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Crystal and Molecular Structure of a Natural Vanadyl Porphyrin

Sarah A. Miller, Trevor W. Hambley and John C. Taylor

Division of Energy Chemistry, CSIRO, Lucas Heights Research Laboratories,
Private Mail Bag 7, Sutherland, N.S.W. 2232.

Abstract

The crystal and molecular structure of a vanadyl deoxophylloerythroetioporphyrin (dpep) extracted from oil shale has been determined by single crystal X-ray diffraction. The compound crystallizes in space group $P2_1/c$ of the monoclinic system with four formula units in a cell of dimensions a 12·912(3), b 14·151(4), c 18·404(8) Å, β 70·34(2)°. Block matrix least-squares refinement gives a final R index of 0·077 for 2296 reflections. The planar molecules are packed almost parallel, with the chloroform solvent molecules lying between the planes and weakly associated with the vanadyl oxygen. The molecular structure establishes the presence of an isocyclic five-membered ring, which suggests that the molecule is a derivative of chlorophyll.

Introduction

The structure and chemistry of metal porphyrins are the subject of considerable interest and research. In particular, the vanadyl and nickel porphyrins found in petrochemical deposits such as crude oils and oil shales are a potential record of the origin and thermal history of these deposits. Despite the fact that porphyrin pigments were first isolated nearly 50 years ago,[1] their exact structures remain largely unknown. While it is generally agreed that the petroporphyrins represent the degradation products of chlorophyll,[2] this view has been questioned.[3]

Shale from the Julia Creek deposit (Toolebuc formation) in Queensland is known to contain high concentrations of porphyrins.[4,5] A vanadyl deoxophylloerythroetioporphyrin (dpep) has been extracted[6] from a sample of this shale and we report here its crystal and molecular structure as determined by single crystal X-ray diffraction.

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[1] Treibs, A., *Justus Liebigs Ann. Chem.*, 1934, **509**, 103.

[2] Baker, E. W., and Palmer, S. E., 'Geochemistry of Porphyrins' in 'The Porphyrins' (Ed. D. Dolphin) Vol. 1, p. 485 (Academic Press: New York 1978).

[3] Hodgson, G. W., and Whiteley, C. G., 'The Universe of Porphyrins' in the Proceedings of the Fourth International Symposium in Environmental Biogeochemistry, p. 35 (Springer: Berlin 1980).

[4] Saxby, J. D., and Riley, K. W., *Chem. Geol.*, 1982, **37**, 265.

[5] Ekstrom, A., Loeh, H. J., and Dale, L., in 'Erogmanga Basin Symposium, Summary Papers' (Compilers P. S. Moore and T. J. Mount) Geol. Soc. Aust. and Pet. Explor. Soc. Aust., Adelaide, 1982.

[6] Ekstrom, A., Fookes, C. J. R., Hambley, T. W., Loeh, H. J., Miller, S. A., and Taylor, J. C., *Nature (London)*, 1983, **306**, 173.

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Experimental

Crystallographic Data Collection

Crystals grown from chloroform form dark red prisms.[6] A crystal measuring 0·20 by 0·22 by 0·26 mm was mounted in a glass tube with epoxy resin. Weissenberg photography with Cu Kα radiation showed systematic absences consistent with $P2_1/c$. This was confirmed with the Lucas Heights Research Laboratories four-circle diffractometer. Lattice parameters were determined by a least-squares fit to the setting angles of 32 high angle reflections.

Crystal data.—$C_{33}H_{35}Cl_3N_4OV$, form. wt 644·97, monoclinic, space group $P2_1/c$; a 12·912(3), b 14·151(4), c 18·404(8) Å, β 70·34(2)°; D_c 1·353, D_o 1·37(2) g cm^{-3}; U 3166·7 Å^3; Z 4; μ(Mo Kα) 5·47 cm^{-1}, λ(Mo Kα) 0·7107 Å, F(000) 1372 electrons.

Intensity data were collected with Zr-filtered Mo Kα radiation on the four-circle diffractometer in the range $0 < 2\theta < 50°$. A reference reflection, measured after every 25 reflections, showed that no decomposition of the crystal occurred. 2925 non-zero independent reflections were collected of which 2296 with $I > 2\sigma(I)$ were retained for structure analysis. Lorentz polarization and absorption correction factors were applied during data reduction.*

Structure Determination and Refinement

The structure was solved by centrosymmetric direct methods which successfully located all non-hydrogen atoms. These were subsequently refined and assigned anisotropic thermal parameters. The hydrogen atoms were included assuming tetrahedral or trigonal geometry about their respective carbon atoms, with fixed C–H bond lengths of 0·97 Å. They were assigned group thermal parameters. Slight hydrogen disorder was apparent, but not investigated, for two ethyl groups. The chloroform solvent hydrogen was located in a difference map and was refined successfully.

Block matrix techniques were used to refine the scale factor and positional and thermal parameters. Overall refinement converged with R 0·077 and R_w 0·083.† At this stage the largest peak in the difference map was less than 0·6 e Å^{-3} in height and located in the vicinity of the solvent.

All scattering factors (neutral V for V^{IV}) and anomalous dispersion terms were taken from International Tables for X-ray Crystallography.[7] Final non-hydrogen atomic positional parameters are listed in Table 1. Thermal parameters, structure factors and calculated hydrogen coordinates have been deposited.‡ All calculations were performed by using the SHELX-76 program package.

Discussion of Structure

Although this molecule is chemically identical with that studied in the structural analysis of Petterson,[8] and the unit cell dimensions and space groups are very similar, the present crystal and that of Petterson are not isostructural as the molecules pack differently.

A stereo ORTEP plot of the crystal packing looking down the y axis is shown in Fig. 1. The planar molecules are packed in an almost parallel arrangement with the closest contact between planes whose vanadyl moieties are related as x, y, z (i) to $1-x,\ 1-y,\ 1-z$ (ii) being 3·531 Å [C(17)(i)–C(24)(ii)]. The closest contact between planes related as (i) to $1-x,\ y-\frac{1}{2},\ \frac{1}{2}-z$ (iii) is 3·595 Å [C(18)(i)–C(27)(iii)]. There is one chloroform molecule associated with each porphyrin and it lies above the plane with its hydrogen directed towards the vanadyl oxygen. The distance between

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* Programs used include local data reduction, structure determination and refinement (SHELX-76, by G. M. Sheldrick), thermal ellipsoid plot (ORTEP by C. K. Johnson) and least-squares plane determination (LSPLANE).

† $R = \Sigma(|F_o|-|F_c|)/\Sigma|F_o|$; $R_w = \Sigma[(|F_o|-|F_c|)w^{1/2}]/\Sigma(|F_o|w^{1/2})$ where $w = 1\cdot8093/(\sigma^2F_o+0\cdot00398F_o^2)$.

‡ Copies are available on request from the Editor-in-Chief, Editorial and Publications Services, CSIRO, 314 Albert Street, East Melbourne, Vic. 3002.

[7] 'International Tables for X-Ray Crystallography', Vol. 4, pp. 99, 149 (Kynoch Press: Birmingham 1974).

[8] Pettersen, R. C., *Acta Crystallogr., Sect. B*, 1969, **25**, 2527.

the oxygen and this hydrogen of 2·17 Å and the C(33)–H(33)–O angle of 159° are consistent with weak hydrogen bonding.

Table 1. Final positional parameters for refined atoms of vanadyl porphyrin

Atom	10^4x	10^4y	10^4z	Atom	10^4x	10^4y	10^4z
V	4176(1)	5884(1)	1411(1)	C(17)	6649(5)	6407(4)	1681(3)
O	3400(3)	5798(2)	2281(2)	C(18)	6473(4)	5477(4)	1553(3)
N(1)	5575(3)	5184(3)	1341(3)	C(19)	7097(4)	4657(4)	1621(3)
N(2)	3776(3)	4682(3)	887(2)	C(20)	6586(4)	3889(4)	1469(3)
N(3)	3263(3)	6679(3)	926(2)	C(21)	6619(5)	2850(4)	1438(4)
N(4)	5072(3)	7080(3)	1410(2)	C(22)	5587(5)	2616(4)	1162(4)
C(1)	5667(4)	4236(4)	1287(3)	C(23)	3547(6)	2071(4)	573(4)
C(2)	5046(4)	3540(4)	1099(3)	C(24)	1709(5)	3335(5)	276(4)
C(3)	4125(4)	3769(4)	897(3)	C(25)	757(5)	6965(5)	342(5)
C(4)	3429(5)	3122(4)	650(3)	C(26)	1741(6)	8890(5)	798(5)
C(5)	2651(5)	3652(4)	520(3)	C(27)	5273(6)	9719(4)	1570(4)
C(6)	2850(4)	4629(4)	670(3)	C(28)	7152(5)	8501(5)	1971(4)
C(7)	2250(5)	5391(4)	574(3)	C(29)	8143(5)	4703(5)	1829(5)
C(8)	2418(4)	6329(4)	682(3)	C(30)	2927(7)	1533(5)	1285(5)
C(9)	1757(5)	7102(4)	584(4)	C(31)	2341(9)	9456(6)	89(6)
C(10)	2168(5)	7905(4)	778(4)	C(32)	8190(7)	8629(7)	1316(7)
C(11)	3121(4)	7642(4)	979(3)	Cl(1)	415(3)	6117(3)	3912(2)
C(12)	3796(5)	8245(4)	1198(3)	Cl(2)	334(3)	5382(3)	2517(2)
C(13)	4711(4)	7997(4)	1386(3)	Cl(3)	455(4)	7351(3)	2702(3)
C(14)	5429(5)	8669(4)	1573(3)	C(33)	855(8)	6251(9)	2910(7)
C(15)	6225(5)	8151(4)	1726(3)	H(33)	170(10)	628(7)	268(6)
C(16)	6009(4)	7170(4)	1609(3)				

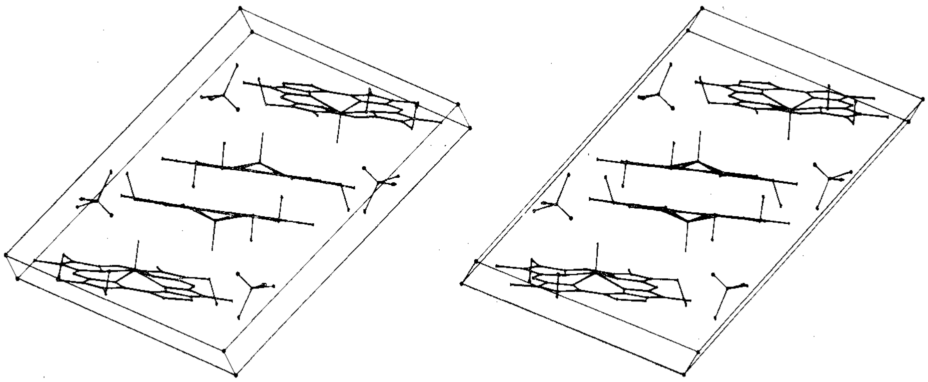

Fig. 1. Stereoview of the unit cell of vanadyl porphyrin as viewed down the y axis with the x axis horizontal and the z axis up the page. The chloroform hydrogen is disposed towards the vanadyl oxygen.

The planarity of the porphyrin ring system can be seen in Fig. 1. The vanadium lies 0·51 Å from the least-squares plane (Table 2), in accord with the 0·5–0·8 Å range predicted from molecular orbital calculations.[9] One of the ethyl groups lies above the plane and the other two below. A different orientation of ethyl groups

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[9] Zerner, M., and Gouterman, M., *Inorg. Chem.*, 1966, **5**, 1699.

Table 2. Displacement of V, O and the methyl and ethyl side groups from the least-squares plane through the porphyrin atoms, N(1–4) and C(1–20)

The equation of the plane is $-0\cdot269X-0\cdot089Y+0\cdot813Z=-0\cdot584$ for orthogonal axes. Deviations of the porphyrin atoms from the plane are <0·05 Å

Atom	*d* (Å)	Atom	*d* (Å)	Atom	*d* (Å)	Atom	*d* (Å)
V	0·506(1)	C(23)	−0·051(6)	C(27)	−0·118(6)	C(31)	−1·279(9)
O	2·089(3)	C(24)	−0·014(6)	C(28)	0·019(7)	C(32)	−1·38(1)
C(21)	0·077(6)	C(25)	−0·039(8)	C(29)	−0·100(7)		
C(22)	0·053(7)	C(26)	0·060(8)	C(30)	1·297(8)		

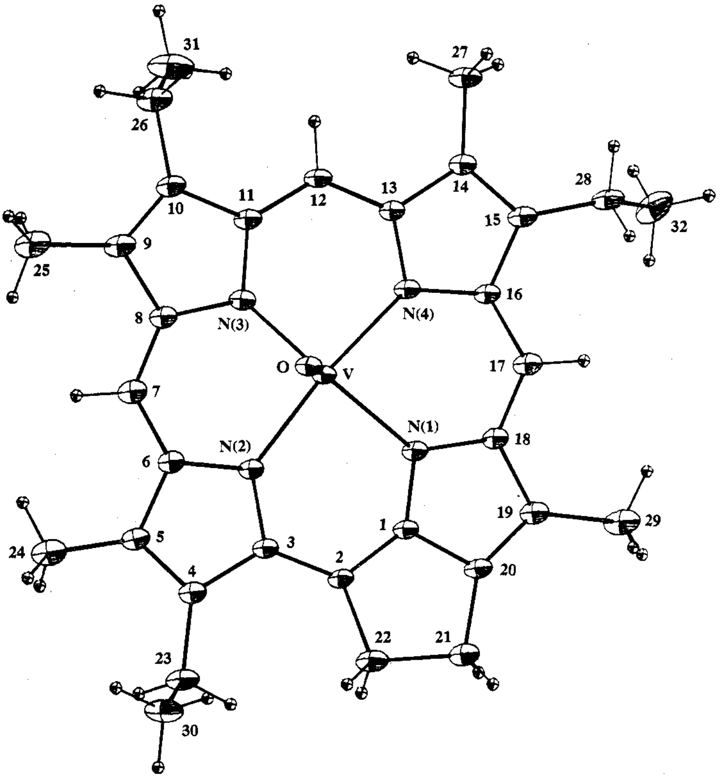

Fig. 2. ORTEP plot of the vanadyl porphyrin molecule with labelling scheme. Vibrational ellipsoids are drawn at the 75% probability level; hydrogen atoms are drawn arbitrarily small. Atoms not otherwise designated are carbons.

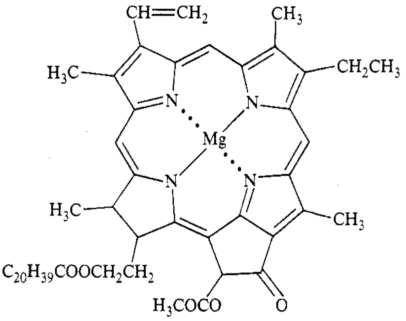

Fig. 3. Chlorophyll *a* structure. Note conformity of the ring skeleton to that of the vanadyl porphyrin.

was observed by Pettersen[8] for a chemically identical vanadyl porphyrin. However, this is not surprising because free rotation of the ethyls would occur in solution and their orientation is a consequence of crystal packing.

Table 3. Bond lengths for vanadyl porphyrin

Atoms	*d* (Å)	Atoms	*d* (Å)	Atoms	*d* (Å)
O–V	1·582(3)	C(4)–C(3)	1·459(9)	C(27)–C(14)	1·501(9)
N(1)–V	2·026(4)	C(5)–C(4)	1·339(9)	C(16)–C(15)	1·447(8)
N(2)–V	2·104(5)	C(23)–C(4)	1·496(8)	C(28)–C(15)	1·50(1)
N(3)–V	2·041(5)	C(6)–C(5)	1·450(8)	C(17)–C(16)	1·394(8)
N(4)–V	2·048(4)	C(24)–C(5)	1·50(1)	C(18)–C(17)	1·369(8)
C(1)–N(1)	1·347(7)	C(7)–C(6)	1·374(9)	C(19)–C(18)	1·443(9)
C(18)–N(1)	1·404(8)	C(8)–C(7)	1·369(9)	C(20)–C(19)	1·348(9)
C(3)–N(2)	1·370(7)	C(9)–C(8)	1·435(9)	C(29)–C(19)	1·52(1)
C(6)–N(2)	1·385(8)	C(10)–C(9)	1·353(9)	C(21)–C(20)	1·472(8)
C(8)–N(3)	1·402(8)	C(25)–C(9)	1·51(1)	C(22)–C(21)	1·61(1)
C(11)–N(3)	1·374(7)	C(11)–C(10)	1·45(1)	C(30)–C(23)	1·49(1)
C(13)–N(4)	1·386(7)	C(26)–C(10)	1·494(9)	C(31)–C(26)	1·50(2)
C(16)–N(4)	1·383(8)	C(12)–C(11)	1·374(9)	C(32)–C(28)	1·48(1)
C(2)–C(1)	1·386(8)	C(13)–C(12)	1·383(8)	C(33)–Cl(1)	1·75(2)
C(20)–C(1)	1·424(9)	C(14)–C(13)	1·448(9)	C(33)–Cl(2)	1·68(2)
C(3)–C(2)	1·399(9)	C(15)–C(14)	1·366(9)	C(33)–Cl(3)	1·72(2)
C(22)–C(2)	1·505(9)				

Table 4. Selected bond angles (degrees)

Atoms	Angle	Atoms	Angle
N(1)–V–O	105·9(2)	C(18)–N(1)–V	129·7(3)
N(2)–V–O	103·4(2)	C(18)–N(1)–C(1)	104·7(5)
N(2)–V–N(1)	85·8(2)	C(3)–N(2)–V	128·6(4)
N(3)–V–O	102·9(2)	C(6)–N(2)–V	123·1(3)
N(3)–V–N(1)	151·1(2)	C(6)–N(2)–C(3)	105·8(5)
N(3)–V–N(2)	88·7(2)	C(8)–N(3)–V	124·9(4)
N(4)–V–O	103·3(2)	C(11)–N(3)–V	126·7(4)
N(4)–V–N(1)	85·0(2)	C(11)–N(3)–C(8)	105·9(5)
N(4)–V–N(2)	153·2(2)	C(13)–N(4)–V	125·3(4)
N(4)–V–N(3)	87·3(2)	C(16)–N(4)–V	128·3(3)
C(1)–N(1)–V	123·1(4)	C(16)–N(4)–C(13)	104·8(4)

The molecular ORTEP plot is shown in Fig. 2. The structure establishes the presence of an isocyclic five-membered ring formed by C(1), C(2), C(20), C(21) and C(22). This ring distinguishes this structure from other porphyrin structures and its presence strongly suggests that the molecule is a derivative of chlorophyll (Fig. 3). The structure obtained is the vanadyl C_{32} dpep structure originally proposed by Treibs[1] and prepared from chlorophyll *a* by Pettersen.[8] Distortion of the vanadium coordination sphere from fourfold symmetry is not obvious from Fig. 2. However this is evident in the extension of the V–N(2) bond (Table 3) by *c.* 0·05 Å, a slight contraction of the V–N(1) bond by *c.* 0·02 Å and the opening of the O–V–N(1) angle by *c.* 2·5° (Table 4). These distortions are presumably due to the isocyclic five-membered ring.

Similar distortions were observed by Pettersen[8] though with the lower accuracy of his determination they were at the limit of crystallographic significance. In both Pettersen's and this structure the tilt of the vanadyl group is away from the isocyclic five-membered ring and towards the solvent. This suggests that the angular distortion of the V–O vector to the plane may not be entirely due to solvent interactions as suggested by Pettersen.

Acknowledgments

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