The Structures of (5,10,15,20-Tetramethylporphyrinato)nickel(II) and (5,10,15,20-Tetramethylchlorinato)nickel(II)

By Judith C. Gallucci, Paul N. Swepston and James A. Ibers

Department of Chemistry, Northwestern University, Evanston, Illinois 60201, USA

Abstract

A metal-assisted template synthesis has led to ease of formation of both (5,10,15,20-tetramethylporphyrinato)nickel(II), Ni(tmp), and (5,10,15,20-tetramethylchlorinato)nickel(II), Ni(tmc). The compound Ni(tmp) ($C_{24}H_{20}N_4Ni$, FW 423·16) crystallizes in space group $P2_1/c$ ($Z = 2$) with unit-cell dimensions $a = 11\cdot332$ (3), $b = 5\cdot664$ (2), $c = 14\cdot162$ (4) Å, $\beta = 104\cdot80$ (1)°, and $V = 879$ Å^3. The structure has been refined to an R index on F^2 of 0·073 based on 7365 reflections (140 K) and 133 variables. The molecule has a crystallographically imposed inversion center. The compound Ni(tmc) ($C_{24}H_{22}N_4Ni$, FW 425·18) crystallizes in space group $P2_1/n$ ($Z = 4$) with unit-cell dimensions $a = 12\cdot593$ (4), $b = 7\cdot489$ (3), $c = 19\cdot296$ (6) Å, $\beta = 94\cdot08$ (1)°, and $V = 1815$ Å^3. The structure has been refined to an R index on F^2 of 0·069 based on 11663 reflections (123 K) and 262 variables. In going from porphyrin to chlorin the reduction of the π-electron system has resulted in markedly different structures. The Ni(tmp) molecule is nearly planar with Ni—N bond lengths of 1·963 (1) and 1·943 (1) Å. The Ni(tmc) molecule exhibits an S_4-ruffled conformation with Ni—N bonds ranging in length from 1·918 (1) to 1·936 (1) Å. The asymmetry in chemically equivalent bonds in Ni(tmc) indicates a reduction in aromaticity relative to Ni(tmp).

Introduction

Metalloporphyrins have been extensively studied as models for coordination sites in metallobiomolecules (Ibers & Holm, 1980). The presence of reduced hemes in certain biological systems (Scott, Irwin, Siegel & Shoolery, 1978a,b; Jacob & Orme-Johnson, 1979) has led to interest in the study of reduced porphyrins, *i.e.* chlorins, bacteriochlorins, and isobacteriochlorins. X-ray diffraction studies of metal-free chlorins have shown the macrocycle to be a planar molecule (Fischer, Templeton, Zalkin & Calvin, 1972; Hoppe, Will, Gassmann & Weichselgartner, 1969; Agius, Ballantine, Ferrito, Jaccarini, Murray-Rust, Pelter, Psaila &

Schembri, 1979). Incorporation of a metal ion such as Zn^{2+} (Spaulding, Andrews & Williams, 1977) or Mg^{2+} (Chow, Serlin & Strouse, 1975; Serlin, Chow & Strouse, 1975) leads to pentacoordination of the metal and to a complex whose slightly puckered conformation is similar to the analogous porphyrin. On the other hand, recently reported structures of nickel octaethylisobacteriochlorin (Kratky, Angst & Johansen, 1981) and nickel octaethylhexahydroporphyrin (Johansen, Piermattie, Angst, Diener, Kratky & Eschenmoser, 1981) have shown extremely puckered macrocycles. A new metal-assisted template synthesis for porphyrins and chlorins (Ulman, Fisher & Ibers, 1982) has led to ease of formation of (5,10,15,20-tetramethylporphyrinato)nickel(II), Ni(tmp), and (5,10,15,20-tetramethylchlorinato)nickel(II), Ni(tmc). An X-ray investigation of these two molecules has revealed strikingly different macrocyclic conformations. A preliminary account of this work has recently appeared (Ulman, Gallucci, Fisher & Ibers, 1980).

Experimental

The compounds Ni(tmp) and Ni(tmc) were prepared as previously described (Ulman, Fisher & Ibers, 1982). Crystals of Ni(tmp) were grown by diffusion of methanol into a chloroform solution, while Ni(tmc) crystals were obtained from hexane diffusion into chloroform. Neither set of crystals was air sensitive. Precession and Weissenberg photographs taken with Cu $K\alpha$ radiation indicated that Ni(tmp) crystallizes in space group $P2_1/c$ (C_{2h}^5) of the monoclinic system. Reflections of the type hkl with $k + l$ odd are systematically weak, but observable. Photographic work for Ni(tmc) showed systematic absences consistent with space group $P2_1/n$ (C_{2h}^5).

Intensity data were collected at low temperature [Ni(tmp), 140 K; Ni(tmc), 123 K] in the usual manner (Jameson & Ibers, 1980; Doedens & Ibers, 1967) on a Picker FACS-I automatic diffractometer using the θ–2θ scan technique. Crystallographic details for both compounds are given in the *Abstract* and in Table 1.

Table 1. *Additional crystallographic details for* Ni(tmp) *and* Ni(tmc)

	Ni(tmp)	Ni(tmc)
Density (calc.) (g cm⁻³)	1·60 (140 K)[a]	1·56 (123 K)
Bounding planes[b]	{100} (0·316), {001}	{101} (0·438),
	(0·170), (013),	{001} (0·319),
	(113), (010)	{101} (0·187),
		(010), (011), (011)
Crystal volume (mm³)	0·0377	0·0460
Radiation	Mo Kα	
	[λ(Kα₁) = 0·7093 Å, graphite monochromator]	
Linear absorption coefficient (cm⁻¹)	11·2	10·9
Transmission factors[c]	0·694 to 0·838	0·657 to 0·831
Temperature[c]	140 K	123 K
Detector aperture	5·5 mm wide × 5·5 mm	4·5 mm wide × 6·0
	high; 32 cm from crystal	mm high; 32 cm
		from crystal
Take-off angle (°)	3·2	3·1
Scan speed (deg min⁻¹ in 2θ)	2	2
2θ limits (°)	3·4 ≤ 2θ < 90·4	3·4 ≤ 2θ ≤ 81
Background counts	10 s at each end of scan	10 s at each end of
	with rescan option[d];	scan with rescan
	increased to 20 s for	option[d]; increased
	2θ > 71°	to 20 s for 2θ > 63°
Scan range	1·2° below Kα₁ to	1·35° below Kα₁ to
	1·3° above Kα₂	1·05° above Kα₂
Data collected	±h,+k,+l	±h,+k,+l
Unique data	7365	11 663
Unique data, with $F_o^2 > 3\sigma(F_o^2)$	4438	6602
Final number of variables	133	262
$R(F^2)$	0·073	0·069
$R_w(F^2)$	0·109	0·100
Error in observation of unit weight, e^2	1·227	1·209
R [on F for $F_o^2 > 3\sigma(F_o^2)$]	0·042	0·043

(a) The low-temperature system is based on a design by Huffman (1974). Note that Ni(tmp) undergoes a sluggish destructive phase transition between 140 and 123 K.

(b) The numbers in parentheses are the distances in mm between the Friedel pairs of the preceding form.

(c) Comparison with sample results of an analytical absorption correction indicated that a Gaussian grid of 4 × 4 × 4 was sufficient for both absorption corrections.

(d) The diffractometer was run under the Vanderbilt disc oriented system (Lenhert, 1975).

The crystals used for data collection were of excellent quality, resulting in large data sets for both molecules. The crystal of Ni(tmp) was a dark-brown, many-sided prism cut from a larger crystal. The crystal of Ni(tmc) was a purple-brown rectangular rod. Both data sets were processed as previously described (Doedens & Ibers, 1967).

There were difficulties associated with the collection of a low-temperature data set for Ni(tmp). During data collection at 123 K, the intensities of the six standards suddenly decreased by about 20%. Subsequently, the standards continued to decrease slowly in intensity and a small piece of the crystal eventually broke away. The resulting data set was corrected for these problems and used in the refinement of Ni(tmp) that was initially reported (Ulman, Gallucci, Fisher & Ibers, 1980). As this decay process occurred with two crystals of Ni(tmp), we believe that a sluggish phase transition may occur in the vicinity of 123 K. The new data set reported here was collected at 140 K with no measurable decrease in the standards.

Solution and refinement of the structures

For both molecules, standard procedures and programs were used for solution and refinement (Waters & Ibers,

1977). Atomic scattering factors for nonhydrogen atoms were those of Cromer & Waber (1974). Scattering factors for H were those of Stewart, Davidson & Simpson (1965). Anomalous-dispersion corrections (Ibers & Hamilton, 1964) for the Ni atom were made in both structures using values of f' and f'' of Cromer & Waber (1974).

The structure of Ni(tmp) was solved with the aid of *MULTAN*78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1977). The data were corrected for absorption by the Gaussian method. After the first

Table 2. *Refined positional parameters and equivalent isotropic thermal parameters for* Ni(tmp) *and* Ni(tmc)

	x	y	z	B_{eq}* (Å²)
(a) Ni(tmp)				
Ni	½	½	1·000	1·06
N(1)	0·508934 (87)	0·22455 (17)	0·920282 (63)	1·46
N(2)	0·321161 (75)	0·49374 (20)	0·955030 (64)	1·50
C(1)	0·61291 (12)	0·10813 (23)	0·911013 (82)	1·89
C(2)	0·58070 (16)	−0·09751 (26)	0·850426 (96)	2·61
C(3)	0·45945 (16)	−0·10402 (26)	0·820421 (93)	2·60
C(4)	0·41341 (12)	0·09748 (23)	0·862079 (81)	1·89
C(5)	0·29151 (12)	0·15413 (26)	0·842172 (87)	2·17
C(6)	0·24994 (10)	0·34163 (25)	0·886980 (88)	1·96
C(7)	0·12312 (12)	0·39730 (33)	0·87298 (12)	2·80
C(8)	0·11612 (12)	0·57641 (33)	0·93286 (12)	2·81
C(9)	0·23900 (10)	0·63889 (25)	0·984097 (94)	2·00
C(10)	0·73208 (12)	0·17454 (26)	0·951677 (94)	2·21
C(11)	0·20134 (17)	0·00329 (34)	0·76928 (12)	3·38
C(12)	0·83282 (17)	0·03392 (33)	0·92509 (14)	3·47
(b) Ni(tmc)				
Ni	0·639478 (13)	0·110646 (24)	0·797882 (9)	1·23
N(1)	0·73355 (8)	0·14129 (15)	0·879732 (57)	1·45
N(2)	0·76012 (8)	0·10901 (16)	0·741018 (56)	1·37
N(3)	0·54488 (8)	0·07226 (15)	0·716937 (58)	1·43
N(4)	0·51909 (8)	0·12122 (16)	0·854242 (56)	1·43
C(1)	0·70778 (11)	0·20017 (20)	0·945119 (69)	1·65
C(2)	0·80177 (12)	0·20476 (22)	0·991411 (73)	2·01
C(3)	0·88310 (12)	0·14530 (22)	0·955432 (77)	2·04
C(4)	0·84089 (10)	0·10956 (20)	0·885724 (70)	1·60
C(5)	0·90388 (10)	0·06577 (19)	0·831485 (76)	1·69
C(6)	0·86492 (10)	0·08136 (18)	0·763827 (72)	1·50
C(7)	0·93704 (11)	0·08104 (20)	0·704772 (78)	1·89
C(8)	0·86569 (11)	0·15084 (20)	0·644210 (75)	1·84
C(9)	0·75619 (10)	0·13766 (18)	0·670511 (68)	1·50
C(10)	0·66640 (11)	0·14077 (19)	0·626161 (68)	1·60
C(11)	0·56737 (10)	0·09141 (19)	0·648976 (67)	1·59
C(12)	0·47726 (11)	0·04286 (23)	0·603547 (74)	2·01
C(13)	0·39970 (11)	−0·01138 (22)	0·643613 (77)	1·96
C(14)	0·43966 (10)	0·01199 (19)	0·714514 (72)	1·61
C(15)	0·37808 (12)	0·00271 (19)	0·770768 (74)	1·65
C(16)	0·41519 (10)	0·07057 (19)	0·835627 (72)	1·60
C(17)	0·34849 (11)	0·10863 (23)	0·890666 (77)	2·02
C(18)	0·41123 (12)	0·18625 (23)	0·942647 (77)	2·05
C(19)	0·51712 (11)	0·18995 (20)	0·920892 (69)	1·63
C(20)	0·60649 (11)	0·23514 (20)	0·964398 (68)	1·71
C(21)	0·59064 (13)	0·30727 (23)	1·036074 (74)	2·26
C(22)	1·02010 (11)	0·01910 (23)	0·84684 (9)	2·20
C(23)	0·67759 (13)	0·18207 (23)	0·550229 (74)	2·13
C(24)	0·26458 (12)	−0·06518 (23)	0·76166 (9)	2·30

* $B_{eq} = \frac{4}{3} [a^2 \beta_{11} + (2ab \cos \gamma) \beta_{12} + \cdots]$.

cycle of full-matrix least-squares anisotropic refinement of the nonhydrogen atoms, the positions of the H atoms of the pyrrole and methyl groups were evident in a difference electron density map. In the spirit of the least-squares method if a given structural feature is known with more precision than can be obtained from the experimental data then it should be included in the model. Accordingly, these H positions were idealized [C—H = 1·0 Å, $B(H) = B(C)_{eq}$ + 1·0 Å^2] and added as fixed contributions to the structure factors. The idealized positions were updated before the final cycle of refinement. The final anisotropic refinement cycle was carried out on F^2 using the 7365 unique reflections (including $F^2 < 0$) and 133 variable parameters. The function $\sum w(F_o^2 - F_c^2)^2$ was minimized, with the weights w being $1/\sigma^2(F^2)$. The final values of R and R_w (based on F^2) are 0·073 and 0·109. In the final cycle of refinement the largest parameter shift was 0·5σ. The largest peak in the final difference map had a peak height of 0·86 e Å^{-3} and was located between atoms C(5) and C(6).

The structure of Ni(tmc) was also solved using *MULTAN*78. After one cycle of structure factor and Fourier calculations based on the 21 nonhydrogen atoms initially found, the remaining nonhydrogen atoms were located. All of the H atoms were found in a difference electron density map. As before, they were included in the model in fixed, idealized positions for the rest of the calculations. An absorption correction was applied and the data were corrected for the slightly increasing intensity (~4%) of the six standards toward the end of data collection. The final refinement was carried out on F^2 using the 11 663 unique reflections (including $F^2 < 0$) to give values of R and R_w on F^2 of 0·069 and 0·100. The final difference electron density map had a maximum peak height of 0·61 (2) e Å^{-3}. The largest parameter shift in the final cycle of refinement was 0·6σ.

Final positional parameters of non-hydrogen atoms with estimated standard deviations are listed in Table 2 for Ni(tmp) and Ni(tmc).*
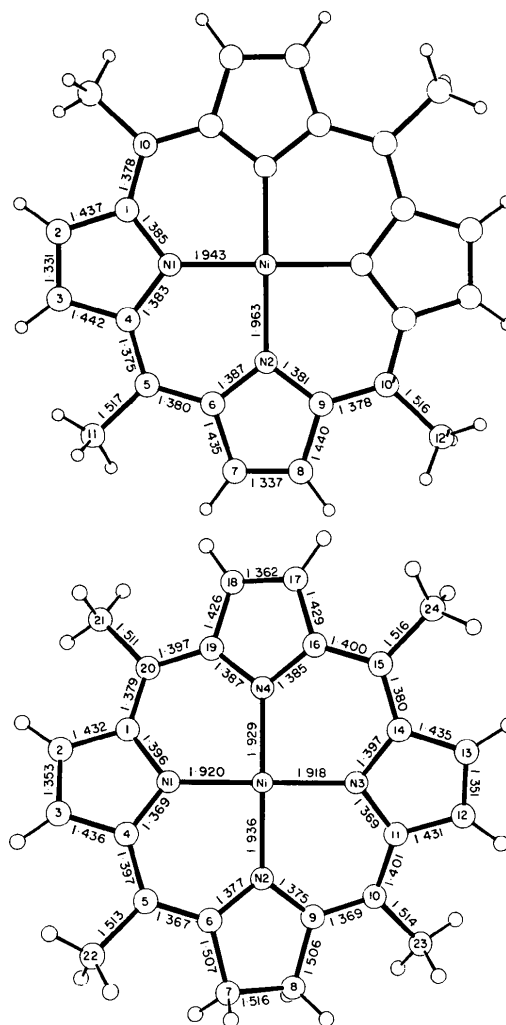

Fig. 1. Projected views of Ni(tmp) (top) and Ni(tmc) (bottom) showing the labeling scheme and bond distances (Å). The Ni(tmp) molecule has an inversion center. Estimated standard deviations for bond lengths in Ni(tmp) are as follows: Ni—N, 0·001; N—C$_a$, 0·001–0·002; C$_a$–C$_b$, 0·002; C$_a$–C$_m$, 0·002; C$_b$–C$_b$, 0·002–0·003; C$_m$–C$_{methyl}$, 0·002 Å. Estimated standard deviations for bond lengths in Ni(tmc) are as follows: Ni—N, 0·001; N—C$_a$, 0·002; C$_a$–C$_b$, 0·002; C$_a$–C$_m$, 0·002; C$_b$–C$_b$, 0·002; C$_m$–C$_{methyl}$, 0·002 Å.

Description of the structures

In order to emphasize the differences in these two structures, bond lengths for Ni(tmp) and Ni(tmc) are displayed in Fig. 1, along with the numbering scheme used for each. The remaining metrical parameters are given in Table 3. For Ni(tmp) the packing consists of two molecules per unit cell in a slipped stack arrangement, as shown in Fig. 2. The distance between symmetry-related mean porphyrin planes is 3·35 Å with each plane making an angle of about 36° with the *b* axis. All intermolecular distances between nonhydrogen atoms are greater than 3·33 Å. The unit cell of Ni(tmc) contains four molecules (Fig. 3), with the shortest intermolecular distance between nonhydrogen atoms being 3·39 Å.

Previous studies on several four-coordinate nickel porphyrin complexes have indicated wide variations of Ni—N bond lengths and puckerings of the macrocycle.

---

* Anisotropic thermal parameters, H-atom parameters, best weighted least-squares-planes parameters, and structure amplitude lists for Ni(tmp) and Ni(tmc) have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36787 (73 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. *Bond angles* (°) *for* Ni(tmp) *and* Ni(tmc)

(a) Ni(tmp)

N(1)—Ni—N(2)	89·98 (4)	N(1)—C(1)—C(10)	126·6 (1)
N(1)—Ni—N(2')	90·02 (4)	N(1)—C(4)—C(5)	126·4 (1)
Ni—N(1)—C(1)	127·51 (8)	N(2)—C(6)—C(5)	126·2 (1)
Ni—N(1)—C(4)	127·94 (9)	N(2)—C(9)—C(10')	126·0 (1)
Ni—N(2)—C(6)	127·27 (9)	C(4)—C(5)—C(6)	121·9 (1)
Ni—N(2)—C(9)	127·67 (9)	C(1)—C(10)—C(9')	121·8 (1)
N(1)—C(1)—C(2)	110·5 (1)	C(5)—C(4)—C(3)	123·4 (1)
N(1)—C(4)—C(3)	110·2 (1)	C(5)—C(6)—C(7)	123·6 (1)
N(2)—C(6)—C(7)	110·1 (1)	C(10)—C(1)—C(2)	122·9 (1)
N(2)—C(9)—C(8)	110·0 (1)	C(10')—C(9)—C(8)	123·9 (1)
C(1)—N(1)—C(4)	104·5 (1)	C(4)—C(5)—C(11)	118·3 (1)
C(6)—N(2)—C(9)	105·1 (1)	C(6)—C(5)—C(11)	119·8 (1)
C(1)—C(2)—C(3)	107·3 (1)	C(1)—C(10)—C(12)	118·2 (1)
C(4)—C(3)—C(2)	107·4 (1)	C(9')—C(10)—C(12)	120·0 (1)
C(6)—C(7)—C(8)	107·4 (1)		
C(9)—C(8)—C(7)	107·4 (1)		

(b) Ni(tmc)

|			
N(1)—Ni—N(2)	90·22 (5)	C(14)—C(13)—C(12)	106·9 (1)
N(1)—Ni—N(3)	178·18 (5)	C(16)—C(17)—C(18)	107·0 (1)
N(1)—Ni—N(4)	89·71 (5)	C(19)—C(18)—C(17)	107·3 (1)
N(2)—Ni—N(3)	90·26 (5)	N(1)—C(1)—C(20)	125·6 (1)
N(2)—Ni—N(4)	178·00 (5)	N(1)—C(4)—C(5)	126·0 (1)
N(3)—Ni—N(4)	89·87 (5)	N(2)—C(6)—C(5)	126·1 (1)
Ni—N(1)—C(1)	127·7 (1)	N(2)—C(9)—C(10)	126·3 (1)
Ni—N(1)—C(4)	126·6 (1)	N(3)—C(11)—C(10)	125·3 (1)
Ni—N(2)—C(6)	126·3 (1)	N(3)—C(14)—C(15)	125·1 (1)
Ni—N(2)—C(9)	125·8 (1)	N(4)—C(16)—C(15)	125·5 (1)
Ni—N(3)—C(11)	127·3 (1)	N(4)—C(19)—C(20)	125·5 (1)
Ni—N(3)—C(14)	127·5 (1)	C(4)—C(5)—C(6)	120·8 (1)
Ni—N(4)—C(16)	127·5 (1)	C(9)—C(10)—C(11)	120·9 (1)
Ni—N(4)—C(19)	127·2 (1)	C(14)—C(15)—C(16)	121·0 (1)
N(1)—C(1)—C(2)	109·7 (1)	C(19)—C(20)—C(1)	120·9 (1)
N(1)—C(4)—C(3)	110·1 (1)	C(5)—C(4)—C(3)	123·6 (1)
N(2)—C(6)—C(7)	112·0 (1)	C(5)—C(6)—C(7)	121·8 (1)
N(2)—C(9)—C(8)	112·0 (1)	C(10)—C(9)—C(8)	121·6 (1)
N(3)—C(11)—C(12)	110·6 (1)	C(10)—C(11)—C(12)	124·0 (1)
N(3)—C(14)—C(13)	109·8 (1)	C(15)—C(14)—C(13)	124·4 (1)
N(4)—C(16)—C(17)	110·3 (1)	C(15)—C(16)—C(17)	124·1 (1)
N(4)—C(19)—C(18)	110·1 (1)	C(20)—C(1)—C(2)	124·5 (1)
C(1)—N(1)—C(4)	105·7 (1)	C(20)—C(19)—C(18)	123·9 (1)
C(6)—N(2)—C(9)	107·8 (1)	C(4)—C(5)—C(22)	120·0 (1)
C(11)—N(3)—C(14)	105·2 (1)	C(6)—C(5)—C(22)	118·9 (1)
C(16)—N(4)—C(19)	105·3 (1)	C(9)—C(10)—C(23)	118·6 (1)
C(1)—C(2)—C(3)	107·1 (1)	C(11)—C(10)—C(23)	120·3 (1)
C(4)—C(3)—C(2)	107·4 (1)	C(14)—C(15)—C(24)	120·3 (1)
C(6)—C(7)—C(8)	103·1 (1)	C(16)—C(15)—C(24)	118·5 (1)
C(9)—C(8)—C(7)	103·0 (1)	C(1)—C(20)—C(21)	120·0 (1)
C(11)—C(12)—C(13)	107·5 (1)	C(19)—C(20)—C(21)	118·9 (1)
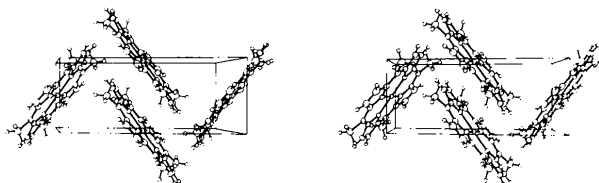
Fig. 2. Stereoscopic view of the packing for Ni(tmp). The origin is in the lower left corner that is nearest the viewer. The horizontal axis is the c axis and is positive moving left to right. The vertical axis is the b axis and is positive moving up the page. The a axis is positive in the direction away from the viewer.

For example, the tetragonal form of Ni(oep) (oep = 2,3,7,8,12,13,17,18-octaethylporphyrinato) has a short Ni—N distance of 1·929 (3) Å with S_4 ruffling of the macrocycle (Meyer, 1972) while the triclinic form is planar with an average Ni—N distance of 1·958 (2) Å (Cullen & Meyer, 1974). More recently, Ni(tmp)I has been found to have an S_4-ruffled macrocycle and an
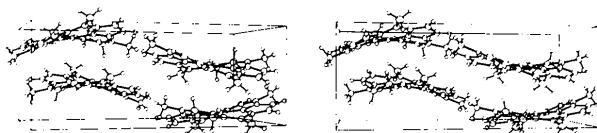
Fig. 3. Stereoscopic view of the packing for Ni(tmc). The origin is in the lower left corner that is nearest the viewer. The horizontal axis is the c axis and is positive moving left to right. The vertical axis is the b axis and is positive moving up the page. The a axis is positive in the direction away from the viewer.

Ni—N bond length of 1·938 (3) Å (Pace, Martinsen, Ulman, Hoffman & Ibers, 1982) while the porphyrin complex in Ni(tmp)(TCNQ) (TCNQ = 7,7,8,8-tetracyano-p-quinodimethane) is a planar molecule with an Ni—N bond length equal to 1·950 (4) Å (Pace, Ulman & Ibers, 1982). The small energy barrier for contraction of the porphyrinato core upon complexation to a small ion such as Ni^{2+} with the resulting non-planarity of the macrocycle has been previously noted (Hoard, 1973).

The Ni(tmp) complex is essentially a planar molecule with metrical parameters characteristic of other planar nickel porphyrins. The NiN_4 coordination is required to be planar by the crystallographically imposed inversion center. However, the two Ni—N bond lengths are significantly different. Moreover, there are two sets of significantly different Ni—C_a* distances, along with two sets of values for the N—C_a—C_m angles. Since the remaining chemically equivalent bond lengths and angles are equal within the standard deviations estimated from the inverse least-squares matrix, it is likely that the Ni—N distances are truly different. The initial results of a bonding electron density study of Ni(tmp) suggest that the Ni—N bond-length differences may arise because of interactions between neighboring molecules in the slipped stacks (Kutzler, Ellis, Berkovitch-Yellin, Swepston & Ibers, 1982).

In Table 4 the metrical parameters have been averaged on the assumption of D_{4h} symmetry and are compared with the averaged parameters for other planar nickel porphyrin structures. The average Ni—N bond length of 1·953 (14) Å is in the range observed for these porphyrins. The major difference among these structures is the previously observed increase in the Ni—C_m distance upon going from the β-carbon substituted to the meso-substituted porphyrin (Cullen & Meyer, 1973). This increase is accompanied by a decrease in the C_a—C_m—C_a angle. The remaining parameters for Ni(tmp) do not differ significantly from those for the other structures in Table 4.

As seen in Figs. 1, 2, and 3, the geometry of Ni(tmc) differs greatly from that of Ni(tmp). As in the

---

* In the text, C_a refers to the a-pyrrole C atoms, C_b refers to the β-pyrrole C atoms and C_m refers to the meso C atoms (Hoard, 1973).

Table 4. *A comparison of averaged bond lengths (Å) and angles (°) for planar nickel porphyrin molecules*

Values are weighted averages in accordance with D_{4h} symmetry. An estimated standard deviation in parentheses is the larger of that estimated for a single observation from the inverse matrix or from the values averaged.

	Ni(tmp)[a]	Ni(tmp) (TCNQ)[b]	Ni(oep)[c] (triclinic)	Ni(deut)[d]
Ni–N	1·953 (14)	1·950 (4)	1·958 (2)	1·960 (14)
N–C_a	1·384 (3)	1·388 (6)	1·376 (6)	1·382 (19)
C_a–C_m	1·378 (2)	1·380 (6)	1·372 (4)	1·374 (25)
C_a–C_b	1·439 (3)	1·435 (6)	1·444 (4)	1·447 (15)
C_b–C_b	1·334 (5)	1·339 (6)	1·346 (4)	1·350 (19)
Ni–C_m	3·422 (2)	3·429 (4)	3·381 (3)	3·403 (13)
Ni–C_a	3·005 (9)	3·006 (6)	3·007 (4)	3·011 (21)
N–Ni–N	90·00 (4)	90·0 (1)	90·15 (9)	90·0 (6)
Ni–N–C_a	127·6 (3)	127·7 (3)	128·0 (2)	127·8 (6)
C_a–N–C_a	104·8 (4)	104·6 (3)	104·0 (4)	104·5 (6)
N–C_a–C_m	126·3 (3)	126·5 (4)	124·4 (3)	125·3 (13)
N–C_a–C_b	110·2 (2)	110·3 (4)	111·6 (3)	111·0 (8)
C_b–C_a–C_m	123·5 (4)	123·2 (6)	124·1 (4)	123·7 (18)
C_a–C_m–C_a	121·9 (1)	121·4 (5)	125·2 (3)	123·9 (13)
C_a–C_b–C_b	107·4 (1)	107·4 (5)	106·5 (4)	106·8 (10)

(a) This work (T = 140 K).
(b) Pace, Ulman & Ibers (1982) (T = 123 K).
(c) Cullen & Meyer (1974) (room temperature).
(d) Hamor, Caughey & Hoard (1965) (deut = 2,4-diacetyl-deuteroporphyrin-IX dimethyl ester) (room temperature).

porphyrin, the chlorin molecule has essentially square-planar coordination about the Ni atom. However, the Ni–N bond lengths range from 1·918 (1) to 1·936 (1) Å and are significantly shorter than those in Ni(tmp). The longest Ni–N bond length involves the N atom of the reduced ring, as observed in other reduced porphyrin molecules (Spaulding, Andrews & Williams, 1977; Chow, Serlin & Strouse, 1975; Serlin, Chow & Strouse, 1975). None of the chemically equivalent bond lengths in the chlorin molecule differs significantly. The C_a–C_m bond lengths are alternately long and short around the ring. As a result, most bond types have two averaged values; one set of distances is longer than and the other set is shorter than the equivalent type in Ni(tmp). A comparison of these averaged distances in Ni(tmp) *vs* Ni(tmc) follows: Ni–N, 1·953 (14) *vs* 1·929 (1) and 1·919 (1); N–C_a,
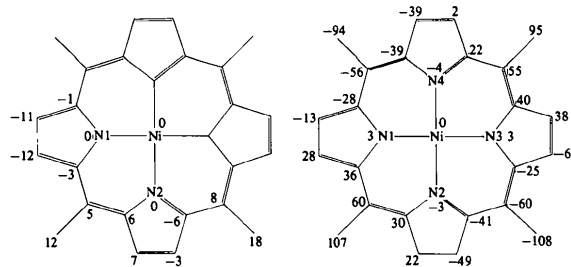

Fig. 4. Deviations of the atoms (Å × 10², e.s.d.'s 0·001–0·002 Å) from a least-squares plane through the 24 endocyclic atoms plus Ni for Ni(tmp) (left) and Ni(tmc) (right). The numbering scheme is the same as in Fig. 1.

1·384 (3) *vs* 1·391 (6) and 1·373 (4); C_a–C_b, 1·439 (3) *vs* 1·432 (4); C_a–C_b, 1·334 (5) *vs* 1·352 (2) and 1·362 (2); C_a–C_m, 1·378 (2) *vs* 1·399 (2) and 1·374 (7) Å.

The C_a–C_b bond lengths of the reduced pyrrole ring of the chlorin are longer than those in the other three pyrrole rings by about 0·08 Å. The C_b–C_b bond length of 1·516 (2) Å in the reduced ring is much longer than that reported for (tetraphenylchlorinato)(pyridine)zinc, Zn(tpc)(py), 1·478 (3) Å (Spaulding, Andrews & Williams, 1977), yet shorter than the analogous bond lengths in ethyl chlorophyllides *a* and *b*, 1·555 (9) and 1·566 (12) Å (Chow, Serlin & Strouse, 1975; Serlin, Chow & Strouse, 1975), methyl pheophorbide *a*, 1·551 (7) Å (Fischer *et al.*, 1972), and perhaps in phyllochlorin ester, 1·53 (3) Å (Hoppe *et al.*, 1969).

Distances of the nonhydrogen atoms from a least-squares plane containing the 24-atom framework and the Ni atom are shown in Fig. 4 for Ni(tmp) and Ni(tmc). The Ni(tmp) molecule is nearly planar with the angle between adjacent pyrrole rings being 6·3°. The Ni(tmc) molecule is extremely non-planar. There is an S_4 ruffling of the core, with angles between adjacent pyrrole rings ranging from 21·7 to 28·6°. These angles are not unusual for S_4-ruffled nickel porphyrins, as Ni(oep) has an angle of about 23° between adjacent rings (Meyer, 1972), while Ni(tmp)I has a value of 17·5° for this angle (Pace, Martinsen, Ulman, Hoffman & Ibers, 1982). It has been suggested that overall puckering, such as that observed here, may result from optimization of Ni–N bonding upon disruption of the π system (Kratky, Angst & Johansen, 1981), with the Ni–N bond distances decreasing in order to approach the normal 1·85 Å bond length for a square-planar monodentate system (Sacconi, 1968).

Each of the three pyrrole rings in Ni(tmc) is planar with the maximum distance from a least-squares plane being 0·02 Å. The reduced ring is not as planar as it is in Zn(tpc)(py) (Spaulding, Andrews & Williams, 1977), with the largest deviation from the best plane through this ring being 0·095 Å for the C(8) atom. As a further measure of this puckering, the C(6)–C(7)–C(8)–C(9) torsion angle is 14·0 (1)°.

The central hole of the reduced macrocycle of Ni(tmc) has decreased considerably upon hydrogenation of the pyrrole ring. Defining C_t as the average of the four N-atom positions, we find the averaged distances for Ni(tmp) *vs* Ni(tmc) are: C_t–C_a, 3·005 *vs* 2·970 Å and C_t–C_m, 3·422 *vs* 3·380 Å. This contraction of the central hole results from the different conformations for the two molecules, as shown in Figs. 2 and 3. This trend is continued in the conformations of two recently reported reduced porphyrins: the *tct* and *ttt* isomers of (2,3,7,8,12,13,17,18-octaethyl-2,3,7,8-tetrahydroporphyrinato)nickel. These molecules are extremely puckered, with angles of 48–49° between opposite five-membered rings (Kratky, Angst & Johan-

sen, 1981). The same angles in Ni(tmc) range from 35 to 38°. Further reduction of the porphyrin ring to form the *tctcc* isomer of (2,3,7,8,12,13,17,18-octaethyl-2,3,7,8,12,13-hexahydroporphyrinato)nickel also results in a severely puckered molecule (Johansen *et al.*, 1981).

In the X-ray studies of the series [5,10,15,20-tetra(4-pyridyl)porphyrinato](pyridine)zinc(II) [Zn(tpyp)(py)] (Collins & Hoard, 1970), (2,3-dihydro-5,10,15,20-tetraphenylporphyrinato)(pyridine)zinc(II) [Zn(tpc)(py)] (Spaulding *et al.*, 1977), and (2,3,7,8-tetrahydro-5,10,15,20-tetraphenylporphyrinato)-(pyridine)zinc(II) [Zn(tpibc)(py)] (Barkigia, Fajer, Spaulding & Williams, 1981), no major conformational changes were observed upon increased reduction of the macrocycle. This may be attributed to the larger size of the Zn atom as compared with the Ni atom and to the fact that the Zn is five-coordinate in this series and lies out of the plane of the macrocycle.

Other reduced metalloporphyin structures, the ethylchlorophyllide *a* and *b* dihydrates (Chow *et al.*, 1975; Serlin *et al.*, 1975), the metal-free chlorins, phyllochlorin ester (Hoppe *et al.*, 1969), methyl pheophorbide *a* (Fischer *et al.*, 1972), and the methyl ester of anhydrobonellin (Agius *et al.*, 1979) are characterized by relatively flat rings in comparison with Ni(tmc). Hence chlorin systems show greater structural variability than do porphyrin systems, a factor of possible biological significance.

The reduction of the pyrrole ring in Ni(tmp) to form Ni(tmc) affords a molecule whose geometrical parameters and conformation are vastly different from the porphyrin. The non-planarity of the Ni(tmc) molecule, along with the alternating long and short C_a–C_m bond lengths, is indicative of a reduction in aromaticity of the chlorin ring relative to the porphyrin. The chlorin structure suggests that an asymmetric charge distribution is present, with charge transfer toward the reduced pyrrole ring.

Because of the extensive data sets available, an experimental and theoretical bonding electron density study is in progress to investigate further the differences between Ni(tmp) and Ni(tmc) (Kutzler, Ellis, Berkovitch-Yellin, Swepston & Ibers, 1982).

References

AGIUS, L., BALLANTINE, J. A., FERRITO, V., JACCARINI, V., MURRAY-RUST, P., PELTER, A., PSAILA, A. F. & SCHEMBRI, P. J. (1979). *Pure Appl. Chem.* **51**, 1847–1864.

BARKIGIA, K. M., FAJER, J., SPAULDING, L. D. & WILLIAMS, G. J. B. (1981). *J. Am. Chem. Soc.* **103**, 176–181.

CHOW, H.-C., SERLIN, R. & STROUSE, C. E. (1975). *J. Am. Chem. Soc.* **97**, 7230–7237.

COLLINS, D. M. & HOARD, J. L. (1970). *J. Am. Chem. Soc.* **92**, 3761–3771.

CROMER, D. T. & WABER, J. T. (1974). In *International Tables for X-ray Crystallography*, Vol. IV. Birmingham: Kynoch Press.

CULLEN, D. L. & MEYER, E. F. JR (1973). *Acta Cryst.* **B29**, 2507–2515.

CULLEN, D. L. & MEYER, E. F. JR (1974). *J. Am. Chem. Soc.* **96**, 2095–2102.

DOEDENS, R. J. & IBERS, J. A. (1967). *Inorg. Chem.* **6**, 204–210.

FISCHER, M. S., TEMPLETON, D. H., ZALKIN, A. & CALVIN, M. (1972). *J. Am. Chem. Soc.* **94**, 3613–3619.

HAMOR, T. A., CAUGHEY, W. S. & HOARD, J. L. (1965). *J. Am. Chem. Soc.* **87**, 2305–2312.

HOARD, J. L. (1973). *Ann. NY Acad. Sci.* **206**, 18–31.

HOPPE, W., WILL, G., GASSMANN, J. & WEICHSELGARTNER, H. (1969). *Z. Kristallogr.* **128**, 18–35.

HUFFMAN, J. C. (1974). PhD Thesis, Indiana Univ.

IBERS, J. A. & HAMILTON, W. C. (1964). *Acta Cryst.* **17**, 781–782.

IBERS, J. A. & HOLM, R. H. (1980). *Science*, **209**, 223–235.

JACOB, G. S. & ORME-JOHNSON, W. H. (1979). *Biochemistry*, **18**, 2967–2980.

JAMESON, G. B. & IBERS, J. A. (1980). *J. Am. Chem. Soc.* **102**, 2823–2831.

JOHANSEN, J. E., PIERMATTIE, V., ANGST, C., DIENER, E., KRATKY, C. & ESCHENMOSER, A. (1981). *Angew. Chem. Int. Ed. Engl.* **20**, 261–263.

KRATKY, C., ANGST, C. & JOHANSEN, J. E. (1981). *Angew. Chem. Int. Ed. Engl.* **20**, 211–212.

KUTZLER, F. W., ELLIS, D. E., BERKOVITCH-YELLIN, Z., SWEPSTON, P. N. & IBERS, J. A. (1982). In preparation.

LENHERT, P. G. (1975). *J. Appl. Cryst.* **8**, 568–570.

MAIN, P., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1977). *MULTAN78. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.

MEYER, E. F. JR (1972). *Acta Cryst.* **B28**, 2162–2167.

PACE, L. J., MARTINSEN, J., ULMAN, A., HOFFMAN, B. M. & IBERS, J. A. (1982). In preparation.

PACE, L. J., ULMAN, A. & IBERS, J. A. (1982). *Inorg. Chem.* **21**, 199–207.

SACCONI, L. (1968). *Transition-Met. Chem.* **4**, 199–298.

SCOTT, A. I., IRWIN, A. J., SIEGEL, L. M. & SHOOLERY, J. N. (1978a). *J. Am. Chem. Soc.* **100**, 316–318.

SCOTT, A. I., IRWIN, A. J., SIEGEL, L. M. & SHOOLERY, J. N. (1978b). *J. Am. Chem. Soc.* **100**, 7987–7994.

SERLIN, R., CHOW, H.-C. & STROUSE, C. E. (1975). *J. Am. Chem. Soc.* **97**, 7237–7242.

SPAULDING, L. D., ANDREWS, L. C. & WILLIAMS, G. J. B. (1977). *J. Am. Chem. Soc.* **99**, 6918–6923.

STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

ULMAN, A., FISHER, D. & IBERS, J. A. (1982). *J. Heterocycl. Chem.* In the press.

ULMAN, A., GALLUCCI, J., FISHER, D. & IBERS, J. A. (1980). *J. Am. Chem. Soc.* **102**, 6852–6854.

WATERS, J. M. & IBERS, J. A. (1977). *Inorg. Chem.* **16**, 3273–3277.