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Crystal Structure of 5,10,15,20-Tetramethyl-21*H*,23*H*-porphine Vanadium(IV) Oxide

Shinsuke SHIMIZU,*, Takamitsu FUKUDA,** Nagao KOBAYASHI,** and Koichi SAITOH*,†**

**Center for the Advancement of Higher Education, Tohoku University, Sendai 980-8576, Japan*
***Department of Chemistry, Graduate School of Science, Tohoku University, Sendai 980-8578, Japan*

The crystal structure of 5,10,15,20-tetramethyl-21*H*,23*H*-porphine vanadium(IV) oxide, VO(TMP), has been determined. Monoclinic, $P2_1/a$, a = 14.298(5), b = 13.445(4), c = 19.895(6)Å, β = 97.487(2). Z = 8, $C_{24}H_{20}N_4OV$.

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Various kinds of vanadyl porphyrin (VOpor) are found in nature within petroleum deposits, shales, and bitumens.[1] Most of them are believed to be derived from ancient chlorophylls. Structural elucidation and an understanding of the global distribution of these complexes would enhance the amount of information obtained from the analysis of VOpor during environmental monitoring.[2] In this study, we succeeded to obtain the crystal structure of 5,10,15,20-tetramethyl-21*H*,23*H*-porphine vanadium(IV) oxide, VO(TMP) (Fig. 1).

VO(TMP) was prepared according to a general method reported by Adler *et al.*[3] from metal-free 5,10,15,20-tetramethyl-21*H*,23*H*-porphine (H_2TMP),[4] followed by purification based on reversed-phase column chromatography (Wakosil 40C18, WAKO, Osaka, Japan/CH_3CN–H_2O 80:20 (v/v)) and recrystallizations from DMF/H_2O. MS (ESI) (*m*/*z*): 454 (M+Na, calcd for $C_{24}H_{20}N_4OVNa$). Single crystals suitable for X-ray analysis were obtained by the slow diffusion of methanol into a solution of VO(TMP) in dichloroethane.

The crystal and experimental data of the compound are given in Table 1. The structure was solved by a direct method and refined by full-matrix least squares to a final reliability value of 0.054. The non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were refined isotropically. The atomic coordinates of the non-hydrogen atoms are given in Tables 2 and 3.

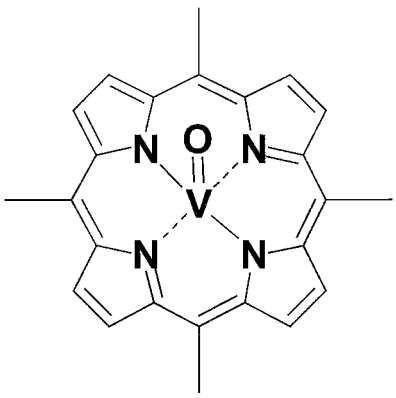

Fig. 1 Structure of VO(TMP).

†To whom correspondence should be addressed.
E-mail: saitoh@high-edu.tohoku.ac.jp

There are two molecules in an asymmetric unit. Their structures are essentially the same. Figure 2 shows ORTEP diagrams of VO(TMP). The V(IV) atom is penta-coordinated with a pseudo square pyramidal geometry, based on four pyrrole nitrogens in the porphyrin macrocycle and the terminal oxygen. The V atom lies (*ca*. 0.49 Å for V2) above the mean plane, defined by the four pyrrole nitrogens. The V–O vector is normal to this plane. The V=O bond length and the V–N distances are comparable to data reported previously for VOpors.[5] A dome-type deformation of the porphyrin ligand was observed, which

Table 1 Crystal and experimental data

Formula: $C_{24}H_{20}N_4OV$
Formula weight = 431.39
Temperature: 223 K
Crystal size: $0.20 \times 0.15 \times 0.10$ mm^3
Crystal color: deep purple
Crystal description: platelet
Crystal system: monoclinic
Space group: $P2_1/a$
a = 14.298(5)Å
b = 13.445(4)Å
c = 19.895(6)Å
β = 97.487(2)°
V = 3792(2)Å^3
Z = 8
Density(calcd): 1.511 g cm^{-3}
Radiation: 0.7107 Å (Mo K_α)
R: 0.054
wR: 0.050
GOF: 1.576
$(\Delta\rho)_{max}$ = 0.38
$(\Delta\rho)_{min}$ = –0.32
No. of reflections collected = 36358
No. of unique reflections = 8484
No. of reflections with $I > 3\sigma(I)$ = 3419
No. of parameters = 541
Diffractometer: Rigaku/MSC Mercury CCD
Monochrometer: graphite
Structure determination: Crystal Structure
Refinement: full-matrix least-squares on F^2

Table 2 Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$)

Atom	*x*	*y*	*z*	*U*(eq)
V(1)	5488.4(7)	1537.7(8)	4252.0(5)	36.0(3)
V(2)	1519.2(7)	553.2(8)	559.7(4)	28.4(3)
O(1)	6322(3)	2124(3)	3973(2)	40.8(13)
O(2)	2640(2)	568(3)	713(2)	32.4(11)
N(1)	4946(4)	2568(5)	4868(3)	62(2)
N(2)	4341(4)	1835(4)	3551(3)	46(2)
N(3)	5517(4)	158(4)	3809(3)	41(2)
N(4)	6100(4)	849(5)	5133(2)	52(2)
N(5)	1083(3)	1630(4)	1193(2)	28(2)
N(6)	1246(3)	1586(4)	-212(2)	30(2)
N(7)	1243(3)	-536(4)	-178(2)	33(2)
N(8)	1134(3)	-484(4)	1243(2)	32(2)
C(1)	4384(7)	3332(7)	4682(6)	87(4)
C(2)	3853(6)	3422(7)	4070(6)	74(3)
C(3)	3774(5)	2721(7)	3544(5)	65(3)
C(4)	3160(7)	2711(10)	2933(7)	122(5)
C(5)	3294(7)	1892(9)	2561(5)	97(4)
C(6)	4059(5)	1356(7)	2961(4)	61(3)
C(7)	4436(6)	487(8)	2745(3)	64(3)
C(8)	5127(6)	-70(6)	3133(4)	54(3)
C(9)	5483(7)	-967(8)	2932(5)	91(4)
C(10)	6102(6)	-1325(6)	3447(5)	78(3)
C(11)	6105(5)	-630(6)	4010(4)	58(3)
C(12)	6593(5)	-743(6)	4638(5)	63(3)
C(13)	6590(5)	-87(7)	5166(4)	59(3)
C(14)	7082(6)	-204(10)	5827(5)	115(5)
C(15)	6931(7)	632(10)	6190(4)	100(4)
C(16)	6320(6)	1266(9)	5763(4)	79(4)
C(17)	5971(8)	2133(10)	5955(5)	86(4)
C(18)	5339(7)	2763(7)	5572(5)	75(4)
C(19)	4920(10)	3647(9)	5754(6)	130(6)
C(20)	4343(9)	4035(8)	5230(7)	106(5)
C(21)	3212(6)	4335(7)	3891(7)	153(5)
C(22)	4046(7)	73(8)	2066(4)	132(4)
C(23)	7230(6)	-1647(7)	4800(5)	121(4)
C(24)	6288(7)	2559(10)	6677(4)	172(5)
C(25)	1050(4)	2641(5)	1074(3)	30(2)
C(26)	1171(4)	3117(5)	467(3)	36(2)
C(27)	1252(4)	2610(5)	-131(3)	32(2)
C(28)	1341(4)	3086(5)	-768(3)	43(2)
C(29)	1358(4)	2361(6)	-1227(3)	46(2)
C(30)	1312(4)	1422(5)	-889(3)	37(2)
C(31)	1351(4)	498(6)	-1190(3)	40(2)
C(32)	1304(4)	-418(5)	-863(3)	36(2)
C(33)	1331(4)	-1379(6)	-1169(3)	47(2)
C(34)	1293(4)	-2075(5)	-691(3)	46(2)
C(35)	1249(4)	-1550(5)	-62(3)	34(2)
C(36)	1225(4)	-2007(5)	559(3)	36(2)
C(37)	1174(4)	-1505(5)	1166(3)	36(2)
C(38)	1147(5)	-1974(5)	1812(3)	47(2)
C(39)	1066(5)	-1254(5)	2265(3)	48(2)
C(40)	1051(4)	-317(5)	1922(3)	37(2)
C(41)	943(4)	610(6)	2211(3)	36(2)
C(42)	933(4)	1511(5)	1862(3)	31(2)
C(43)	802(4)	2470(5)	2148(3)	42(2)
C(44)	877(4)	3161(5)	1682(3)	42(2)
C(45)	1177(5)	4243(5)	462(3)	53(2)
C(46)	1482(5)	467(6)	-1943(3)	65(3)
C(47)	1232(5)	-3142(5)	582(3)	54(2)
C(48)	790(5)	666(6)	2952(3)	55(2)

Table 3 Selected bond lengths [Å] and angles [°]

V(1)-O(1)	1.588(4)	O(1)-V(1)-N(1)	102.9(2)
V(1)-N(1)	2.055(7)	O(1)-V(1)-N(2)	103.7(2)
V(1)-N(2)	2.050(5)	O(1)-V(1)-N(3)	103.9(2)
V(1)-N(3)	2.057(5)	O(1)-V(1)-N(4)	105.3(2)
V(1)-N(4)	2.073(5)	N(1)-V(1)-N(2)	87.3(2)
V(2)-O(2)	1.592(3)	N(1)-V(1)-N(3)	153.2(2)
V(2)-N(5)	2.068(5)	N(1)-V(1)-N(4)	86.7(2)
V(2)-N(6)	2.069(5)	N(2)-V(1)-N(3)	86.7(2)
V(2)-N(7)	2.074(5)	N(2)-V(1)-N(4)	151.0(2)
V(2)-N(8)	2.071(5)	N(3)-V(1)-N(4)	86.0(2)
		O(2)-V(2)-N(5)	104.5(2)
		O(2)-V(2)-N(6)	102.8(2)
		O(2)-V(2)-N(7)	103.8(2)
		O(2)-V(2)-N(8)	103.3(2)
		N(5)-V(2)-N(6)	86.6(2)
		N(5)-V(2)-N(7)	151.7(2)
		N(5)-V(2)-N(8)	86.8(2)
		N(6)-V(2)-N(7)	87.0(2)
		N(6)-V(2)-N(8)	153.9(2)
		N(7)-V(2)-N(8)	86.9(2)

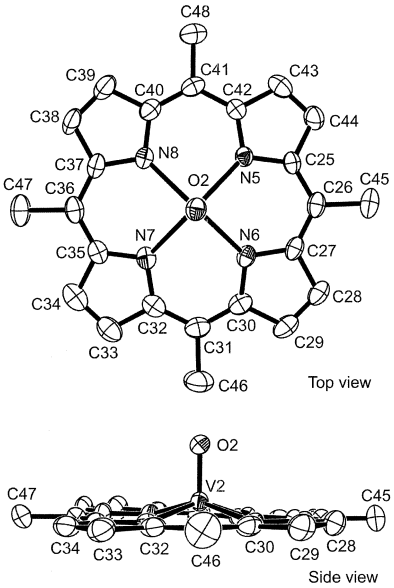

Fig. 2 ORTEP drawings of VO(TMP) with the atom labels. Displacement ellipsoids are shown at the 50% level. Hydrogen atoms are omitted for clarity.

is characteristic of penta-dentate metalloporphyrins. The *meso*-carbon atoms maintain a high degree of planarity.

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