Vanadium(II) Porphyrins: Synthesis and Physicochemical Properties. Crystal Structures † of Bis(dimethylphenylphosphine)- and Bis(tetrahydrofuran)-(2,3,7,8,12,13,17,18-octaethylporphyrinato)-vanadium(II)

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The vanadium(II) porphyrins $[\mathrm{V^{II}L(PPhMe_2)_2}]$ and $[\mathrm{V^{II}L(thf)_2}]$ have been prepared from $[\mathrm{V^{IV}LX_2}]$ [L = 2,3,7,8,12,13,17,18-octaethylporphyrinate (oep), *meso*-tetraphenylporphyrinate (tpp), *meso*-tetra-*m*-tolylporphyrinate (tmtp), or *meso*-tetra-*p*-tolylporphyrinate (tptp); X = halide]. The crystal structures of $[\mathrm{V^{II}(oep)(PPhMe_2)_2}]$ and $[\mathrm{V^{II}(oep)(thf)_2}]$ have been solved by *X*-ray diffraction methods. Crystals of $[\mathrm{V^{II}(oep)(PPhMe_2)_2}]$ are orthorhombic, space group *Pbca*, with a = 14.540(2), b = 21.431(3), c = 15.305(5) Å, and Z = 4. Crystals of $[\mathrm{V^{II}(oep)(thf)_2}]$ are triclinic, space group $P\bar{1}$, with a = 10.078(1), b = 10.202(3), c = 10.815(1) Å, α = 75.54(1), β = 87.63(1), γ = 66.43(1)°, and Z = 1. In both complexes the two non-porphyrin ligands are in a *trans* configuration. The vanadium atom, being on an inversion centre, lies in the perfect plane of the four nitrogen atoms and is octahedrally co-ordinated $\{\mathrm{V^{II}}$–P 2.523(1), $\mathrm{V^{II}}$–O 2.174(4), mean V–N 2.046(4) Å for $[\mathrm{V^{II}(oep)(thf)_2}]$ and 2.051(4) Å for $[\mathrm{V^{II}(oep)(PPhMe_2)_2}]\}$.

Low-valent metal porphyrin complexes have been extensively studied for many years [1–7] and have shown some promise in understanding the reactions of haems with molecular oxygen. The poor reactivity of oxovanadium(IV) porphyrins has restricted their co-ordination chemistry to that of the $\mathrm{VO^{2+}}$ unit, and to the best of our knowledge no vanadium(II) or vanadium(III) complexes have hitherto been characterized. However, we have recently [8] described the synthesis and structure determination of dihalogenovanadium(IV) porphyrins $[\mathrm{V^{IV}LX_2}]$ (1), X = Cl or Br, which could act as precursors of low-valent vanadium porphyrins.

In a preliminary communication [9] we have pointed out that the reduction of higher oxidation state vanadium halogeno-derivatives gives vanadium(II) porphyrins, $[\mathrm{V^{II}L(PPhMe_2)_2}]$. In this paper we present the synthesis and characterization of $[\mathrm{V^{II}L(thf)_2}]$ (2) and $[\mathrm{V^{II}L(PPhMe_2)_2}]$, (3), as well as the crystal structure determinations of $[\mathrm{V^{II}(oep)(PPhMe_2)_2}]$, (3a), and $[\mathrm{V^{II}(oep)(thf)_2}]$, (2a).‡

Experimental

Synthesis and Spectroscopic Measurements.—All experimental procedures were performed under an argon atmosphere using dry oxygen-free solvents. The dichlorovanadium(IV) complexes, $[\mathrm{V^{IV}LCl_2}]$, were prepared as reported previously.[9]

Typical preparations of vanadium(II) complexes are illustrated below.

$[\mathrm{V^{II}(oep)(thf)_2}]$, (2a). Reduction by zinc amalgam (2 g) of a dry oxygen-free tetrahydrofuran solution (40 $\mathrm{cm^3}$) containing $[\mathrm{V^{IV}(oep)Cl_2}]$ (0.58 mmol) led to a brown solution after vigorous stirring for 12 h at room temperature. After evaporation *in vacuo*, the residue was recrystallized from heptane. Yield 200 mg (47%).

$[\mathrm{V^{II}(oep)(PPhMe_2)_2}]$, (3a). A solution of well dried $[\mathrm{V^{IV}(oep)Cl_2}]$ (0.46 mmol) with an excess of dimethylphenylphosphine (0.2 $\mathrm{cm^3}$) in tetrahydrofuran (30 $\mathrm{cm^3}$) was reduced by zinc amalgam (2 g). The reaction mixture was treated as described above yielding 197 mg (50%) of the product after recrystallization from heptane (30 $\mathrm{cm^3}$).

The reactions conditions, yields, and elemental analyses for the complexes are summarized in Table 1.

Physical Measurements.—Elemental analyses were performed by the Service de Microanalyse du C.N.R.S. Infrared spectra were recorded on a Perkin-Elmer 580B apparatus for 1% dispersions in Nujol mulls. Visible and u.v. spectra were obtained on a Perkin-Elmer 559 spectrophotometer using 10^{-6} mol $\mathrm{dm^{-3}}$ dry oxygen-free tetrahydrofuran solutions. Magnetic measurements were performed on a Foner magnometer using a field of 10 000 Oe ($10^7/4\pi$ A $\mathrm{m^{-1}}$).

Crystallography.—*Crystal data.* $[\mathrm{V^{II}(oep)(PPhMe_2)_2}]$, $\mathrm{C_{52}H_{66}N_4P_2V}$, M = 839, orthorhombic, a = 14.540(2), b = 21.431(3), c = 15.305(5) Å, U = 4 769 $\mathrm{Å^3}$, Z = 4, D_c = 1.208 g $\mathrm{cm^{-3}}$, space group *Pbca*, μ(Cu-K_α) = 27 $\mathrm{cm^{-1}}$, λ(Cu-K_α) = 1.540 54 Å, F(000) = 1 836.

$[\mathrm{V^{II}(oep)(thf)_2}]$, $\mathrm{C_{44}H_{60}N_4O_2V}$, M = 707, triclinic, a = 10.078(1), b = 10.202(3), c = 10.815(1) Å, α = 75.54(1), β = 87.63(1), γ = 66.43(1)°, U = 985 $\mathrm{Å^3}$, Z = 1, D_c = 1.23 g $\mathrm{cm^{-3}}$, space group $P\bar{1}$, μ(Cu-K_α) = 26 $\mathrm{cm^{-1}}$, F(000) = 368.

X-Ray data collection and crystal structure determination. Deep red crystals of $[\mathrm{V^{II}(oep)(PPhMe_2)_2}]$ were obtained by recrystallization of the complex from heptane. They were in the form of orthorhombic bipyramids truncated by a pinacoïd. A crystal of dimensions 0.21 × 0.21 × 0.10 mm was sealed into a glass capillary and mounted on a CAD 4 Enraf-Nonius diffractometer. Unit-cell dimensions were refined by a least-

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† *Supplementary data available* (No. SUP 56038, 9 pp.): thermal parameters, H-atom co-ordinates, least-squares planes. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1984, Issue 1, pp. xvii—xix. Structure factors are available from the editorial office.

‡ Abbreviations used: thf = tetrahydrofuran; L = porphyrinate(2−); oep = 2,3,7,8,12,13,17,18-octaethylporphyrinate(2−); tpp = 5,10,15,20-tetraphenylporphyrinate(2−); tmtp = 5,10,15,20-tetra-*m*-tolylporphyrinate(2−); and tptp = 5,10,15,20-tetra-*p*-tolylporphyrinate(2−).

Table 1. Reaction conditions and yields

Complex	Recrystallization solvent [a]	Yield (%)	Analysis [b] (%) C	H	N	V	P
(3a) $[V^{II}(oep)(PPhMe_2)_2]$	A	50	72.6	7.80	6.45	5.45	7.25
			(72.75)	(7.70)	(6.50)	(5.90)	(7.15)
(2a) $[V^{II}(oep)(thf)_2]$	A	47	73.1	7.95	7.90	6.45	
			(72.6)	(8.30)	(7.70)	(7.00)	
(3c) $[V^{II}(tmtp)(PPhMe_2)_2]$	B	41	77.45	5.65	5.45	5.45	6.05
			(77.15)	(5.85)	(5.60)	(5.10)	(6.20)
(3d) $[V^{II}(tptp)(PPhMe_2)_2]$	B	60	77.1	5.85	5.60	5.20	6.30
			(77.15)	(5.85)	(5.60)	(5.10)	(6.20)

[a] A = Heptane; B = heptane–toluene (1 : 1). [b] Calculated values are given in parentheses.

Table 2. Fractional co-ordinates of $[V^{II}(oep)(PPhMe_2)_2]$ (3a)

Atom	*X/a*	*Y/b*	*Z/c*	Atom	*X/a*	*Y/b*	*Z/c*
V	0	0	0	C(12)	0.244 3(6)	−0.173 6(4)	−0.210 6(6)
P	0.078 5(1)	0.102 8(1)	0.030 0(1)	C(13)	0.318 5(4)	−0.148 9(3)	0.041 9(5)
N(1)	0.123 0(3)	−0.044 0(2)	−0.021 2(3)	C(14)	0.280 7(6)	−0.212 2(3)	0.057 1(6)
N(2)	0.011 3(3)	−0.019 0(2)	0.131 0(3)	C(15)	0.130 6(4)	−0.077 5(3)	0.333 4(4)
C(1)	0.163 7(4)	−0.054 0(2)	−0.101 3(3)	C(16)	0.115 7(7)	−0.144 7(4)	0.348 4(6)
C(2)	0.243 5(4)	−0.094 2(2)	−0.090 5(3)	C(17)	−0.061 9(5)	−0.006 8(3)	0.365 5(4)
C(3)	0.251 6(4)	−0.106 4(2)	−0.002 8(4)	C(18)	−0.042 8(6)	0.058 7(4)	0.397 9(5)
C(4)	0.176 2(4)	−0.074 7(2)	0.039 7(3)	C(30)	0.203 4(4)	0.098 9(4)	0.036 9(6)
C(5)	0.158 5(4)	−0.074 2(2)	0.129 3(3)	C(40)	0.047 9(5)	0.136 7(4)	0.134 8(5)
C(6)	0.083 4(4)	−0.048 4(2)	0.172 8(3)	C(50)	0.055 1(4)	0.164 4(3)	−0.048 0(4)
C(7)	0.067 1(4)	−0.049 2(3)	0.266 3(3)	C(51)	−0.003 9(5)	0.213 1(3)	−0.030 6(5)
C(8)	−0.015 7(4)	−0.020 7(2)	0.280 4(3)	C(52)	−0.026 3(6)	0.257 0(4)	−0.093 5(7)
C(9)	−0.050 3(3)	−0.001 2(2)	0.195 9(3)	C(53)	0.012 0(7)	0.253 0(4)	−0.172 9(7)
C(10)	−0.131 4(4)	0.031 2(2)	0.180 6(4)	C(54)	0.070 4(8)	0.206 2(5)	−0.192 4(5)
C(11)	0.296 9(4)	−0.122 2(3)	−0.165 4(4)	C(55)	0.092 8(6)	0.160 2(3)	−0.131 2(4)

squares analysis of the observed setting angles of the K_{α_1} peaks of 25 reflections in the range $6 \leqslant \theta \leqslant 18°$. Scans for systematically absent reflections ($hk0$, $h = 2n + 1$; $h0l$, $l = 2n + 1$; $0kl$, $k = 2n + 1$) verified the space group determined by the Weissenberg method. *X*-Ray intensities were collected with monochromatized Cu-K_α radiation using a θ—2θ scan technique between $\theta = 2$ and 70°. Two standard reflections were monitored (every 2 h), but no statistically significant deviations were observed. A total of 4 101 reflections was collected in an eighth of the reciprocal space and 1 733 having $\sigma(I)/I < 0.33$ were used to solve and refine the structure. Each reflection was corrected for Lorentz and polarization effects, but not for absorption [$\mu R_{\text{max.}}$(Cu-K_α) = 0.57].

From the *U*, *M*, *Z*, and D_c values, the vanadium atom lies unambiguously on the 000 inversion centre of the space group. The structure was solved by the heavy-atom method which gave the atomic positions of the phosphorus atoms. The remaining atoms of the half-molecule including the hydrogens were located from Fourier difference maps. All positional and thermal parameters (four reflections per parameter) were refined with the full-matrix least-squares program SHELX [10] to $R(F) = 0.045$ and $R'(F) = 0.046$ where $w = 1/\sigma^2(F)$ and $\sigma^2(F) = \sigma^2(\text{count}) + 0.0025\,F^2$. Final positional parameters are listed in Table 2.

Deep red crystals of $[V^{II}(oep)(thf)_2]$ were crystallized from heptane in a form limited by three pinacoïds. A crystal of dimensions 0.15 × 0.13 × 0.08 mm was mounted as above. Unit-cell dimensions were refined by least-squares analysis of the observed setting angles of the K_{α_1} peaks of 25 reflections in the range $20 \leqslant \theta \leqslant 30°$. *X*-Ray intensities were collected as above. Three standard reflections were used for periodic checking of the alignment of the crystal (every 100 reflections) and three others for testing for possible deterioration of the crystal (every 2 h). No statistically significant deviations were observed. A total of 4 462 reflections was collected in the reciprocal sphere and 2 360 having $\sigma(I)/I < 0.33$ were used to solve and refine the structure. Each reflection was corrected for Lorentz and polarization effects, but not for absorption [$\mu R_{\text{max.}}$(Cu-K_α) = 0.39].

The structure was solved by the heavy-atom method in the space group $P\bar{1}$. The vanadium atom lies on the inversion centre of the space group. The remaining atoms of the half-molecule including the hydrogens were located from Fourier difference maps. All positional and thermal parameters (seven reflections per parameter) were refined with SHELX to $R(F) = 0.073$ and $R'(F) = 0.057$, where $w = 1/\sigma^2_{\text{count}}(F)$. Final positional parameters are listed in Table 3.

For both structures the scattering factors and the anomalous dispersion correction for V and P atoms were taken from ref. 11.

Results and Discussion

The vanadium(II) porphyrins $[V^{II}L(L')_2]$ were obtained by reduction of dihalogenovanadium(IV) porphyrins (Scheme). One of the major difficulties encountered during the synthesis was oxidation of the products obtained, and it is necessary to work under dry and anaerobic conditions. Interaction of vanadium(II) complexes with molecular oxygen occurs in solution and in the solid state, leading to the stable vanadyl compounds.

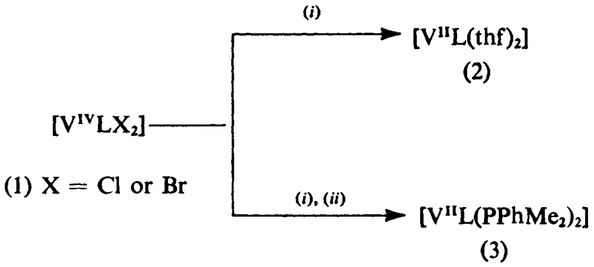
The proposed formula for compounds (2) and (3) is in accordance with the analytical results (Table 1). The electronic spectra of these complexes at room temperature are typical of hyperporphyrinic systems (Table 4), the intensities of bands I

Table 3. Fractional co-ordinates of $[V^{II}(oep)(thf)_2]$, (2a)

Atom	X/a	Y/b	Z/c	Atom	X/a	Y/b	Z/c
V	0	0	0	C(11)	−0.464 7(5)	0.506 3(6)	−0.285 5(5)
N(1)	−0.160 7(4)	0.207 2(4)	−0.061 6(3)	C(12)	−0.410 9(6)	0.575 4(7)	−0.403 7(6)
N(2)	0.050 5(4)	0.056 7(4)	0.154 8(3)	C(13)	−0.379 6(5)	0.600 7(5)	−0.050 1(5)
C(1)	−0.253 0(5)	0.259 2(5)	−0.170 7(5)	C(14)	−0.300 5(7)	0.696 6(6)	−0.107 5(6)
C(2)	−0.349 0(5)	0.412 8(5)	−0.180 6(5)	C(15)	0.033 6(8)	0.331 1(9)	0.347 4(7)
C(3)	−0.312 8(5)	0.452 0(5)	−0.080 9(5)	C(16)	−0.076 8(9)	0.335 5(9)	0.424 6(8)
C(4)	−0.195 9(5)	0.323 9(5)	−0.005 9(4)	C(17)	0.307 8(12)	0.000 5(8)	0.445 6(7)
C(5)	−0.129 2(5)	0.314 2(5)	0.106 7(5)	C(18)	0.237 6(10)	−0.058 5(10)	0.530 7(10)
C(6)	−0.014 8(5)	0.192 5(6)	0.181 7(5)	O	0.151 3(4)	0.078 2(4)	−0.109 9(3)
C(7)	0.055 0(7)	0.187 5(7)	0.297 7(5)	C(20)	0.301 1(7)	0.001 7(7)	−0.093 8(6)
C(8)	0.161 2(7)	0.052 4(6)	0.337 8(5)	C(21)	0.368 4(7)	0.093 5(8)	−0.179 0(6)
C(9)	0.159 0(5)	−0.032 2(6)	0.249 8(5)	C(22)	0.248 0(8)	0.227 7(7)	−0.249 8(6)
C(10)	−0.251 8(5)	0.176 1(6)	−0.253 5(4)	C(23)	0.114 5(7)	0.215 9(7)	−0.196 0(6)

Table 4. U.v.-visible spectroscopic data (in thf)

Complex	λ/nm ($10^{-4}\varepsilon$/dm^3 mol^{-1} cm^{-1})			
(3a) $[V^{II}(oep)(PPhMe_2)_2]$	366 (6.7)	381 (7.7)	447 (4.2)	504 (2.0)
(2a) $[V^{II}(oep)(thf)_2]$	367 (4.4)	419 (4.1)	479 (0.8)	505 (0.8)
(3b) $[V^{II}(tpp)(PPhMe_2)_2]$	369 (3.5)	439 (3.4)	535 (1.1)	
(2b) $[V^{II}(tpp)(thf)_2]$	365 (2.3)	403 (3.5)	522 (0.8)	
(3c) $[V^{II}(tmtp)(PPhMe_2)_2]$	368 (3.5)	436 (4.3)	534 (1.1)	
(2c) $[V^{II}(tmtp)(thf)_2]$	365 (2.7)	405 (3.5)	523 (0.9)	
(3d) $[V^{II}(tptp)(PPhMe_2)_2]$	371 (3.8)	448 (3.1)	545 (1.4)	
(2d) $[V^{II}(tptp)(thf)_2]$	365 (2.2)	405 (3.0)	524 (0.8)	



Scheme. (*i*) Zn–Hg, thf; (*ii*) $PPhMe_2$ (excess)

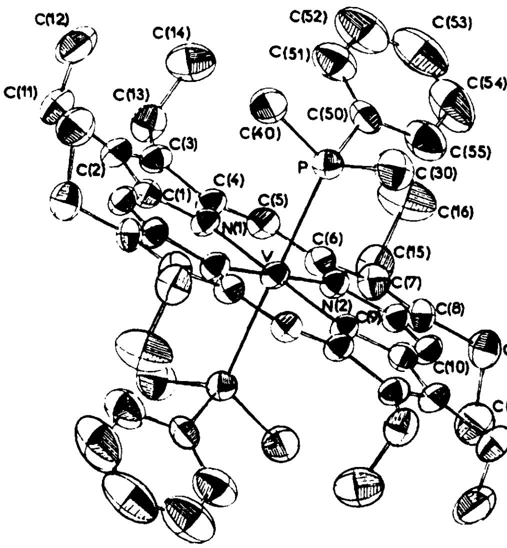


Figure 1. ORTEP view of $[V^{II}(oep)(PPhMe_2)_2]$, (3a)

and II being of the same magnitude. The i.r. spectra of the isolated complex $[V^{II}(oep)(thf)_2]$, (2a), shows two bands at 885 and 1 040 cm^{-1} respectively assigned to v(C–O) and v(C–C) of the co-ordinated thf (the corresponding bands of thf itself appear at 910 and 1 070 cm^{-1}). No absorptions typical of co-ordinated $PPhMe_2$ [for complexes (3)] or metal–ligand vibrations [for (2) and (3)] could be assigned.

Even at 77 K, no e.s.r. spectrum corresponding to the vanadium(II) porphyrins was found. The postulated low valence state of the vanadium was checked by magnetic moment measurement. The magnetic moment of $[V^{II}(oep)(PPhMe_2)_2]$, (3a), is $\mu_{eff.} = 3.52$ B.M. (B.M. $\approx 9.27 \times 10^{-24}$ A m^2) ($S = 1.33$, calculated with a Landé factor of 2). This value is consistent with a d^3 complex. The results indicate a symmetrical axial ligation of two ligands (thf or $PPhMe_2$) in either a *trans* or a *cis* configuration. Structural data which allow a discrimination between these two possible configurations were obtained from the *X*-ray analyses.

Tables 5 and 6 give the main distances and angles in both molecules. Figures 1 and 2 are ORTEP [12] views of the complexes and give the atom numbering scheme used. In the two molecules, both non-porphyrin ligands are in a *trans* configuration. Furthermore, the vanadium atom being on an inversion centre lies in the perfect plane of the four nitrogen atoms and is octahedrally co-ordinated. The symmetry of the octahedron is almost D_{4h} in $[V^{II}(oep)(thf)_2]$ [N(1)–V–O 89.2(1) and N(2)–V–O 89.9(2)°], but differs significantly from this in $[V^{II}(oep)(PPhMe_2)_2]$ [N(1)–V–P 92.0(1) and N(2)–V–P 88.0(1)°]. This distortion may be due to the crystal packing. The mean V–N distances are statistically equivalent {2.051(4) Å in $[V^{II}(oep)(PPhMe_2)_2]$ and 2.046(4) Å in $[V^{II}(oep)(thf)_2]$}. They are comparable to those observed in bis[bis(diphenylphosphino)methane](*meso*-tetraphenylporphyrinato)ruthenium(II) [2.041(8) Å] [13] and in bis(tetrahydrofuran)(*meso*-tetraphenylporphyrinato)iron(II) [2.057(2) Å].[14] As expected

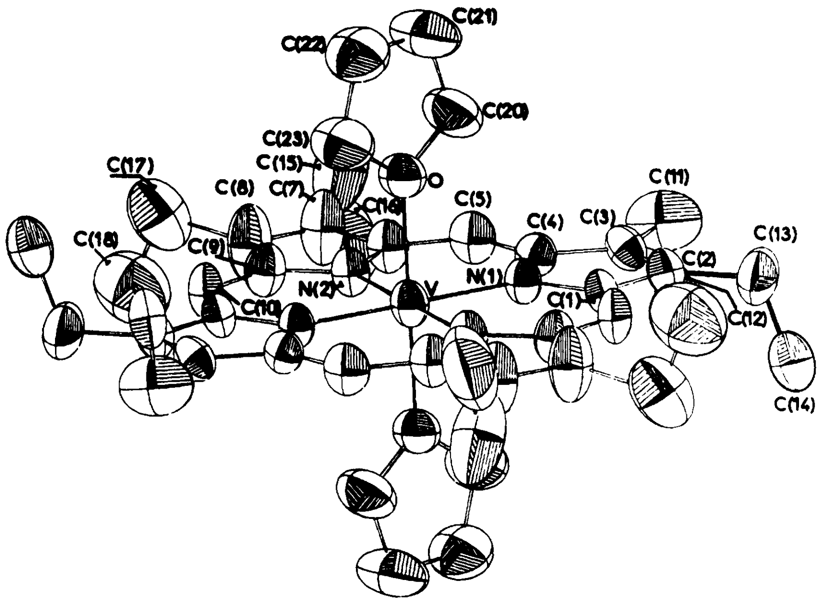


Figure 2. ORTEP view of [V^{II}(oep)(thf)$_2$], (2a)

Table 5. Bond distances (Å) in [V^{II}(oep)(thf)$_2$], (2a), and [V^{II}(oep)(PPhMe$_2$)$_2$], (3a)

(*a*) Co-ordination polyhedron

	(2a)	(3a)		(2a)	(3a)
V–N(1)	2.045(3)	2.048(4)	N(1)–N(2)	2.892(5)	2.890(6)
V–N(2)	2.046(4)	2.053(4)	$N(1^{i})$–N(2) *	2.893(6)	2.909(6)
V–X	2.174(4) (X = O)	2.523(1) (X = P)			

(*b*) Macrocycle

	(2a)	(3a)		(2a)	(3a)
N(1)–C(1)	1.387(6)	1.378(6)	C(11)–C(12)	1.491(8)	1.508(10)
N(1)–C(4)	1.383(7)	1.379(6)	C(4)–C(5)	1.377(8)	1.394(7)
N(2)–C(6)	1.376(7)	1.380(7)	C(2)–C(11)	1.496(6)	1.509(8)
N(2)–C(9)	1.382(5)	1.391(6)	C(3)–C(13)	1.511(8)	1.498(8)
C(1)–C(2)	1.455(6)	1.455(7)	C(7)–C(15)	1.616(12)	1.508(8)
C(2)–C(3)	1.349(8)	1.372(8)	C(8)–C(17)	1.740(12)	1.495(8)
C(3)–C(4)	1.439(5)	1.445(7)	C(13)–C(14)	1.502(9)	1.483(10)
C(5)–C(6)	1.400(6)	1.393(7)	C(15)–C(16)	1.357(12)	1.476(10)
C(7)–C(8)	1.340(7)	1.367(8)	C(17)–C(18)	1.311(15)	1.514(10)
C(8)–C(9)	1.442(9)	1.449(7)	$C(1)$–$C(10^{i})$	1.375(9)	1.390(7)
C(9)–C(10)	1.381(7)	1.389(7)	C(6)–C(7)	1.444(9)	1.450(7)

(*c*) Ligands

Tetrahydrofuran		Dimethylphenylphosphine		Dimethylphenylphosphine	
O–C(20)	1.389(7)	P–C(30)	1.822(6)	C(51)–C(52)	1.384(12)
O–C(23)	1.391(7)	P–C(40)	1.816(7)	C(52)–C(53)	1.339(15)
C(20)–C(21)	1.487(10)	P–C(50)	1.813(6)	C(53)–C(54)	1.349(15)
C(21)–C(22)	1.469(8)	C(50)–C(51)	1.377(9)	C(54)–C(55)	1.398(12)
C(22)–C(23)	1.481(11)	C(50)–C(55)	1.389(9)		

* i = $\bar{x}, \bar{y}, \bar{z}$.

for a d^3 ion, these distances are slightly greater (0.02 Å) than the mean distance $C_t \cdots N$ [2.031(2) Å] observed [15] in [V^{IV}(oep)O] and characterize a small expansion of the porphyrinic core.

In [V^{II}(oep)(thf)$_2$] the axial bond length V^{II}–O [2.174(4) Å] is statistically similar to that quoted in tetrakis(2,4,6-trimethoxyphenyl)divanadium(II) bis(tetrahydrofuran) [16] [mean V–O 2.213(7) Å] and much shorter than that observed in [Fe^{II}(tpp)(thf)$_2$] [Fe–O 2.351(3) Å at room temperature [14a] and 2.288(1) Å at liquid-nitrogen temperature [14b]]. This can be explained as follows. The iron(II) complex is high spin $S = 2$, the d_{z^2} orbital is populated and repels the thf ligand; in the vanadium(II) complex, this orbital is empty and the ligand can be approached more closely to the metal. It can also be noted that the group $H_2C(20)$–O–$C(23)H_2$ of the thf ligand eclipses the N(1)–V–N(1′) bond. This conformation of the two methylene groups allows closer packing compared with the staggered configuration. Therefore the V–O bond length

Table 6. Bond angles (°) in [V^{II}(oep)(thf)$_2$], (2a), and [V^{II}(oep)(PPhMe$_2$)$_2$], (3a)

(*a*) Co-ordination polyhedron

	(2a)	(3a)		(2a)	(3a)
N(1)–V–N(2)	90.0(1)	90.4(2)	N(1)–V–X	89.2(1) (X = O)	92.0(1) (X = P)
N(1^I)–V–N(2)	90.0(1)	89.6(2)	N(1^I)–V–X	90.8(1) (X = O)	87.7(1) (X = P)
N(1)–N(2)–N(1^I)	90.0(1)	89.9(2)	N(2)–V–X	89.9(2) (X = O)	88.0(1) (X = P)
N(2^I)–N(1)–N(2)	90.0(1)	90.1(2)	N(2^I)–V–X	90.1(2) (X = O)	92.3(1) (X = P)

(*b*) Macrocycle

	(2a)	(3a)		(2a)	(3a)
C(1)–N(1)–C(4)	106.5(3)	106.7(4)	N(1)–C(4)–C(5)	123.7(4)	123.9(5)
C(6)–N(2)–C(9)	107.1(4)	106.5(4)	C(3)–C(4)–C(5)	126.4(5)	125.9(5)
N(1)–C(1)–C(2)	108.7(5)	109.4(4)	C(4)–C(5)–C(6)	128.1(5)	128.2(5)
C(1)–C(2)–C(3)	107.7(4)	107.0(5)	N(2)–C(6)–C(5)	124.6(5)	123.7(4)
C(2)–C(3)–C(4)	107.2(4)	106.6(5)	C(5)–C(6)–C(7)	126.6(5)	125.2(5)
N(1)–C(4)–C(3)	109.9(4)	110.2(4)	C(6)–C(7)–C(15)	124.5(4)	125.2(5)
N(2)–C(6)–C(7)	108.8(4)	109.8(4)	C(8)–C(7)–C(15)	126.2(6)	127.6(5)
C(6)–C(7)–C(8)	107.7(6)	107.2(5)	C(7)–C(8)–C(17)	126.8(7)	128.5(5)
C(7)–C(8)–C(9)	107.7(5)	107.0(4)	C(9)–C(8)–C(17)	123.2(5)	124.3(5)
N(2)–C(9)–C(8)	108.7(4)	109.6(4)	N(2)–C(9)–C(10)	124.1(5)	124.3(4)
N(1)–C(1)–C(10)	124.4(4)	125.3(5)	C(8)–C(9)–C(10)	127.1(5)	126.1(4)
C(2)–C(1)–C(10)	126.9(4)	125.3(5)	C(2)–C(11)–C(12)	113.8(5)	111.2(6)
C(1)–C(2)–C(11)	124.3(5)	124.0(5)	C(3)–C(13)–C(14)	111.6(4)	112.8(6)
C(3)–C(2)–C(11)	128.0(4)	127.9(5)	C(7)–C(15)–C(16)	99.9(8)	114.1(6)
C(2)–C(3)–C(13)	127.8(4)	128.2(5)	C(8)–C(17)–C(18)	86.6(8)	112.8(6)
C(4)–C(3)–C(13)	125.0(5)	125.0(5)			

(*c*) Ligands

Tetrahydrofuran		Dimethylphenylphosphine		Dimethylphenylphosphine	
V–O–C(20)	123.8(3)	V–P–C(30)	114.5(4)	P–C(50)–C(55)	118.9(5)
V–O–C(23)	125.5(3)	V–P–C(40)	113.7(3)	C(51)–C(50)–C(55)	118.2(6)
C(20)–O–C(23)	110.4(5)	V–P–C(50)	115.7(5)	C(50)–C(51)–C(52)	121.8(7)
O–C(20)–C(21)	108.4(4)	C(30)–P–C(40)	101.4(4)	C(51)–C(52)–C(53)	119.4(8)
C(20)–C(21)–C(22)	106.3(6)	C(30)–P–C(50)	106.1(3)	C(52)–C(53)–C(54)	120.6(9)
C(21)–C(22)–C(23)	105.5(5)	C(40)–P–C(50)	104.0(4)	C(53)–C(54)–C(55)	121.5(8)
O–C(23)–C(22)	109.1(4)	P–C(50)–C(51)	122.7(5)	C(54)–C(55)–C(50)	118.5(7)

seems to be determined by the overlap of the d_{z^2} orbital with the oxygen lone pair and by steric hindrance. The thf molecule exhibits relatively large thermal parameters as observed in the room-temperature study of [Fe^{II}(tpp)(thf)$_2$].[14a] The average C–O and C–C bond distances, uncorrected for thermal motion [1.39(1) and 1.48(1) Å], are in good agreement with the data in ref. 5*a*, but smaller than those observed for the liquid-nitrogen-temperature study of [Fe^{II}(tpp)(thf)$_2$][14b] [C–O 1.45(1) and C–C 1.53(1) Å] where the thermal motion was found to be much reduced.

In [V^{II}(oep)(PPhMe$_2$)$_2$] the V–P distance is 2.523(1) Å; this is to our knowledge the first example of a vanadium(II)–phosphorus bond length. It is slightly longer than those observed in vanadium phosphine complexes: 2.442(2) Å in *cis*-[V(η^5-C$_5$H$_5$)(CO)$_2$(Ph$_2$PCH$_2$CH$_2$PPh$_2$)][17] and 2.360(2) Å in [{V(CO)$_4$(PMe$_2$)}$_2$].[18] The P–C distances in PPhMe$_2$ [1.817(6) Å] are in good agreement with those found in other metal phosphine complexes.[17–19]

The bond distances and angles of the macrocycle in both complexes are in the range expected for an expanded porphyrinate core[20] [mean N–C$_a$ 1.382(9), C$_a$–C$_b$ 1.447(9), C$_b$–C$_b$ 1.36(1), and C$_a$–C$_m$ 1.387(8) Å; C$_a$–N–C$_a$ 106.7(5), N–C$_a$–C$_m$ 124.3(4), C$_a$–C$_m$–C$_a$ 128.1(8), and N–C$_a$–C$_b$ 109.4(5)°. C$_a$ = C(1),(4),(6),(9); C$_b$ = C(2),(3),(7),(8); C$_m$ = C(5),(10)].

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