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Synthesis and structural studies of early transition metalloporphyrin complexes. 1. X-ray structures of *meso*-5,10,15,20 tetratolyl hafnium(IV) μ-dioxo dimer complex and *meso*-5,10,15,20 tetratolyl porphyrin vanadium(IV) oxo complex

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Synthesis and structural studies of early transition metalloporphyrin complexes.1. X-ray structures of *meso*-5,10,15,20 tetratolyl hafnium(IV) μ-dioxo dimer complex and *meso*-5,10,15,20 tetratolyl porphyrin vanadium(IV) oxo complex

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(TTP) hafnium dichloride, 1, where TTP = *meso*-5,10,15,20 tetratolyl porphyrin dianion, has been synthesized and spectroscopically characterized as a precursor to 2. Hydrolysis of 1 gives (TTP) hafnium μ-dioxo dimer, 2. (TTP) vanadium oxo complex, 3, can be obtained by hydrolysis of the corresponding chloro complex. Compound 2 has been characterized by spectroscopic and single crystal X-ray diffraction analyses. $[(TTP)HfO]_2$·toluene crystalizes in the space group C2/c, a = 31.906(6) Å, b = 16.864(3) Å, c = 19.180(4) Å, β = 117.52(3)°, V = 9152(3) $Å^3$, d_{calcd} = 1.369 g/cm^3, Z = 8, 6029 unique observed reflections, final R = 0.077. The Hf atom is 1.02 Å from the plane of the porphyrin ring; Hf-O bond lengths are 2.1 Å. The hafnium atoms are 3.06(1) Å from each other and the average Hf-O-Hf angle is 94°. The porphyrin rings are 5.4° from being parallel and the distance between the centers of the porphyrin rings is ~5.1 Å. TTPVO·mesitylene, 3, crystallizes from mesitylene in the space group $P\bar{1}$, a = 8.365(2), b = 10.320(3), c = 14.380(5) Å, α = 91.91(3), β = 91.44(3), γ = 108.26(2)°, V = 1177.2(6) $Å^3$, d_{calcd} = 1.27 g/cm^3, Z = 1, 1851 observed unique reflections, final R = 0.069. The average V − N distance = 2.016 Å. The coordination geometry around the vanadium is distorted C_{4V}. The V = O group is disordered about the center of inversion. The vanadium atom resides 0.57 Å above the plane of the nitrogens. The (ring center) −V = O angle is 165.9° while the V = O vector is essentially colinear with the vector normal to the plane of nitrogens.

INTRODUCTION

There has been considerable interest in metal oxo complexes, and several types of terminal and bridging oxo compounds are known[1]. However, there have been very few cases of well characterized group IV oxo-bridged compounds reported[2]. Linear μ-oxo bridged complexes of the type $[\{MX(\eta\text{-}C_5H_5)_2\}_2O]$ (M = Zr or Hf; X = Cl, Me or C_6H_5) are known[2,3]. Although single MOM bridges may be bent or linear, in the cases of zirconium and hafnium complexes μ-oxo bridges are almost linear[3]. In the case of some homo- and hetero-binuclear metalloporphyrin complexes, linear M-O-M bridges are reported[4].

We report here in a non-linear binuclear μ-dioxo bridged hafnium porphyrin complex. To the best of our knowledge, this represents the first example of a structurally characterized symmetric μ-dioxo bridged dinuclear metalloporphyrin complex.

Recently, there has been considerable interest in studying cofacial dinuclear metalloporphyrin and bis porphyrin complexes as model compounds for bacterochlorophyll[5,6]. This special attention to the study of cofacial porphyrins has a twofold origin: (a) spectral properties of the complexes and their relationship to chlorophyll pair interactions and (b) metal-metal interaction[7]. Our bis hafnium μ-dioxo porphyrin complex, 2, represents a new case of a cofacial metalloporphyrin.

Vanadyl porphyrins have been the subject of much interest due to their presence in fossil fuels which poses problems when refining and burning high-vanadium-content fuels. Triebs postulated that the principal com-

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pound in geological samples is vanadyl deoxophyllo erythroetioporphyrin (DPEP) and developed a detailed scheme to point out how this compound was formed from chlorophyll[8,9]. X-ray structures of (DPEP)VO, (OEP)VO, (ETP)VO and (TPP)VO have been reported[10]. We report the X-ray structure of (TTP)VO which shows differences in some key bond distances from the reported values of a very closely related structure (TPP)VO (where TPP = *meso* 5,10,15,20 tetraphenyl porphyrin dianion)[11].

RESULTS AND DISCUSSION

(TTP)HfCl$_2$, **1**, [(TTP)HfO]$_2$, **2**, and (TTP)VO, **3**, are synthesized in good yields though no special effort was made to optimize any yields other than making sure visible spectra showed no unreacted porphyrin (limiting reagent) in the reaction mixture. Complexes **2** and **3** have been characterized by spectroscopic and single crystal X-ray diffraction analyses. Prior to the time of the symposium we had not succeeded in obtaining X-ray quality crystals for **1**.

Both the visible spectra and ^{1}H NMR of the hafnium μ-dioxo dimer, **2**, indicate the influence the porphyrin rings exert on one another, similar to what has been reported for the bisporphyrin complexes[5,6]. The visible spectra of complex **2** shows a blue-shifted Soret band at 406 nm, whereas the Soret band for the monomeric complex **1** is observed at 416 nm. The ^{1}H NMR of complex **2** shows the β-pyrrole signals at 8.4 ppm, which is ~0.6 ppm upfield from the monomeric complex **1**. The extent of the ring current in complex **2** is somewhat less than the reported Zr and Hf bisporphyrin TPP complexes where the β-pyrrole signals are observed at ~8.2 ppm. This can be rationalized by the fact that the rings are much closer to each other in these bis-porphyrin complexes and as a result the Soret bands are also more blue-shifted for these complexes. The FAB mass spectral data of **2**, shows a molecular ion peak at 1727.4 a.m.u., which agrees well with theoretical isotopic mass analysis for the formula [(TTP)HfO]$_2$ of 1726.47 a.m.u. Based on this and the X-ray analyses, we propose a μ-dioxo structure.

The X-ray analysis indicates doming and ruffling of the porphyrin ring towards the hafnium atom. The TTP rings are twisted with respect to each other by approximately 23.6°. The distance between the porphyrin ring centers is ~5.1 Å. The porphyrin rings are almost parallel, with an angle of 5.4° between the ring planes defined by the four nitrogens. The hafnium atoms are 1.02 Å away from the center of the plane of four nitrogens. The non-bonded distance between Hf and Hf#1 is 3.06 Å. One of the bridging oxygens (O2) is disordered and appears in two symmetry related positions, refined each as O2 and O2#1, with nearly 0.50 occupancy (O2 and O2#1 are related by the symmetry operation 1 − x, y, −3/2 − z). The Hf-O1-Hf#1 angle is 91° whereas the the disordered oxygen Hf-O2-Hf angle is 97°. The four-membered ring made up of [Hf-O1-Hf#1-O2] is puckered. It is interesting to note that the Hf-O-Hf angle in reported structures is almost linear[3]. Furthermore, the Hf-O bonds are longer than the reported Hf-O distances in $(Cp_2HfMe)_2O$[3]. The individual Hf-N distances are 2.26 to 2.28 Å, in good agreement with reported Hf-N single bonds[2]. The phenyl rings are close to being perpendicular to the plane of the ring (77–104° to the plane of the four nitrogens). The solvent molecule toluene was disordered and could not be refined and hence was treated as fixed ring during the least squares refinement.

A study of the reaction chemistry of complexes **1** and **2** is in progress. Preliminary results indicate the formation of air and moisture sensitive alkyl and alkoxide complexes from complex **1** upon reaction with alkyl lithium or lithium alkoxide. Cyclic voltammetry on these complexes is also currently in progress.[12]

In **3** the coordination geometry around the vanadium is distorted C_{4V}. The structure displays a center of symmetry in each unit cell at the center of the porphyrin ring. Since the complex cannot support such a symmetry element, the V = O group is disordered with the V atom 0.57 Å out of the plane of the nitrogens. The (ring center) −V = O angle is 165.9° while the V = O vector is essentially colinear with the vector normal to the plane of nitrogens. The four V − N distances are not identical: the V − N1 distance is 2.092 Å and the V − N2 distance is 2.236 Å (see Table 3). Comparison of the X-ray results of (TTP)VO, **3**, with the closely related reported (TPP)VO structure[11] indicates some interesting differences. Compound **3** crystallizes in a triclinic space group (P$\bar{1}$) whereas (TPP)VO crystallizes in I4/m. The V = O bond distance for complex **3**, 1.582(8) Å, is not significantly shorter than the 1.625(16) Å reported in (TPP)VO. The vanadium atom lies 0.57 Å out of the plane of the porphyrin ring for complex **3**, while the related distance for TPPVO is 0.53 Å. Though the V − N distances for **3** are unequal, the average is <3σ of the V − N distance in (TPP)VO [2.080(6) Å]. Furthermore, the V = O vector makes an angle of 1.3° with the normal to the porphyrin ring in keeping with the V = O vector being colinear with normal to the ring in reported TPPVO.

Due the paramagmetic nature of the complex, ^{1}H NMR did not give interpretable signals. Preliminary results indicate that the reaction of two equivalents of Grignard reagent with **3** results in a (TTP) V − R type of complex, where R = phenyl or phenylacetylide. This is in agreement with literature results for a tetra-aza annu lene vanadyl complex[13]. We are currently continuing further studies in these alkyl complexes.

MATERIALS AND METHODS

All reactions and manipulations were performed under air or dry nitrogen using Schlenk techniques. Petroleum ether and THF (Fisher) were dried over Na/K benzophenone ketyl and freshly distilled before use, CH_2Cl_2 was dried and distilled over CaH_2 before use, DMF (ACS certified, Aldrich) and 1,2,4 trichlorobenzene (ACS certified, Aldrich) were dried over 4Å Molecular Sieves prior to use. Anhydrous VCl_3 and $HfCl_4$ were purchased from Strem chemicals and used without further purification. $TTPH_2$ was synthesized by a literature method[14]. ^1H NMR spectra were recorded on a Varian XL-200 spectrometer, at 200 MHz field strenght, in $CDCl_3$ at room temperature. Visible spectra were recorded by a Beckman DU-70 spectrophotometer at room temperature as a CH_2Cl_2 solution. Elemental analyses were done by Onieda Research Labs, Whitesboro, NY. FAB mass spectra were run at the University of Illinois-Urbana mass-spectrometry lab.

Synthesis of $TTPHfCl_2$, **1**: 0.41 g (0.61 mmol) of $TTPH_2$ and 0.40 g (1.2 mmol) of anydrous $HfCl_4$ were refluxed in 1,2,4 trichlorobenzene under nitrogen for 48 hrs. The metal insertion was monitored by visible spectra and was found to be complete at the end of this time. Solvent was removed under reduced pressure from the resulting moisture and air sentitive solution to give an oily deep red mass. This oily mass was washed with petroleum ether and extracted with 5 × 20 mL of CH_2Cl_2. The resulting CH_2Cl_2 solution was passed through a 2.5 × 5 cm basic alumina column under nitrogen. Removal of the solvent from the eluent gave 0.24 g (isolated yield of 39.3% based on porphyrin). Vis: λ_{max} = 416 (Soret), 538 nm. ^1H NMR $CHCl_3$, 9.1 (s, 8, β-pyrrole), 8.4 and 8.2 (broad unresolved peaks, 16), 2.68 (s, 12, CH_3 p-tolyl). FAB MS: m/z 847.2 [(TTP)Hf] Anal. Calcd for $C_{48}H_{36}N_4Cl_2$: C, 62.77; H, 3.92; N, 6.10. Found C, 61.99; H, 4.50; N, 61.5.

Synthesis of $[TTPHfO]_2$ **2**: This compound can be synthesized in several ways. Hydrolysis of $(Por)HfCl_2$, $(Por)HfR_2$ or $(Por)Hf(OR)_2$ can be used, where, por = a porphyrin dianion. However, hydrolysis of $(Por)HfCl_2$, **1**, probably represents the most straightforward synthesis. 0.20g of **1** (0.21 mmol) in 1,2,4-trichlorobenzene was refluxed in open air and slowly cooled. The solvent was removed under reduced pressure to give a maroon-red oily mass. This was extracted in CH_2Cl_2 and passed through a dry basic alumina column and rinsed with 5% methanol in CH_2Cl_2. Evaporation of solvent resulted in 0.12 g of maroon-red color product (isolated yield = 61 %). ^1H NMR $CHCl_3$, δ 8.40 (s, 16, β-pyrrole), 7.55 and 7.37 (broad unresolved peaks, 32), 2.664 (s, 24, CH_3 p-tolyl). FAB MS: m/z 1727.4 a.m.u [molecular ion peak $(TTPHfO)_2$]. Vis Spec λ_{max} = 406, 539 nm.

Table 1 Selected crystal data and structure refinement for **2** and **3**

Molecular formula	$[TTPHfO]_2 \cdot C_7H_8$	$TTPVO \cdot C_9H_{12}$
Crystal system	Monoclinic	Triclinic
Space group	C2/c	$P\bar{1}$
a(Å)	31.906(6)	8.365(2)
b(Å)	16.864(3)	10.320(3)
c(Å)	19.180(4)	14.380(5)
V(Å^3)	9152(3)	1177.2(6)
α	90	91.91(3)
β	117.52(3)	91.44(3)
γ	90	108.26(2)
Z	8	1
Density (calculated) Mg/m^3	1.369	1.207
wavelength (λÅ)	0.71073	1.5418
Scan Type	ω-2θ	ω-2θ
Total number of independent reflections	6029	2958
Crystal size (mm)	0.56 × 0.44 × 0.39	0.19 × 0.14 × 0.14
θ range for data collection	1.41 to 22.55°	3.07 to 55°
data/restraints/parameters	6025/9/487	2958/0/307
Final R	0.077 [I > 2σ(I)]	0.069 [I > 3σ(I)]

Synthesis of TTPVO, **3**: 1.11g (7 mmol) of anhydrous vanadium trichloride was added to a boiling solution of 1.50g (2.2 mmol) of $TTPH_2$ in 130 mL of DMF. This solution was refluxed for four days and metal insertion was monitored by visible spectra. At the end of this period, visible spectra indicated no free base porphyrin present. The workup consisted of removing the DMF under reduced pressure. The solid red mass obtained was washed repeatedly with petroleum ether (5 × 20 mL) and chromatographed on a 2.5 × 25 cm column(neutral alumina, activity one). Pure TTPVO was obtained by CH_2Cl_2 elution. Removal of the CH_2Cl_2 solution provided 1.403 g of purple red product (75.5% based on porphyrin). Vis (CH_2Cl_2) λ_{max} = 423 (Soret), 548 nm. ^1H NMR ($CDCl_3$) δ 10-8 (br unresolved lines, 24, β pyrrole and aromatic), 2.3 (br s, 12, CH_3 p-tolyl). Anal. Calcd for $C_{48}H_{36}N_4VO \cdot 1/2$ DMF: C, 77.0; H, 8.10; N, 5.31. Found: C, 77.3; H, 8.00; N, 5.21.

X-ray Crystal structure determination

X-ray diffraction data was collected on a Siemens P3 automated diffractometer at 20°C using Mo Kα radiation for $[(TTP)HfO]_2$, **2**, and Cu Kα graphite-monochromated radiation for TTPVO, **3**. Crystallographic data are summarized in *Table 1*.

Single crystals of $[TTPHfO]_2 \cdot C_7H_8$, **2**, were obtained by slow evaporation of a toluene solution at room temperature. The structure of **2** was solved by the SHELXTL PC^{TM} software package[15]. The Hf and most C positions were initially found; subsequent non-hydrogens were found from difference maps. The structure was refined by full-matrix least-squares based on F^2. All non-hydrogens, except those of the toluene, were refined anisotropically. Hydrogen positions were incorporated at their calculated positions (C-H = 1.00 Å) and were not refined. There is a disordered toluene (solvent)

Table 2 Selected Interatomic Distances (Å) and angles (°) for $[(TTP)HfO]_2$. Toluene

Hf-O(2)#1	2.02(11)	Hf-O(2)	2.07(12)
Hf-O(1)	2.15(9)	Hf-N(2)	2.26(10)
Hf-N(3)	2.26(9)	Hf-N(1)	2.27(9)
Hf-N(4)	2.28(10)	Hf-Hf#1	3.06(1)
O(1)-Hf#1	2.15(9)	O(2)-Hf#1	2.02(11)
O(2)#1-Hf-O(2)	74(9)	O(2)#1-Hf-O(1)	71(5)
O(2)-Hf-)(1)	70(5)	N(2)-Hf-N(3)	79(3)
N(3)-Hf-N(1)	126(3)	N(3)-Hf-N(4)	78(4)
N(2)-Hf-N(4)	127(4)	N(1)-Hf-N(4)	77(3)
Hf-O(1)-Hf#1	*91(5)*	*Hf#1-O(2)-Hf*	*97(5)*

Symmetry transformations used to generate equivalent atoms:
#1 −x + 1, y, −z + 3/2

molecule in the unit cell which was treated as fixed in the final refinement cycle. Selected distances and angles are given in *Table 2*. A thermal ellipsoid plot of this molecule is given in Figure 1.

Table 3 Selected Interatomic Distances (Å) and angles (°) for (TTP)VO:Mesitylene

V-O	1.582(8)		
V-N1	2.092(5)	V-N1[a]	2.103(5)
V-N2	2.236(6)	V-N2[a]	1.940(5)
N1-C2	1.380(7)	N1-C5	1.386(7)
N1-V-O	105.1(3)	N2-V-O	105.8(3)
N1-V-N2	82.1(2)	V-N1-C5	122.6(3)
V-N1-C2	129.8(4)	V-N2-C7	125.6(5)

[a] Through inversion: 1 − x, 1 − y, 1 − z

A single crystal of $(TTP)VO{\cdot}C_9H_{12}$, 3, was obtained by slow evaporation of a 1:1 solution CH_2Cl_2 and mesitylene at room temperature. The structure was solved by direct method [MULTAN 76][16]. Aromatic hydrogen positions were set to 1.00 Å from the respective C, alkyl hydrogens, in tetrahedral positions at 1.10 Å. Refinement was done a full-matrix least-squares procedure[17] minimizing $\Sigma\omega(|F_o|-|F_c|)^2$, where $w = 1/\sigma^2(F)$. Anisotropic thermal parameters were used for all nonhydrogen atoms and hydrogen atoms were assigned isotropic thermal parameters. Selected distances and angles are given in *Table 3*. and a thermal ellipsoid plot (ORTEP)[18] of this molecule is shown in Figure 2.

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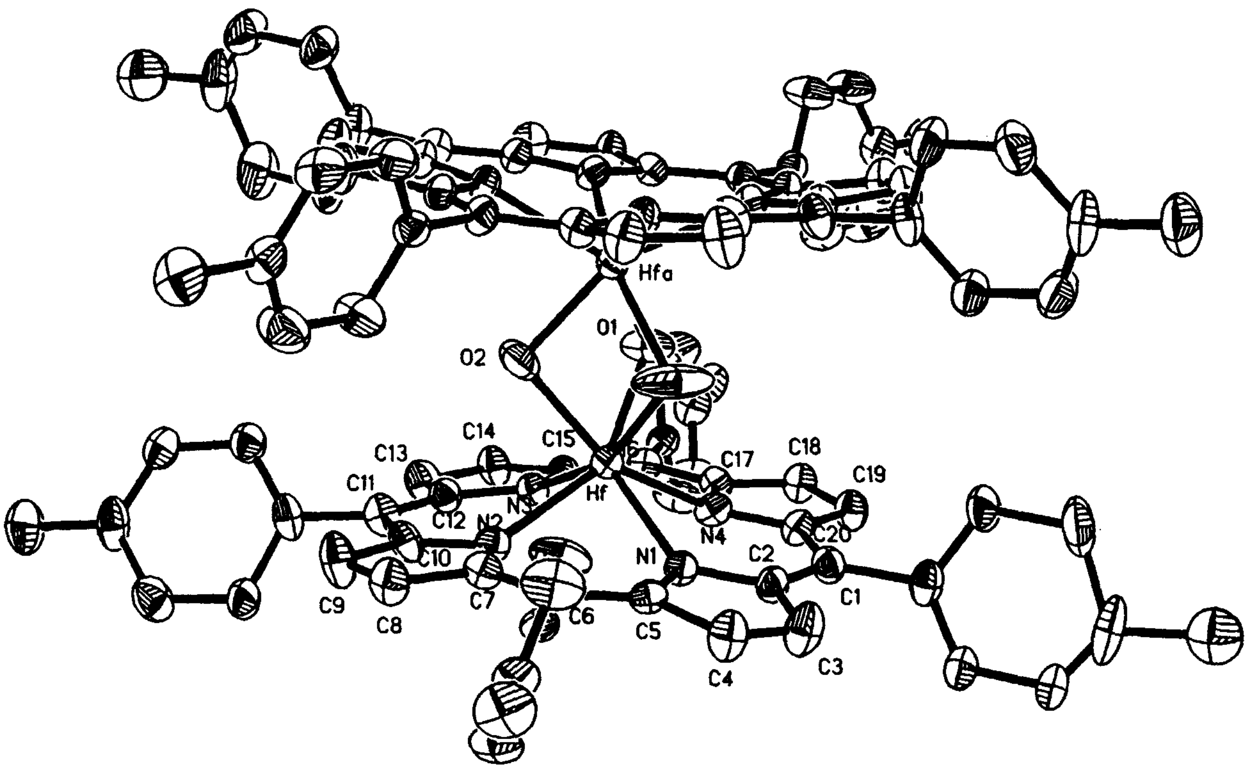

Figure 1 Structure of $[(TTP)HfO)]_2$, **2** with atom labels (20% thermal ellipsoids).

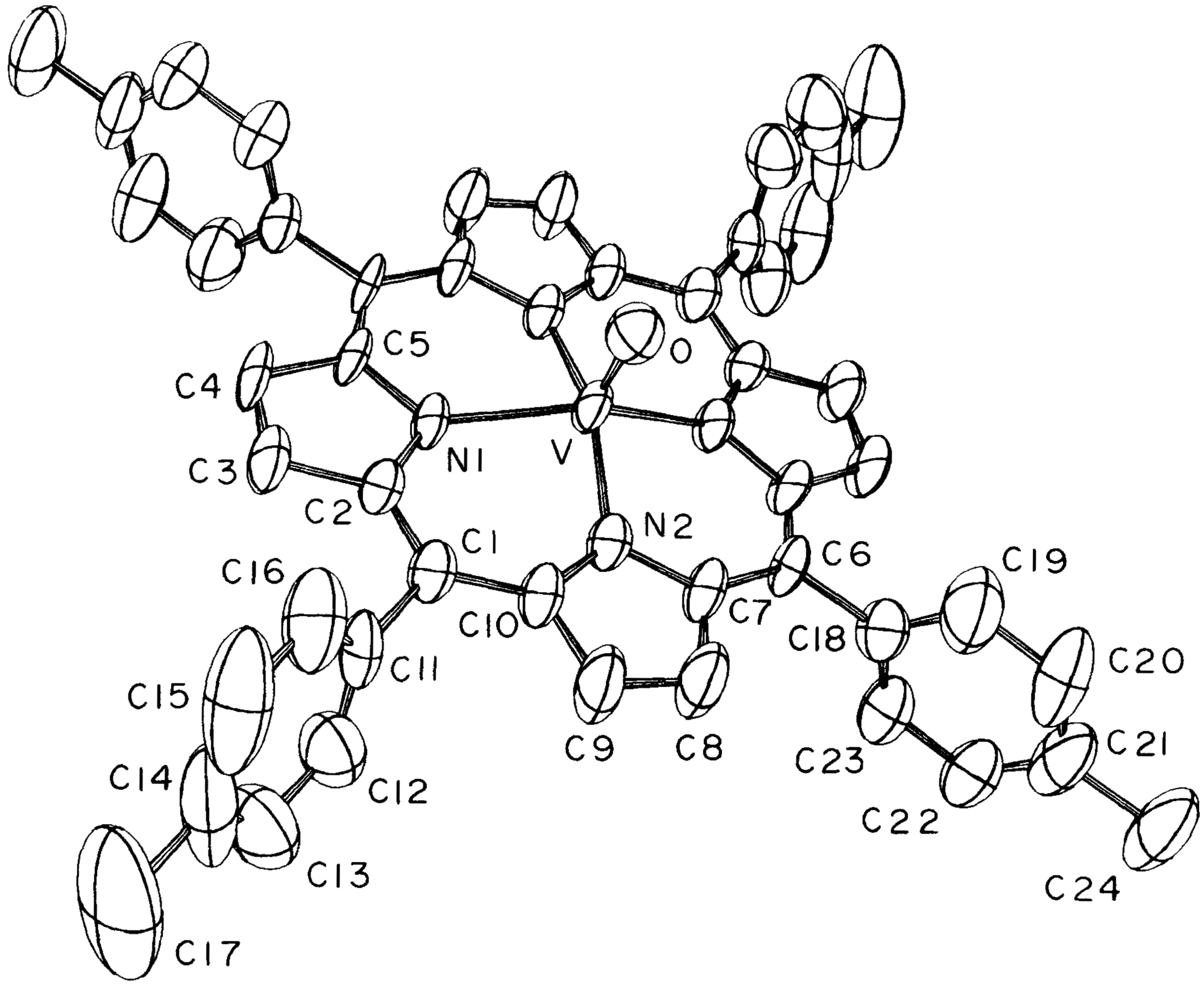

Figure 2 Structure of (TTP)VO, **3** with atom labels (50% thermal ellipsoids).

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