Metal Complexes of Sterically Hindered Porphyrins. Crystal and Molecular Structure of *meso*-Tetrakis(3,5-di-t-butyl-4-hydroxyphenyl)porphyrin-nickel(II)

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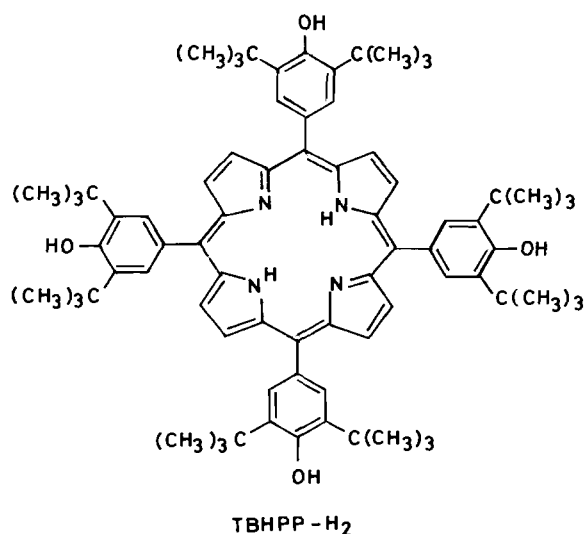
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Abstract

The structure of the title complex has been determined by single crystal X-ray diffraction methods. The complex crystallised in the triclinic system, space group $P\bar{1}$ with unit cell dimensions $a = 14.820(2)$, $b = 15.398(2)$, $c = 18.822(1)$ Å, $\alpha = 75.35(6)$, $\beta = 69.74(3)$, $\gamma = 87.31(3)°$, $V = 3894.5$ Å^3, $Z = 2$. The geometry about the nickel is square planar and the Ni–N bond distances (1.91 Å) are among the shortest so far reported for metalloporphyrin complexes. In order to accommodate this 'undersized' metal ion the porphyrin core undergoes severe S_4 ruffling with angles of 23.4–35.1° between adjacent pyrrole rings. The dihedral angles between the phenyl rings and the mean porphyrin plane are between 63.3 and 83.4°.

Introduction

The chemistry of phenolic porphyrins and their metal complexes has in recent years attracted considerable interest [1–6]. Some of these compounds have been synthesised as prospective sensitisers in the photocatalytic oxidation and reduction of water [4, 5], and others to mimic chemical and spectroscopic properties of various haemoproteins [1–3]. We have recently synthesised *meso*-tetrakis(3,5-di-t-butyl-4-hydroxyphenyl)porphyrin, TBHPP-H$_2$, and have found that some of its complexes, when oxidised, display chemical and spectroscopic properties similar to those of peroxidase compound I [1, 2]. While the structures of the oxidised complexes have not been established it is probable that phenoxyl radicals are involved and that the steric protection afforded by the t-butyl substituents plays a vital role in stabilising such radicals. The iron(III) complex of this porphyrin in the presence of thiolate ligands has also been shown to mimic certain spec-

troscopic characteristics of cytochrome P-450 derivatives [7]. In order to assess the steric effects of the t-butyl substituents we have decided to investigate the structure of a metalloporphyrin by X-ray diffraction and in this paper we report the crystal and molecular structure of the nickel(II) complex, Ni–TBHPP.

Experimental

Preparations

The porphyrin TBHPP-H$_2$ was synthesised and purified by previously reported methods [5]. The complex Ni–TBHPP was prepared by the addition of excess NiCl$_2$·6H$_2$O (2 g, 8.4×10^{-3} mol) to a stirred solution of TBHPP-H$_2$ (30 mg, 2.7×10^{-5} mol) in *N,N*-dimethylformamide at 100 °C. Complex formation, which was monitored spectrophotometrically (the porphyrin has Q bands [8] at 651, 596, 560 and 523 nm — these disappear as a result of complex formation and are replaced by a single Q

TBHPP-H$_2$

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TABLE I. Positional Parameters and Isotropic Temperature Factors for Ni–TBHPP[a]

Atom	x	y	z	B (Å²)	Atom	x	y	z	B (Å²)
Ni	0.71233(3)	0.34212(3)	0.27699(3)	2.29(1)	C(35)	0.5646(3)	0.0607(3)	0.2880(2)	3.3(1)
O(1)	0.1465(3)	0.6051(3)	0.4115(3)	7.0(1)	C(36)	0.5847(3)	0.0410(3)	0.2164(3)	3.6(1)
O(2)	0.4649(3)	−0.1793(2)	0.2752(2)	6.5(1)	C(37)	0.5522(3)	−0.0393(3)	0.2109(3)	3.7(1)
O(3)	1.2162(2)	0.0769(3)	0.3880(2)	6.2(1)	C(38)	0.5754(4)	−0.0607(3)	0.1312(3)	4.8(1)
O(4)	1.0533(3)	0.8673(2)	0.0440(2)	7.4(1)	C(39)	0.4829(5)	−0.0740(4)	0.1142(3)	6.4(2)
N(1)	0.6763(2)	0.4649(2)	0.2606(2)	2.95(8)	C(40)	0.6376(6)	0.0151(5)	0.0640(3)	7.1(2)
N(2)	0.5831(2)	0.3024(2)	0.3001(2)	2.84(8)	C(41)	0.6326(5)	−0.1471(4)	0.1282(4)	6.8(2)
N(3)	0.7492(2)	0.2200(2)	0.2920(2)	2.47(7)	C(42)	0.4991(4)	−0.0991(3)	0.2808(3)	4.4(1)
N(4)	0.8420(2)	0.3810(2)	0.2560(2)	2.53(7)	C(43)	0.4786(4)	−0.0824(3)	0.3543(3)	4.8(1)
C(1)	0.7359(3)	0.5409(3)	0.2235(3)	3.2(1)	C(44)	0.4231(5)	−0.1512(4)	0.4320(3)	6.5(2)
C(2)	0.6807(3)	0.6192(3)	0.2199(3)	4.5(1)	C(45)	0.3206(6)	−0.1696(5)	0.4373(5)	9.1(2)
C(3)	0.5882(3)	0.5920(3)	0.2594(3)	4.6(1)	C(46)	0.4178(7)	−0.1192(5)	0.5008(4)	10.7(2)
C(4)	0.5846(3)	0.4957(3)	0.2825(3)	3.4(1)	C(47)	0.4754(7)	−0.2371(5)	0.4388(5)	9.9(2)
C(5)	0.5012(3)	0.4426(3)	0.3146(3)	3.4(1)	C(48)	0.5130(4)	−0.0009(3)	0.3549(3)	4.3(1)
C(6)	0.5013(3)	0.3515(3)	0.3195(3)	3.4(1)	C(49)	0.9886(3)	0.1933(3)	0.3244(2)	3.1(1)
C(7)	0.4180(3)	0.2977(3)	0.3344(3)	4.9(1)	C(50)	0.9975(3)	0.1959(3)	0.3943(3)	3.4(1)
C(8)	0.4476(3)	0.2178(3)	0.3206(3)	5.1(1)	C(51)	1.0727(3)	0.1585(3)	0.4173(3)	3.6(1)
C(9)	0.5499(3)	0.2195(3)	0.3009(3)	3.4(1)	C(52)	1.0790(4)	0.1641(4)	0.4962(3)	4.4(1)
C(10)	0.6059(3)	0.1467(3)	0.2911(2)	3.0(1)	C(53)	1.1727(5)	0.2139(5)	0.4821(4)	7.0(2)
C(11)	0.6987(3)	0.1464(3)	0.2926(2)	2.74(9)	C(54)	0.9983(4)	0.2161(5)	0.5387(3)	6.3(2)
C(12)	0.7506(3)	0.0669(3)	0.3055(3)	3.7(1)	C(55)	1.0707(5)	0.0702(5)	0.5510(3)	7.2(2)
C(13)	0.8301(3)	0.0904(3)	0.3164(3)	3.7(1)	C(56)	1.1413(3)	0.1166(3)	0.3661(3)	3.9(1)
C(14)	0.8313(3)	0.1858(3)	0.3060(2)	2.74(9)	C(57)	1.1373(3)	0.1139(3)	0.2925(3)	3.8(1)
C(15)	0.9071(3)	0.2366(3)	0.3026(2)	2.77(9)	C(58)	1.2142(3)	0.0698(4)	0.2358(3)	5.1(1)
C(16)	0.9129(3)	0.3299(3)	0.2743(2)	2.74(9)	C(59)	1.1968(5)	0.0821(4)	0.1598(4)	6.6(2)
C(17)	0.9987(3)	0.3835(3)	0.2516(3)	3.7(1)	C(60)	1.2124(5)	−0.0318(4)	0.2712(4)	7.3(2)
C(18)	0.9812(3)	0.4662(3)	0.2172(3)	3.7(1)	C(61)	1.3146(4)	0.1110(5)	0.2174(4)	8.0(2)
C(19)	0.8830(3)	0.4659(3)	0.2209(2)	2.75(9)	C(62)	1.0591(3)	0.1524(3)	0.2736(3)	3.5(1)
C(20)	0.8355(3)	0.5425(3)	0.2004(2)	2.85(9)	C(63)	0.8927(3)	0.6292(3)	0.1585(2)	3.1(1)
C(21)	0.4061(3)	0.4860(3)	0.3395(3)	3.6(1)	C(64)	0.9586(4)	0.6383(3)	0.0850(3)	3.9(1)
C(22)	0.3545(3)	0.4721(3)	0.4182(3)	3.9(1)	C(65)	1.0151(4)	0.7176(3)	0.0438(3)	4.6(1)
C(23)	0.2665(3)	0.5118(3)	0.4451(3)	4.1(1)	C(66)	1.0869(5)	0.7269(4)	−0.0394(3)	7.5(2)
C(24)	0.2135(4)	0.4978(4)	0.5335(3)	5.6(2)	C(67)	1.0922(7)	0.6390(5)	−0.0630(4)	9.5(2)
C(25)	0.2669(6)	0.4398(6)	0.5809(4)	9.1(3)	C(68)	1.0555(9)	0.7962(6)	−0.0970(4)	13.4(4)
C(26)	0.1126(5)	0.4528(5)	0.5574(5)	8.9(2)	C(69)	1.1841(7)	0.7558(7)	−0.0495(6)	15.2(3)
C(27)	0.2039(6)	0.5885(5)	0.5551(4)	8.4(2)	C(70)	1.0003(4)	0.7867(3)	0.0819(3)	4.5(1)
C(28)	0.2338(3)	0.5643(3)	0.3880(3)	4.2(1)	C(71)	0.9350(3)	0.7800(3)	0.1565(3)	3.5(1)
C(29)	0.2838(3)	0.5803(3)	0.3077(3)	4.1(1)	C(72)	0.9205(4)	0.8568(3)	0.1977(3)	4.5(1)
C(30)	0.2467(4)	0.6402(4)	0.2473(3)	5.2(1)	C(73)	1.0128(5)	0.8755(4)	0.2105(4)	7.4(2)
C(31)	0.3163(6)	0.6491(6)	0.1647(4)	8.9(2)	C(74)	0.8885(5)	0.9402(4)	0.1498(4)	7.0(2)
C(32)	0.2370(5)	0.7362(5)	0.2576(4)	7.1(2)	C(75)	0.8431(5)	0.8324(3)	0.2778(3)	6.0(2)
C(33)	0.1515(5)	0.6048(5)	0.2509(4)	8.5(2)	C(76)	0.8827(3)	0.6989(3)	0.1939(2)	3.2(1)
C(34)	0.3704(3)	0.5383(3)	0.2854(3)	3.7(1)					

[a]e.s.d.s given in parentheses.

band [8] at 531 nm) was complete after ~10 min at this temperature. The reaction solution was partitioned between water and chloroform (1:1, 200 cm³), the chloroform phase then washed several times with water, dried over anhydrous sodium sulphate and evaporated to dryness under reduced pressure. The solid residue (~28 mg) was characterised as pure Ni–TBHPP by microanalysis and ¹H NMR spectroscopy.

Found: C, 77.0; H, 7.6; N, 4.5. Calc. for Ni(C₇₆-H₉₂N₄O₄): C, 77.1; H, 7.9; N, 4.7%. ¹H NMR spectrum in CDCl₃ solution: δ = 8.81 (8 β-pyrrole H),

7.81 (8 phenyl H), 5.45 (4 phenolic H), 1.56 (72 t-butyl H) ppm relative to TMS. Suitable crystals of the complex in the form of violet rectangular plates were obtained from a concentrated dichloromethane solution of Ni-TBHPP over which cyclohexane was carefully layered.

Crystal Data

C₇₆H₉₂N₄O₄Ni, $M = 1184.32$, triclinic, $a = 14.820(2)$, $b = 15.398(2)$, $c = 18.822(1)$ Å, $\alpha = 75.35(6)$, $\beta = 69.74(3)$, $\gamma = 87.31(3)°$, $V = 3894.5$ Å³ (by least-squares refinement on diffractometer
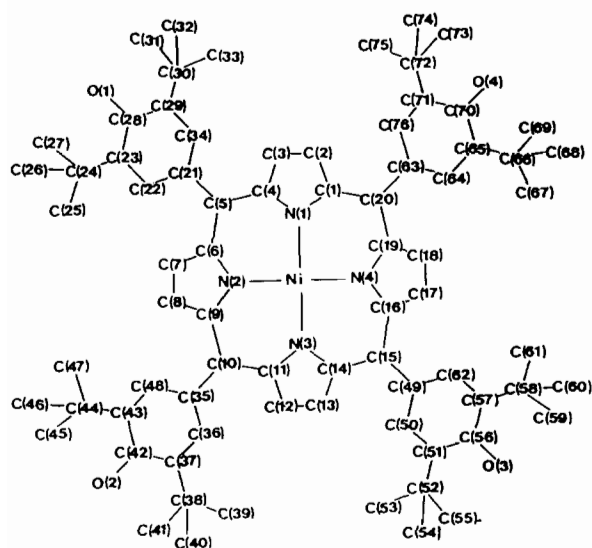
Fig. 1. Structure of TBHPP–Ni showing the numbering scheme used.

for 25 automatically centred reflections), $Z = 2$, $D_c = 1.01$ g cm^{-3}, λ(Mo Kα) = 0.7069 Å), $F(000) = 1272$, space group $P\bar{1}$ (No. 2). Violet rectangular plates 0.88 × 0.75 × 0.18 mm, μ(Mo Kα) = 2.9 cm^{-1}.

Data Collection and Processing

An Enraf Nonius CAD-4 diffractometer in ω–2θ zigzag scan mode was used with graphite monochromated Mo Kα radiation; 12 725 reflections were measured ($1 \leqslant \theta \geqslant 24°$, $+h$, $\pm k$, $\pm l$) giving 8919 unique observed reflections $I > 3\sigma(I)$, after averaging and correcting for absorption (transmission 83.9–99.8%). Linear and approximately isotropic crystal decay *ca.* 2% was corrected for during processing.

Structure Analysis and Refinement

Using direct methods (MULTAN) 52 non-hydrogen atoms including most of the porphyrin core and fragments of the phenyl rings were found in the E-map. Full-matrix least-squares refinement and Fourier maps revealed the remainder of the non-hydrogen atoms. Positional and anisotropic thermal parameters were refined for non-hydrogen atoms with hydrogen atoms (not hydroxyl) calculated (0.97 Å) but not refined. $R = 0.068$, $R_w = 0.103$. A statistical weighting scheme, $w = 4F_o^2/(\sigma I^2 + pF^2)^2$ which allows for counting statistics, the Lp factor and an experimental instability factor p (=0.07) to downweight intense reflections was used. A better weighting scheme could not be determined, the large data set making multiple calculations impractical. All calculations were performed with the SDP package of crystallographic programs [9] on a DEC PDP 11/73 computer; atomic scattering factors are as supplied with the program.

TABLE II. Selected Average Interatomic[a] Distances (Å) and Angles (°) for Ni–TBHPP

Ni–N	1.913(3)	C_o–C_{Ph}	1.394(5)
N–C_α	1.379(4)	C_{Ph}–O	1.389(4)
C_α–C_β	1.429(5)	C_o–C_t	1.535(6)
C_β–C_β	1.340(5)	C_t–C_{Me}	1.519(7)
C_α–C_{ms}	1.382(5)	Ni–C_α	2.961(6)
C_{ms}–C_p	1.497(4)	Ni–C_{ms}	3.367(9)
C_p–C_m	1.377(5)	N–N'	2.706(6)
C_m–C_o	1.390(5)	N–N''	3.826(8)
N–Ni–N'	90.0(1)	C_α–M_{ms}–C_p	119.2(6)
N–Ni–N''	179.1(1)	C_{ms}–C_p–C_m	120.3(3)
Ni–N–C_α	127.4(2)	C_p–C_m–C_o	121.3(3)
C_α–N–C_α	105.2(3)	C_m–C_o–C_{Ph}	116.5(3)
N–C_α–C_β	110.1(3)	C_o–C_{Ph}–O	118.2(3)
N–C_α–C_{ms}	125.3(3)	C_m–C_o–C_t	120.6(4)
C_α–C_β–C_β	107.3(3)	C_{Ph}–C_o–C_t	122.9(3)
C_α–C_{ms}–C_α	121.3(3)	C_o–C_t–C_{Me}	111.0(4)
C_β–C_α–C_{ms}	124.3(3)	C_{me}–C_t–C_{Me}	107.9(5)

[a]C_α = carbons adjacent to nitrogen atoms in pyrrole rings; C_β = carbons remote from nitrogen atoms in pyrrole rings; Cms = *meso* carbons; C_{Ph} = carbons attached to phenolic OH groups; C_o, C_m, C_p = carbons *ortho, meta* and *para* to C_{Ph}; C_t = tertiary carbons in Bu^t groups; C_{Me} = methyl carbons in Bu^t groups; N,N' = adjacent nitrogens; N,N'' = opposite nitrogens.

Results and Discussion

Description of the Structure

The structure of the complex illustrating the numbering scheme adopted is shown in the Fig. 1. Fractional atomic coordinates are listed in Table I with selected bond lengths and bond angles given in Table II.

X-ray analysis shows that the geometry about the nickel is essentially square planar with N–Ni–N bond angles all very close (within 0.7°) to 90° and with equal (within 3σ) Ni–N bond distances (1.913 ± 0.008 Å). Chemically equivalent bond distances and angles in the ligand are virtually identical. An interesting aspect of the structure is the marked non-planarity of the porphyrin core, which undergoes severe S_4 ruffling such that the angles between adjacent pyrrole rings lie between 23.4 and 35.1°. The methine carbon atoms are alternately displaced by ±0.54 Å from the least-squares plane defined by the N_{1-4} and C_1–C_{20} atoms. The phenyl rings lie at angles 75.1, 83.4, 77.9 and 63.3° to this plane. Some of these structural aspects are evident from the stereoview of the complex in Fig. 2.

The compatibility between hole size and metal ion radius for macrocyclic ligands [10], and more specifically for porphyrins [11], has been discussed. Most so-called planar porphyrins have angles of
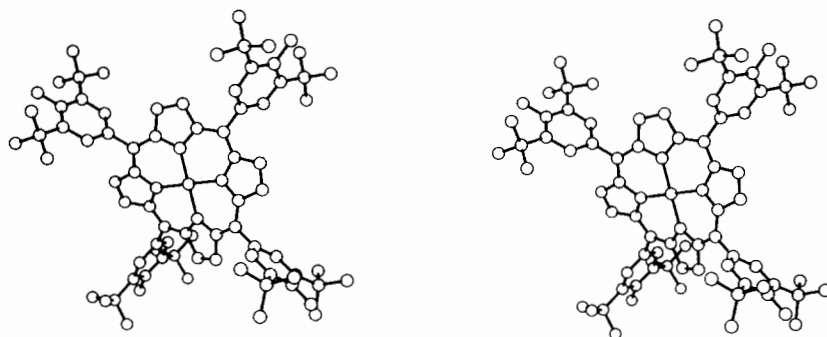
Fig. 2. Stereoview of TBHPP–Ni showing puckering of the porphyrin core and orientation of the phenyl rings.

TABLE III. Metal–Nitrogen Bond Distances and Angles Between Adjacent Pyrrole Rings in some Nickel(II) and other Metalloporphyrins

Complex	M–N (Å)	Angles between adjacent pyrrole rings (°)	Reference
Ni–TBHPP[a]	1.913(8)	23.4–35.1	this work
Ni–OEP[b] (tetragonal)	1.929(3)	32.8	14
(triclinic)	1.958(2)	2.1	15
Ni–DEUT[c]	1.960(14)	1.9–5.2	16
Ni–TMP[d]	1.953(14)	6.3	17
Mn–TPP[e]	2.082–2.092	8.1[f]	18
Fe–TPP	1.972(4)	18.0[f]	19
Co–TPP	1.949(3)	19.0[f]	18
Ni–TPP	1.928(3)	–	18
Cu–TPP	1.981(7)	26.8	12
Zn–TPP	2.037(15)	6.5	20
Ag–TPP	2.092(3)	7.5	20
Pd–TPP	2.009(9)	25.2	12

[a]TBHPP = tetrakis(3,5-di-tert-butyl-4-hydroxyphenyl)porphyrin. [b]OEP = octaethylporphyrin. [c]DEUT = 2,4-diacetyl-deuteroporphyrin IX dimethyl ester. [d]TMP = 5,10,15,20-tetramethylporphyrin. [e]TPP = tetraphenylporphyrin. [f]Calculated from atomic coordinates withdrawn from the Cambridge Data Base.

$2–5°$ between adjacent pyrrole rings with atom displacements from the mean plane of ~ 0.02 Å. A planar metalloporphyrin is estimated to have a hole radius of 2.01 Å and it has been postulated that in order to retain planarity this radius should not be less than 1.96 Å. Consequently smaller hole radii give rise to non-planar porphyrins. On the other hand Ni–N bond lengths in square planar complexes containing imine type ligands are generally *ca.* 1.85 Å [10], and so the porphyrin core must contract if it is to accommodate this undersized metal ion. The rigidity of the porphyrin system however permits only partial radial contraction and results in a Ni–N bond length of 1.91 Å, the shortest so far reported for nickel(II)–porphyrin complexes. This bond distance, although shorter than that necessary for porphyrin planarity is longer than Ni–N bond distances in square planar complexes containing monodentate ligands. As has been previously pointed out for metallo–tetraphenylporphyrin (M–TPP) derivatives crystal packing may also contribute somewhat to puckering of the porphyrin core [12, 13]. Ni–N

bond distances for a number of nickel(II) and other metalloporphyrin complexes are listed in Table III.

The dihedral angles between the phenyl rings and the mean porphyrin plane in Ni–TBHPP lie in the range $63.3–83.4°$. These angles are similar to those in TPP derivatives and the deviation from $90°$ has been attributed to minor conjugation between rings through the $C_p–C_{ms}$ bonds [11]. The closest contact between nickel atoms (*i.e.* x, y, z and $1 - x, 1 - y, 1 - z$) in symmetry related molecules is 10.7 Å and this compares with intermetal distances of ~ 8 Å which are typical of M–TPP complexes (e.g. 8.3 Å in Cu–TPP*) [12]. The increased separation in the present case is undoubtedly due to the steric demands of the t-butyl substituents. These steric effects would also result in poorer crystal packing and would account for the lower unit cell density (1.01 g cm^{-3}) compared to those of M–TPP complexes ($1.29–1.48$ g cm^{-3}; M = Fe^{II}, Co^{II}, Cu^{II}, Zn^{II}, Pd^{II}) [12, 18–

*This value was calculated from the unit cell dimensions given in Table I, ref. 12.

20]. Molecular modelling shows that theses substituents also sterically protect the phenolic groups and indeed would stabilise phenoxy radicals that might result from oxidation of the porphyrin ligand. Such stabilisation against 'self reactions' has previously been reported in the case of the 2,4,6-tri-t-butylphenoxy radical [21].

Supplementary Material

A complete list of bond distances, angles, thermal parameters, least-square planes and structure factors can be obtained from the authors.

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