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CHEMISTRY OF VANADYL PORPHYRINS

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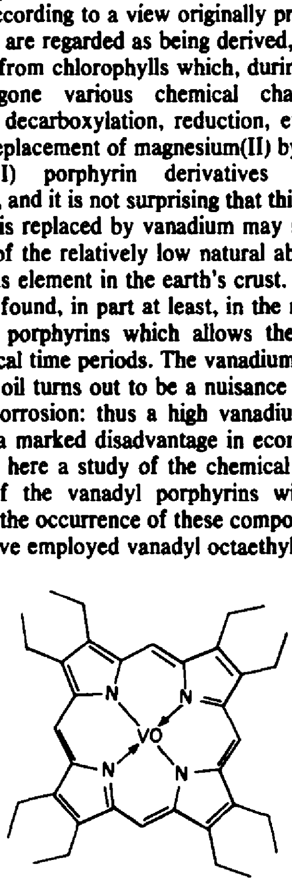
Abstract—The chemistry of vanadyl porphyrins has been explored using vanadyl octaethylporphyrin as the type substance, and with special reference to the occurrence of such substances in petroporphyrins. Spectroscopic properties (electronic spectra, IR spectra, mass spectra) are described, and electronic spectra are employed to detect the occupation of the vacant axial coordination site. Direct substitution of vanadyl octaethylporphyrin furnishes *meso*-substituted products: various nitro, chloro and benzoyloxy derivatives are characterised. Trans alkylation is observed when vanadyl octaethylporphyrin is heated *in vacuo* on various supports, including clay minerals: the reaction provides a model for the generation of the homologous series of vanadyl polyalkylporphyrins found in crude oils and bitumens.

Vanadyl porphyrins are found in many crude oils and bitumens. According to a view originally propounded by Treibs,[1] they are regarded as being derived, in this situation, mainly from chlorophylls which, during diagenesis, have undergone various chemical changes (dehydrogenation, decarboxylation, reduction, etc.) including the overall replacement of magnesium(II) by vanadyl(II). Magnesium(II) porphyrin derivatives are readily demetallated, and it is not surprising that this metal ion is lost. That it is replaced by vanadium may seem surprising in view of the relatively low natural abundance (*ca.* 0.02%) of this element in the earth's crust. The explanation may be found, in part at least, in the robustness of the vanadyl porphyrins which allows them to persist over geological time periods. The vanadium thus appearing in crude oil turns out to be a nuisance since it leads to furnace corrosion: thus a high vanadium content in crude oil is a marked disadvantage in economic terms.[2]

We report here a study of the chemical and physical properties of the vanadyl porphyrins with particular reference to the occurrence of these compounds in fossil fuels. We have employed vanadyl octaethylporphyrin (1) as the type substance. This is particularly appropriate because the petroporphyrins are complex mixtures of polyalkyl derivatives.[3] Preliminary accounts of part of this work have appeared.[4]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Metallation and demetallation. Various methods have been reported for inserting the vanadyl ion into a porphyrin. Treibs[5] employed vanadium tetrachloride but the reaction was not very satisfactory and is thought to have led to a partially chlorinated product.[6] Two metal salt/acid systems[6,7] were evaluated for the preparation of 1: of these Erdman's method (vanadyl sulphate, pyridine, acetic acid, heat)[6] proved the superior and gave a near quantitative yield. However, some protodesubstitution was observed when this method was applied to certain *meso*-substituted derivatives: this effect was particularly noticeable with 5-nitrooctaethylporphyrin. More recently the preparation of 1 by heating vanadyl acetylacetonate and the porphyrin in phenol has been reported.[8]

The *removal* of the metal from vanadyl porphyrins requires vigorous conditions. Vanadyl octaethylporphyrin was not demetallated by trifluoracetic acid (reflux, 18 hr), nor by 85% phosphoric acid (180°, 1 hr). It was partially demetallated (*ca.* 40%) by treatment with HBr-HOAc[1] at 100° for 4 hr. Sulphuric acid caused efficient demetallation: concentrated sulphuric acid at room temperature (15 min), or 75% sulphuric acid at 100° (1 hr) were both effective, but 50% sulphuric acid at 100° (15 min) did not generate a detectable amount of the free base.

Spectroscopic properties. In neutral solvents such as chloroform vanadyl octaethylporphyrin shows[4] a normal two-banded visible spectrum with $\epsilon_\alpha > \epsilon_\beta$. *meso*-Substituted derivatives possess similar spectra, but as the degree of substitution increases (for $-NO_2$, $-Cl$, $-OCOPh$) λ_{max} moves to lower energy and the $\epsilon_\beta/\epsilon_\alpha$ ratio increases. The electronic spectra are collected in Table 1. In trifluoroacetic acid (but not in acetic acid) a considerable change occurs[9] to give a haemin-like spectum. We ascribe this change, which recalls that observed when titanyl octaethylporphyrin is treated with methanolic HCl,[10] to O-protonation.

In basic solvents which are good unencumbered nucleophiles the electronic spectrum also changes: the changes here are thought to be due to further coordination in the vacant axial position. With moderately hindered nucleophiles such as quinoline and triethylamine the spectra are very similar to that observed in chloroform: moderately good ligands (e.g. pyridine) split the Soret band,[6,11] while good unencumbered ligands (e.g. primary amines) cause the lower energy bands to

Table 1. Electronic spectra of vanadyl porphyrins ($CHCl_3$, λ nm, ϵ_{max})

Vanadyl complex of	Soret	β	α
Octaethylporphyrin (OEP)	407 (292,000)	534 (13,300)	572 (28,400)[a]
Porphyrin	401(293,000)	524 (12,100)	560 (9700)
5-Nitro OEP	410 (224,000)	537 (12,500)	577 (21,500)
5,10-Dinitro OEP	412 (190,000)	539 (11,400)	579 (19,400)
5,15-Dinitro OEP	413 (130,000)	539 (8900)	579 (13,400)
5-Chloro OEP	418 (274,000)	542 (13,500)	581 (12,300)
5,10-Dichloro OEP	438 (222,000)	556 (11,900)	596 (6100)
5,15-Dichloro OEP	425 (275,000)	552 (11,400)	596 (5500)[b]
5,10,15-Trichloro OEP	438 (192,000)	573(10,200)	610i (5100)
5,10,15,20-Tetrachloro OEP	452 (174,000)	591 (8400)	634 (6900)
5-Benzoyloxy OEP	414 (281,000)	537 (14,000)	574 (17,000)
5-Hydroxy OEP	419 (204,000)	539 (13,000)	573 (7300)

[a] Inflection at 498 (2000).
[b] Inflection at 517 (2700).

Table 2. Further coordination of vanadyl octaethylporphyrin: electronic spectra in basic solvents (λ_{max})

	Soret	
Little or no further coordination		
$CHCl_3$	408	534, 572
Quinoline	412	536, 573
2-Picoline	408	535, 572
Triethylamine	406	532, 570
Weakly coordinating		
Pyridine	408, 423	535, 572
4-Picoline	408, 428	536, 572
t-Butylamine	407, 420	534, 572
Strongly coordinating		
n-Butylamine	405,422	537i, 547, 572, 584
Ethylenediamine	408, 428	549, 572, 585
2-Phenylethylamine	407, 426	547, 571, 582

split as well. Some typical spectra[9] are recorded in Table 2. The sensitivity of this further coordination to steric factors may be associated with the requirement for the incoming ligand to enter a shallow cavity in order to effect coordination, since in the starting material the vanadium atom is expected to be displaced out of the porphyrin plane towards the oxygen atom by about 0.5 A.[12] That *primary* amines give spectra which are rather characteristic led to the supposition that an interaction with vanadyl might occur in another way, for example to give complexes of V = NR(II), the aza analogue of vanadyl(II). We found no support for this view: when a solution of vanadyl octaethylporphyrin in *N*-butylamine was taken to dryness and kept in vacuo overnight the residue was indistinguishable (TLC) from the starting material.

All the vanadyl porphyrins studied here showed an infrared band near 1000 cm^{-1} which, in agreement with earlier workers,[6,13] is assigned to the V=O stretching mode. Table 3 lists the bands occurring in the 1000 cm^{-1} region for magnesium(II) and nickel(II) octaethylporphyrin, and for a series of vanadyl(II) porphyrins.

Mass spectrometry has been used extensively in the examination of petroporphyrins (see below): the direct examination of vanadyl complexes is facilitated by the robustness of such complexes, and by the isotopic purity of natural vanadium (99.75% ^{51}V). The mass spectrum of 1 shows three features which are regarded as characteristic of vanadyl polyalkylporphyrins: (i) a molecular ion appearing as the base peak, (ii) a doubly charged molecular ion with an appreciable relative abundance (*ca.* 10%) and (iii) successive losses (here, up to the maximum of eight) of benzylic-type alkyl (here, Me) groups. The mass spectrum of vanadyl(II) octaethylporphyrin is shown in Fig. 1. When certain *meso*-substituents (e.g. $-NO_2$, $-OCOPh$) are present, fragments are also seen which arise from the loss of the *meso*-substituent and/or from its replacement by hydrogen. Table 4 shows the relative abundance of such fragments. These fragmentations are considered to reflect the well known overcrowding of the *meso*-substituents in octaalkylporphyrins.[14,15]

Table 3. Bands in the 1000 cm^{-1} region for some vanadyl porphyrins (KBr discs)

Porphyrin	Bands between 1020–970 cm^{-1}
Mg OEP	1011, 975
Ni OEP	1018, 991
VO OEP	1013, 999, 982
VO 5-nitro OEP	1016, 999, 982
VO 5-chloro OEP	1014, 1000, 983i
VO 5-benzoyloxy OEP	1020, 1000i, 990

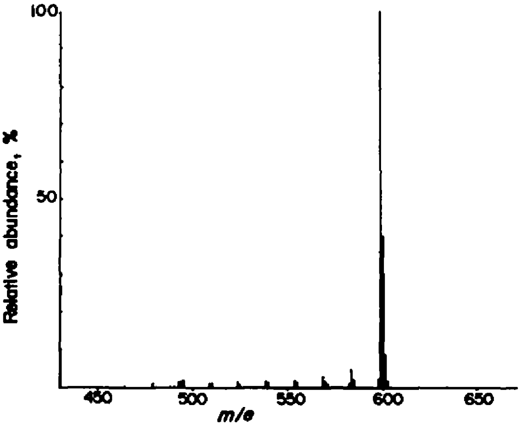
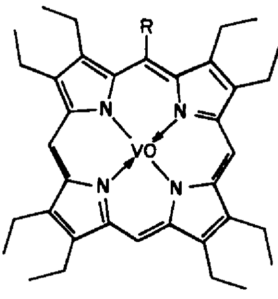


Fig. 1. Mass spectrum of vanadyl octaethylporphyrin (AEI Ltd. MS902, 70ev, direct insertion at 250°).

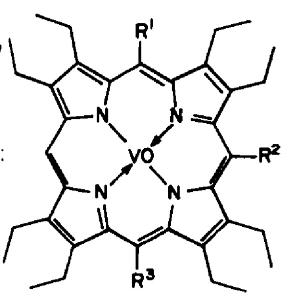
Table 4. Relative abundances of fragment ions in the mass spectra of vanadyl octaethylporphyrins arising from loss of *meso*-substituents

Vanadyl complex	Desubstitution	Protodesubstitution
OEP	M-1 (2.5%)	
5-Nitro OEP	M-46 (4%)	M-45 (11%)
5-Chloro OEP	M-35 (2%)	M-34 (6%)
5-Benzoyloxy OEP	M-121 (65%)	M-120 (31%)
5-Hydroxy OEP	M-17 (9%)	M-16 (71%)

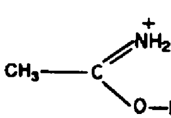
meso-*Substitution*. Conditions were established under which vanadyl octaethylporphyrin could be directly substituted at *meso*-positions. Thus treatment with nitric acid in acetonitrile at 0° for 5 min gave a 61% yield of vanadyl 5 - nitrooctaethylporphyrin (2). A possible nitrating species in this medium is protonated acetimidoyl nitrate (3). Under more vigorous conditions the two dinitro derivatives (4 and 5) were obtained and were separated by crystallisation, together with a small amount of the trinitro derivative (6). Nitration was also observed using sodium nitrite—HCl in aqueous acetonitrile. The identities of the vanadyl nitroporphyrins were confirmed by comparison with samples made by metallation of the appropriate nitroporphyrins.[16]



2 : R—NO_2
7 : R—Cl
9 : R—OCOPh
12 : R—OH



4 : R^1—R^2—NO_2, R^3—H
5 : R^1—R^3—NO_2, R^2—H
6 : R^1—R^2—R^3—NO_2



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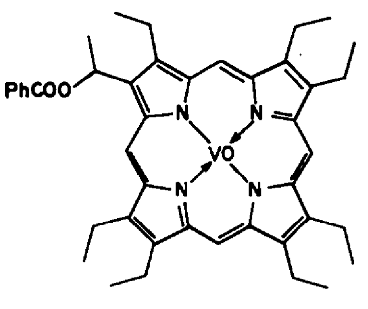
Similarly, chlorination with hydrogen peroxide-hydrogen chloride in tetrahydrofuran generated the mono chloro derivative (7) together with the di, tri and tetra substituted compounds, the latter becoming principal products when the reaction was prolonged. With benzoyl peroxide in 1,2,4-trichlorobenzene at *ca.* 98° a complex mixture was obtained, which included products of benzoyloxylation at side chain "benzylic" positions and at *meso*-positions. The side chain substituted compound, vanadyl 2 - (1^1 - benzoyloxyethyl)heptaethylporphyrin (8), was obtained crystalline in 5% yield. It had $\nu_{C=O}$ = 1711 cm^{-1} and the mass spectrum showed only a weak molecular ion with strong peaks at *m/e* 597 (M-$PhCO_2H$), 122 ($PhCO_2H$) and 105 (PhCO). In contrast the *meso*-benzoyloxy derivative (9), isolated in 18% yield, had a strong molecular ion, and had $\nu_{C=O}$ = 1743 cm^{-1}. These distinctions paralleled those observed in the metal-free benzoyloxy porphyrins.[17]



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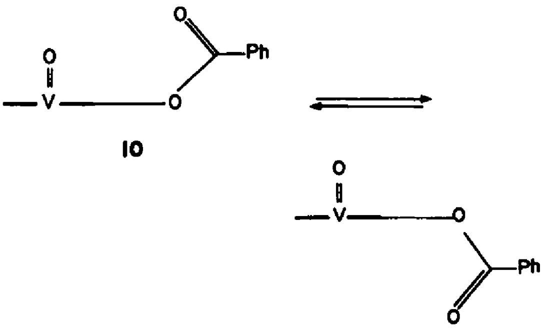
Remarkably, careful analytical TLC (SiO_2, 23% acetone in petroleum) of vanadyl 5 - benzoyloxyoctaethylporphyrin (9) showed two spots. When each component was rechromatographed the same two spots appeared. We suppose that the two components are atropisomers (10, 11), analogous to those observed with tetra(*meso* - *o* - hydroxyphenyl)porphyrin.[18] Such isomers are another consequence of the overcrowding of *meso*-substituents mentioned above: in this case the immediate effect of overcrowding is the steric inhibition of free rotation about the *meso*-C–O bond.



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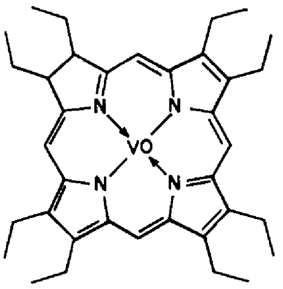
11

Alkaline hydrolysis of 9 gave the corresponding hydroxy compound (12). The visible spectrum in chloroform (red solution) was of the normal two banded type (Table 1) and the infrared showed no absorption in the CO region, confirming, as with other divalent metal complexes of this type,[19] that the substance exists predominantly as shown, and not as an oxophlorin derivative.

The relative susceptibilities of a variety of metallo porphyrins in *meso*-electrophilic substitution have been assessed by following deuteriation[20] in chloroform-deuteriotrifluoroacetic acid mixtures.[21,22] The apparent half life for the formation of the [*meso*-$^2H_4$] vanadyl octaethylporphyrin at room temperature was *ca.* 5 hr, which is considerably longer than has been observed for the deuteriation under these conditions (< 20 min) of the analogous iron(III), platinum(II) and palladium(II) complexes.[21] The reaction of the vanadyl derivative was complicated when carried out in air for a prolonged period by the formation of a *meso*-trifluoroacetoxy derivative (accurate mass measurement for the molecular ion of vanadyl 5,10,15 - trideuterio - 20 - trifluoroacetoxyoctaethylporphyrin). The origin of this is not clear: it may arise from a 5,15-addition of trifluoroacetic acid followed by a dehydrogenation step, but other routes (e.g. involving radical or cation radical species) can be envisaged.

Redox reactions. According to Zerner and Gouterman[23] the vanadium(II) porphyrin is predicted to be thermodynamically stable but readily oxidised. Our attempts to isolate this, or the vanadium(III), complex were unsuccessful. Attempted metallation of octaethylporphyrin with vanadium(III) chloride in various solvents failed in an inert atmosphere: in the presence of air the vanadyl complex was obtained.

Treatment of vanadyl octaethylporphyrin with lithium aluminium hydride in tetrahydrofuran gave a striking colour change (red → green). The intermediate had a phlorin-like spectrum, and it seems likely that reduction occurred with interruption of the conjugated system rather than by reduction of the metal to the V(II) state, since the latter complex would be expected to have a normal metalloporphyrin spectrum. Quenching regenerated the starting material (64%) although some demetallation occurred, and a trace of the vanadyl chlorin (13) was formed. Reduction to the metallochlorin(13) also occurred with sodium-isopentyl alcohol. The product is regarded as the *trans* derivative since equilibration is expected to occur under the preparative conditions. Attempts to metallate *trans*-octaethylchlorin using the Erdman method were unsuccessful: dehydrogenation intervened and the product was a mixture of octaethylporphyrin and its vanadyl derivative. A clean dehydrogenation of 13 to 1 occurred with DDQ.



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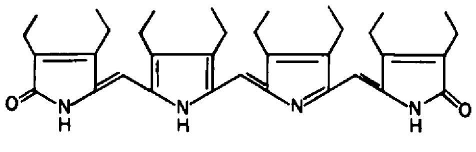

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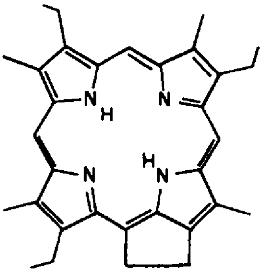
Vanadyl octaethylporphyrin resisted photoxidation[24] (PhH, 500 W tungsten lamp, O_2 flush) and coupled oxidation with ascorbic acid and hydrogen peroxide in pyridine.[25] Preliminary experiments with hydrogen peroxide—trifluoroacetic acid gave a complex mixture in which octaethyl - 1,19(21*H*, 24*H*)bilindione (14) was identified as a minor component.

Transalkylation. Triebs[26] concluded that the most important petroporphyrins from bitumen were 17^2 - decarboxy - 13^1 - deoxophytoporphyrin (15, name based on phytoporphyrin, 16. Compound 15 is desoxophylloerythroetioporphyrin in the Fischer nomenclature) and etioporphyrin (17). Twenty years after the original work reports began to appear suggesting that the situation was more complicated.[27] The most decisive evidence came from mass spectrometry.[3,28] Thus petroporphyrins extracted from asphaltenes with methylsuphonic acid (-V, Ni) were reported to fall into one minor series and two major series. The two major series were mixtures of homologues of 15 and etioporphyrin (17), the relative distribution in each series of homologues forming a roughly Gaussian distribution peaking at 15 and 17.[28] While the formation of these two porphyrins from chlorophyll *a* (or *b*) and, possibly, from haem pigments during diagenesis is plausible, the origin of their homologues—lower and higher—is not clear.† Of the suggested explanations[29] that postulating transalkylation[28,30] seemed to us the most reasonable since not only did it find example as an acid-catalysed reaction in simpler aromatic systems[31] (e.g. the Jacobson rearrangement)[32] but it accounted, for example, for the distribution (*ca.* C_{27}–C_{37}) of homologues of 15 (C_{32}). The suggestion, then, was that the alkylporphyrins might undergo transalkylation on acidic minerals over geological time periods. This suggestion was subjected to experimental test.



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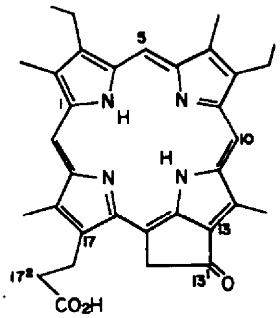
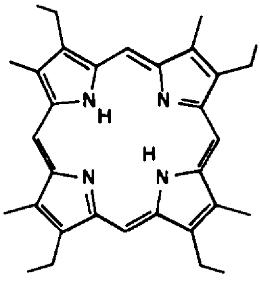


16 Phytoporphyrin (phylloerythrin in Fischer nomenclature)



17 Etioporphyrin III

Octaethylporphyrin did not suffer transalkylation when left in concentrated sulphuric acid at room temperature for 22 days. However, when vanadyl octaethylporphyrin (M = 599) was mixed (by grinding) with alumina and heated in vacuo at 245° for 19 days, and the metalloporphyrin was recovered and crystallised, mass spec-

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†Another uncertainty, which is not resolved here, but needs to be stated, is that it does not appear to be established beyond dispute that the etioporphyrin component of the petroporphyrin mixture is entirely (or at all) the type III isomer drawn in (17).

trometry showed clearly the presence of higher homologues (M + Me (613) and M + Et (627)). The most convincing results were obtained by impregnating the support, including the natural clay minerals illite and montmorillonite, with the vanadyl octaethylporphyrin in solution; and recording the mass spectrum of the total extract after thermal treatment. Results obtained in this way are recorded in Table 5. The result with alumina at 300° for 12 hr is shown in Fig. 2, and compared with the high mass region of the mass spectrum of the starting material. Clearly there is evidence for transethylation, a conclusion confirmed by accurate mass determinations on the peaks at 571 and 627. The entering Et groups are presumed to be located at *meso*-positions. There is also some indication in the minor peaks around 613 and 639 for transmethylation, presumably involving benzylic cleavage, but evidently this is a much lese favourable process.

As Table 5 shows, vanadyl octaethylporphyrin suffered little change when heated alone (300°, 12 hr) but under the same conditions on alumina pronounced transethylation occurred. On silica gel extensive decomposition occurred at 300°, but some transethylation was observed at 250° (though not at 200°). On the clay minerals transethylation was in evidence even at 200°. The results support the hypothesis that the various homologous series of petroporphyrins have arisen by intermolecular transalkylation processes catalysed by natural supports such as aluminosilicates.

EXPERIMENTAL

General. General experimental methods and conventions have been indicated previously.[17,25] Unless otherwise noted, electronic spectra (λ in nm) refer to solutions in chloroform, NMR spectra to soln in [^{2}H]chloroform, and IR spectra (ν in cm^{-1}) to KBr discs. Some of the spectra are collected in the Tables.

Metallation of porphyrins

Vanadyl octaethylporphyrin. Octaethylporphyrin (155 mg) and vanadyl sulphate dihydrate (235 mg) in HOAc–pyridine (2:1, 15 ml) were refluxed (7 hr) and the cold mixture was diluted with water (15 ml). The crude metalloporphyrin was removed, washed well with water, sat NaHCO$_3$ and water, and recrystallised from CHCl$_3$–MeOH to give purple crystals (170 mg, 98%) of vanadyl octaethylporphyrin, m.p. > 320°. (Found: C, 71.94; H, 7.31; N, 9.24; V, 8.34%; M$^+$ = 599.296. $C_{36}H_{44}N_4OV$ requires: C, 72.10; H, 7.40; N, 9.34; V, 8.49%; M = 599.295). λ (PhH) 408 (320,000), 534 (16,000), 572 (36,000). λ (HOAc) 404 (290,000), 532 (15,000), 570 (32,000). λ (CF$_3$CO$_2$H) 387 (110,000), 470 (4400), 513 (6600), 541 (5600), 562i (5300), 613i (4400). λ (pyridine) 408 (256,000), 423 (111,000), 536 (14,200), 572 (25,500).

Vanadyl porphyrin. This was prepared from porphyrin (20 mg) in an analogous way, except that the period of reflux was 20 hr. The red precipitate was washed as before, and dried *in vacuo* to afford vanadyl porphyrin in 48% yield. It could not be recrystallised. M.p. > 310° (Found: M$^+$ 375.045. $C_{20}H_{12}N_4OV$ requires: M$^+$ 375.045).

Reactions of Vanadyl octaethylporphyrin

Nitration. (a) Vanadyl octaethylporphyrin (20 mg) in acetonitrile (40 ml) was added to conc. HNO$_3$ (d, 1.4) in acetonitrile (1:49, 80 ml) both solns being at 0°. After 5 min without further cooling the soln was poured into water (200 ml) and extracted with CHCl$_3$. The extract was washed (NaHCO$_3$ aq, water), dried, and chromatographed on neutral alumina (Grade III). Elution with 30% benzene in petroleum gave *vanadyl 5 - nitrooctaethylporphyrin* (13 mg, 61%) as cherry-red rhomboids (from CHCl$_3$–MeOH), m.p. > 320°. (Found: C, 66.77; H, 6.66; N, 10.91%; M$^+$ 644.281. $C_{36}H_{43}N_5O_3V$ requires: C, 67.06; H, 6.72; N, 10.86%; M$^+$ 644.281. ν 1528, 1375, 999. The same compound was prepared by metallation of 5 - nitrooctaethylporphyrin.

(b) Vanadyl octaethylporphyrin (36 mg) in acetonitrile (80 ml) was treated with a soln of conc. HNO$_3$ (d, 1.4) in acetonitrile (2:25, 30 ml) for 1 min, both solns being at 22°. The mixture was then worked up as before. Chromatography on neutral alumina

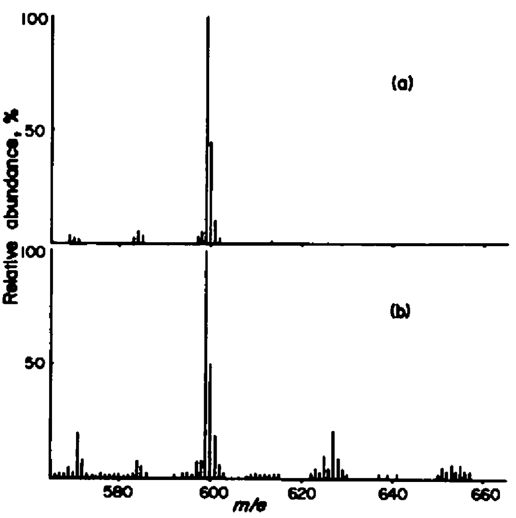

Fig. 2. Mass spectrum of vanadyl octaethylporphyrin: (a) after being heated (300°, vacuum, 12 hr); (b) after being heated on alumina under the same conditions.

Table 5. Transalkylation of vanadyl octaethylporphyrin (12 hr, *in vacuo*, relative abundances at *m/e* values given)

Support	Temperature	543	554	569 (−30)	571 (−28)	584 (−15)	585 (−14)	599	613 (+14)	615 (+16)	627 (+28)	637	655 (+56)
Nil	—	0	2.2	3.2	1.0	5.0	2.1	100	0	0	0	0	0
Nil	300°	0.4	3.1	3.6	2.1	6.0	3.1	100	0.7	0.3	0	0	0
Al$_2$O$_3$[a]	300°	2.5	3.6	4.8	20.0	7.6	5.0	100	2.0	1.2	21.0	1.2	5.8
SiO$_2$[b]	200°	0.2	2.2	3.0	1.9	5.0	2.5	100	0.6	0.2	0	0	0
SiO$_2$	250°[c]	13.5	5.3	6.0	48.0	7.8	32.0	100	4.6	1.8	3.6	1.8	1.2
Montmorillonite[d]	150°	4.5	2.7	4.5	22.0	6.0	3.4	100	1.1	1.9	1.0	0.2	0.5
Montmorillonite	200°[e]	10.0	3.5	5.1	26.0	6.5	20.5	100	5.0	6.3	10.5	0.8	1.2
Illite[f]	200°	2.1	3.2	4.0	14.0	6.4	4.3	100	1.2	2.4	7.9	0.2	1.8

[a] Al$_2$O$_3$: Hopkins and Williams "Camag" M.F.C. Grade, neutral.
[b] SiO$_2$: Hopkins and Williams M.F.C. grade.
[c] Some decomposition noted: gross decomposition at 300°.
[d] From Amory, Mississippi: sample number 48W1222.
[e] Gross decomposition at 300°.
[f] From Morris, Illinois: sample number 48W1536.

(Grade II) gave the mixed dinitro derivatives eluted with benzene–petroleum (13:7) which were crystallised from $CHCl_3$–MeOH as red prisms (17.7 mg, 43%).

The mixed vanadyl dinitroporphyrins (31.2 mg) for several experiments were fractionally crystallised twice from chloroform–methanol (1:3) to give *vanadyl* 5,15 - *dinitrooctaethylporphyrin* (17 mg, 19%) as red prisms, m.p. > 310°. (Found: M^+ 689.263. $C_{36}H_{42}N_6O_5V$ requires: M^+ 689.266). ν 1531, 1375, 1000. The residues from the mother liquors were crystallised from chloroform–methanol (1:10) to give *vanadyl* 5,10 - *dinitrooctaethylporphyrin* (8.9 mg, 10%) as red crystals m.p. > 310°. (Found: N, 12.13%, M^+ 689.264. $C_{36}H_{42}N_6O_5V$ requires: N, 12.19%). ν 1538, 1371, 1365, 1001, 999. Each of the two metal complexes was identical with the compound prepared by metallation of the appropriate dinitroporphyrin.[16]

(c) Treatment of vanadyl octaethylporphyrin (20.4 mg) in acetonitrile (80 ml) with sodium nitrite (36.4 mg) in 2N HCl (15 ml) over 30 min at room temp. followed by work up as before gave vanadyl 5,10,15 - trinitrooctaethylporphyrin (1 mg, 4%), vanadyl dinitrooctaethylporphyrin (6 mg, 25%), and vanadyl 5 - nitrooctaethylporphyrin (6.4 mg, 29%).

Chlorination. (a) H_2O_2 (28%, 1 ml) was added to 0.5 N HCl (99 ml), and 72 ml of this soln was immediately added to vanadyl octaethylporphyrin (59.5 mg) in THF (100 ml). The mixture was refluxed (1 hr), diluted with $CHCl_3$ (50 ml) and washed with water, $NaHCO_3$ aq and then water again. Chromatography (neutral alumina, Grade III) afforded (i) a green fraction eluted with toluene - n - heptane (1:4) which gave metallic blue needles (2.1 mg, 3%) of *vanadyl* 5,10,15,20 - *tetrachlorooctaethylporphyrin*, m.p. 267–9°, from $CHCl_3$–MeOH. (Found: M^+ 735.140. $C_{36}H_{40}{}^{35}Cl_4N_4OV$ requires: M^+ 735.140). (ii) A green fraction with toluene - n - heptane (2:3) which gave blue crystals (4.7 mg, 7%) of *vanadyl* 5,10,15 - *trichlorooctaethylporphyrin*, m.p. 253–5° from $CHCl_3$–MeOH. (Found: M^+ 701.180. $C_{36}H_{41}{}^{35}Cl_3N_4OV$ requires: M^+ 701.179). Continued elution with this solvent gave (iii) A red fraction which was crystallised from chloroform-methanol to give *vanadyl* 5,15 - *dichlorooctaethylporphyrin*, (2.1 mg, 3%) as red needles, m.p. > 300°. (Found: C, 65.03; H, 6.53%; M^+ = 667.216. $C_{36}H_{42}Cl_2N_4OV$ requires: C, 64.67; H, 6.33%; M = 667.218 for ^{35}Cl). (iv) Toluene - n - heptane (1:1) eluted a reddish-green fraction which gave blue rhomboids, m.p. 254–6°, of *vanadyl* 5,10 - *dichlorooctaethylporphyrin* (1.7 mg, 3%) from $CHCl_3$–MeOH. (Found: M^+ 667.218). (v) Toluene - n - heptane (7:3) eluted a red component which gave red crystals, m.p. > 310°, of *vanadyl 5-chlorooctaethylporphyrin* (13.6 mg, 21%) from $CHCl_3$–MeOH. (Found: C, 68.02; H, 6.98; M^+ 633.255. $C_{36}H_{43}ClN_4OV$ requires: C, 68.18; H, 6.83%; M^+ 633.257 for ^{35}Cl).

(b) Under similar conditions continued treatment with the chlorinating mixture (70 ml for 1.5 hr reflux, then an additional 40 ml for a further 1.5 hr reflux) gave the vanadyl complexes of the tetrachloro derivative (37%) and the trichloro derivative (11%) as the main isolated products.

(c). Metallation of 5 - chlorooctaethylporphyrin and 5,15 - dichlorooctaethylporphyrin gave products identical (ES, TLC) with those formed by chlorination of the vanadyl porphyrin.

Benzoyloxylation. To vanadyl octaethylporphyrin (106 mg) in 1,2,4 - trichlorobenzene (20 ml) at *ca.* 98° under N_2 was added benzoyl peroxide (54.5 mg) in the same solvent (2 ml) over 75s. The soln was kept under N_2 at *ca.* 98° for 30 min and the solvent was removed under reduced pressure. TLC (23% acetone in petroleum) yielded in order of decreasing mobility: (i) Vanadyl octaethylporphyrin (35% recovery). (ii) *Vanadyl* 2 - (1′ - *benzoyloxethyl)heptaethylporphyrin* (6.9 mg, 5%) as purple crystals, m.p. 205–8° (dec.), from $CHCl_3$–MeOH. (Found: C, 71.75; H, 6.8%; M^+ = 719.315. $C_{43}H_{48}N_4O_3V$ requires: C, 71.75; H, 6.7%; M = 719.317). λ 411 (285,000), 535 (12,600) and 574 (23,000). λ 1711, 1017, 993, (iii) *Vanadyl* 5 - *benzoyloctaethylporphyrin* (22.7 mg, 18%) as purple crystals, m.p. > 310°, from $CHCl_3$–MeOH. (Found: C, 71.26; H, 6.95%; M^+ = 719.315). ν 1743, 1020, 990. This material was identical (TLC, ES, IR) with a sample made by metallation. (iv) *Vanadyl di* - (meso - *benzoyloxyoctaethylporphyrin* (8.2 mg, 6%) as purple crystals, m.p. > 310°, phase change at 224–6°, from chloroform–petroleum. (Found: M^+ = 839.337. $C_{50}H_{52}N_4O_5V$ requires: M^+ = 839.338). λ 419 (279,000), 541 (15,100) and 577 (10,600). ν 1744, 1020, 1000i, 990.

Hydrolysis of vanadyl 5 - *benzoyloxyoctaethylporphyrin.* Vanadyl 5 - benzoyloxyoctaethylporphyrin (23.9 mg) was refluxed in pyridine (20 ml) and 4N KOH (2 ml) for 90 min. The soln was poured into water (200 ml) and extracted with $CHCl_3$ (6 × 50 ml). The combined $CHCl_3$ extracts were washed with water and dried. The concentrate was chromatographed on neutral alumina (Grade III). Chloroform-benzene (1:1) eluted *vanadyl* 5 - *hydroxyoctaethylporphyrin* (2.5 mg, 12%) isolated as deep blue crystals, m.p. > 310°. (Found: M^+ = 615.290. $C_{36}H_{44}N_4O_2V$ requires: M^+ = 615.290). λ (pyridine + KOH) 539, 574, 624, 676. ν, no strong band in the 1600 region, 1018, 994, 978.

Reduction of vanadyl octaethylporphyrin

(a) *With lithium aluminium hydride.* To a stirred soln of vanadyl octaethylporphyrin (7 mg) in THF (12 ml) was added LAH (100 mg) (colour change: red → green; λ 462, 495, 585, 613, 650 and 734) and the solution was refluxed for 2.5 hr. The THF was removed, sufficient methanol was added to destroy the LAH, followed by benzene. The inorganic precipitate was removed by filtration, and the filtrate was concentrated and chromatographed on neutral alumina (Grade III) to give (i) octaethylporphyrin (35% spectroscopic) eluted with benzene–petroleum (1:1); (ii) vanadyl octaethylchlorin (trace) and (iii) vanadyl octaethylporphyrin (64% spectroscopic) eluted with benzene.

(b) *With sodium in isopentyl alcohol.* To vanadyl octaethylporphyrin (21 mg) in isopentyl alcohol (15 ml) refluxing under N_2 was added Na (20 mg). After 15 min the cooled soln was treated with MeOH (10 ml) and water (10 ml) and the soln was extracted with $CHCl_3$ (20 ml) which was washed with water (2 × 30 ml) and dried. Concentration and chromatography on neutral alumina (Grade III) gave (i) *trans*-octaethylchlorin (2%, spectroscopic), eluted with benzene-petroleum (1:1); (ii) octaethylporphyrin (3%, spectroscopic); (iii) *vanadyl* trans-*octaethylchlorin* (1.7 mg, 9%) eluted with benzene and crystallised from chloroform-petroleum, m.p. > 310°. (Found: M^+ = 601.311. $C_{36}H_{44}N_4OV$ requires: M = 601.311). λ 409 (114,000), 506 (4200), 541 (4900), 574 (7000), 632 (33,000). ν 2961, 2932, 2875, 1635, 1572, 1206, 1052, 1011, 995, 958; and (iv) vanadyl octaethylporphyrin (6.5 mg, 31%) eluted with benzene and crystallised from $CHCl_3$–MeOH.

Transalkylation experiments

(*a*) Octaethylporphyrin (3 mg) in conc H_2SO_4 (3 ml) was left at room temp. for 22 days. The mixture was worked up in the usual way: the mass spectrum of the crystallised product showed no significant peak at *m/e* 562(M + 28).

(b) Vanadyl octaethylporphyrin (2 mg portions) was heated (i) alone and (ii) mixed (by grinding) with neutral alumina (1 g) in each case *in vacuo* at 245° for 19 days. The porphyrin from the alumina experiment was recovered by extraction with chloroform, and both samples were crystallised from $CHCl_3$–MeOH. Mass spectrometry gave the relative abundances shown below.

	m/e	599	613	614	627	628
Starting material	%	100	0.2	0.1	0	0
Heated alone	%	100	1.2	0.6	0.4	0.2
Heated with Al_2O_3	%	100	0.8	0.4	1.6	0.7

(c) Vanadyl octaethyl porphyrin (1 mg) was applied in a little chloroform solution to a support (250 mg). The solvent was removed and the sample sealed, both *in vacuo*. The sample was heated at the stated temperature for 12 hr. The product was extracted with chloroform and the crude extract was subjected to mass spectrometry with the results shown in Table 5.

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