C_{2h}{}^5\text{-}P2_1/c$.

The crystal selected for data collection was a monoclinic prism with bounding faces of the forms {101}, {011}, {100}, and {010}. Approximate dimensions of the crystal are 0.207 × 0.221 × 0.162 mm. The calculated volume is 0.0066 mm^3. The crystal was mounted with the [100] direction approximately along the spindle axis.

The lattice parameters, obtained as previously described[6,7] by hand centering of 13 reflections in the range $40 < 2\theta < 60°$ on a Picker four-circle automatic diffractometer using Cu Kα_1 radiation (λ 1.540 562 Å), are $a = 14.334$ (3), $b = 23.061$ (8), $c = 9.815$ (2) Å, $\beta = 104.18$ (2)°. The calculated density, based on four molecules per unit cell, of 1.269 g/cm^3 agrees well with the value of 1.25 (1) g/cm^3 measured by flotation in aqueous zinc chloride solution.

Data were collected in shells of 2θ for $5 < 2\theta < 160°$ by the θ–2θ scan method using Cu Kα radiation prefiltered with Ni foil. The scan range in 2θ was from 0.80° below the Cu Kα_1 peak to 0.80° above the Cu Kα_2 peak. The takeoff angle was 3.0° and the scintillation counter was positioned 32 cm from the crystal preceded by an aperture 3.1 mm high by 3.1 mm wide. The pulse height analyzer was set to admit about 90% of the Cu Kα peak. Background counts were taken for 10 s at each end of the scan range and a scan rate of 2° in 2θ per minute was used. Attenuators were automatically inserted if the intensity of the diffracted beam exceeded approximately 7000 counts/s during a scan. During the course of data collection six standard reflections from diverse regions of reciprocal space were measured

Table II. Positional and Thermal Parameters for the Atoms of 2,3,7,8,12,13,17,18,-Octaethylporphinatooxovanadium(IV)

ATOM	X[A]	Y	Z	B11[B]	B22	B33	B12	B13	B23
V	-0.250994(44)	0.058132(24)	0.488995(63)	43.90(35)	12.35(10)	106.60(74)	2.46(18)	5.84(38)	-3.07(24)
N(1)	-0.13014(20)	0.06200(11)	0.65981(28)	41.9(16)	13.57(51)	94.6(32)	3.98(80)	3.0(18)	-5.0(11)
N(2)	-0.29546(19)	0.13557(11)	0.56694(28)	36.8(16)	12.17(49)	101.4(33)	1.20(73)	11.0(19)	-4.5(10)
N(3)	-0.39794(20)	0.04100(11)	0.40748(29)	41.0(17)	12.16(49)	109.4(36)	1.33(76)	0.6(20)	-2.7(10)
N(4)	-0.23258(21)	-0.03264(12)	0.50200(30)	47.4(19)	12.62(50)	114.2(37)	4.25(80)	-0.4(21)	-3.3(12)
O	-0.21082(19)	0.07858(11)	0.35605(25)	68.8(18)	17.80(52)	110.5(32)	3.73(80)	32.8(20)	0.6(10)
C(1)	-0.05653(25)	0.02224(15)	0.68836(35)	40.8(21)	17.14(71)	96.0(41)	4.51(98)	1.8(23)	-6.0(13)
C(2)	0.02916(26)	0.04730(16)	0.77711(37)	42.1(21)	19.73(82)	108.5(44)	4.1(10)	1.9(24)	-6.6(14)
C(3)	0.00685(26)	0.10264(16)	0.80377(36)	42.9(21)	18.69(75)	105.7(44)	1.6(10)	4.3(24)	-4.3(14)
C(4)	-0.09304(25)	0.11169(14)	0.73117(35)	41.0(20)	15.12(66)	101.2(41)	-0.18(94)	1.6(23)	-5.5(13)
C(5)	-0.14345(25)	0.16319(14)	0.72822(36)	42.9(21)	14.52(65)	110.7(43)	-1.46(96)	7.0(24)	-10.4(14)
C(6)	-0.23682(25)	0.17483(13)	0.65334(34)	46.3(21)	12.30(60)	97.6(39)	1.07(92)	14.9(23)	-4.6(12)
C(7)	-0.28585(26)	0.22985(14)	0.64911(36)	48.2(21)	12.19(59)	106.8(42)	0.56(94)	20.6(24)	-4.9(12)
C(8)	-0.37472(25)	0.22334(13)	0.56265(35)	44.6(20)	11.87(59)	104.2(40)	2.49(90)	22.6(24)	-1.3(12)
C(9)	-0.38105(24)	0.16403(14)	0.51127(34)	39.7(19)	13.41(60)	98.1(39)	2.19(90)	20.6(23)	-1.0(12)
C(10)	-0.46052(25)	0.13898(14)	0.42235(36)	40.5(20)	12.90(60)	115.2(43)	2.80(91)	9.5(24)	1.2(13)
C(11)	-0.46979(25)	0.08187(14)	0.37421(36)	40.8(21)	13.79(63)	111.1(43)	0.78(93)	7.2(24)	1.1(13)
C(12)	-0.55664(24)	0.05630(15)	0.28923(37)	37.9(19)	15.77(66)	120.0(44)	-0.1(10)	6.4(24)	1.6(15)
C(13)	-0.53737(26)	-0.00089(15)	0.27362(37)	43.4(21)	15.61(69)	114.8(45)	-2.69(98)	7.1(25)	1.9(14)
C(14)	-0.43853(26)	-0.01008(15)	0.34735(37)	46.7(22)	13.93(64)	108.8(43)	-2.61(99)	3.2(25)	-0.7(13)
C(15)	-0.39016(28)	-0.06273(15)	0.36015(39)	57.2(24)	12.99(64)	131.3(49)	-0.2(11)	-8.6(27)	-4.8(15)
C(16)	-0.29707(30)	-0.07431(15)	0.43258(40)	63.9(27)	12.67(65)	131.0(49)	3.8(10)	-1.3(29)	-6.9(14)
C(17)	-0.25261(32)	-0.13078(16)	0.45431(44)	71.7(29)	13.54(70)	163.4(60)	8.0(12)	-10.9(34)	-8.5(16)
C(18)	-0.16127(31)	-0.12349(17)	0.53308(45)	69.9(30)	15.76(76)	156.1(58)	8.7(12)	-8.5(33)	-11.1(17)
C(19)	-0.14814(28)	-0.06156(15)	0.56099(39)	60.1(24)	14.00(67)	123.8(46)	8.6(11)	-3.4(27)	-7.6(15)
C(20)	-0.06588(28)	-0.03532(16)	0.64221(39)	52.2(23)	18.03(74)	120.0(47)	11.5(11)	-12.1(26)	-9.9(15)
C(21)	0.12346(28)	0.01672(19)	0.83066(46)	44.7(23)	25.44(98)	160.1(60)	8.8(12)	-1.5(30)	-17.0(20)
C(22)	0.12781(35)	-0.01847(22)	0.96255(53)	68.6(32)	31.2(13)	196.6(77)	14.4(17)	-11.9(40)	9.7(25)
C(23)	0.07212(28)	0.14793(17)	0.88852(42)	44.4(23)	22.08(89)	142.5(55)	-0.5(12)	-1.9(29)	-5.3(17)
C(24)	0.06912(36)	0.14998(22)	1.03821(47)	86.1(36)	33.2(13)	133.7(59)	-8.7(18)	14.0(37)	-21.0(22)
C(25)	-0.24138(28)	0.28392(15)	0.72396(41)	58.6(25)	14.14(68)	141.8(52)	2.0(11)	16.9(29)	-14.6(15)
C(26)	-0.17830(33)	0.31506(18)	0.64519(52)	74.6(32)	18.52(87)	217.0(75)	-9.3(14)	39.5(41)	-11.3(21)
C(27)	-0.45174(27)	0.26787(15)	0.52184(40)	48.7(22)	14.46(66)	130.4(48)	5.3(10)	17.5(27)	-4.0(14)
C(28)	-0.45329(34)	0.29505(19)	0.38078(47)	77.3(33)	21.10(93)	167.7(65)	9.0(15)	10.4(38)	10.9(20)
C(29)	-0.64895(27)	0.08853(17)	0.23128(45)	34.7(21)	20.06(84)	174.3(61)	-0.5(11)	2.6(28)	-1.7(18)
C(30)	-0.64848(31)	0.12141(21)	0.09813(47)	59.0(27)	29.0(12)	173.6(68)	7.7(15)	13.4(34)	19.2(22)
C(31)	-0.60376(27)	-0.04594(16)	0.19143(44)	42.4(22)	17.70(80)	151.4(55)	-4.2(11)	0.3(28)	-2.5(16)
C(32)	-0.59796(34)	-0.05116(19)	0.04105(49)	75.8(32)	24.8(11)	168.8(65)	-9.6(15)	7.2(37)	-15.7(21)
C(33)	-0.30454(33)	-0.18931(18)	0.40598(44)	75.2(31)	21.01(91)	138.3(58)	4.5(14)	7.7(34)	-5.6(18)
C(34)	-0.28313(40)	-0.20775(25)	0.27381(58)	97.1(43)	38.5(16)	220.1(86)	-4.4(21)	25.9(51)	-24.0(30)
C(35)	-0.08722(35)	-0.17039(18)	0.59264(45)	87.8(35)	19.57(86)	146.6(60)	3.3(14)	21.6(38)	-4.7(18)
C(36)	-0.01896(38)	-0.17592(25)	0.50456(54)	79.3(37)	40.2(16)	175.8(73)	4.0(19)	16.5(43)	-6.6(27)

[A] ESTIMATED STANDARD DEVIATIONS IN THE LEAST SIGNIFICANT FIGURE(S) ARE GIVEN IN PARENTHESES IN THIS AND ALL SUBSEQUENT TABLES. [B] THE FORM OF THE ANISOTROPIC THERMAL ELLIPSOID IS: $EXP[-(B11H^2+B22K^2+B33L^2+2B12HK+2B13HL+2B23KL)]$. THE QUANTITIES GIVEN IN THE TABLE ARE THE THERMAL COEFFICIENTS X 10^4.

every 100 reflections. The deviations of these standards were all within counting statistics.

The data were processed as previously described[6,7] using a value of 0.04 for p. Of the 6662 reflections measured, 6299 were unique and of these 3971 have $F_o^2 > 3\sigma(F_o^2)$. The data were corrected for absorption,[8] using a linear absorption coefficient of 29.11 cm^{-1}. The transmission factors ranged from 0.583 to 0.680.

Solution and Refinement of Structure. A sharpened, origin removed, Patterson map was calculated but the solution obtained from this map would not refine. Because of a nonstatistical distribution of the $|E|$'s, they were separated into two classes, i.e., $h + k + l$ even and $h + k + l$ odd. These two classes were separately rescaled such that $\langle E^2 \rangle = 1.0$ for each set. The top 200 $|E|$'s from each class were used in the direct methods program MULTAN. An $|E|$ map constructed from the solution with the highest figure of merit showed the position of the vanadium, oxygen, four nitrogen, and 20 carbon atoms. A least-squares refinement of the above atoms followed by a difference Fourier map clearly displayed the positions of the eight ethyl groups.

The structure was refined using full-matrix least-squares techniques. Initially the quantity minimized was $\Sigma w(|F_o| - |F_c|)^2$ where $|F_o|$ and $|F_c|$ are the observed and calculated structure amplitudes and where the weights, w, are taken as $4F_o^2/\sigma^2(F_o^2)$. In the final two cycles of refinement the quantity minimized was $\Sigma w(F_o^2 - F_c^2)^2$ and $w = 1/\sigma^2(F_o^2)$. The agreement indices are defined as $R = \Sigma|F_o^2 - F_c^2|/\Sigma F_o^2$ and $R_w = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w F_o^4]^{1/2}$. For refinements on $|F_o|$ the agreement indices are $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w F_o^2]^{1/2}$. Atomic scattering factors were taken from Cromer and Waber's tabulation.[9] The anomalous dispersion terms for V were included in F_c[10]. After the penultimate cycle of anisotropic least-squares refinement the positions of all hydrogen atoms, including those on the methyl groups, could be readily located. These positions were idealized, using C–H = 0.95 Å, and the fixed contributions of these atoms were included in the last cycle of refinement. The final agreement indices, based on refinement of F_o^2 with 6482 reflections (including $F_o^2 \leq 0$) and 379 variables, are $R = 0.084$ and $R_w = 0.16$. The conventional agreement index on F_o for $F_o^2 > 3\sigma(F_o^2)$ is 0.060.

An analysis of $\Sigma w(F_o^2 - F_c^2)^2$ as a function of F_o^2, setting angles, and Miller indices shows no unusual trends. The standard deviation of an observation of unit weight is 1.71 e^2. A final difference Fourier synthesis is essentially featureless with the highest peak equal to 0.74 (7) e/Å^3. A listing of the observed and calculated structure amplitudes (×10) for those data used in the refinement is given in Table I.[11] Entries with $F_o < 0$ are for those reflections having $F_o^2 < 0$.

The final atomic parameters and their errors are listed in Table II. The atomic parameters for all the hydrogen atoms are given in Table III.

Discussion

The numbering scheme employed in this paper is shown in Figure 2. Figure 3 is a stereoview of the unit cell and Figure 4 shows a stereoview of a VO(OEP) molecule. Table IV gives

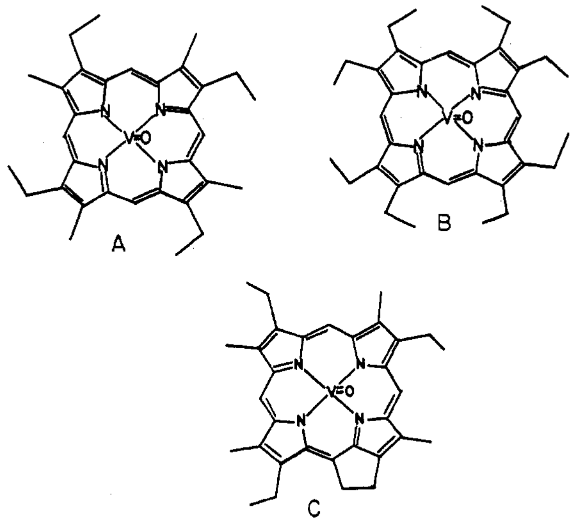

Figure 1. (A) Vanadyl etioporphyrin I, (B) vanadyl octaethylporphyrin, (C) vanadyl deoxophylloerythroetioporphyrin (VO(DPEP)).

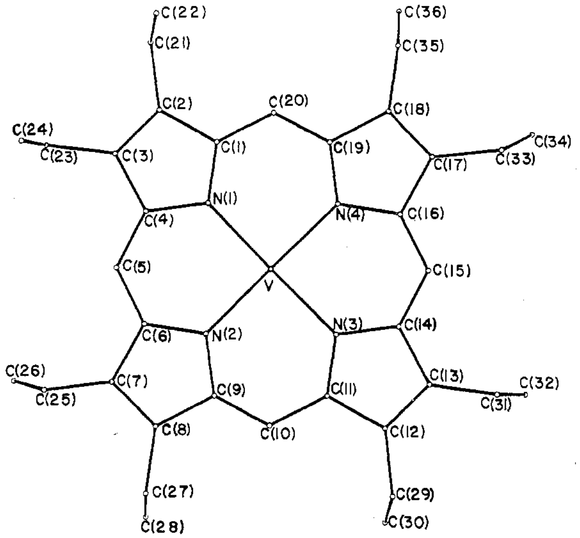

Figure 2. A sketch of the VO(OEP) molecule showing the labeling scheme.

the bond distances and angles within the molecule. Figure 5 shows the inner coordination sphere around the vanadium atom.

Table III. Atomic Coordinates for the Hydrogen Atoms

Atom	x	y	z
C(5)-H	−0.110	0.194	0.787
C(10)-H	−0.516	0.165	0.388
C(15)-H	−0.426	−0.095	0.310
C(20)-H	−0.009	−0.059	0.671
C(21)-H(1)	0.135	−0.009	0.760
C(21)-H(2)	0.174	0.045	0.850
C(23)-H(1)	0.137	0.142	0.883
C(23)-H(2)	0.053	0.186	0.847
C(25)-H(1)	−0.293	0.310	0.733
C(25)-H(2)	−0.205	0.274	0.816
C(27)-H(1)	−0.514	0.251	0.515
C(27)-H(2)	−0.443	0.298	0.593
C(29)-H(1)	−0.702	0.061	0.210
C(29)-H(2)	−0.661	0.114	0.302
C(31)-H(1)	−0.590	−0.083	0.240
C(31)-H(2)	−0.669	−0.036	0.194
C(33)-H(1)	−0.054	−0.160	0.687
C(33)-H(2)	−0.120	−0.207	0.595
C(35)-H(1)	−0.284	−0.219	0.476
C(35)-H(2)	−0.373	−0.185	0.392
C(22)-H(1)	0.121	0.007	1.037
C(22)-H(2)	0.076	−0.045	0.946
C(22)-H(3)	0.187	−0.038	0.992
C(24)-H(1)	0.120	0.171	1.096
C(24)-H(2)	0.009	0.168	1.049
C(24)-H(3)	0.069	0.111	1.075
C(26)-H(1)	−0.122	0.293	0.647
C(26)-H(2)	−0.212	0.323	0.552
C(26)-H(3)	−0.158	0.352	0.691
C(28)-H(1)	−0.386	0.298	0.370
C(28)-H(2)	−0.488	0.274	0.305
C(28)-H(3)	−0.476	0.335	0.375
C(30)-H(1)	−0.589	0.145	0.115
C(30)-H(2)	−0.649	0.097	0.022
C(30)-H(3)	−0.701	0.149	0.073
C(32)-H(1)	−0.645	−0.078	−0.011
C(32)-H(2)	−0.606	−0.015	−0.006
C(32)-H(3)	−0.535	−0.067	0.037
C(34)-H(1)	0.028	−0.206	0.536
C(34)-H(2)	−0.050	−0.183	0.408
C(34)-H(3)	0.019	−0.140	0.506
C(36)-H(1)	−0.317	−0.242	0.239
C(36)-H(2)	−0.302	−0.178	0.205
C(36)-H(3)	−0.216	−0.214	0.289

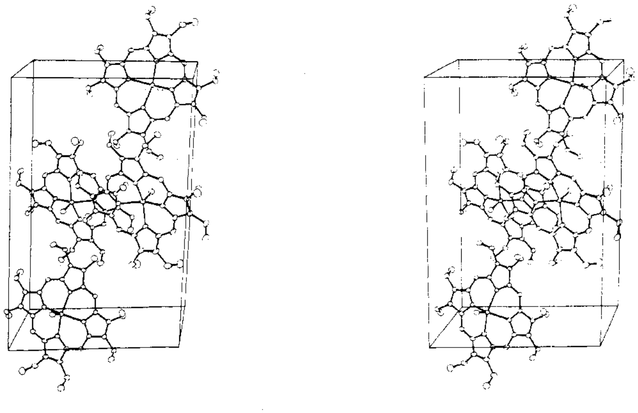

Figure 3. Stereoview of a unit cell of VO(OEP). The x axis is horizontal to the right, the y axis is vertical, and the z axis is perpendicular coming toward the reader. The vibrational ellipsoids are drawn at the 20% probability level. All the hydrogen atoms have been omitted.

The V(IV) atom is five coordinate (Figure 5) and is displaced out of the plane of the porphyrin toward the axially bound oxygen atom. The vanadium atom is displaced 0.543 Å from the mean plane of the four nitrogen atoms and 0.591 Å from the mean plane of the porphyrin core (Table V). This distance is in the range 0.48–0.72 Å predicted by Extended Hückel Molecular Orbital Calculations performed by Zerner and Gouterman.[12] A comparison with other vanadyl structures (Table VI) shows that this distance is typical of five-coordinate vanadium complexes. For example, in tetrasodium divanadyl(IV)-D-tartrate-L-tartrate dodecahydrate,[13] $Na_4(VO\text{-}DL\text{-}C_4H_2O_6)_2 \cdot 12H_2O$, the vanadium atom is 0.546 Å above the plane of the four oxygen atoms. However, we see that the vanadium atom is farther out of the plane in the OEP structure than in the DPEP structure. Originally it was proposed[14] that the vanadium atom should be closer to the plane in DPEP than in other vanadyl structures because in DPEP the vanadium atom is bonded to four nitrogen atoms whereas in other then known structures the vanadium atom was bonded to four oxygen atoms or at the most to two nitrogen and two oxygen atoms. It was thought that the V–N interaction was stronger than the V–O interaction. But in the present structure the vanadium atom is also bonded to four nitrogen atoms and it is as far out of the plane as in most of the other vanadyl complexes. Since the DPEP porphyrin is unsymmetrical there may be steric factors that cause the vanadium to be closer to the plane.

Table IV. Selected Bond Distances (Å) and Angles (deg) in VO(OEP)

V-O	1.620 (2)		
V-N(1)	2.097 (3)	V-N	2.102 (6)[a]
V-N(2)	2.102 (3)		
V-N(3)	2.099 (3)		
V-N(4)	2.110 (3)		
N(1)-C(1)	1.374 (4)	N-C_a[b]	1.379 (5)
N(1)-C(4)	1.380 (4)		
N(2)-C(6)	1.377 (4)		
N(2)-C(9)	1.381 (4)		
N(3)-C(11)	1.375 (4)		
N(3)-C(14)	1.380 (4)		
N(4)-C(16)	1.391 (4)		
N(4)-C(19)	1.379 (4)		
C(1)-C(2)	1.441 (5)	C_a-C_b	1.447 (6)
C(3)-C(4)	1.450 (4)		
C(6)-C(7)	1.446 (4)		
C(8)-C(9)	1.453 (4)		
C(11)-C(12)	1.444 (4)		
C(13)-C(14)	1.440 (5)		
C(16)-C(17)	1.442 (5)		
C(18)-C(19)	1.458 (5)		
C(2)-C(3)	1.357 (5)	C_b-C_b	1.358 (5)
C(7)-C(8)	1.355 (5)		
C(12)-C(13)	1.364 (5)		
C(17)-C(18)	1.358 (5)		
C(1)-C(20)	1.398 (5)	C_a-C_m	1.387 (7)
C(4)-C(5)	1.387 (4)		
C(5)-C(6)	1.386 (5)		
C(9)-C(10)	1.380 (4)		
C(10)-C(11)	1.395 (4)		
C(14)-C(15)	1.389 (5)		
C(15)-C(16)	1.376 (5)		
C(19)-C(20)	1.389 (5)		
N(1)-C(1)-C(20)	124.0 (3)	N-C_a-C_m	124.3 (3)
N(1)-C(4)-C(5)	124.5 (3)		
N(2)-C(6)-C(5)	124.3 (3)		
N(2)-C(9)-C(10)	124.5 (3)		
N(3)-C(11)-C(10)	124.3 (3)		
N(3)-C(14)-C(15)	123.9 (3)		
N(4)-C(16)-C(15)	124.3 (3)		
N(4)-C(19)-C(20)	124.3 (3)		
C(4)-C(5)-C(6)	127.4 (3)	C_a-C_m-C_a	127.4 (5)
C(9)-C(10)-C(11)	127.2 (3)		
C(14)-C(15)-C(16)	128.0 (3)		
C(19)-C(20)-C(1)	126.8 (3)		
N(1)-C(1)-C(2)	110.7 (3)	N-C_a-C_b	110.0 (4)
N(1)-C(4)-C(3)	109.9 (3)		
N(2)-C(6)-C(7)	109.9 (3)		
N(2)-C(9)-C(8)	109.6 (3)		
N(3)-C(11)-C(12)	110.3 (3)		
N(3)-C(14)-C(13)	110.4 (3)		
N(4)-C(16)-C(17)	109.6 (3)		
N(4)-C(19)-C(18)	109.6 (3)		
C(1)-C(2)-C(3)	106.7 (3)	C_a-C_b-C_b	107.0 (3)
C(4)-C(3)-C(2)	107.0 (3)		
C(8)-C(7)-C(6)	107.2 (3)		
C(7)-C(8)-C(9)	106.9 (3)		
C(11)-C(12)-C(13)	106.9 (3)		
C(12)-C(13)-C(14)	106.7 (3)		
C(16)-C(17)-C(18)	107.6 (3)		
C(17)-C(18)-C(19)	106.9 (3)		
C(20)-C(1)-C(2)	125.2 (3)	C_m-C_a-C_b	125.6 (3)
C(5)-C(4)-C(3)	125.5 (3)		
C(5)-C(6)-C(7)	125.7 (3)		
C(10)-C(9)-C(8)	125.8 (3)		
C(10)-C(14)-C(12)	125.4 (3)		
C(15)-C(14)-C(13)	125.6 (3)		
C(15)-C(16)-C(17)	126.1 (3)		
C(20)-C(19)-C(18)	125.9 (3)		
C(1)-C(2)-C(21)	125.7 (3)	C_a-C_b-C_α(Et)	125.2 (4)
C(4)-C(3)-C(23)	125.1 (3)		
C(6)-C(7)-C(25)	124.6 (3)		
C(9)-C(8)-C(27)	125.2 (3)		
C(11)-C(12)-C(29)	124.8 (3)		
C(14)-C(13)-C(31)	125.7 (3)		
C(16)-C(17)-C(33)	125.2 (4)		
C(19)-C(18)-C(35)	125.2 (4)		
C(2)-C(21)	1.501 (5)	C_b-C_α(Et)	1.512 (21)
C(3)-C(23)	1.509 (5)		
C(7)-C(25)	1.507 (5)		
C(8)-C(27)	1.489 (4)		
C(12)-C(29)	1.503 (5)		
C(13)-C(31)	1.503 (5)		
C(17)-C(33)	1.527 (5)		
C(18)-C(35)	1.558 (5)		
C(21)-C(22)	1.516 (6)	C_α(Et)-C_β(Et)	1.495 (22)
C(23)-C(24)	1.481 (6)		
C(25)-C(26)	1.508 (6)		
C(27)-C(28)	1.515 (5)		
C(29)-C(30)	1.512 (6)		
C(31)-C(32)	1.503 (6)		
C(33)-C(34)	1.461 (7)		
C(35)-C(36)	1.467 (6)		
N(1)-V-N(3)	150.2 (1)		
N(2)-V-N(4)	149.9 (1)		
N(1)-V-N(2)	86.4 (1)		
N(1)-V-N(4)	85.8 (1)		
N(2)-V-N(3)	86.2 (1)		
N(3)-V-N(4)	86.3 (1)		
C(1)-N(1)-C(4)	105.6 (3)	C_a-N-C_a	106.0 (4)
C(6)-N(2)-C(9)	106.3 (3)		
C(11)-N(3)-C(14)	105.7 (3)		
C(16)-N(4)-C(19)	106.3 (3)		
C(3)-C(2)-C(21)	127.5 (3)	C_b-C_b-C_α(Et)	127.7 (4)
C(2)-C(3)-C(23)	127.9 (3)		
C(8)-C(7)-C(25)	128.1 (3)		
C(7)-C(8)-C(27)	127.8 (3)		
C(13)-C(12)-C(29)	128.3 (3)		
C(12)-C(13)-C(31)	127.5 (3)		
C(17)-C(18)-C(35)	127.8 (3)		
C(18)-C(17)-C(33)	127.0 (3)		

[a] The figure in parentheses following an average value is the larger of that estimated for an individual value from the inverse matrix or on the assumption that the values averaged are from the same population. [b] The notation C_a, C_b, and C_m is that of J. L. Hoard, *Science*, 174, 1293 (1973).

The average V–N distance of 2.102 (6) Å is longer than that of 2.053 (9) Å found in *N,N'*-ethylenebis(acetylacetoneiminato)oxovanadium(IV),[15] VO($C_{12}H_{18}N_2O_2$). It is somewhat longer than that found in cobalt and iron porphyrins (e.g., Co(1-Me-Im)(OEP),[16] Co–N = 1.96 (1) Å, and FeCl(PP-IX),[17] Fe–N = 2.062 (10) Å). However, this V–N bond distance is smaller than the Ti–N distance of 2.111 (3) Å found in (α,γ-dimethyl-α,γ-dihydrooctaethylporphinato)oxotitanium(IV).[18] The V═O bond length of 1.620 (2) Å is very similar to those found in other structures (Table VI). The V═O vector is tilted 1.5° with respect to the normal to the porphyrin plane.

The bond distances within the porphyrin (Table IV) are similar to those observed in Co(3-Pic)$_2$(OEP),[19] Co(1-Me-Im)(OEP),[16] and Ni(OEP).[20,21]

A comparison of this structure with that of octaethylporphyrin[22] free base shows that the insertion of VO for H_2 has minimal effect on the geometry of the porphyrin core. Of course the porphyrin core is far less planar in the vanadyl complex (Table V).

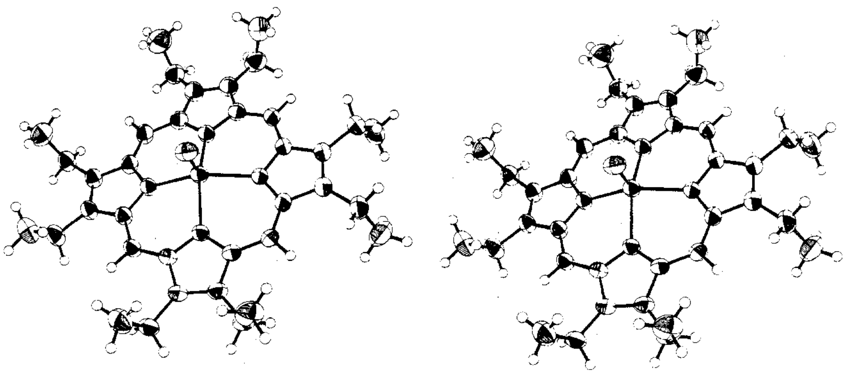

Figure 4. Stereoview of a VO(OEP) molecule. The vibrational ellipsoids are drawn at the 50% probability level, except for the hydrogen atoms.

Table V. Deviations A (×10^2) and Equations of Weighted Least-Squares Planes[a]

	Plane 1	Plane 2	Plane 3	Plane 4	Plane 5	Plane 6	Plane 7
V	61.6	59.1	54.3				
N(1)	3.4 (3)	1.6 (3)	0.4 (3)	0.4 (3)			
C(1)	11.8 (4)	8.8 (4)		−0.6 (4)			
C(2)	12.2 (4)	10.4 (4)		0.2 (4)			
C(3)	2.5 (4)	2.5 (4)		0.2 (4)			
C(4)	−4.0 (4)	−4.0 (4)		−0.6 (4)			
C(5)	−10.9 (4)	−9.3 (4)					
N(2)	1.4 (3)	1.5 (3)	−0.3 (2)		0.6 (3)		
C(6)	−8.9 (3)	−7.2 (3)			−0.9 (3)		
C(7)	−11.6 (4)	−8.2 (4)			0.6 (4)		
C(8)	−6.0 (3)	−3.1 (3)			−0.03 (34)		
C(9)	1.6 (4)	−2.5 (3)			−0.5 (3)		
C(10)	6.2 (4)	5.9 (4)					
N(3)	12.2 (4)	8.8 (3)	0.4 (3)			0.4 (3)	
C(11)	9.9 (4)	7.7 (4)				−0.7 (4)	
C(12)	5.0 (4)	1.7 (4)				0.6 (4)	
C(13)	1.4 (4)	−3.7 (4)				−0.2 (4)	
C(14)	6.0 (4)	0.8 (4)				−0.2 (4)	
C(15)	1.9 (4)	−4.9 (4)					
N(4)	12.7 (3)	7.4 (3)	−0.4 (3)				−0.9 (3)
C(16)	1.9 (4)	−5.1 (4)					1.4 (4)
C(17)	−11.8 (5)	−19.9 (5)					−0.8 (5)
C(18)	−15.4 (5)	−24.1 (5)					−0.6 (5)
C(19)	8.3 (4)	2.2 (4)					1.4 (4)
C(20)	13.5 (4)	8.5 (4)					
C(21)	19.4 (5)						
C(23)	2.2 (4)						
C(25)	−14.0 (4)						
C(27)	−3.4 (4)						
C(29)	4.3 (4)						
C(31)	−1.3 (4)						
C(33)	−34.9 (5)						
C(35)	−45.1 (5)						

Plane A	Plane B	Angle, deg	Plane A	Plane B	Angle, deg
2	1	0.8	2	7	7.9
2	3	1.3	4	5	4.1
2	4	3.6	4	7	11.0
2	5	3.0	5	6	6.1
2	6	3.1	6	7	5.8

Coefficients of the Plane Equation $Ax + By + Cz = D^b$

Plane	A	B	C	D	
1	7.685	5.661	−8.975	−6.605	Porphyrin + 8 α-C atoms
2	7.682	5.975	−8.935	−6.540	Porphyrin
3	7.832	6.347	−8.841	−6.463	Nitrogens
4	7.191	7.187	−8.885	−6.357	Pyrrole 1
5	8.049	6.771	−8.712	−6.405	Pyrrole 2
6	7.292	5.101	−9.141	−6.422	Pyrrole 3
7	7.709	2.877	−9.227	−6.510	Pyrrole 4

[a] The entries for which an error is not indicated are for atoms which were not included in the calculation of the plane. [b] The plane is in crystal coordinates as defined by W. C. Hamilton, *Acta Crystallogr.*, 18, 502 (1965).

There are small metrical differences between VO(OEP) and VO(DPEP). Whereas three of the V–N distances in VO(DPEP) average 2.10 Å, the same as in VO(OEP), the fourth is considerably shorter at 1.96 Å. This may be a reflection

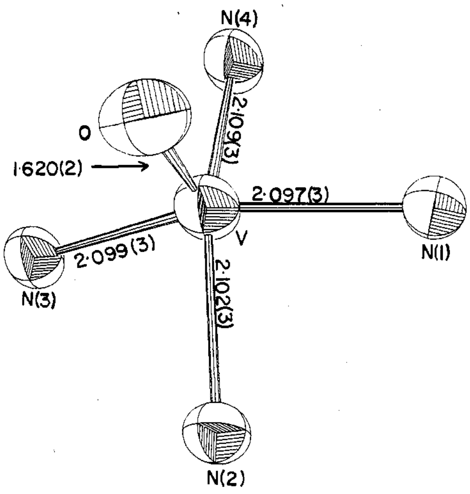

Figure 5. Perspective view of the inner coordination sphere around the vanadium atom in VO(OEP). The vibrational ellipsoids are drawn at the 50% probability level.

Table VI. Structural Data for Some Vanadyl Complexes

Compd	V=O, Å	V–basal plane, Å	Ref
VO(OEP)	1.620 (2)	0.543	*a*
$Na_4(VO\text{-DL-}C_4H_2O_6)_2$	1.62	0.546	*b*
VO(DPEP)	1.619 (7)	0.48	*c*
$VO(C_6H_5COCHCOCH_3)_2$	1.612 (10)	0.537	*d*
$VOCl_2(C_5H_{12}N_2O)_2$	1.61	0.502	*e*
$VO(C_{12}H_{18}N_2O_2)$	1.585	0.58	15
$VO(C_5H_7O_2)_2$	1.56	0.548	*f*

[a] This work. [b] R. E. Tapscott, R. L. Belford, and I. C. Paul, *Inorg. Chem.*, 7, 356 (1968). [c] R. C. Pettersen, *Acta Crystallogr., Sect. B,* **25**, 2527 (1969). [d] P. K. Hon, R. L. Belford, and C. E. Pfluger, *J. Chem. Phys.*, **43**, 1323 (1965). [e] J. Coltzer, *Acta Crystallogr., Sect. B*, **26**, 872 (1970). [f] R. P. Dodge, D. H. Templeton, and A. Zalkin, *J. Chem. Phys.*, **35**, 55 (1961).

of the unsymmetrical nature of the DPEP porphyrin.

The porphyrin itself is nonplanar, although as expected the individual pyrrole groups are planar within experimental error. The ruffling of the porphyrin core is not consistent with any of the idealized distortions.[23] We do observe a slight doming characteristic of five-coordinate metalloporphyrins.

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Registry No. VO(OEP), 27860-55-5.

Supplementary Material Available: Table I, a listing of structure amplitudes of octaethylporphinatooxovanadium(IV) (44 pages). Ordering information is given on any current masthead page.

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(8) The Northwestern absorption program AGNOST includes the Coppens–Leiserowitz–Rabinovich logic for Gaussian integration. In addition to local programs for the CDC 6400 computer, local modifications of the following programs were employed: Zalkin's FORDAP Fourier program, Johnson's ORTEP II thermal ellipsoid plotting program, Busing and Levy's ORFFE error function program, Dewar's program FAME for Wilson statistics and generation of normalized structure factors, and Main, Wolfson, and Germain's MULTAN direct methods program. Our full-matrix, least-squares program, NUCLS, in its nongroup form, closely resembles the Busing–Levy ORFLS program. Final calculations were carried out by remote hook-up to the Lawrence Berkeley Laboratory CDC 7600 computer. These same programs were used. The diffractometer was run under the disk-oriented system developed by P. G. Lenhert, *J. Appl. Crystallogr.*, **8**, 568 (1975).
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