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Crystal and Molecular Structure of three Oxovanadium(IV) Porphyrins: Oxovanadium Tetraphenylporphyrin(I), Oxovanadium(IV) Etioporphyrin(II) and the 1:2 Adduct of (II) with 1,4-Dihydroxybenzene(III). Hydrogen Bonding Involving the VO Group. Relevance to Catalytic Demetallisation

MICHAEL G. B. DREW, PHILIP C. H. MITCHELL and CARLOS E. SCOTT

Department of Chemistry, The University, Whiteknights, Reading RG6 2AD, U.K.

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The structures of the three title compounds have been determined by X-ray Crystallography. (I) is tetragonal, spacegroup $I4/m$ *with* $Z = 2$, $a = 13.345(7)$, $c = 9.745(8)$ Å. *(II) is triclinic, spacegroup* $P\bar{1}$, $Z = 2$, $a = 10.52(1)$, $b = 11.70(1)$, $c = 12.97(1)$ Å, $\alpha = 70.7(1)$, $\beta = 113.8(1)$, $\gamma = 108.8(1)°$; *(III) is orthorhombic, spacegroup Pnaa,* $Z = 8$, $a = 17.72(1)$, $b = 18.14(1)$, $c = 18.57(1)$ Å. *Data for all three compounds have been collected on a diffractometer and 556 (I), 2316 (II), 1263 (III)) above background reflections have been refined to R (0.099, 0.086, 0.082) respectively.*

(I) has disordered C_{4h} *symmetry following a well-known structure type. The features of the oxovanadium(IV) etioporphyrin structures in (II) and (III) are similar. Compound (III), the adduct with 1,4-dihydroxybenzene (quinol,* H_2Q*)* $[VO(ETP)]_2[H_2Q]$*, which crystallised from a solution of [VO(ETP)] in tetrahydrofuran stabilised with 0.1% quinol, consists of [VO(ETP)] molecules linked by H-bonds through the VO groups to the quinol OH groups. We discuss the general phenomenon of H-bonding to VO groups and its possible relevance to binding of VO porphyrins to OH groups at catalyst surfaces.*

Introduction

In this paper we report the structures of oxovanadium(IV)tetraphenylporphyrin, VO(TTP), (I), oxovanadium(IV)(etioporphyrin), VO(ETP) (II), and an adduct of (II) with 1,4-dihydroxybenzene (quinol, H_2Q){$[VO(ETP)]_2[H_2Q]$} (III). This work is part of a program on catalytic demetallisation of oxovanadium(IV) porphyrins which occur in petroleum crudes [1, 2] directed towards determining possible ways in which oxovanadium porphyrins might bind to catalyst surfaces. The quinol adduct(III) was formed when we tried to crystallise the parent compound(II) from tetrahydrofuran stabilised with 0.1% quinol. A feature of the structure is intermolecular hydrogen bonding between the VO group and the quinol OH groups.

Experimental

We prepared VO(TTP) by the following method. Mesotetraphenylporphyrin (abbreviated H_2TPP) was prepared by the method previously reported [3] and purified by dry column chromatography on alumina with chloroform as the eluent [4, 5], the resulting product being at least 98.7% pure [6, 7]. Then (I) was synthesised by the literature method [5] and the unreacted H_2TPP extracted with trifluoroacetic acid [8] to give the final product. Crystals were prepared by slow evaporation of a solution of the compound (0.0150 g) in dichloromethane (5 cm^3).

We prepared the compounds etioporphyrin (abbreviated H_2ETP) and oxovanadium(IV)etioporphyrin(II) (abbreviated [VO(ETP)]) by literature methods [9, 10]. Deep purple crystals of (II) suitable for X-ray Crystallography were obtained by slow evaporation of a solution of the compound (0.0215 g) in dichloromethane (5 cm^3). The adduct with 1,4-dihydroxybenzene (quinol, abbreviated H_2Q) {$[VO(ETP)]_2[H_2Q]$} (II) crystallised much to our surprise when a solution of [VO(ETP)] (0.0163 g) in tetrahydrofuran (10 cm^3) stabilised with 0.1% quinol slowly evaporated. The yield of the adduct(III) was insufficient for analysis; the nature of the crystals was shown by the X-ray crystallography.

Structure Determination

Crystal data for compounds (I), (II), and (III) are given in Table I. The three crystals were mounted in turn on a Stoe STADI2 diffractometer and data were collected via variable width w scan. Background counts were 20 s and the scan rate of 0.033°/s was applied to a width of ($1.5 + \sin \mu/\tan \theta$). Absorption and extinction corrections were not applied. A starting set of coordinates for (I) was obtained from

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TABLE I. Crystal Data and Refinement Details.

Compound	(I) VO(TPP)	(II) VO(ETP)	(III) VO(ETP)1/2H$_2$Q
Formula	VON$_4$C$_{44}$H$_{28}$N$_4$	VON$_4$C$_{32}$H$_{36}$	VO$_2$N$_4$C$_{32}$H$_{36}$
M	679.1	543.2	598.2
Class	Tetragonal	Triclinic	Orthorhombic
Spacegroup	I4/m	$P\bar{1}$	Pnaa (No 57)
Absences	h + k + 1 = 2n + 1	none	hk0, h = 2n + 1 h0l, l = 2n + 1 0kl, k + 1 = 2n + 1
a(A)	13.345(7)	10.52(1)	17.72(1)
b(A)	13.345(7)	11.70(1)	18.14(1)
c(A)	9.745(8)	12.97(1)	18.57(1)
α (deg)	(90)	70.7(1)	(90)
β (deg)	(90)	113.8(1)	(90)
γ (deg)	(90)	108.8(1)	(90)
U (Å^3)	1735.5	1345.7	5970.1
Z	2	2	8
F(000)	702	574	2528
μ (cm^{-1})	3.46	4.16	3.94
dm (g cm^{-3})	1.31	1.34	1.28
dc (g cm^{-3})	1.31	1.31	1.33
λ (Å)	0.7107	0.7107	0.7107
Rotation axis	c	b	a
2*theta max	45	50	40
No of data	827	3500	3133
Criteria for data inclusion	$I > 2\sigma(I)$	$I > 3\sigma(I)$	$I > 2\sigma(I)$
No of data in refinement	556	2316	1265
R	0.099	0.086	0.082
R$_w$	0.102	0.092	0.082

isomorphous structures. The structure of (II) was solved simply by the Patterson method. (II) proved surprisingly difficult to solve because the V···V vector in the Patterson function was obscured by other vectors between the planar molecules. Direct methods did not work and eventually we solved the structure in spacegroup P1 by placing the vanadium atom at the origin and locating most of the atoms of the porphyrin ring around it. The second vanadium was then located in the Fourier map and we then reverted to spacegroup $P\bar{1}$. In both (II) and (III) all non-hydrogen atoms were located by Fourier methods. In all three structures, hydrogen atoms were placed in trigonal or tetrahedral positions and those bonded to the same atom were given a common thermal parameter. Methyl hydrogen atoms were included as rigid groups. Surprisingly in view of the intermolecular hydrogen bond formed between the HO groups of the quinol and the O atom of the VO group (see below) we could not locate the hydrogen on the oxygen of the quinol in a difference Fourier map or refine it in an assumed position with a reasonable thermal parameter. However the data for (III) were weak compared to (II) and it is possible that the hydrogen atom has a spread of acceptable positions which cause the peak to be too broad to locate.

In (I) all atoms were refined in ordered positions apart from the vanadium and oxygen atoms. Several compounds of TPP crystallise in this spacegroup I/4m with the metal in position (2a) with site symmetry 4/m. Examples include Fe(TPP)(NO) [11], Co(TTP)-(NO)(piperidine) [12] and TiBr$_2$(TTP) [13]. In the latter structure the molecule is ordered with the Ti atom at the origin. However in the other structures the metal atom is disordered on either side of the z = 0 mirror plane. In five-co-ordinate structures the terminal ligand is disordered also. The structure of (I) proved typical with the vanadium and oxygen atom refined with 50% occupancy in 0, 0, z positions. However we could detect no signs of disorder in the porphyrin ligand.

All three structures were refined by full-matrix least squares with a weighting scheme $w = 1/(\sigma^2(I) + 0.003F^2)$. Final R values were 0.099, 0.086 and 0.082 respectively. Calculations were carried out using Shelx76 [14] at the University of Manchester Computing Centre. Atomic scattering factors and dispersion corrections were taken from ref. 15. Atomic parameters are given in Tables II, III and IV. Molecular dimensions in the coordination spheres are given in Table V. Remaining dimensions, thermal parameters and structure factors are included in the Supplementary Publication.

TABLE II. Atomic Co-Ordinates ($\times 10^4$) for (I) Deviations in Parentheses.

Atom	X	Y	Z
V(1)	0	0	548(4)
C(1)	2283(6)	−278(6)	0
C(10)	3618(5)	−2186(6)	1199(7)
C(11)	4471(6)	−2746(7)	1203(11)
C(2)	3188(6)	275(7)	0
C(3)	2943(6)	1242(7)	0
C(4)	1855(6)	1308(7)	0
C(5)	2201(6)	−1321(6)	0
C(6)	3171(6)	−1908(6)	0
C(7)	4938(7)	−3005(7)	0
N(1)	1461(5)	365(4)	0
O(1)	0	0	2215(16)

TABLE III. Atomic Co-Ordinates ($\times 10^4$) for (II) Standard Deviations in Parentheses.

Atom	X	Y	Z
V(1)	−1047(1)	1968(1)	8125(1)
N(1)	−1781(7)	366(5)	9208(7)
C(2)	−2688(9)	−716(7)	8870(8)
C(3)	−2920(9)	−986(7)	7857(8)
C(4)	−2338(9)	−275(7)	7021(8)
N(5)	−1397(7)	869(5)	7056(7)
C(6)	−1066(8)	1260(7)	6049(8)
C(7)	−150(9)	2363(7)	5734(8)
C(8)	573(8)	3258(7)	6386(8)
N(9)	482(6)	3162(5)	7427(6)
C(10)	1360(8)	4247(7)	7734(8)
C(11)	1567(9)	4524(7)	8747(8)
C(12)	1032(8)	3802(7)	9611(8)
N(13)	100(7)	2638(5)	9593(6)
C(14)	−172(8)	2246(7)	10604(8)
C(15)	−1080(9)	1119(7)	10907(8)
C(16)	−1814(9)	234(7)	10277(8)
C(17)	−2756(9)	−926(7)	10634(9)
C(18)	−3280(9)	−1498(7)	9757(8)
C(19)	−3081(10)	−1362(8)	11724(9)
C(20)	−4401(14)	−994(14)	11618(13)
C(21)	−4326(11)	−2709(8)	9687(10)
C(22)	−2588(9)	−607(7)	5966(8)
C(23)	−1808(9)	344(7)	5360(8)
C(24)	−3582(10)	−1737(8)	5594(9)
C(25)	−5044(11)	−1548(9)	4792(11)
C(26)	−1723(12)	423(9)	4249(9)
C(27)	1502(9)	4409(7)	6005(8)
C(28)	1985(9)	5028(7)	6864(8)
C(29)	1865(9)	4842(8)	4941(9)
C(31)	2953(10)	6263(8)	6903(9)
C(30)	3263(13)	4565(13)	5106(12)
C(32)	1296(9)	4127(7)	10674(8)
C(33)	567(9)	3162(7)	11266(7)
C(34)	2230(9)	5293(7)	11007(8)
C(35)	3748(11)	5179(9)	11800(10)
C(36)	447(11)	3061(9)	12406(9)
O(1)	−2343(6)	2661(5)	7500(5)

TABLE IV. Atomic Co-Ordinats ($\times 10^4$) for (III) Estimated Standard Deviations in Parentheses.

Atom	X	Y	Z
V(1)	3392(1)	125(1)	86(1)
O(1)	2662(5)	90(6)	604(5)
N(1)	3497(7)	1219(7)	−157(7)
C(2)	3826(8)	1764(11)	268(8)
C(3)	4295(9)	1628(10)	844(8)
C(4)	4530(8)	939(10)	1091(9)
N(5)	4309(5)	298(7)	770(6)
C(6)	4681(8)	−261(9)	1135(7)
C(7)	4629(9)	−984(10)	1012(8)
C(8)	4221(8)	−1353(10)	506(8)
N(9)	3755(7)	−965(7)	12(7)
C(10)	3420(11)	−1510(10)	−409(10)
C(11)	2930(9)	−1360(11)	−991(10)
C(12)	2729(9)	−666(11)	−1244(9)
N(13)	2933(6)	−15(8)	−928(6)
C(14)	2646(8)	531(12)	−1347(8)
C(15)	2712(9)	1283(12)	−1237(10)
C(16)	3136(9)	1622(11)	−680(10)
C(17)	3198(8)	2416(10)	−588(8)
C(18)	3625(8)	2496(11)	24(10)
C(19)	2923(11)	3005(10)	−1051(10)
C(20)	3441(12)	3231(12)	−1645(11)
C(21)	3872(9)	3210(10)	352(9)
C(23)	5178(8)	29(9)	1693(7)
C(24)	5454(10)	1387(9)	2088(8)
C(25)	5114(12)	1520(13)	2790(10)
C(26)	5638(9)	−367(10)	2214(8)
C(27)	4137(8)	−2109(9)	357(9)
C(28)	3663(9)	−2262(9)	−216(9)
C(29)	4552(9)	−2693(10)	771(10)
C(30)	4265(11)	−2855(14)	1522(13)
C(31)	3453(9)	−2958(9)	−562(9)
C(32)	2283(9)	−510(12)	−1869(8)
C(33)	2197(8)	210(10)	−1919(8)
C(34)	1945(10)	−1112(10)	−2327(9)
C(35)	2437(11)	−1409(11)	−2900(10)
C(36)	1775(10)	635(10)	−2525(10)
O(40)	1130(6)	94(8)	1024(6)
C(41)	587(9)	35(9)	505(9)
C(42)	−153(8)	−96(9)	713(8)
C(43)	726(7)	145(9)	−218(10)

Discussion

In all three structures, the vanadium atom is five-co-ordinate being bonded to the four nitrogen atoms of the porphyrin and one terminal oxygen atom. The metal geometry is square pyramidal. The dimensions of the vanadium coordination spheres are given in Table V.

The structure of (I) is shown in Fig. 1 together with the atomic numbering scheme. The V–O bond

TABLE V. Dimensions in the Coordination Sphere.

Dimensions in (I)

V(1)–N(1)	2.080(6)
V(1)–O(1)	1.625(16)
N(1)–V(1)–O(1)	104.88(10)
N(1)–V(1)–N(1**)	150.23(20)
N(1)–V(1)–N(1*)	86.21(23)

Symmetry elements

*–Y, X, –Z
**–X, –Y, –Z

Dimensions in (II) and (III)

	(II)	(III)
V(1)–N(1)	2.071(13)	2.044(6)
V(1)–N(5)	2.042(9)	2.086(12)
V(1)–N(9)	2.063(12)	2.083(7)
V(1)–N(13)	2.054(12)	2.067(7)
V(1)–O(1)	1.599(6)	1.614(9)
N(1)–V(1)–N(5)	86.7(5)	85.3(3)
N(1)–V(1)–N(9)	152.84(27)	151.64(42)
N(5)–V(1)–N(9)	87.2(3)	86.7(5)
N(1)–V(1)–N(13)	86.11(27)	87.4(6)
N(5)–V(1)–N(13)	152.13(28)	151.64(42)
N(9)–V(1)–N(13)	87.08(28)	86.9(4)
N(1)–V(1)–O(1)	104.4(3)	104.0(5)
N(5)–V(1)–O(1)	104.1(3)	105.5(4)
N(9)–V(1)–O(1)	102.71(5)	104.43(28)
N(13)–V(1)–O(1)	103.8(3)	102.9(4)

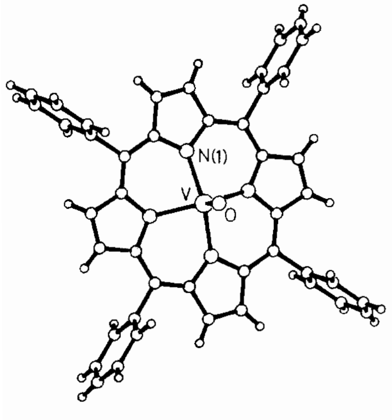

Fig. 1. The Structure of VO(TPP), (I).

length is 1.625(16) Å with the vanadium atom 0.53 Å above the plane of the four nitrogen atoms. Despite the restrictions of the spacegroup there are no signs of disorder in the porphyrin. In particular the phenyl rings are perpendicular to the N_4 plane. This is not the case when there is no spacegroup restriction, *i.e.* 71.7, 68.0° in Zn(TPP) [15], 83.9, 78.3, 85.0, 65.5° in $MoCl_2$(TPP) [16], 81.9, 56.1, 70.5, 61.8° in MoClO(TPP) [17]. Similarly the ring is usually less planar with distortions of carbon atoms (apart from C(10), C(11)) by up to 0.6 Å from the N_4 plane.

The structure of VO(ETP) (II) in a projection down the V=O bond is shown in Fig. 2. The geometry of [VO(ETP)] in the quinol adduct (III) is the same as in the parent compound (II) apart from some small conformational change in the methyl atom positions. The numbering scheme in the two structures is equivalent. However in (III) two [VO(ETP)] molecules are associated via intramolecular hydrogen bonds with one quinol molecule as shown in Fig. 3.

In (II) and (III), the vanadium to terminal oxygen bond lengths are (1.599(6), 1.614(9) Å) with the vanadium atoms 0.49(1) (II), 0.51(1) Å above the N_4 plane in the direction of the oxygen atom.

The V–N bond lengths to the four nitrogen atoms of the porphyrin ligand fall within the normal range (2.049(9) to 2.086(12) Å). The V=O distance in (III) at (1.614(9) Å) is slightly longer than in (II) (1.599(6) Å) possibly because of the hydrogen bond. Though we note that the distance in (I) is 1.625(16) Å but the s.d. may be an underestimate because of the disorder. The V–N distances are unexceptional ranging from 2.042(9) to 2.086(12) Å.

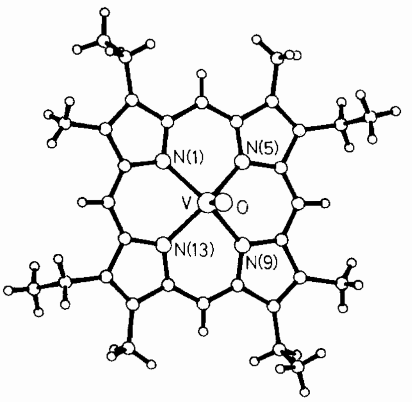

Fig. 2. The structure of VO(ETP), (II).

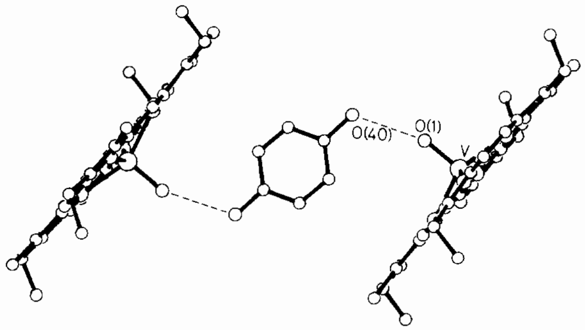

Fig. 3. The structure of $(VO(ETP))_2(H_2Q)$, (III). Hydrogen bonds are represented by the dotted lines.

Dimensions within the porphyrin rings are similar to those in the few etioporphyrin structures previously reported.

In the Cambridge Data Files we found nickel(II) etioporphyrin bis(tetranitrofluorenone) [18], nickel-etioporphyrin [19], bis(dimethylamine)–etio(I)porphinato–Rhodium(III) chloride dihydrate, [20] and Vanadyl Deoxophylloerythro–etioporphyrin, 1,2-dichloroethane solvate [21].

It is interesting that the prophyrin ring of the adduct (III) deviates from planarity more than the porphyrin ring of (II). For compound (II) a least squares plane through all atoms bar V, O and the four $-CH_3$ of the ethyl groups has a maximum deviation of a contributing atom of 0.05 Å whereas the deviation for (III) is 0.21 Å. The plane through the 4N atoms in (II) also shows considerable deviation even among some of the ring carbon atoms. The reason for this distortion of the porphyrin ring in (III) is not obvious. For example there are no close contacts between the quinol molecule and the porphyrin ring.

The main interest in structure (III) is the intermolecular hydrogen bond formed between the quinol and the VO group. The O···O distances of 2.82 Å and the V=O···O and C–O···O angles of 159.3 and 118.9° are acceptable for intermolecular hydrogen bonds [22]. To check whether oxovanadium groups had a general propensity for forming hydrogen bonds and whether any such interactions weakened the V=O bond, we searched the Cambridge Data Centre files for structures containing oxovanadium groups. Of the 75 structures, there were only six with V=O···O distances of <3.0 Å and all involved water molecules; four were dioxovanadium(V) [23–26] one oxovanadium(IV) [27] and one an oxoperoxovanadate [28]. None was directly comparable to our quinol adduct. These structures and ours do however indicate the VO_n groups can form H bonds to water and HO groups. We list in Table VI, V=O and O···O distances and V=O···O angles. There does seem to be some tendency for the V=O distance to increase with (a) decreasing O···O and (b) increasing V=O···O angle, *i.e.* with an increase of H-bonding.

Finally we discuss the rather remarkable circumstance that the compound we were able to crystallise from tetrahydrofuran (THF) containing only 0.1% quinol was the quinol adduct $\{[VO(ETP)]_2[H_2Q]\}$ (III) and not the parent compound (II) or an adduct with THF. The failure to obtain a THF adduct is consistent with the general reluctance of the VO porphyrins to engage in axial coordination [29] a consequence of the *trans*-repulsive effect of the terminal oxo-group and the inaccessibility of the vanadium atom raised above the plane of the porphyrin ring. Formation of the quinol adduct does not reflect any propensity of the VO group for strong H-bonding. Most probably formation of the crystalline adduct is due to a particularly favourable crystal lattice energy resulting from the H-bonding. Nevertheless we have shown that H-bonding involving a VO group is possible. Part of the purpose of our work was to determine the possible ways in which VO porphyrins might bind to $Co-Mo/Al_2O_3$ hydrodesulpherisation catalysts and to acidic cracking catalysts. Clearly a H bonding interaction between VO and surface HO groups is possible. Whether such interactions do arise we discuss in a forthcoming paper.

Apart from the intramolecular hydrogen bond there are no intramolecular distances shorter than the sum of van der Waals radii. Indeed packing efficiency is similar with both (II) and (III) in that both have only two contacts between non-hydrogen atoms less than 3.5 Å and these are ca. 3.48 Å.

TABLE VI. Dimensions Found in Vanadyl Structures Containing Intermolecular Hydrogen Bonds.

Compound	V=O	O···O	V=O···O	Ref.
(a)	1.638	2.965	162.1	27
(b)	1.615	2.984	112.5	23
(c)	1.658	2.796	109.6	24
(c)	1.624	2.912	125.7	24
(d)	1.579	2.971	120.3	28
(e)	1.625	2.797	113.5	25
(e)	1.658	2.772	143.1	25
(f)	1.619	2.908	111.9	26
(f)	1.619	2.874	122.8	26

Compounds:

(a) Potassium Diperoxo–(oxalato)–oxo–vanadium)Monohydrate.
(b) Cesium *cis*-dioxo–dipicolinato–vanadium(V) Monohydrate.
(c) Ammonium (dihydrogenethylenediaminetetraaacetato) Dioxovanadate(V) trihydrate.
(d) Ammonium Oxo–Peroxo–(pyridine–2,6-dicarboxylato)-vanadate(V) dihydrate.
(e) Ammonium (Salicylaldehyde–S–methyl–thiosemicarbazonato)-dioxo–vanadate(V) monohydrate.
(f) Tetrasodium Divanadyl(IV) D-tartrate L-tartrate Dodecahydrate.

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