Vanadium(II) Porphyrin Complexes: Synthesis and Characterization. Crystal Structure of 2,3,7,8,12,13,17,18-Octaethylporphinatobis-(dimethylphenylphosphine)vanadium(II)

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The vanadium(II) porphyrins $V^{II}(PPhMe_2)_2$(porp) containing phosphine ligands have been prepared from $V^{IV}(X_2)$(porp) [porp = octaethylporphinato(oep), meso-tetraphenylporphinato, meso-tetra-m-tolylporphinato, meso-tetra-p-tolylporphinato] and the crystal structure of $V^{II}(PPhMe_2)_2$(oep) has been solved by X-ray diffraction methods; the first observations of interactions between vanadium(II) porphyrins and molecular oxygen are described.

Low-valent metalloporphyrins have been shown to interact with molecular oxygen; it has been found that synthetic iron(II),[1] ruthenium(II),[2] cobalt(II),[3] chromium(II),[4] and manganese(II)[5] porphyrins can be reversibly or irreversibly oxygenated. On the basis of the M^{II}–M^{III} redox potentials, it has also been postulated that V^{II} should bind O_2 more strongly than Fe, Mn, and Co metalloporphyrin complexes,[5a,6] but to the best of our knowledge such vanadium(II) complexes have not hitherto been characterized. However, we have recently[7] described the synthesis and structure determination of dihalogenovanadium(IV) porphyrins which could act as precursors to low-valent vanadium porphyrins. We report here a convenient synthetic procedure for the isolation of vanadium(II) porphyrins by the reduction of higher oxidation state halogeno-derivatives, and their definitive structural characterization, together with the first observation of interactions between vanadium(II) porphyrins and dioxygen.

Reduction by zinc amalgam (2 g) of a dry oxygen-free tetrahydrofuran solution (30 cm³) containing $V^{IV}Cl_2$(oep)† (0.46 mmol) and an excess of dimethylphenylphosphine (0.2 cm³) led to a brown solution after vigorous stirring for 12 h at room temperature. After evaporation in vacuo, the residue was recrystallized from heptane (197 mg, 51%). The conditions, yields, and spectroscopic data for this reaction and reactions of other porphyrins are summarized in Table 1. Elemental analyses of the compounds obtained are consistent with the molecular formula $V^{II}(PPhMe_2)_2$(porp). Reduction of $V^{IV}Cl_2$(porp) in the absence of dimethylphenylphosphine affords the THF solvates $V^{II}(THF)_2$(porp). The u.v.–visible spectra obtained at room temperature (under Ar) for the $V^{II}(PPhMe_2)_2$(porp) complexes are typical of hyperporphyrinic

Table 1. Yields and u.v.–visible data for the vanadium(II) porphyrin complexes $V^{II}(PPhMe_2)_2$ (porp).

porp	% Yield	λ_{max}/nm (10^{-4} ϵ/dm³ mol⁻¹ cm⁻¹)
oep	51[a]	366 (13.4), 381 (15.4), 447 (8.5), 504 (4.0)
tpp	46[b]	369 (7.6), 439 (7.4), 535 (2.4)
tmtp	41[b]	368 (12.5), 436 (15.3), 534 (4.0)
tptp	60[b]	371 (10.0), 448 (8.0), 545 (3.2)

[a] From heptane. [b] From toluene–heptane (1 : 1).

systems (see Table 1). Two structural possibilities are consistant with the analytical data: (a) a cis-form with the metal significantly out of the porphyrin plane and (b) a trans-form. To distinguish between the two possibilities, the structure of $V^{II}(PPhMe_2)_2$(oep) was determined by X-ray diffraction,‡ and Figure 1 shows a projection of the molecular structure. The vanadium(II) atom is on the (0,0,0) inversion centre and has a pseudo-octahedral co-ordination. Hence the two phosphine ligands are trans and the vanadium atom lies strictly within the plane of the four nitrogen atoms {average V–N 2.050(4) Å; cf. 2.041(8) Å in (5,10,15,20-tetraphenylporphinato)bis-[bis(diphenylphosphino)methane]ruthenium(II)–dichloromethane[8] }. The metal–phosphorus distance [2.523(1) Å] is longer than those observed in the ruthenium porphyrin just

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† Abbreviations used: THF = tetrahydrofuran; porp = porphinato; oep = octaethylporphinato; tpp = meso-tetraphenyl-porphinato; tmtp = meso-tetra-m-tolylporphinato; tptp = meso-tetra-p-tolylporphinato.
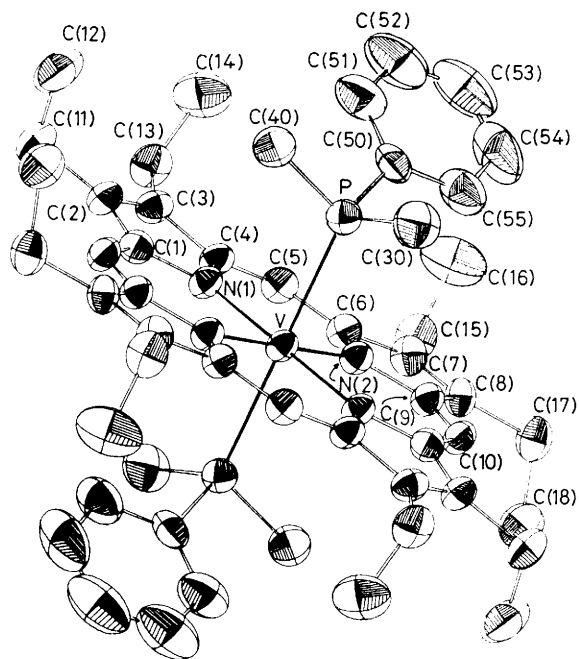
Figure 1. ORTEP drawing of the structure of $V^{II}(PPhMe_2)_2$ (oep). All atoms are represented by 50% probability thermal ellipsoids.

mentioned[8] [2.398(3) Å] and in other vanadium complexes {2.442(2) Å in cis-$[(\eta^5-C_5H_5)V(CO)_2(Ph_2PCH_2CH_2PPh_2)]$[9] 2.360(2) Å in $[(CO)_4V(PMe_3)]_2$[10] }. This long bond length could be explained by steric hindrance considerations: the nitrogen-methyl [N(1)–C(40), N(2)–C(30)] distances would be much shorter than the sum of the van der Waals radii (3.25 Å) if the metal–phosphorus bond were of normal length. The geometry of the porphinato-ligand is normal and agrees with that observed in other metalloporphyrins.[11]

One of the major difficulties encountered in attempts to study the reaction of vanadium(II) porphyrin complexes with molecular oxygen is the large driving force towards the irreversible formation of the stable vanadyl compounds [reaction (1)]. We have observed the following. (i) Exposure at

$$V^{II} + O_2 \rightleftharpoons V(O_2) \rightarrow V^{IV}{=}O \qquad (1)$$

room temperature of a toluene solution of $V^{II}(PPhMe_2)_2(porp)$ to O_2 results in a rapid, irreversible reaction giving $V^{IV}(O)$-(porp); no reaction occurs below $-50\,°C$. Optical and e.s.r. spectra do not support the existence of a vanadium–dioxygen adduct throughout the temperature range (from 25 to $-50\,°C$). (ii) Oxidation of vanadium(II) complexes occurs in the solid state leading to a mixture of $V^{IV}(O)(porp)$ and another

product (A). I.r. spectra of oxidized samples dispersed in Nujol were recorded to monitor the reaction; the characteristic V=O stretch of $V^{IV}(O)(porp)$ appears at ca. 1000 cm^{-1} while bands at 1177 (for porp = oep) and ca. 1140 cm^{-1} (for porp = tpp, tmtp, and tptp) are attributable to the second complex (A). When $V^{II}(PPhMe_2)_2(oep)$ is oxidized with $^{18}O_2$§ the 1177 cm^{-1} band is absent, and the band at 1111 cm^{-1} becomes stronger than the ligand band at 1110 cm^{-1}. This result clearly indicates that the 1177 cm^{-1} band was shifted to 1111 cm^{-1} by the $^{16}O_2$–$^{18}O_2$ substitution. Thus the i.r. data for the product (A) are consistent with dioxygen co-ordinated to vanadium, which may be described as superoxide-like. In view of these results, we are studying the possible use of such vanadium(II) complexes as oxygen carriers.

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§ Oxygen-18 (98.5%) was obtained from Service des Isotopes Stables, Saclay, France.