

Metal Complexes with Tetrapyrrole Ligands, LVII¹⁾

Synthesis, Spectra, and Structure of Nitridorhenium(V) Porphyrins

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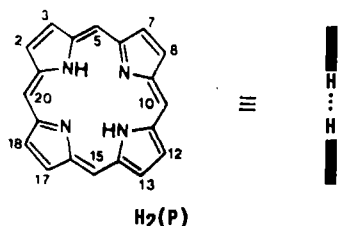
Key Words: Rhenium(V) porphyrins / Nitridorhenium(V) complexes / Rhenium-Nitrogen triple bonds / Metalloporphyrins

Oxorhenium(V) porphyrins ReO(P)X ($X = \text{Cl, Br}$) or $[\text{ReO(P)}]_2\text{O}$, or trichlororhenium(V) porphyrins $\text{ReCl}_3(\text{P})$ ($\text{P} = \text{OEP, TPP, TTP, TAP, TCIP, TMP}$)^{2,3)}, respectively, are transformed into nitridorhenium(V) porphyrins ReN(P) with hydrazine hydrate in the presence of ethanol, in good yields. The diamagnetic complexes are stable towards hydrolysis and con-

tain pentacoordinate Re^{V} in a square pyramid of nitrogen donor atoms. Their structure is deduced spectrometrically and is proven in the case of ReN(OEP) by X-ray crystallography. The UV/Vis- and ¹H-NMR spectra of the new nitrido complexes are compared with those of the corresponding zinc(II) porphyrins.

Coordination compounds with transition metal-to-nitrogen triple bonds have many fascinating aspects⁴⁾. The nitridomanganese(V) unit was first realized in nitridomanganese(V) porphyrins^{4,5,6)}, e.g. in MnN(TTP) ^{2,4,5a)}, which is a square-pyramidal complex of type A (see Schemes 1 and 2).

Scheme 1. Substitution pattern of the porphyrins $\text{H}_2(\text{P})$, the dianions of which are used as equatorial ligands $(\text{P})^{2-}$ in the rhenium porphyrins

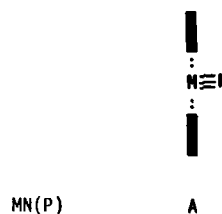


No.	Short formula	Names of the tetrapyrroles
	$\text{H}_2(\text{P})$	General, or unsubstituted porphyrin
1	$\text{H}_2(\text{OEP})$	2,3,7,8,12,13,17,18-Octaethylporphyrin ^{a)}
2	$\text{H}_2(\text{TPP})$	5,10,15,20-Tetraphenylporphyrin ^{b)}
3	$\text{H}_2(\text{TTP})$	5,10,15,20-Tetra- <i>p</i> -tolylporphyrin
4	$\text{H}_2(\text{TAP})$	5,10,15,20-Tetrakis(4-methoxyphenyl)-porphyrin
5	$\text{H}_2(\text{TCIP})$	5,10,15,20-Tetrakis(4-chlorophenyl)-porphyrin
6	$\text{H}_2(\text{TMP})$	5,10,15,20-Tetramesitylporphyrin
	$\text{H}_2(\text{Pc})$	Phthalocyanine
7 ^{c)}	$\text{H}_2(\text{TDCCP})$	5,10,15,20-Tetrakis(2,6-dichlorophenyl)-porphyrin
	$\text{H}_2(\text{OEPMe}_2)$	5,15-2,3,7,8,12,13,17,18-Octaethyl-5,15-dimethyl-5 <i>H</i> ,15 <i>H</i> -porphyrin

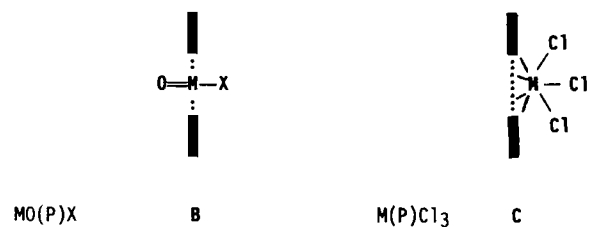
^{a)} The positions 2–18 as a set are called *peri* positions. — ^{b)} The positions 5,10,15,20 are called *meso* positions. — ^{c)} The rhenium(V) complexes of this porphyrin were obtained only in an impure form^{2)b)} and not transformed into a nitride, but the zinc(II) complex of 7 is described in experiment 3 and Table 7.

Scheme 2. Short formulas of complexes and coordination types A–C

a) Nitridometal(V) Porphyrins, MN(P)



b) Mononuclear Oxo or Trichloro Complexes, MO(P)X or $\text{MCl}_3(\text{P})$

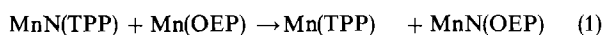


M: central metal
X: Cl, Br, O/2^{a)}

(M = Re in this work)

a) Dinuclear μ -oxo complexes $[\text{MO(P)}]_2\text{O}$

An interesting reaction of terminal nitrido ligands is nitrogen atom transfer from a nitridometal(V) unit to either olefins⁷⁾ or metal(II) or metal(III) systems [reactions (1)⁸⁾ or (2)⁹⁾], which has been observed with various porphyrin complexes recently.

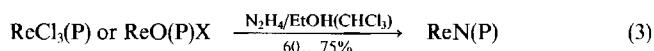


Since rhenium, the heavier homologue of manganese, forms a variety of porphyrin complexes^{10,11} in the oxidation states -1 ¹², $+2$ ¹³, and $+5$ ¹⁴, but also a large variety of nitridorhenium complexes with chloro and phosphane ligands^{4,15}, it seemed worthwhile to look for nitridorhenium porphyrins. The corresponding nitridometal(V) phthalocyanines Mn(Pc) (**A**) were discovered in the sequence $\text{M} = \text{Tc}$ ^{16a}, Re ^{16b}, and, very recently, Mn ¹⁷. With other metals, the nitridometal porphyrin systems OsN(OEP)OMe ¹⁸, $[\text{MoN(TPP)}]\text{Br}_3$ ¹⁹, and MoN(TPP) (**A**)²⁰ are already known.

The original protocol^{14b} for the synthesis of oxorhenium(V) porphyrins ReO(P)X , type **B** (Scheme 2), started from Re_2O_7 but was rather inefficient¹³. Recently, we have described an efficient procedure for the insertion of Re^{V} into porphyrin systems²¹ using ReCl_5 in refluxing trichlorobenzene, which provided access not only to oxorhenium(V) complexes ReO(P)X but also to the trichlororhenium(V) porphyrins $\text{ReCl}_3(\text{P})$, type **C**. The latter seemed especially useful candidates for the replacement of chloride by nitride. At first glance, an exchange of oxo ligands by nitride seemed rather difficult. Nevertheless it turned out that both types of rhenium(V) porphyrins, **B** and **C**, can be transformed into nitridorhenium(V) porphyrins. These results are described here.

Synthesis of Nitridorhenium(V) Porphyrins

Following the procedure of Chatt and coworkers¹⁵, the trichlororhenium(V) or the oxorhenium(V) derivatives of the porphyrins **1–6** (see Scheme 1) were treated with hydrazine hydrate in boiling 1:1 mixtures of chloroform and ethanol, yielding nitridorhenium(V) porphyrins according to reaction (3). As Chatt had already stated, the presence of ethanol is essential. The mechanism of this reaction is not known.



The μ -oxo complex $[\text{ReO(P)}]_2\text{O}$ [$\text{X} = \text{OReO(P)}$ in **B**] was subjected to this nitridation as well. For details, see experiments 1 and 2.

The new nitridorhenium(V) porphyrins resemble their manganese(V) analogues in their stability, their red colour in solution, their nonpolar behaviour during chromatography on alumina, and their diamagnetism. The complexes do not react with organic acids, mineral acids, or 30% hydrogen peroxide. Prolonged boiling of toluene solutions of the nitrido complexes with aqueous potassium hydroxide produces μ -oxobis[oxorhenium(V)] porphyrins.

For the spectroscopic characterization described in the next section, the zinc complexes Zn(P) of the porphyrins **1–6** were required as reference compounds. Their preparation is described in experiment 3. Although the nitridorhenium(V) derivative of the porphyrin **7** was not studied (see footnote ⁹, Scheme 1), its Zn^{II} complex is also presented there.

Spectroscopic Characterization

Along with the elemental analyses, the mass spectra (see Table 6) clearly prove the compositions of the new complexes. The $\text{Re} \equiv \text{N}$ triple bond should give rise to IR bands between 950 and 1150 cm^{-1} ²². In ReNCl_3 ²³, such a band appears at 1080 cm^{-1} . In the IR spectra of porphyrin complexes, a location of a band typical for the metal-nitrogen triple bond is not very easy because the porphyrin ring has prominent bands at about 1000 cm^{-1} . Comparison of the IR spectra of the nitrides ReN(P) with those of the zinc complexes of the corresponding porphyrins, Zn(P) , clearly shows extra absorption at the wave numbers indicated in Table 6; thus, the $\text{Re} \equiv \text{N}$ vibration should appear between 1077 and 1090 cm^{-1} .

UV/Vis Spectra: The spectra of the oxo- and trichlororhenium(V) porphyrins of the types **B** and **C** belong to the so-called "hyper" type^{24,25} and thus have extra bands in the visible region, which normally give these complexes a green or brown colour. The spectra of the nitridomanganese(V) systems have been assigned a weak "hypso" type^{24,5a}, in which a hypsochromic shift of the Q(0,0) band of about 10–22 nm as compared with the corresponding zinc porphyrin indicates some metal-to-porphyrin back bonding. This back bonding of the Mn^{V} ion is caused by the nitride ligand which acts as a strong π -donor and produces a *cis* effect on the optical spectrum of the porphyrin system²⁵.

The optical spectrum of ReN(OEP) is shown in Figure 1, and spectral data of the nitridorhenium(V) porphyrins are compiled in Table 1 along with those of the zinc(II) complexes of the respective porphyrins **1–6**. The latter serve as reference compounds defining the so-called "normal" type of the optical spectrum. This is defined by the wavelength found for the Q(0,0) or α band, in octaalkylporphyrin systems like Zn(OEP) , or the Q(0,1), or β band, in tetraarylporphyrin systems like Zn(TPP) .

Like the nitridomanganese(V) porphyrins^{5–7}, their rhenium(V) analogues are red showing essentially Q(0,0), Q(0,1),

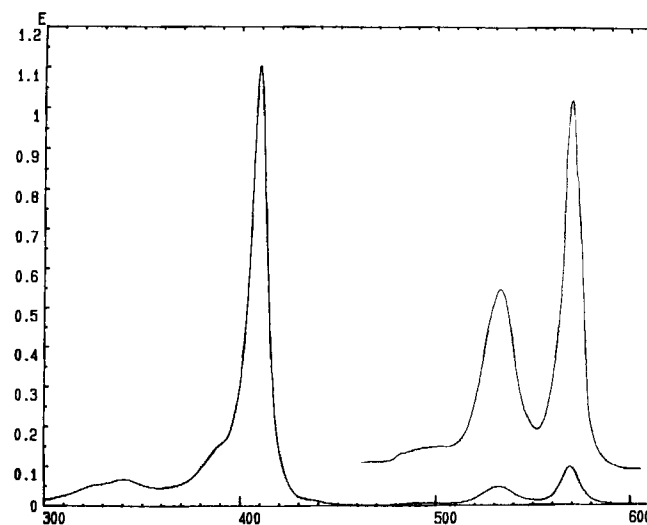


Figure 1. UV/Vis spectrum of ReN(OEP) in CH_2Cl_2 .

Table 1. UV/Vis spectra of corresponding nitridorhenium(V) and zinc(II) porphyrins, ReN(P) and Zn(P), in CH₂Cl₂

Complex	λ_{\max} [nm], lg ϵ in parentheses			
	Soret (B)	B [Q(0,1)]	α [Q(0,0)]	
ReN(OEP)	342 (4.22)	410 (5.15)	534 (4.12)	570 (4.44)
Zn(OEP)		400 (5.51)	530 (4.15)	570 (4.31)
ReN(TPP)	318 (3.95)	432 (5.15)	552 (3.98)	590 (3.34)
Zn(TPP)		418 (5.74)	548 (4.34)	586 (3.72)
ReN(TTP)	318 (4.00)	430 (5.28)	550 (3.78)	590 (3.39)
Zn(TTP)		418 (5.74)	548 (4.34)	588 (3.72)
ReN(TAP)	314 (4.22)	426 (5.27)	548 (4.17)	588 (3.43)
Zn(TAP)		424 (5.56)	550 (4.28)	592 (3.81)
ReN(TC1P)	344 (4.41)	430 (5.08)	550 (3.88)	593 (3.37)
Zn(TC1P)		422 (5.57)	552 (4.23)	594 (3.59)
ReN(TMP)	320 (4.27)	430 (5.59)	550 (4.27)	584 (3.47)
Zn(TMP)		420 (5.73)	548 (4.38)	
Zn(TDCP) ^{a)}		424 (5.30)	552 (4.25)	

^{a)} See footnote ^{c)}, Scheme 1.

Table 2. ¹H-NMR spectra of nitridorhenium(V) porphyrins ReN(P) and the corresponding zinc(II) complexes Zn(P) in CD₂Cl₂

Complex	Assignments Signals (δ [ppm], multiplicity)			
	meso-H	-CH ₂ -	-CH ₃	
ReN(OEP)	10.59 (s)	4.32 (q)	2.00 (t)	
Zn(OEP)	10.15 (s)	4.14 (q)	1.97 (t)	
	peri-H	ortho-H	meta-H	para-H
ReN(TPP)	9.19 (s)	8.44 (d)	7.80 _g (m)	7.60 (m) ^{a)}
Zn(TPP)	8.81 (s)	8.13 (d)	7.78 (m)	7.71 (t)
ReN(TTP)	9.19 (s)	8.31 (d)	7.62 (d)	2.73 (s) ^{b)}
Zn(TTP)	8.83 (s)	8.02 (d)	7.57 (d)	2.67 (s)
ReN(TAP)	9.21 (s)	8.34 (d)	7.36 (d)	4.12 (s) ^{b)}
Zn(TAP)	8.97 (s)	8.04 (s)	7.28 (s)	4.10 (s) ^{b)}
ReN(TC1P)	9.18 (s)	8.65 (m) ^{a)}	7.80 (m) ^{a)}	
Zn(TC1P)	8.94 (s)	8.13 (d)	7.74 (d)	
ReN(TMP)	8.93 (s)	2.12 (s) _{b)}	7.32 (s)	2.64 (s)
Zn(TMP)	8.64 (s)	1.63 (s) _{b)}	7.26 (s)	2.62 (s)
		1.84 (s) _{b)}		
		1.53 (s) _{b)}		
Zn(TDCP) ^{c)}	8.62 (s)	7.80, 7.79 7.77	7.71/7.70 ^{d)} 7.68/7.66	

^{a)} Unresolved multiplets. — ^{b)} Methyl resonances of CH₃ or CH₃O groups. — ^{c)} See footnote ^{c)}, Scheme 1. — ^{d)} AB₂ System.

and B ("Soret") bands (see Table 1). Nevertheless, there is a weak extra band between 318 and 344 nm, which is absent in the Zn^{II} derivatives, and the Q band is somewhat bathochromically shifted. Comparison of the wavelengths of the α -bands of ReN(OEP) and Zn(OEP), and the β bands of the respective ReN and Zn tetraarylporphyrins (see Table 1) reveals that there is no hypsochromic shift of these bands in the nitridorhenium(V) porphyrins. Contrary to the nitr-

domanganese(V) porphyrins, the spectral type of the former is thus close to normal (red colour) with some "hyper" character (weak band at 320 to 340 nm). This means that the nitride ligand induces much less electron density at the Re^V ion than at the Mn^V ion.

¹H-NMR Spectra: The ¹H-NMR spectra of the nitridorhenium(V) porphyrins are given in Table 2 along with the data for the corresponding Zn^{II} porphyrins. The diamagnetism of the nitrides is evident from the narrow peaks which appear very close to the corresponding signals of the Zn^{II} complexes. The spectra do not show any signals due to hydrogen-containing axial ligands, which might be coordinated in *trans* position to the nitride ligand. This is in line with the strong *trans*-labilizing effect of multiply bound donor ligands in metal porphyrins^{5a,25}.

The chemical shifts and the multiplicities of the signals shown in Table 2 are in accord with the square pyramidal structure of the N \equiv ReN₄ coordination group. Hindered rotation of the phenyl groups about the C—C bond to the porphyrin ring was earlier observed with oxotitanium(IV)²⁶ porphyrins and at lower temperatures with nitridomanganese(V) porphyrins^{5a}). This gives rise to anisochronous protons in *ortho* and *meta* positions of the phenyl groups, which is typical for the axial asymmetry of these configurationally stable square pyramidal systems.

Axial asymmetry is not indicated for the zinc porphyrins apart from Zn(TMP) which, like ReN(TMP), shows two signals for the *ortho*-methyl groups, and Zn(TDCP). In the latter and in Zn(TMP), the water adducts Zn(P)OH₂ appear to be rather reluctant to exchange of water with the solvent. The coordinated water molecule may be protected from exchange by the *ortho*-methyl or *ortho*-chloro substituents. It is well-known that Zn^{II} porphyrins pick up donor ligands to form square-pyramidal complexes^{27,28,29}). The Zn^{II} porphyrins shown in Table 2 are all expected to add a water molecule, but this probably suffers rapid exchange with free water molecules from both sides of the porphyrin plane in the *ortho*-unsubstituted complexes, and axial asymmetry is not effective.

The strong donor capacity of the nitride ligand in MnN(P) was already mentioned. It was likewise deduced from the chemical shifts of the *meso*-protons in MnN(OEP) or the *peri*-protons in MnN(TTP)^{5a}) which fell between the values for Zn^{II} and Ti^{IV} porphyrins, thus indicating a "quasitetravalent" character of the Mn^V ion in these systems. Generally, the chemical shifts of those protons that are directly bound to the porphyrin system are susceptible to the oxidation state of the central metal ion^{30,31}). In ReN(TTP), the chemical shift of the *peri*-protons is close to the corresponding value for TiO(TTP), thus rather indicating "quasi-tetravalent" character of the Re^V ion in the ReN system. The *meso*-proton signals of ReN(OEP) are indeed shifted towards higher field as compared with ReO(OEP)Cl ($\delta = 10.80^{21b}$); the same is true for the *peri*-protons of ReN(TMP) relative to ReO(TMP)Cl ($\delta = 9.12^{21b}$). In the other tetraarylporphyrin systems, the values observed for ReO(P)X practically do not differ from those found for ReN(P). Nitride is therefore only

slightly stronger donating than oxide in the rhenium(V) porphyrins. However, in the manganese(V) porphyrins nitride is very much more donating than oxide. As a consequence, the nitridomanganese(V) porphyrins are diamagnetic and stable^{5–7}, whereas the oxomanganese(V) porphyrins are paramagnetic and highly reactive^{32–35}.

Molecular Structure of Nitrido(octaethylporphyrinato)-rhenium(V)

Crystals of ReN(OEP) were grown from a pyridine solution. Details of the structure determination are collected in Table 3⁶. Fractional atomic coordinates and thermal parameters are listed in Table 4. The asymmetrical unit contains one discrete ReN(OEP) molecule (Figure 2) and a pyridine molecule, which is not coordinated to the rhenium atom. The numbering scheme of the porphyrin skeleton and the deviations of the C, N, and Re atoms from the mean

plane, “P_C”^{3,27}, of the 20 C and 4 N atoms of the porphyrin core are displayed in Figure 3. Individual Re–N bond lengths of the coordination polyhedron and mean values of bond lengths and bond angles of the porphyrinato core are given in Table 5.

Table 3. Crystallographic data of ReN(OEP) · C₅H₅N

C₄₁H₄₉N₆Re, molecular mass 812.09, crystal system triclinic, space group $P\bar{1}$; $a = 1306.8(3)$, $b = 1354.2(4)$, $c = 1170.9(3)$ pm; $\alpha = 111.38(2)$, $\beta = 94.75(2)$, $\gamma = 69.85(2)^\circ$; $V = 1809 \cdot 10^6$ pm³, $Z = 2$; $d(\text{calcd.}) 1.491$ g cm⁻³, crystal size $0.18 \times 0.20 \times 0.28$ mm. Diffractometer PW1100/16, Cu-K α radiation, graphite monochromator, $\mu = 65.88$ cm⁻¹, temperature 173 K, $\Theta/2\Theta$ flying step-scan, $\Delta\omega = 0.80 + 0.14 \text{ tg}(\Theta)^\circ$, step width 0.05° , scan speed $0.024^\circ/\text{s}$, Θ limits $3/50^\circ$, octants $\pm h$, $\pm k$, $\pm l$, number of measured data 3543, number of observed data 3295 [rejection criterion $I \geq 3\sigma(I)$], Lorentz, polarization, and empirical absorption corrections, abs. min. and max. $0.86/1.20$, solution of the structure by means of the heavy atom method, number of variables refined: 433, residual electron density not exceeding 0.2 e/Å³, $R_1 = 0.025$; $R_2 = 0.041$; ERRFIT = 1.016

The four equatorial pyrrole nitrogen atoms of the porphyrinato ligand and the axial nitride ligand set up a square pyramid about the rhenium(V) ion. The apical and basal Re–N bond lengths and the displacement of the Re atom from the basal plane “P_N”^{3,27} of the pyramid which is likewise the mean plane of the four pyrrole nitrogen atoms, are discussed below.

1. *The Re–N(nitrido) Bond Distance:* The length of the axial Re≡N bond, 163.3(4) pm, lies in the range of Re≡N bond distances of 160.3 and 165.6 pm found in other square pyramidal nitridorhenium(V) complexes⁴. The Mn≡N or Cr≡N triple bonds in MnN(OEPMe₂)^{5b} and MnN(TAP)⁶ (151 pm) or CrN(TTP)³⁷ (156 pm) are much shorter, their metal(V) ions belonging to the smaller species of the first transition metal series. In the only other structurally characterized nitridometal(V) porphyrin containing a second- or third-row transition metal, i.e. MoN(TPP)^{20b}, the Mo≡N distance was found to be 178(4) pm. At the 3- σ level of significance this bond distance is 178 ± 12 pm. Thus, it can lie very close to the value of 163.3(4) found in ReN(OEP) and to the Mo≡N bond lengths found in other square pyramidal nitridomolybdenum derivatives (observed range: 163–166 pm⁴). The Re≡N bond lies almost perpendicular to P_N and P_C (see above). The tipping angles relative to the normals of these mean planes, 0.4 and 0.3° respectively, are very small indeed.

2. *The Re–N(porphyrin) Bond Distances and the Out-of-Plane Displacement of the Metal, $\Delta(N_A)$, relative to P_N:* The average Re–N(porphyrin) bond length of 208.1(2) pm in ReN(OEP) is slightly shorter than in the five-coordinate porphyrin derivatives VO(OEP)³⁸ (210 pm), TiO(OEP)³⁹ (211 pm), and low-spin MoO(TPP)⁴⁰ (211 pm), but longer than in CrN(TTP)³⁷ (204 pm) and the low-spin MnN(TAP)⁶ (202 pm). Dehnicke and Strähle⁴ state that in all square-pyramidal second- and third-row nitridometal complexes the central metal is located about 55 pm above the basal

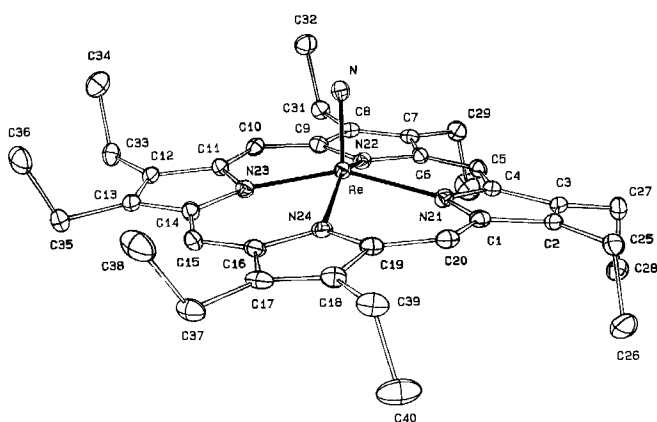


Figure 2. ORTEP plot of a ReN(OEP) molecule in the crystal. Ellipsoids are scaled to enclose 50% of the electronic density. Hydrogen atoms are omitted

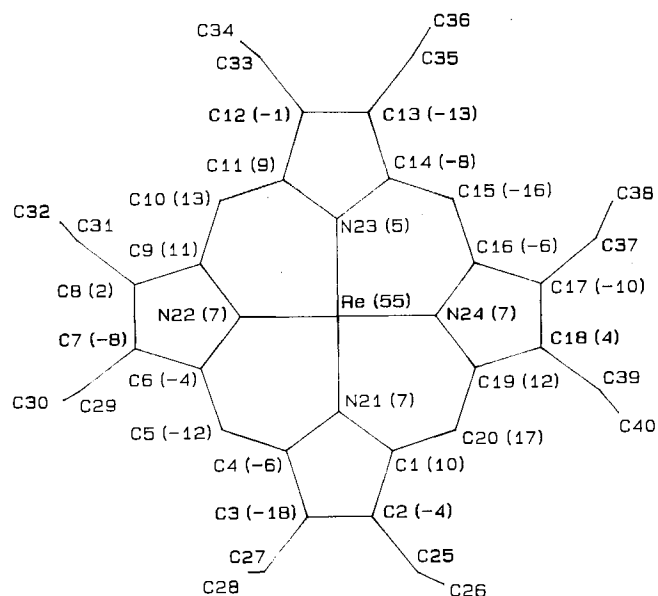


Figure 3. Stick-bond model projection of ReN(OEP) along the ReN axis. The labeling scheme of all but the hydrogen atoms of the OEP ring is given. Also shown are the deviations of the porphyrin core atoms and the rhenium atom (in pm) from the plane P_C³

Table 4. Fractional atomic coordinates^{a,b)} and equivalent thermal parameters^{c)} for ReN(OEP)

Atom	X	Y	Z	B(Å ²)
Re	0.05940(1)	0.36670(1)	0.24030(2)	2.292(6)
N	0.0199(3)	0.2856(3)	0.1171(3)	2.8(1)
C1	0.1377(4)	0.4992(4)	0.1194(4)	2.7(1)
C2	0.2326(4)	0.4947(4)	0.0610(4)	2.7(1)
C3	0.3192(4)	0.4121(4)	0.0788(4)	2.7(1)
C4	0.2776(4)	0.3599(4)	0.1443(4)	2.7(1)
C5	0.3397(4)	0.2687(4)	0.1782(4)	2.8(1)
C6	0.3031(4)	0.2190(4)	0.2427(4)	2.4(1)
C7	0.3679(4)	0.1234(4)	0.2749(4)	2.9(1)
C8	0.3004(4)	0.1024(4)	0.3377(4)	2.8(1)
C9	0.1935(4)	0.1845(4)	0.3457(4)	2.8(1)
C10	0.1032(4)	0.1961(4)	0.4099(4)	2.8(1)
C11	0.0030(4)	0.2805(4)	0.4282(4)	2.8(1)
C12	0.0876(4)	0.2961(4)	0.5073(4)	3.0(1)
C13	0.1678(4)	0.3926(4)	0.5081(4)	3.1(1)
C14	0.1296(4)	0.4355(4)	0.4305(4)	2.8(1)
C15	0.1881(4)	0.5328(4)	0.4069(4)	3.0(1)
C16	0.1545(4)	0.5734(4)	0.3291(4)	2.9(1)
C17	0.2186(4)	0.6730(4)	0.3019(5)	3.3(1)
C18	0.1572(4)	0.6823(4)	0.2212(4)	3.1(1)
C19	0.0543(4)	0.5924(4)	0.2009(4)	2.9(1)
C20	0.0341(4)	0.5774(4)	0.1299(4)	2.9(1)
N21	0.1665(3)	0.4162(3)	0.1708(3)	2.7(1)
N22	0.1961(3)	0.2556(3)	0.2866(3)	2.67(9)
N23	0.0256(3)	0.3665(3)	0.3833(3)	2.7(1)
N24	0.0544(3)	0.5260(3)	0.2660(3)	2.7(1)
C25	0.2308(4)	0.5733(4)	-0.0030(4)	3.5(1)
C26	0.2438(6)	0.6824(4)	0.0867(6)	5.9(2)
C27	0.4382(4)	0.3827(4)	0.0502(2)	3.7(1)
C28	0.4953(4)	0.4355(5)	0.1627(6)	4.8(2)
C29	0.4880(4)	0.0662(4)	0.2493(5)	3.5(1)
C30	0.5529(5)	0.1198(6)	0.3506(6)	6.8(2)
C31	0.3280(4)	0.0088(4)	0.3867(5)	3.5(1)
C32	0.2963(5)	-0.0920(4)	0.2994(5)	4.7(2)
C33	0.0896(4)	0.2160(4)	0.5650(5)	3.7(1)
C34	0.1164(5)	0.1152(4)	0.4756(6)	5.1(2)
C35	0.2796(4)	0.4450(4)	0.5725(5)	3.8(1)
C36	0.3611(5)	0.3945(6)	0.4990(6)	5.7(2)
C37	0.3312(4)	0.7456(4)	0.3552(5)	3.8(1)
C38	0.4192(5)	0.6948(6)	0.2961(6)	6.7(2)
C39	0.1900(5)	0.7712(4)	0.1631(5)	3.8(1)
C40	0.1577(6)	0.8729(4)	0.2397(6)	6.3(2)
N41	0.6948(6)	0.0683(5)	0.0337(6)	10.3(2)
C42	0.6672(7)	0.1632(7)	0.1091(7)	8.4(3)
C43	0.7404(9)	0.1962(6)	0.1675(6)	9.4(3)
C44	0.8485(7)	0.1425(7)	0.1485(8)	11.7(2)
C45	0.8724(7)	0.026(1)	0.058(1)	12.8(4)
C46	0.7931(8)	-0.0010(8)	-0.0018(8)	9.3(3)

^{a)} Figure 2 displays the numbering of all nonhydrogen atoms of the ReN(OEP)Py molecule. N41 and C42-C46 belong to the pyridine molecule. — ^{b)} The estimated standard deviations of the least significant digit are given in parentheses. — ^{c)} Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $(4/3) \cdot [a^2 \cdot \beta(1,1) + b^2 \cdot \beta(2,2) + c^2 \cdot \beta(3,3) + ab(\cos \gamma) \cdot \beta(1,2) + ac(\cos \beta) \cdot \beta(1,3) + bc(\cos \alpha) \cdot \beta(2,3)]$.

plane. This parameter corresponds to the displacement $\Delta(N_4)$ of the metal relative to P_N . It amounts to 48 pm in ReN(OEP) and hence is small for a third-row transition metal porphyrin. As regards other square pyramidal metal porphyrins of the type MX(P), where X = O or N, this value lies between those found for MnN(TAP)⁶⁾ (39 pm) and CrN(TTP)³⁷⁾ (42 pm) on one hand and VO(OEP)³⁸⁾ (54 pm) and TiO(OEP)³⁹⁾ (56 pm) on the other hand. The variation of the metal—N(porphyrin) bond distances, M—N_p, and the displacements of the metals from the porphyrin planes, $\Delta(N_4)$, are, in general, related to the spin state of the central metal (occupation of the $d_{x^2-y^2}$ orbital), to the radius $Ct \cdots N_p$ of the cavity in the different porphyrins, and to the size of the metal ion. However, in all these compounds the metal $d_{x^2-y^2}$ orbital is empty. Thus, the parameters which play a role in the observed variations of the M—N_p and $\Delta(N_4)$

distances are the slight variations of the cavity size in the different porphyrins⁴¹⁾ and, more importantly, the dimensions of the various metal ions which are present in the above-mentioned complexes under different oxidation states (+4 for Ti, V, Mo and +5 for Cr, Mn, and Re).

Table 5. Bond distances [pm] and bond angles [deg] with their standard deviations (in parentheses) of the ReN₅ square pyramid and the porphyrinato core in the ReN(OEP) molecule

Bond distances		Bond angles		Bond angles	
Re-N	1.633(4)	N-Re-N21	103.2(2)	N21-Re-N23	153.0(2)
Re-N21	2.074(4)	N-Re-N22	103.6(2)	N21-Re-N24	86.7(2)
Re-N22	2.081(4)	N-Re-N23	103.8(2)	N22-Re-N23	87.1(2)
Re-N23	2.086(4)	N-Re-N24	103.0(2)	N22-Re-N24	153.4(2)
Re-N24	2.085(4)	N21-Re-N22	87.1(2)	N23-Re-N24	86.8(2)
Core bond lengths ^{a)}			Core bond angles ^{a)}		
N-C _α	138.2(6)	C _α -N-C _α	106.2(4)		
C _α -C _β	144.7(9)	N-C _α -C _β	109.7(2)		
C _α -C _β	135.6(4)	C _α -C _β -C _β	107.1(6)		
C _α -C _m	138.7(7)	C _α -C _m -C _α	126.4(4)		
C _β -C _α (Et)	149.8(10)	N-C _α -C _m	124.8(6)		
C _α (Et)-C _β (Et)	152.2(11)	C _β -C _α -C _m	125.4(5)		

^{a)} C_α, C_β, C_m, C_α(Et), and C_β(Et) denote the α and β carbon atoms of the pyrrole ring, the methine carbon atom, and the two carbon atoms of the ethyl group, respectively. Averaged bond lengths and bond angles are given.

3. *Porphyrinato Core Conformation in ReN(OEP)*: The porphyrin ring represents a domed-ruffled conformation. The doming is indicated by the separation between P_C and P_N which amounts to 7 pm. A domed conformation is typical for five-coordinate metal complexes in which the metal lies, in general, out of P_N. This increases the overlap of the sp²-hybridized electron pair at the pyrrole nitrogen atoms with the equatorial dsp³ acceptor orbitals of the metal. The doming is, in ReN(OEP), superimposed by a ruffling of the core indicated by the location of the *meso*-carbons above and below P_C (see Figure 3). The dihedral angles of P_C with the mean planes of the pyrrole rings, which are individually almost planar, range from 4.8 to 6.1°.

4. *Dimerization of ReN(OEP) in the Crystal*: The ReN(OEP) molecules are paired in the solid state, forming a π dimer involving a crystallographic inversion centre. The planes of the two porphyrin systems, P and P', are parallel, and their separations amount to 355.4 pm (P_N—P'_N) or 366.7 pm (P_C—P'_C), respectively. The shortest Re⋯Re distance is 584.2 pm and the "lateral shift"²⁹⁾ of one rhenium atom parallel to the mean plane of the porphyrin ring containing the other rhenium atom is 356.1 pm. This value of the lateral shift allows the dimer of ReN(OEP) molecules to be classified as "I" ("moderate lateral shifts") in the large series of porphyrin π dimers compared recently by Scheidt²⁹⁾.

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Experimental

MS: Varian MAT 311 A with data system SS 100 MS (direct insertion, ion source at 150°C , field ion desorption). — IR: Perkin-Elmer 397, KBr pellets. — UV/Vis: Hewlett Packard HP 8451 A. — $^1\text{H NMR}$: Bruker WM 300 (300 MHz). — Elemental analyses: Mr. F. Roth, Institut für Organische Chemie und Biochemie der Techn. Hochschule Darmstadt. — Diffraction data: Philips PW1100/16 automated diffractometer equipped with a low-temperature device built in Strasbourg. Details of the procedure of structure determination may be taken from Table 3 and previous papers⁴².

The following chemicals were purchased from the companies indicated in brackets: Octaethylporphyrin, $\text{H}_2(\text{OEP})$ (Strem Chemicals), hydrazine hydrate, $[\text{D}_1]$ chloroform, $[\text{D}_2]$ dichloromethane, $[\text{D}_8]$ toluene (Merck). 1,2,4-Trichlorobenzene (TCB) was a gift of Bayer AG. Alumina type W 200 basic super I (Woelm-ICN Bio-medicals) was deactivated with water to grade II. The tetraarylporphyrins were prepared and purified by literature methods^{43–45}. Chloroform and dichloromethane were distilled and passed an alumina column (super I, basic) prior to use. — Trichlororhenium(V), μ -oxobis[oxorhenium(V)], and oxohalogenorhenium(V) porphyrin complexes were prepared as previously described^{21b}.

Experiment 1: General Procedure for the Preparation of Nitrido-rhenium(V) Porphyrins, $\text{ReN}(\text{P})$, from Oxohalogenorhenium(V) or μ -Oxobis[oxorhenium(V)] Porphyrins, $\text{ReO}(\text{P})\text{X}$ ($\text{X} = \text{Cl}, \text{Br}$) or $[\text{ReO}(\text{P})]_2\text{O}$: 2 ml of hydrazine hydrate was added to a solution of 0.1 mmol of red $\text{ReO}(\text{P})\text{X}$ ($\text{B}, \text{X} = \text{Cl}, \text{Br}; \text{P} = \text{OEP}, \text{TPP}, \text{TTP}, \text{TAP}, \text{TCIP}, \text{TMP}$) or green $[\text{ReO}(\text{P})]_2\text{O}$ ($\text{B}, \text{X} = 0/2; \text{P} = \text{OEP}, \text{TPP}, \text{TTP}, \text{TAP}, \text{TCIP}$) in 10 ml of chloroform/ethanol (1:1). The solution was gently heated to reflux. In the case of the green μ -oxo complexes, a colour change to red occurred after a few minutes. Heating was terminated when the UV/Vis spectrum of the solution did not indicate any further progress of the reaction. After removal of the chloroform in vacuo, the product precipitated in the remaining hydrazine hydrate, was dried in vacuo after filtering and washing with water, and purified by chromatography on an alumina column (grade II, basic, 25×2.5 cm). Fractions 1 and 2 were eluted with dichloromethane, fraction 3 with dichloromethane/methanol (99:1). The brown fraction 1 contained traces of residual $\text{ReCl}_3(\text{P})$ from the preparation of the starting materials and was discarded. Some starting material could be recovered from the green fraction 3 as the methoxides, $\text{ReO}(\text{P})\text{OMe}$. The deep red fraction 2 was freed from the solvent in vacuo and the residue recrystallized from dichloromethane, yielding the nitrido complex $\text{ReN}(\text{P})$ [0.5 to 0.7 mmol, 50 to 70%] as dark violet microcrystals (for specific compounds, see Table 6).

Experiment 2: General Procedure for the Preparation of Nitrido-rhenium(V) Porphyrins, $\text{ReN}(\text{P})$, from Trichlororhenium(V) Porphyrins, $\text{ReCl}_3(\text{P})$: 1 ml of hydrazine hydrate was added to a solution of 0.05 mmol of $\text{ReCl}_3(\text{P})$ ($\text{C}; \text{P} = \text{OEP}, \text{TPP}, \text{TTP}, \text{TAP}, \text{TCIP}, \text{TMP}$) in 50 ml of chloroform/ethanol (1:1), and the mixture was stirred at room temp. for 1 h and then heated at reflux for about 30 min. The progress of the reaction was monitored by UV/

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Vis spectroscopy; vanishing of the bands due to the trichlorides and appearance of new bands at 430, 550, and 590 nm indicated the end of the reaction. Workup of the reaction mixture was done as described in experiment 1. Fraction 1 was larger, fraction 3 smaller than in experiment 1; the oxo complexes $\text{ReO}(\text{P})\text{OMe}$ were formed by hydrolysis of either $\text{ReN}(\text{P})$ or $\text{ReCl}_3(\text{P})$ at the alumina during chromatography. The red fraction 2 contained $\text{ReN}(\text{P})$ [30 to 37 mol; 60 to 75%].

Note: Application of hydrazine hydrate of concentrations > 80% and use of boiling toluene as solvent may lead to complexes of chlorins (porphyrin ring hydrogenation) and metal-free porphyrins.

Experiment 3: Synthesis of Zinc(II) Porphyrins, $\text{Zn}(\text{P})$: A solution of about 0.2 to 0.5 mmol of a porphyrin $\text{H}_2(\text{P})$ in 50 ml of TCB

Table 6. Names, IR data, mass spectral data, and elemental analyses of individual rhenium(V) porphyrins $\text{ReN}(\text{P})$

<i>Nitrido(2,3,7,8,12,13,17,18-octaethylporphyrinato)rhenium(V)</i> , $\text{ReN}(\text{OEP})$: IR: $\tilde{\nu} = 1090$ cm^{-1} . — MS: calcd. 733, found 733 (M^+).	
$\text{C}_{36}\text{H}_{44}\text{N}_5\text{Re}$ (733.0)	Calcd. C 58.99 H 6.05 N 9.55 Found C 58.89 H 5.93 N 9.59
<i>Nitrido(5,10,15,20-tetraphenylporphyrinato)rhenium(V)</i> , $\text{ReN}(\text{TPP})$: IR: $\tilde{\nu} = 1075$ cm^{-1} . — MS: calcd. 813, found 813 (M^+).	
$\text{C}_{44}\text{H}_{28}\text{N}_5\text{Re}$ (813.0)	Calcd. C 65.01 H 3.47 N 8.61 Found C 64.40 H 3.42 N 8.50
<i>Nitrido[5,10,15,20-tetrakis(4-methylphenyl)porphyrinato]rhenium(V)</i> , $\text{ReN}(\text{TTP})$: IR: $\tilde{\nu} = 1080$ cm^{-1} . — MS: calcd. 869, found 870 (M^+).	
$\text{C}_{48}\text{H}_{36}\text{N}_5\text{Re}$ (869.1)	Calcd. C 66.34 H 4.18 N 8.06 Found C 66.19 H 4.03 N 8.14
<i>Aquanitrido[5,10,15,20-tetrakis(4-methoxyphenyl)porphyrinato]rhenium(V)</i> , $\text{ReN}(\text{TAP}) \cdot \text{H}_2\text{O}$. — IR: $\tilde{\nu} = 1080$ cm^{-1} . — MS: calcd. for $\text{ReN}(\text{TAP})$ 933, found 933 (M^+).	
$\text{C}_{48}\text{H}_{38}\text{N}_5\text{O}_5\text{Re}$ (951.1)	Calcd. C 60.62 H 4.03 N 7.36 Found C 60.39 H 3.94 N 7.16
<i>Nitrido[5,10,15,20-tetrakis(4-chlorophenyl)porphyrinato]rhenium(V)</i> , $\text{ReN}(\text{TCIP})$: IR: $\tilde{\nu} = 1080$ cm^{-1} . — MS: calcd. 949, found 949 (M^+).	
$\text{C}_{44}\text{H}_{24}\text{N}_5\text{Re}$ (950.7)	Calcd. C 55.59 H 2.57 N 7.37 Found C 55.28 H 2.43 N 7.19
<i>Nitrido[5,10,15,20-tetrakis(2,4,6-trimethylphenyl)porphyrinato]rhenium(V)</i> , $\text{ReN}(\text{TMP})$: IR: $\tilde{\nu} = 1095$ cm^{-1} . — MS: calcd. 981, found 981 (M^+).	
$\text{C}_{56}\text{H}_{52}\text{N}_5\text{Re}$ (981.3)	Calcd. C 68.55 H 5.34 N 7.14 Found C 68.45 H 5.38 N 6.92

Table 7. Names, yields, and analytical data of zinc porphyrins, $\text{Zn}(\text{P})$, prepared along experiment 3

<i>[5,10,15,20-Tetrakis(4-methoxyphenyl)porphyrinato]zinc(II)</i> , $\text{Zn}(\text{TAP})$: 285 mg (71%) of a red powder.	
$\text{C}_{48}\text{H}_{36}\text{N}_4\text{O}_4\text{Zn}$ (798.2)	Calcd. C 72.22 H 4.55 N 7.02 Found C 71.81 H 4.42 N 6.87
<i>[5,10,15,20-Tetrakis(4-chlorophenyl)porphyrinato]zinc(II)</i> , $\text{Zn}(\text{TCIP})$: 353 mg (86%) of red microcrystals.	
$\text{C}_{44}\text{H}_{24}\text{Cl}_4\text{N}_4\text{Zn}$ (815.9)	Calcd. C 64.77 H 2.96 N 6.87 Found C 64.39 H 2.95 N 6.76
<i>[5,10,15,20-Tetrakis(2,6-dichlorophenyl)porphyrinato]zinc(II)</i> , $\text{Zn}(\text{TDCP})$: 231 mg (96%) of a red powder.	
$\text{C}_{44}\text{H}_{20}\text{Cl}_8\text{N}_4\text{Zn}$ (935.7)	Calcd. C 55.42 H 2.11 N 5.87 Found C 55.39 H 1.99 N 5.82
<i>[5,10,15,20-Tetrakis(2,4,6-trimethylphenyl)porphyrinato]zinc(II)</i> , $\text{Zn}(\text{TMP})$: 184 mg (96%) of red microcrystals.	
$\text{C}_{56}\text{H}_{52}\text{N}_4\text{Zn}$ (846.4)	Calcd. C 79.46 H 6.19 N 6.62 Found C 79.40 H 6.40 N 6.54

was heated at reflux with 0.4 to 1.0 mmol of $Zn(acac)_2$. After 30 to 35 min, an UV/Vis spectrum of the solution indicated complete reaction to Zn(P). After removal of the solvent in high vacuum the residue was chromatographed on an alumina column (grade II, basic or neutral, 2.5×12 cm) with chloroform. The brownish red forerun [traces of $H_2(P)$] was discarded. The red main fraction was evaporated in vacuo and the residue recrystallized from chloroform [dichloromethane for Zn(TMP)]. Specific examples are given in Table 7.

CAS Registry Numbers

ReN(OEP) · C_6H_5N : 128842-63-7 / ReN(TPP): 128709-55-7 / ReN(TTP): 128709-56-8 / ReN(TAP) · H_2O : 128709-57-9 / ReN(TCIP): 128709-58-0 / ReN(TMP): 128731-79-3 / Zn(TAP): 57715-42-1 / Zn(TCIP): 29116-33-4 / Zn(TDCP): 100506-72-7 / Zn(TMP): 104025-54-9 / Zn(OEP): 17632-18-7 / Zn(TPP): 14074-80-7 / Zn(TTP): 19414-67-6 / $ReCl_3(OEP)$: 128709-59-1 / $ReCl_3(TPP)$: 128709-60-4 / $ReCl_3(TTP)$: 128709-61-5 / $ReCl_3(TAP)$: 128709-62-6 / $ReCl_3(TCIP)$: 128709-63-7 / $ReCl_3(TMP)$: 128731-80-6 / $ReO(OEP)Br$: 128709-64-8 / $ReO(TPP)Br$: 128709-65-9 / $ReO(TTP)Br$: 122402-90-8 / $ReO(TAP)Br$: 128709-66-0 / $ReO(TCIP)Br$: 128709-67-1 / $ReO(TMP)Br$: 128731-81-7 / $[ReO(OEP)]_2O$: 37338-88-8 / $[ReO(TPP)]_2O$: 128709-68-2 / $[ReO(TTP)]_2O$: 122402-87-3 / $[ReO(TAP)]_2O$: 128709-69-3 / $[ReO(TCIP)]_2O$: 128109-70-6 / $Zn(acac)_2$: 14024-63-6 / $ReO(OEP)Cl$: 117201-90-8 / $ReO(TPP)Cl$: 128709-71-7 / $ReO(TTP)Cl$: 117201-86-2 / $ReO(TAP)Cl$: 128709-72-8 / $ReO(TCIP)Cl$: 128709-73-9 / $ReO(TMP)Cl$: 128731-82-8 / $N_2H_4 \cdot H_2O$: 7803-57-8

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