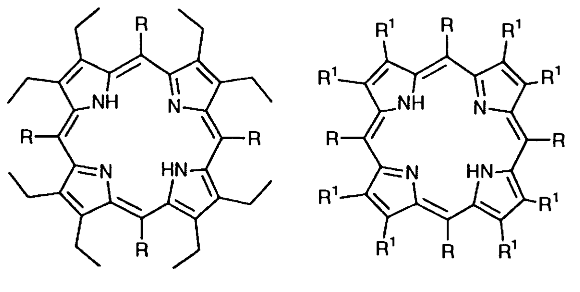
Prevention of Out-of-plane Macrocycle Distortion by Thallium in the Sterically Strained 2,3,7,8,12,13,17,18-Octaethyl-5,10,15,20-tetranitroporphyrin *

Mathias O. Senge
Department of Chemistry, University of California, Davis, CA 95616, USA

Dodecaalkyl/aryl-substituted porphyrins have been shown to exhibit severely non-planar macrocycle conformations with displacement of the C_b-atoms of up to 1.2 Å. 2,3,7,8,12,13,17,18-Octaethyl-5,10,15,20-tetranitroporphyrin (H_2oetnp) presents an easily available model compound for studies on the conformational flexibility of tetrapyrroles. In contrast to most known structures of dodecasubstituted porphyrins, which exhibit severely non-planar macrocycle conformations, the thallium(III) complex [Tl(oetnp)Cl], shows only a moderately distorted macrocycle with an average displacement of the C_b-atoms of 0.19 Å. This is the first example of a dodecasubstituted porphyrin where the effect of the large main-group metal ion counterbalances the conformational distortion induced by steric strain of the peripheral substituents. Out-of-plane relief of the steric strain is prevented by the thallium atom; rather, in-plane distortion of the macrocycle, with widened C_a–C_m–C_a angles, is observed. Structural investigations of the free-base porphyrin and its nickel(II) complex show very non-planar conformations and severe saddle-shaped distortion indicated by displacements of the C_b-atoms of up to 1.05 Å. The mode and degree of distortion are similar to those described for dodecaalkyl/aryl-porphyrins indicating that the oetnp ligand is non-planar and that the much smaller degree of distortion observed in the thallium derivative is due to a metal effect. This striking difference of conformational distortion on dependence of the central metal is the first example where such large differences in non-planarity of a given tetrapyrrole ligand have been characterized by structural means. Crystal data: H_2oetnp, orthorhombic, $Pna2_1$, a = 11.114(4), b = 12.409(5), c = 25.905(11) Å, Z = 4, R = 0.046 for 2783 reflections with $I > 2.5\sigma(I)$; [Ni(oetnp)], triclinic, $P\bar{1}$, a = 10.610(2), b = 13.678(5), c = 24.884(8) Å, α = 95.89(3), β = 93.19(2), γ = 92.70(2)°, Z = 4 (2 independent molecules), R = 0.063 for 8649 reflections with $I > 2.0\sigma(I)$; [Tl(oetnp)Cl], triclinic, $P\bar{1}$, a = 13.968(4), b = 14.091(3), c = 18.737(4) Å, α = 94.80(2), β = 99.94(2), γ = 90.43(2)°, Z = 4 (2 independent molecules), R = 0.079 for 7640 reflections with $I > 1.5\sigma(I)$.

The study of non-planar tetrapyrrole conformations has attracted interest recently with respect to studies of their conformational flexibility.[1a] Different macrocycle shapes are believed to be responsible for the often unique physicochemical properties observed in protein–tetrapyrrole complexes *in vivo*.[1b,c,2] Non-planar tetrapyrrole macrocycles have been observed in several chlorophyll[3] and haem[4] protein complexes. Considerable conformational flexibility has been found in studies on chlorophyll derivatives,[1b,5] chlorins,[6] corrins[7] and other porphyrins.[1a,8,9]

Special interest has been given to the study of highly substituted porphyrins as model compounds for non-planar chromophores. The zinc(II) complexes of H_2omtpp,† H_2oetpp and the free base H_2dpp have been shown to exhibit severely saddle-shaped macrocycle conformations induced by steric crowding of the peripheral substituents.[10–12] Molecular-mechanics calculations predicted a wide range of different conformations possible for nickel(II) complexes of dodecasubstituted porphyrins, which was confirmed by resonance-Raman spectroscopy and X-ray crystallography.[13–15] Spectroscopic studies showed that the non-planar conformations are retained in solution. Theoretical calculations indicated a direct correlation between degree of non-planarity and strongly red-shifted absorption bands.[1b] Similar results were obtained with derivatives of H_2obtpp, which had very distorted macrocycles and exhibited bathochromic shifted absorption bands compared to H_2oep and H_2tpp derivatives.[16]



R = NO_2 H_2oetnp
R = Ph H_2oetpp
R = H H_2oep

R^1 = R = Ph H_2dpp
R^1 = Me, R = Ph H_2omtpp
R^1 = Br, R = Ph H_2obtpp
R^1 = H, R = Ph H_2tpp

Several other cases are described in the literature where dodecasubstituted porphyrins exhibit considerable red-shifted absorption bands when compared to less substituted parent compounds. Examples include tetra-*meso*-halogenated (*i.e.* 5,10,15,20-substituted) H_2oep derivatives[17,18] and tetra-*meso*-nitroporphyrins, *e.g.* H_2oetnp.[19,20] In the context of our

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* *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

† Abbreviations used: H_2dpp = 2,3,5,7,8,10,12,13,15,17,18,20-dodecaphenylporphyrin; H_2obtpp = 2,3,7,8,12,13,17,18-octabromo-5,10,15,-20-tetraphenylporphyrin; H_2oep = 2,3,7,8,12,13,17,18-octaethylporphyrin; H_2oetpp = 2,3,7,8,12,13,17,18-octaethyl-5,10,15,20-tetraphenylporphyrin; H_2omtpp = 2,3,7,8,12,13,17,18-octamethyl-5,10,15,-20-tetraphenylporphyrin; H_2oetnp = 2,3,7,8,12,13,17,18-octaethyl-5,10,15,20-tetranitroporphyrin; H_2tpp = 5,10,15,20-tetraphenylporphyrin.

ongoing studies on the conformational distortion of tetrapyrroles, it is therefore of interest to establish the structure of highly substituted porphyrins with substituents other than *meso*-alkyl or -aryl groups. The ease with which *meso*-nitroporphyrins can be prepared, compared with the more laborious total syntheses of dodecaalkyl- and dodecaarylporphyrins, makes these molecules promising model compounds for the study of metal effects in highly substituted porphyrins.

Experimental

Spectroscopic Measurements.—Proton NMR spectra were recorded at a frequency of 300 MHz on a General Electric QE-300 instrument. All chemical shifts are given in ppm and have been converted to the δ scale using the residual solvent signal at δ 5.30 for CD_2Cl_2. Electronic absorption spectra were recorded on a Hewlett Packard 8450A spectrophotometer using methylene chloride as solvent. Melting points are uncorrected and were determined with a Thomas Bristoline apparatus.

Syntheses.—The free base H_2oetnp and its nickel(II) complex [Ni(oetnp)] were prepared according to published procedures and gave satisfactory spectroscopic and analytical data.[20a]

Chloro(2,3,7,8,12,13,17,18-*octaethyl*-5,10,15,20-*tetranitroporphyrinato*)*thallium*(III), [Tl(oetnp)Cl]. To a solution of H_2oetnp (65 mg) in $CHCl_3$ (50 cm^3) was added a solution of thallium(III) trifluoroacetate (100 mg) in tetrahydrofuran (100 cm^3). The mixture was stirred at room temperature for 2 h, diluted with water and extracted into $CHCl_3$. The organic phase was dried over Na_2SO_4 and the solvent removed *in vacuo*. The residue of [Tl(O_2CCF_3)(oetnp)] was not further characterized but was directly taken up in CH_2Cl_2 (50 cm^3) and stirred with a solution of KCl (0.1 g) in MeOH (50 cm^3). The mixture was stirred overnight, mixed with water and extracted with methylene chloride. The organic phase was dried and evaporated. The bright purple residue was recrystallized from CH_2Cl_2-*n*-hexane (78 mg, 90%), m.p. 240 °C (decomp.) (Found: C, 45.40; H, 4.20; N, 11.75. $C_{36}H_{40}ClN_8O_8Tl$ requires C, 45.50; H, 4.10; N, 11.90%); $\lambda_{max}(CH_2Cl_2)$/nm 438 (log ε/dm^3 mol^{-1} cm^{-1} 5.72), 566 (4.87) and 608 (sh); δ_H(300 MHz; $CDCl_3$) 3.626 (16 H, q, CH_2) and 1.566 (24 H, t, CH_3).

X-Ray Crystallography.—Brown parallelepipeds of H_2oetnp were grown by slow diffusion of *n*-hexane into a concentrated solution of the compound in methylene chloride, while crystals for the two metal complexes were grown from $CHCl_3$–MeOH. The crystals were immersed in hydrocarbon oil, a single crystal selected, mounted on a glass fibre and placed in a low-temperature N_2 stream.[21] A Siemens R3m/V automatic diffractometer with a graphite monochromator and equipped with a locally modified Siemens low-temperature device was used for data collection of H_2oetnp and [Ni(oetnp)] (Mo-Kα radiation, λ = 0.710 73 Å), while intensities for [Tl(oetnp)Cl] were collected on a Siemens P4 instrument equipped with a Siemens rotating anode (Cu-Kα radiation, λ = 1.514 78 Å). Cell parameters were determined from 20–25 automatically centred reflections with $20 \leqslant 2\theta \leqslant 25°$ for H_2oetnp and [Ni(oetnp)] and in the range $45 \leqslant 2\theta \leqslant 65°$ for [Tl(oetnp)Cl]. Cell parameters are listed in Table 1. The intensities were measured in the range $0 < 2\theta \leqslant 55°$ at 130 K using the ω-scan technique for the data collections on H_2oetnp and [Ni(oetnp)]. Data for [Tl(oetnp)Cl] were collected in the range $0 < 2\theta \leqslant 108.5°$ using the θ–2θ scan technique. Two standard reflections were measured every 198 reflections and showed only statistical variation in intensity during the data collections.

Table 1 Structure determination summary for H_2oetnp, [Ni(oetnp)] and [Tl(oetnp)Cl]

	H_2oetnp	[Ni(oetnp)]	[Tl(oetnp)Cl]
Formula	$C_{36}H_{42}N_8O_8$	$C_{36}H_{40}N_8NiO_8$	$C_{36}H_{40}ClN_8O_8Tl$
M	714.8	771.5	952.6
Crystal size/mm	0.62 × 0.51 × 0.4	0.65 × 0.6 × 0.4	0.25 × 0.18 × 0.09
Space group	$Pna2_1$	$P\bar{1}$	$P\bar{1}$
a/Å	11.114(4)	10.610(2)	13.968(4)
b/Å	12.409(5)	13.678(5)	14.091(3)
c/Å	25.905(11)	24.884(8)	18.737(4)
α/°	90	95.89(3)	94.80(2)
β/°	90	93.19(2)	99.94(2)
γ/°	90	92.70(2)	90.43(2)
U/Å^3	3573(2)	3582(2)	3618.7(14)
F(000)	1512	1616	1896
Z	4	4[a]	4[a]
D_c/g cm^{-3}	1.329	1.431	1.748
μ(Mo-Kα)/mm^{-1}	0.096	0.606	9.807 (Cu-Kα)
Diffractometer	Siemens R3m/V	Siemens R3m/V	Siemens P4 (RA)
λ/Å	0.710 73	0.710 73	1.541 78
T/K	130	130	124
2θ range/°	$0 < 2\theta \leqslant 55$	$0 < 2\theta \leqslant 55$	$0 < 2\theta \leqslant 108.5$
Scan type	ω	ω	2θ–θ
Scan speed/° min^{-1}	14.65	14.65	58.59
Scan range/°	2.0	2.20	2.0 plus Kα separation
Octants collected	$+h, +k, +l$	$\pm h, \pm k, +l$	$\pm h, \pm k, +l$
Independent reflections	4180	13 754	8852
Observed reflections	2783 [$I > 2.5\sigma(I)$]	8649 [$I > 2.0\sigma(I)$]	7640 [$I > 1.5\sigma(I)$]
No. of Parameters	468	955	773
Data-to-parameter ratio	5.9:1	9.1:1	9.9:1
Largest Δ/σ	0.062	0.008	0.188
ρ_{max}/e Å^{-1}	0.29	0.55	4.09 (near Tl)
R[b]	0.046	0.063	0.079
R'[c]	0.057	0.067	0.124
g	0.0016	0.0007	0.0432
S	0.96	1.20	0.60

[a] Two independent molecules. [b] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [c] $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w F_o^2]^{\frac{1}{2}}$, where $w^{-1} = \sigma^2(F) + gF^2$.

The intensities were corrected for Lorentz and polarization effects. An absorption correction was applied using the program XABS,[22] and extinction was disregarded. The structures were solved *via* direct methods (for H_2oetnp) or *via* Patterson syntheses and subsequent structure expansion {for [Ni(oetnp)] and [Tl(oetnp)Cl]} using the SHELXTL PLUS program system.[23] Structure solution for [Ni(oetnp)] was only possible in the non-centrosymmetric space group $P1$, followed by transfer of the coordinates of the macrocycle atoms to the centrosymmetric space group $P\bar{1}$. The missing side-chain atoms were located in subsequent difference maps. The refinement was carried out by full-matrix least squares on $|F|$ using the same program system. The function minimized was $\Sigma w(F_o - F_c)^2$. Hydrogen atoms were included at calculated positions by using a riding model [C–H 0.96 Å, N–H 0.9 Å, $U_{iso}(H) = 0.04$]. Calculations were carried out on a Vax-station 3200. All non-hydrogen atoms were refined with anisotropic thermal parameters. For [Tl(oetnp)Cl] only the thallium, chlorine, nitrogen, oxygen and the ethyl side-chain atoms were refined with anisotropic thermal parameters. The structure of [Tl(oetnp)Cl], measured on a diffractometer equipped with a copper rotating anode, showed a very high residual electron density. Application of different methods for absorption correction did not overcome this problem. Trials to overcome this problem by collecting data with Mo-Kα radiation on a conventional instrument failed due to the small crystal size. Final R values for the observed data are listed in Table 1 and additional refinement details are given in the supplementary material. Tables 2 to 4 list the atomic coordinates.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Results and Discussion

Structure of the Free Base.—In order to study the influence of the peripheral substituents on the macrocycle conformation and to establish the basic conformation of the free ligand we first crystallized H_2oetnp. Fig. 1 shows the molecular structure and labelling scheme. Atomic coordinates are listed in Table 2 while selected structural parameters for the free base and metal complexes studied here are compiled in Table 5. The H_2oetnp molecule is strikingly non-planar with a severe saddle distortion (Fig. 2). Similar types and degrees of distortion have been described for [Zn(omtpp)(MeOH)], [Zn(oetpp)(py)] (py = pyridine),[10] the copper(II) and cobalt(II) complexes of H_2oetpp,[15] H_2dpp,[11] and 2,3,7,8,12,13,17,18-octabromotetraarylporphyrins.[16b]

The macrocycle distortion is characterized in all cases by an alternating displacement of the pyrrole rings above and below the mean plane of the molecule. The average deviation from the plane of the 24 core atoms is 0.4 Å for H_2oetnp. The plane of the four nitrogens (4N-plane) shows deviations from planarity in the order of 0.08 Å, while the *meso*-carbons deviate by 0.05 Å from the least-squares plane of the macrocycle atoms (Table 5). The individual pyrrole rings are all planar with deviations < 0.02 Å. They are tilted with respect to the mean plane of the 24 core atoms by an average angle of 20.6°. The distortion mode in the free base H_2oetnp can thus be best described as a saddle, according to the definition given by Scheidt and Lee.[8] In order to minimize steric interaction between the *meso*-substituents and the neighbouring C_b-substituents the plane of the nitro substituents (O–N–O plane) is twisted with respect to the plane of the 24 core atoms by 58.7° (average value for all four groups). This conformation minimizes the contacts between neighbouring substituents. Hence, there are no unreasonable short intramolecular distances.

The degree of non-planarity in dodecasubstituted porphyrins is best described by the skeletal deviations of the macrocycle atoms (Fig. 3). The mean deviation from the least-squares 4N-plane is 0.32 Å for the C_a-, 0.04 Å for the C_m- and 0.84 Å for the C_b-positions. These values indicate that the distortion in the free base H_2oetnp is somewhat smaller than that observed in dodecaalkyl/aryl- or octabromotetraaryl-porphyrins. The deviations of the C_b-atoms from the plane of the 24 core atoms is 1.05 Å in [Zn(omtpp)(MeOH)], 1.08 Å in [Zn(oetpp)(py)],[10] 1.2 Å in [Cu(oetpp)] and [Co(oetpp)],[15] 1 Å in H_2dpp[11] and 0.96 Å in 2,3,7,8,12,13,17,18-octabromo-5,10,15,20-tetramesitylporphyrin.[16b] Thus the degree of distortion in octaethylporphyrin with four *meso*-nitro groups is about 10% smaller than in other free bases with *meso*-alkyl or -aryl groups.

A different, monoclinic modification of H_2oetnp has recently been described by Zhu *et al.*[19b] While this structure exhibits the same overall structural features as the one described in

Table 2 Atomic coordinates (× 10^4) for H_2oetnp

Atom	x	y	z
N(21)	923(3)	4065(3)	2240
N(22)	1165(2)	4149(3)	1111(1)
N(23)	2936(3)	5838(3)	1250(1)
N(24)	2903(3)	5576(3)	2381(1)
C(1)	821(4)	4233(3)	2756(2)
C(2)	−339(4)	3852(3)	2951(2)
C(21)	−915(4)	4099(4)	3460(2)
C(22)	−1289(4)	5286(4)	3491(2)
C(3)	−907(4)	3385(3)	2543(2)
C(31)	−2183(4)	3004(4)	2536(2)
C(32)	−3041(4)	3848(4)	2316(2)
C(4)	−79(4)	3504(3)	2102(2)
C(5)	−186(3)	3054(3)	1615(2)
C(6)	437(4)	3268(3)	1161(2)
C(7)	362(4)	2753(3)	662(2)
C(71)	−158(4)	1651(3)	545(2)
C(72)	613(5)	747(3)	756(2)
C(8)	975(4)	3383(3)	316(2)
C(81)	1100(5)	3127(4)	−252(2)
C(82)	2188(6)	2423(6)	−367(2)
C(9)	1488(4)	4267(3)	606(2)
C(10)	2144(4)	5173(3)	446(2)
C(11)	2731(4)	5974(3)	731(2)
C(12)	3275(4)	6980(3)	542(2)
C(121)	3096(4)	7534(4)	29(2)
C(122)	1916(5)	8158(5)	4(2)
C(13)	3854(4)	7415(3)	952(2)
C(131)	4362(4)	8540(3)	979(2)
C(132)	3516(5)	9302(4)	1261(3)
C(14)	3670(4)	6652(3)	1384(2)
C(15)	4220(4)	6699(3)	1874(2)
C(16)	3949(4)	6136(3)	2329(2)
C(17)	4622(4)	6042(3)	2804(2)
C(171)	5881(4)	6408(4)	2921(2)
C(172)	5953(5)	7437(4)	3256(2)
C(18)	3919(4)	5446(3)	3140(2)
C(181)	4351(4)	5049(4)	3656(2)
C(182)	4877(5)	3895(4)	3619(2)
C(19)	2818(4)	5174(3)	2875(2)
C(20)	1801(4)	4647(3)	3039(2)
N(1)	−1179(3)	2274(3)	1552(2)
O(1)	−1063(3)	1377(3)	1735(2)
O(2)	−2072(3)	2594(3)	1315(1)
N(2)	2197(4)	5318(3)	−122(2)
O(3)	1329(3)	5721(3)	−329(1)
O(4)	3122(3)	5023(3)	−341(1)
N(3)	5272(3)	7418(3)	1908(2)
O(5)	6175(3)	7147(3)	1671(2)
O(6)	5181(3)	8238(3)	2168(2)
N(4)	1721(3)	4443(3)	3608(2)
O(7)	1560(3)	5212(3)	3888(1)
O(8)	1832(3)	3509(3)	3751(1)

Table 3 Atomic coordinates (× 10^4) for [Ni(oetnp)]

Atom	x	y	z	Atom	x	y	z
Molecule 1				Molecule 2			
Ni(1)	7 534(1)	7 852(1)	−26(1)	Ni(2)	12 705(1)	8 001(1)	4 984(1)
N(21)	7 939(4)	8 590(3)	−616(2)	N(25)	12 339(4)	9 014(3)	4 530(2)
N(22)	7 265(4)	6 662(3)	−511(2)	N(26)	12 516(4)	7 012(3)	4 366(2)
N(23)	7 450(4)	7 105(3)	582(2)	N(27)	12 711(4)	6 989(3)	5 463(2)
N(24)	7 433(4)	9 044(3)	436(2)	N(28)	13 197(4)	8 988(3)	5 571(2)
C(1)	8 426(5)	9 550(3)	−581(2)	C(21)	12 417(5)	10 016(4)	4 660(2)
C(2)	9 063(5)	9 733(4)	−1 067(2)	C(22)	11 707(5)	10 515(4)	4 262(2)
C(2a)	9 808(5)	10 635(4)	−1 189(2)	C(22a)	11 432(5)	11 592(4)	4 278(2)
C(2b)	9 118(6)	11 203(5)	−1 609(2)	C(22b)	10 273(6)	11 832(4)	4 593(3)
C(3)	8 897(5)	8 879(4)	−1 408(2)	C(23)	11 206(5)	9 801(4)	3 880(2)
C(3a)	9 585(6)	8 645(4)	−1 918(2)	C(23a)	10 244(5)	9 934(4)	3 431(2)
C(3b)	10 665(6)	7 981(5)	−1 801(3)	C(23b)	8 944(6)	9 492(5)	3 535(3)
C(4)	8 125(5)	8 196(4)	−1 137(2)	C(24)	11 689(5)	8 883(4)	4 027(2)
C(5)	7 515(5)	7 324(4)	−1 352(2)	C(25)	11 769(5)	8 011(4)	3 697(2)
C(6)	6 984(5)	6 627(4)	−1 062(2)	C(26)	12 279(5)	7 154(4)	3 833(2)
C(7)	6 302(5)	5 706(4)	−1 266(2)	C(27)	12 575(5)	6 296(4)	3 482(2)
C(7a)	5 587(6)	5 474(4)	−1 802(2)	C(27a)	12 539(7)	6 156(4)	2 873(2)
C(7b)	4 440(6)	6 114(4)	−1 851(2)	C(27b)	11 351(8)	5 627(5)	2 627(3)
C(8)	6 315(5)	5 131(4)	−847(2)	C(28)	12 923(5)	5 615(4)	3 808(2)
C(8a)	5 689(6)	4 107(4)	−870(2)	C(28a)	13 411(6)	4 620(4)	3 609(2)
C(8b)	6 425(7)	3 322(4)	−1 175(3)	C(28b)	14 830(6)	4 641(5)	3 645(3)
C(9)	6 949(5)	5 724(4)	−384(2)	C(29)	12 825(5)	6 039(4)	4 359(2)
C(10)	7 320(5)	5 470(3)	121(2)	C(30)	12 767(5)	5 566(3)	4 822(2)
C(11)	7 684(5)	6 114(3)	575(2)	C(31)	12 551(5)	5 987(4)	5 340(2)
C(12)	8 098(5)	5 892(4)	1 112(2)	C(32)	12 187(5)	5 504(4)	5 805(2)
C(12a)	8 752(6)	4 989(4)	1 260(2)	C(32a)	11 861(6)	4 422(4)	5 848(2)
C(12b)	10 057(6)	4 931(5)	1 031(3)	C(32b)	10 473(6)	4 132(5)	5 713(3)
C(13)	7 956(5)	6 718(4)	1 455(2)	C(33)	12 117(5)	6 239(4)	6 218(2)
C(13a)	8 291(6)	6 839(4)	2 054(2)	C(33a)	11 520(6)	6 139(4)	6 746(2)
C(13b)	7 338(7)	6 329(5)	2 391(2)	C(33b)	10 234(6)	6 621(5)	6 759(3)
C(14)	7 508(5)	7 457(4)	1 121(2)	C(34)	12 554(5)	7 134(4)	6 014(2)
C(15)	7 120(5)	8 386(4)	1 277(2)	C(35)	13 029(5)	7 994(4)	6 307(2)
C(16)	6 964(5)	9 133(4)	947(2)	C(36)	13 511(5)	8 827(4)	6 097(2)
C(17)	6 573(5)	10 136(4)	1 088(2)	C(37)	14 249(5)	9 671(4)	6 385(2)
C(17a)	5 770(6)	10 473(4)	1 545(2)	C(37a)	14 971(5)	9 728(4)	6 929(2)
C(17b)	4 415(6)	10 051(5)	1 456(3)	C(37b)	16 161(6)	9 165(5)	6 898(2)
C(18)	6 955(5)	10 670(4)	692(2)	C(38)	14 289(5)	10 369(4)	6 036(2)
C(18a)	6 643(5)	11 721(4)	626(2)	C(38a)	14 972(5)	11 372(4)	6 165(2)
C(18b)	5 463(6)	11 745(4)	242(3)	C(38b)	14 261(6)	12 095(4)	6 538(2)
C(19)	7 513(5)	9 991(4)	294(2)	C(39)	13 592(5)	9 955(3)	5 541(2)
C(20)	8 141(5)	10 216(3)	−158(2)	C(40)	13 151(5)	10 433(3)	5 112(2)
N(1)	7 453(5)	7 121(3)	−1 946(2)	N(5)	11 415(5)	8 067(4)	3 115(2)
O(1)	6 727(4)	7 581(3)	−2 210(2)	O(9)	12 180(5)	8 489(3)	2 853(2)
O(2)	8 152(4)	6 502(3)	−2 137(2)	O(10)	10 395(4)	7 695(3)	2 946(2)
N(2)	7 223(5)	4 413(3)	200(2)	N(6)	12 833(5)	4 484(3)	4 752(2)
O(3)	7 986(4)	3 887(3)	−6(2)	O(11)	11 861(5)	4 004(3)	4 585(2)
O(4)	6 382(4)	4 157(3)	487(2)	O(12)	13 856(5)	4 142(3)	4 855(2)
N(3)	6 917(5)	8 630(3)	1 858(2)	N(7)	13 085(5)	8 032(3)	6 904(2)
O(5)	5 984(4)	8 251(3)	2 034(2)	O(13)	13 893(4)	7 574(3)	7 127(2)
O(6)	7 693(4)	9 205(3)	2 123(2)	O(14)	12 323(4)	8 532(3)	7 140(2)
N(4)	8 502(4)	11 259(3)	−189(2)	N(8)	13 450(4)	11 502(3)	5 136(2)
O(7)	9 375(4)	11 625(3)	113(2)	O(15)	12 828(4)	12 051(3)	5 428(2)
O(8)	7 907(4)	11 687(3)	−522(2)	O(16)	14 310(4)	11 772(3)	4 861(2)

the present paper, large differences occur in the structural parameters of the nitro groups. The C_m–N–O bond angles in the present structure are 117.4(4)° and the O–N–O angles are 125.2(4)°. In contrast, for the monoclinic structure determination physically unreasonable large bond angles and short bond lengths were reported, indicating some problem in the structure determination.[19b] The values determined in the present orthorhombic form for H_2oetnp are almost identical with those found in the other two nitro structures described here and agree well with those found in 5-nitrooctaethylporphyrin structures[24] and with those described for a peripheral nitro group in 8^1(*E*)-8^2-nitroprotoporphyrin dimethyl ester.[25]

A number of mononitro octaethylporphyrin derivatives (*e.g.* the 5-nitro derivative) and different zinc(II) complexes have recently been structurally characterized and showed no strong distortion of the macrocycle.[24] This indicates that for H_2oetnp only the 'overloading' of the peripheral positions leads to the observed macrocycle distortion. The structure of a zinc(II) 5,15-dinitrooctaethylporphyrin derivative also showed no significant macrocycle distortion.[19b]

Structure of [Ni(oetnp)]. The nickel(II) complex of H_2oetnp, [Ni(oetnp)], crystallized in a triclinic cell with two crystallographically independent molecules per asymmetric unit. Table 3 lists the atomic coordinates while structural data are compiled in Table 5. The molecular structure and numbering scheme of one of the molecules is shown in Fig. 4. The overall molecular structure and deformation is rather similar to that described for the free base H_2oetnp and other dodecasubstituted porphyrins. However, the degree of distortion is larger in the case of the nickel(II) structure than is observed in the free base. In addition the macrocycle shows a ruffled distortion due to the presence of the small nickel(II) ion which

Table 4 Atomic coordinates (× 10^4) for [Tl(oetnp)Cl]

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Molecule 1				Molecule 2			
Tl(1)	143(1)	2084(1)	3414(1)	Tl(2)	4730(1)	−2959(1)	1484(1)
Cl(1)	−189(2)	1973(2)	2096(1)	Cl(2)	4919(2)	−2786(2)	2797(1)
N(21)	1130(6)	953(6)	3817(5)	N(25)	3470(6)	−2098(6)	1075(5)
N(22)	−975(6)	1238(6)	3799(5)	N(26)	5584(7)	−1754(6)	1215(5)
N(23)	−680(6)	3349(6)	3751(4)	N(27)	5900(6)	−3878(6)	1162(5)
N(24)	1439(6)	3029(6)	3749(4)	N(28)	3734(6)	−4178(6)	1019(5)
C(1)	2110(7)	921(7)	3744(6)	C(21)	2496(8)	−2370(8)	933(6)
C(2)	2431(7)	−52(7)	3670(5)	C(22)	1880(7)	−1548(7)	877(5)
C(2a)	3368(7)	−453(7)	3502(6)	C(22a)	784(8)	−1527(8)	695(7)
C(2b)	4028(8)	−809(9)	4159(7)	C(22b)	446(9)	−1480(8)	−126(7)
C(3)	1618(7)	−647(7)	3694(6)	C(23)	2479(7)	−770(8)	1013(6)
C(3a)	1600(7)	−1673(8)	3517(5)	C(23a)	2088(7)	237(9)	1038(6)
C(3b)	1263(9)	−1960(8)	2713(6)	C(23b)	1900(10)	611(10)	1782(7)
C(4)	844(7)	−8(8)	3805(6)	C(24)	3484(7)	−1107(7)	1122(5)
C(5)	−92(7)	−230(7)	3911(5)	C(25)	4347(7)	−595(7)	1219(5)
C(6)	−933(7)	284(8)	3934(6)	C(26)	5309(6)	−838(7)	1259(5)
C(7)	−1884(7)	−34(7)	4062(5)	C(27)	6185(7)	−200(8)	1288(6)
C(7a)	−2200(7)	−950(7)	4308(6)	C(27a)	6264(8)	864(7)	1322(6)
C(7b)	−2762(8)	−1667(9)	3678(7)	C(27b)	6279(9)	1214(9)	571(6)
C(8)	−2464(7)	731(8)	3979(6)	C(28)	6940(7)	−800(7)	1264(5)
C(8a)	−3586(7)	625(8)	3915(6)	C(28a)	7975(7)	−418(7)	1331(6)
C(8b)	−4049(8)	420(8)	3136(6)	C(28b)	8490(7)	−276(7)	2123(6)
C(9)	−1896(8)	1545(8)	3857(6)	C(29)	6589(7)	−1789(7)	1215(6)
C(10)	−2169(7)	2507(8)	3815(6)	C(30)	7102(7)	−2619(8)	1168(6)
C(11)	−1651(7)	3345(8)	3755(6)	C(31)	6836(7)	−3595(8)	1133(6)
C(12)	−1990(8)	4326(8)	3765(6)	C(32)	7442(8)	−4409(8)	1083(6)
C(12a)	−2999(8)	4726(8)	3743(6)	C(32a)	8529(7)	−4421(7)	1172(5)
C(12b)	−3569(9)	4795(10)	2991(6)	C(32b)	8964(7)	−4353(7)	1967(6)
C(13)	−1195(7)	4891(8)	3749(6)	C(33)	6851(7)	−5206(7)	995(6)
C(13a)	−1263(7)	5971(7)	3783(6)	C(33a)	7171(8)	−6193(8)	888(6)
C(13b)	−1233(8)	6444(8)	4537(7)	C(33b)	7638(9)	−6680(8)	1561(7)
C(14)	−351(7)	4288(7)	3751(5)	C(34)	5861(7)	−4832(7)	1074(5)
C(15)	589(8)	4537(8)	3784(6)	C(35)	5009(7)	−5390(7)	1032(5)
C(16)	1460(6)	4022(7)	3803(5)	C(36)	4034(8)	−5152(8)	1035(6)
C(17)	2471(7)	4368(8)	3970(6)	C(37)	3185(7)	−5746(7)	1030(6)
C(17a)	2865(8)	5388(8)	4038(7)	C(37a)	3189(8)	−6755(7)	1219(6)
C(17b)	3125(9)	5691(9)	3349(8)	C(37b)	3453(9)	−6810(8)	2016(6)
C(18)	3053(8)	3589(8)	3990(6)	C(38)	2405(7)	−5185(7)	945(5)
C(18a)	4148(7)	3628(8)	4230(6)	C(38a)	1365(8)	−5575(8)	858(6)
C(18b)	4445(8)	3574(10)	5059(7)	C(38b)	1045(9)	−5748(9)	1561(8)
C(19)	2396(7)	2735(7)	3860(5)	C(39)	2744(7)	−4202(7)	951(5)
C(20)	2628(8)	1765(8)	3818(6)	C(40)	2242(7)	−3374(7)	916(5)
N(1)	−208(6)	−1281(6)	4021(5)	N(5)	4193(6)	472(7)	1245(5)
O(1)	126(5)	−1502(5)	4616(4)	O(9)	4127(5)	878(5)	1817(4)
O(2)	−621(5)	−1788(5)	3504(4)	O(10)	4137(5)	812(5)	658(4)
N(2)	−3167(7)	2671(6)	3915(6)	N(6)	8086(7)	−2418(6)	1053(5)
O(3)	−3792(6)	2671(6)	3368(5)	O(11)	8230(5)	−2422(5)	410(4)
O(4)	−3322(6)	2825(5)	4549(5)	O(12)	8737(5)	−2312(5)	1595(5)
N(3)	806(6)	5550(6)	3848(5)	N(7)	5130(6)	−6427(6)	933(5)
O(5)	855(5)	6001(6)	4451(5)	O(13)	5409(5)	−6842(5)	1460(4)
O(6)	901(5)	5940(5)	3306(4)	O(14)	4905(5)	−6798(5)	304(4)
N(4)	3698(6)	1635(6)	3849(5)	N(8)	1148(6)	−3525(6)	762(5)
O(7)	4033(6)	1676(5)	3289(4)	O(15)	763(5)	−3619(6)	125(4)
O(8)	4174(5)	1421(6)	4438(4)	O(16)	760(5)	−3572(5)	1283(4)

causes contraction of the core.[7,26] The mean Ni–N bond length of 1.920(4) Å is only marginally shorter than the value observed in the S_4-ruffled form of [Ni(oep)].[27] The different degree and type of distortion can clearly be seen in the displacements of the macrocycle atoms from the least-squares plane of the 24 core atoms (Table 5). The displacements for the C_a-atoms are much larger (0.45 and 0.41 Å) (for the two independent molecules, respectively) than observed in the free base. The displacement of the C_b-atoms (1.05 and 0.93 Å) is about 20% larger than in the free base. The different distortion mode in the nickel complexes is evident from the displacement of the C_m-atoms. While in the free base almost no deviations from planarity are observed the two nickel molecules show average deviations of 0.22 and 0.3 Å from the 4N-plane. Thus, in addition to a saddle distortion a ruffling effect induced by the nickel(II) is observed. The different types of distortion become evident by comparing a linear display of the skeletal deviations as shown in Fig. 3.

The latter values also indicate one of the main structural differences between the two crystallographically independent molecules. Molecule 1 has a slightly higher degree of displacements for the C_b-positions while the displacement of the *meso*-carbons is higher in molecule 2. A second difference between both molecules is the orientation of the ethyl groups with respect to the mean plane (see below).

The ruffling effect of the nickel(II) is also evident from the tilt angles of the individual pyrrole rings with the mean plane of the macrocycle. The average tilt angle in molecule 1 is 24.9°, while in molecule 2 a slightly smaller value of 22.6° is observed. These values are larger than the ones observed for H_2oetnp, reflecting

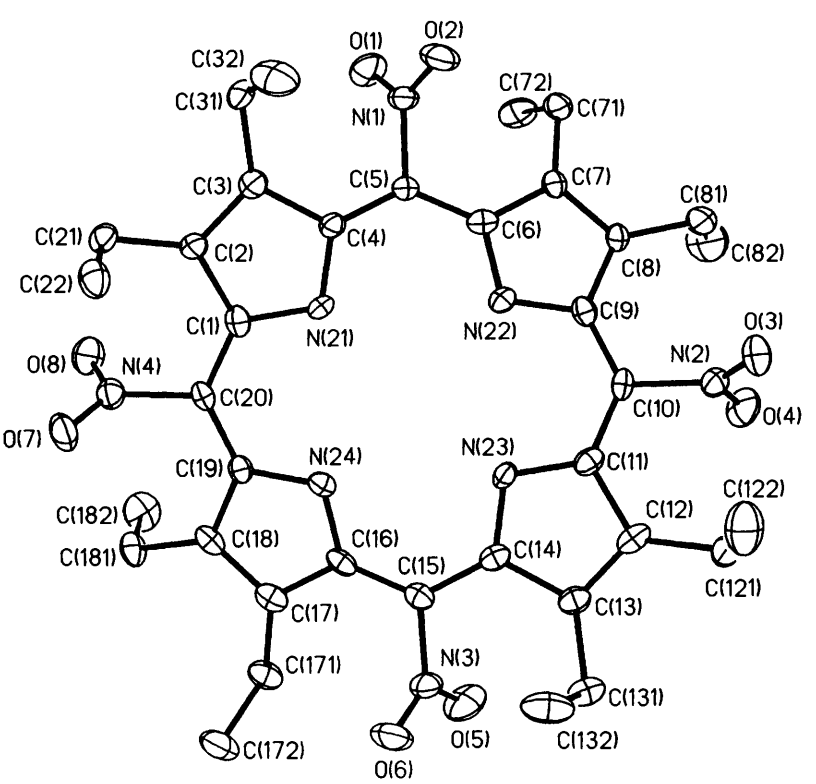

Fig. 1 The molecular structure and labelling scheme for 2,3,7,8,12,13,17,18-octaethyl-5,10,15,20-tetranitroporphyrin (H_2oetnp). Ellipsoids are drawn for 50% occupancy

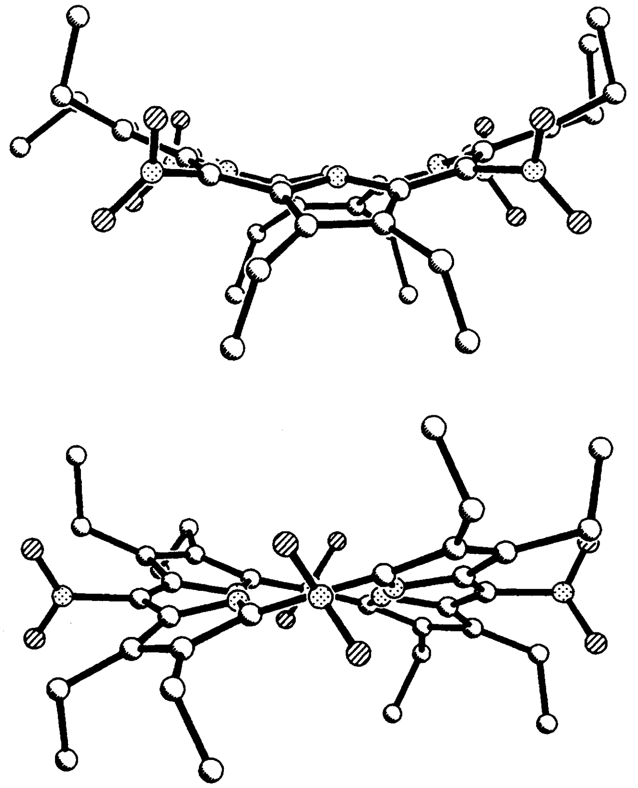

Fig. 2 Two different side views of the structure of H_2oetnp. Both views are related by a 45° rotation orthogonal to the plane of the paper

the influence of the nickel ion. A similar situation was found in a comparison of the free-base and nickel(II) complex of octabromotetramesitylporphyrin.[16b] Major differences occur also in the degree of displacement for neighbouring C_b-atoms, which are much larger in molecule 2. As was the case for the free base, the plane of the nitro groups are not orthogonal to the plane of the macrocycle. The angles are 50.6° for molecule 1 of [Ni(oetnp)] and 59.3° for molecule 2. Note that the orientation of the phenyl groups in all dodecasubstituted porphyrins with *meso*-phenyl groups deviated also strongly from the orthogonal orientation.[10,11,16b]

The bond lengths and bond angles of the three non-planar oetnp macrocycles {in H_2oetnp and the two molecules of [Ni(oetnp)]} agree well with values found in other non-planar dodecasubstituted porphyrins. The effect of the distorted macrocycle leads generally to an increase in the C_m–C_a–C_b angle and a decrease in the N–C_a–C_m and M–N–C_a angles. The free base H_2oetnp has C_m–C_a–C_b angles of 129.2(4)° similar to those of 128.8(5) and 128.3(5)° found in [Ni(oetnp)]. These are even slightly larger than the value of *ca.* 127° found in [Zn(omtpp)] and [Zn(oetpp)][10] and are significantly larger than the average of 124° found for planar porphyrins.[8] The N–C_a–C_m bond angles are 121.1(4)° for H_2oetnp and 120.0(5)° in [Ni(oetnp)], compared to about 122.5° in [Zn(omtpp)] and [Zn(oetpp)][10] and 126° in an average planar porphyrin.

Structure of [Tl(oetnp)Cl]. The thallium(III) complex [Tl(oetnp)Cl] crystallized with two crystallographically independent molecules in the space group $P\bar{1}$. Table 4 lists the atomic coordinates while structural data are compiled in Table 5. The molecular structure and numbering scheme for one molecule is shown in Fig. 5. Surprisingly the structure shows a much lesser degree of conformational distortion than observed in [Ni(oetnp)], H_2oetnp or other dodecasubstituted porphyrins with steric strain. While in the strongly distorted structures displacements of the C_b-atoms of about 0.9 Å are observed, the two thallium derivatives show displacements of 0.3 and 0.17 Å, respectively. The molecules still show significant deviations from planarity (Fig. 6) but the degree of distortion is more comparable to that observed in thallium(III) derivatives of tpp or oep, which show deviations of the C_b-atoms in the order of 0.1–0.2 Å.[28,29] These are much smaller than those observed in other dodecasubstituted porphyrins and were attributed to the

Table 5 A comparison of selected structural data for H_2oetnp, [Ni(oetnp)] and [Tl(oetnp)Cl]

		[Ni(oetnp)]		[Tl(oetnp)Cl]	
	H_2oetnp	Molecule 1	2	Molecule 1	2
Displacements[a]/Å					
M	—	0.01 (0.02)	0.02 (0.03)	0.67 (0.76)	0.68 (0.74)
N	0.08 (0.08)	0.18 (0.19)	0.18 (0.18)	0.01 (0.09)	0.00 (0.06)
C_a	0.28 (0.32)	0.45 (0.44)	0.41 (0.41)	0.11 (0.09)	0.08 (0.06)
C_b	0.83 (0.84)	1.05 (1.05)	0.93 (0.93)	0.30 (0.26)	0.17 (0.13)
C_m	0.05 (0.04)	0.22 (0.22)	0.30 (0.30)	0.10 (0.06)	0.10 (0.08)
Bond lengths[b]/Å					
M–N	—	1.917(4)	1.922(4)	2.216(8)	2.217(9)
N–C_a	1.363(6)	1.382(6)	1.379(6)	1.389(13)	1.382(14)
C_a–C_b	1.459(6)	1.455(7)	1.450(7)	1.459(15)	1.468(15)
C_a–C_m	1.397(6)	1.380(7)	1.384(7)	1.393(15)	1.398(15)
C_b–C_b	1.368(6)	1.364(8)	1.358(8)	1.378(15)	1.358(14)
C_b–CH_2	1.505(6)	1.507(8)	1.512(8)	1.511(15)	1.506(15)
CH_2–CH_3	1.529(7)	1.532(9)	1.519(9)	1.521(16)	1.517(17)
C_m–NO_2	1.482(6)	1.476(7)	1.480(7)	1.482(14)	1.490(13)
N–O	1.222(6)	1.222(7)	1.225(7)	1.227(12)	1.221(15)
Bond angles[b]/°					
N–M–N (opp)	—	169.0(2)	169.2(0)	144.7(3)	144.5(3)
N–M–N (adj)	—	90.5(2)	90.5(2)	84.7(3)	84.7(3)
M–N–C_a	—	126.5(3)	127.1(3)	124.9(7)	125.0(7)
N–C_a–C_m	121.1(4)	120.0(5)	120.0(5)	121.2(9)	121.6(9)
N–C_a–C_b	109.6(4)	110.7(4)	110.1(4)	109.3(9)	109.2(9)
C_a–N–C_a	107.5(4)	104.9(4)	104.4(4)	107.1(8)	107.2(8)
C_a–C_m–C_a	130.4(4)	126.0(5)	126.9(5)	134.3(10)	133.8(10)
C_a–C_b–C_b	106.5(4)	106.5(5)	106.4(5)	107.1(9)	107.1(9)
C_m–C_a–C_b	129.2(4)	128.8(5)	128.3(5)	129.3(10)	129.1(10)
C_a–C_b–CH_2	128.1(4)	127.4(5)	128.4(5)	129.9(9)	128.8(9)
C_b–C_b–CH_2	124.8(4)	125.6(5)	125.0(5)	122.6(10)	123.9(10)
C_b–CH_2–CH_3	112.3(4)	112.0(5)	112.2(5)	113.3(9)	112.7(9)
C_a–C_m–NO_2	114.8(4)	117.0(5)	116.5(5)	113.2(9)	113.0(9)
C_m–N–O	117.4(4)	117.3(5)	117.3(5)	117.6(9)	116.9(8)
O–N–O	125.2(4)	125.4(5)	125.5(5)	124.8(9)	126.1(9)

[a] From least-squares plane of the 4N-plane; values in parentheses refer to the plane of the 24 macrocycle atoms. [b] Average values for the geometrically equivalent positions.

influence of the large thallium atom.[28] The thallium co-ordination is very similar to that observed in other chlorothallium(III) porphyrins.[28] The Ti–N bond lengths of around 2.216(8) Å agree well with those found in [Tl(tpp)Cl] [2.21(1) Å] and [Tl(oep)Cl] [2.212(6) Å].[28] The bond length to the axial chloride 2.422(2) Å agrees also well with data in the literature, as does the displacement of the thallium atoms by 0.69 Å from the 4N-plane.[28]

The differences in macrocycle distortion are best seen by inspection of the linear display of the skeletal deviations (Fig. 6). While the 24 core atoms in molecule 1 show an average deviation from planarity of 0.14 Å, molecule 2 exhibits an average deviation of 0.09 Å. This is also reflected in the different deviation from the 4N-plane of the C_b-atoms, which is 0.3 Å in molecule 1 and 0.17 Å in molecule 2. The much smaller degree of macrocycle distortion is also reflected in the average angles of the individual pyrrole rings with the 4N-plane, which are 8° (molecule 1) and 5.7° (molecule 2). These angles are much smaller than those found in [Ni(oetnp)] and H_2oetnp. Major differences are also found in the twist angles between the nitro groups and the 4N-plane. While in [Ni(oetnp)] strong deviations from an orthogonal orientation was observed (average angle = 55.0°), in [Tl(oetnp)Cl] the average angles are 87.4° in molecule 1 and 91.95° in molecule 2. In general the structural parameters observed in [Tl(oetnp)Cl] resemble more those observed in sterically not overloaded tpp or oep derivatives,[28] than those observed in the very non-planar structures of [Ni(oetnp)], H_2oetnp or other dodecasubstituted porphyrins. Thus the much smaller degree of distortion in [Tl(oetnp)Cl] represents a remarkable exception from the conformational distortion observed in other highly substituted porphyrins. One important difference can be observed in the C_a–C_m–C_a angles. In [Tl(oep)Cl] an angle of 129.6° is observed while [Tl(oetnp)Cl] exhibits angles of 134.3 and 133.8°, respectively, for the two molecules. These values are considerably larger than those observed in the nickel(II) complex or the free base and indicate that part of the steric strain in the molecule is released by opening of the C_a–C_m–C_a angles, *i.e.* by in-plane distortion of the macrocycle. Significant out-of-plane distortion of the macrocycles as observed in the other dodecasubstituted porphyrins is prevented here by the large main-group metal. This is a unique case of a dodecasubstituted porphyrin where relief of the steric strain by out-of-plane distortion is counteracted by the thallium atom leading to in-plane distortion and only moderate out-of-plane distortion of the macrocycle.

One of the reasons for this effect of the thallium atom seems to be the inability to contract sufficiently the core of the macrocycle in thallium porphyrins. A study of the metal dependence of the non-planarity in octaalkyltetraphenylporphyrins found that the core size for the non-planar metallooctaethyltetraphenylporphyrins is smaller than that for the corresponding planar metallooctaethylporphyrins.[15] Thallium porphyrins have generally large core sizes (≈2.1 Å) and the present structures of [Tl(oetnp)Cl] exhibit core sizes of 2.11 Å. Thus no core contraction, compared to *e.g.* [Tl(oep)Cl] (2.10 Å), was found. In the metallooctaethyltetraphenylporphyrin series an inverse relationship between the degree of non-planarity and metal size was found. However, the changes in macrocycle conformation were small, contrary to the situation found here for the nickel(II) and thallium(III) complexes of H_2oetnp. Thus considerable differences in the conformational flexibility of different dodecasubstituted porphyrins occur.

Another special feature of the thallium structures is the orientation of the pyrrole rings with regard to the thallium centre. Thallium porphyrins have often been described as having a 'doming' of the macrocycle towards the thallium. This is evidenced by the difference of the thallium displacement from the plane of the 24 core atoms and the 4N-plane. These differences are 0.09 Å in the molecule with Tl(1) and 0.06 Å for molecule 2. However the distortion is not of C_{4v} type as required for a domed structure. In both molecules three pyrrole rings point away from the thallium centre, while one ring is oriented towards the thallium (Fig. 6). Such a conformation has been observed in other thallium porphyrins,[28a] however the pyrrole ring deviating from C_{4v} symmetry was found to be in plane with the 24 core atom plane or slightly above. Here the C_b-positions in the unique pyrrole rings are displaced by 0.3 Å (molecule 1) or 0.13 Å (molecule 2) towards the thallium, a rather unique feature.

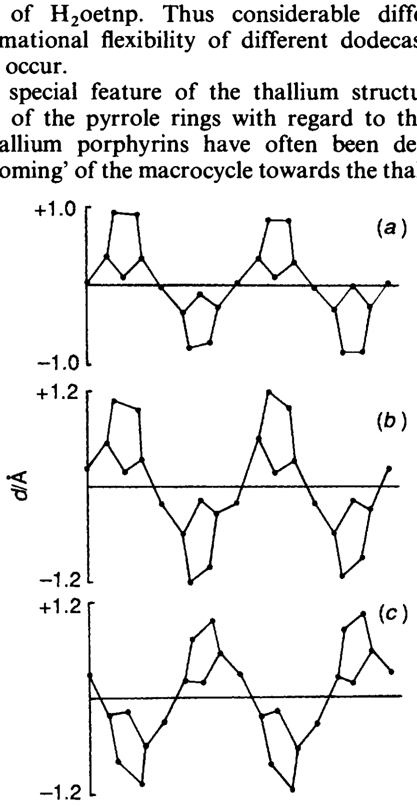

Fig. 3 Linear display of the skeletal deviations (*d*/Å) from the 4N-plane for H_2oetnp (*a*) and the two molecules of [Ni(oetnp)] (*b*), (*c*). The *x*-axis is not to scale and shows in sequence the atoms C(20), C(1), C(2), N(21), C(3), C(4) ··· N(24), C(18), C(19), C(20)

The only other case known of a planar, dodecasubstituted porphyrin is the structure of the copper(II) complex of 2,3:7,8:12,13:17,18-tetrapropano-5,10,15,20-tetra(3,4,5-trimethoxyphenyl)porphyrin.[30] However, steric strain in that case is eased by small internal C_b–C_b–CH_2 angles (112°) which move the methylene groups away from the *meso*-aryl groups, minimizing the effect of steric crowding at the porphyrin periphery. In the structure of [Tl(oetnp)Cl] these angles are in the range of 122–124°, which are typical values for other strongly non-planar dodecasubstituted porphyrins.

Ethyl Group Orientation.—With regard to future comparisons of calculated and experimental structures it might be useful to list the orientation of the ethyl groups in the five molecules described. In all cases the ethyl orientation around the macrocycle is not symmetric. In H_2oetnp the arrangement of the ethyl groups is DDUUDDUD (U = ethyl orientation up, D = down) with respect to the molecular plane. In [Ni(oetnp)] molecule 1 has an UDUDDUUU orientation while molecule 2 shows a UUUDUUDU arrangement. In [Tl(oetnp)Cl] the molecule with Tl(1) has UDDDDUDU and the molecule with Tl(2) has a DUDUUUUU orientation. The orientation of the ethyl groups is also of interest with regard to the size and form of potential substrate binding pockets in highly distorted

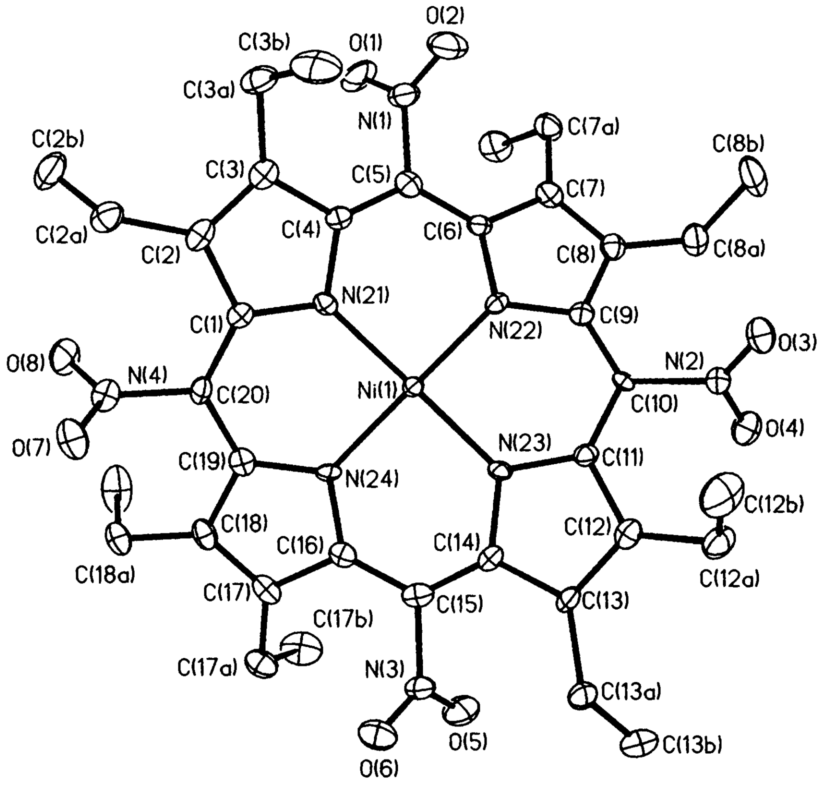

Fig. 4 The molecular structure and labelling scheme for one of the two crystallographically independent molecules of (2,3,7,8,12,13,17,18-octaethyl-5,10,15,20-tetranitroporphyrinato)nickel(II), [Ni(oetnp)]. Ellipsoids are drawn for 50% occupancy

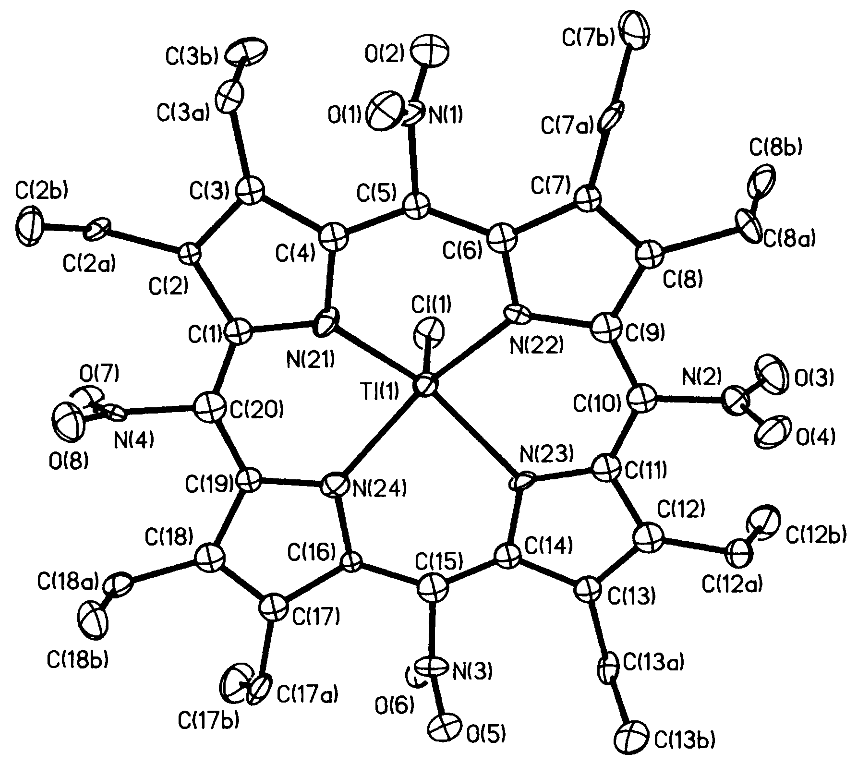

Fig. 5 The molecular structure and labelling scheme for one of the two crystallographically independent molecules of chloro(2,3,7,8,12,13,17,18-octaethyl-5,10,15,20-tetranitroporphyrinato)thallium(III), [Tl(oetnp)Cl]. Ellipsoids are drawn for 50% occupancy

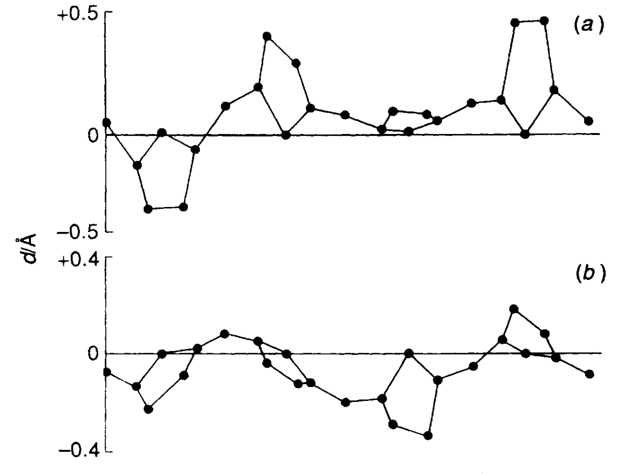

Fig. 6 Linear display of the skeletal deviations (d/Å) from the 4N-plane for the two molecules of [Tl(oetnp)Cl]. The x-axis is not to scale and shows in sequence the atoms C(20), C(1), C(2), N(21), C(3), C(4)... N(24), C(18), C(19), C(20). Note the difference in the y-axis scale compared to Fig. 3

porphyrins. Often small solvent molecules are located in the cavity of the metallooctaalkyltetraphenylporphyrins.[10,15] In these cases a symmetric arrangement of the ethyl groups of the type UUDDUUDD is observed. With the asymmetric orientation of the ethyl groups in the solid-state structures described here, different cavity types are realized.

Packing Analysis.—An important factor in the structural analysis of tetrapyrrole conformations is the question of intermolecular interactions. Several cases are known where π-stacking and short intermolecular contacts are responsible for the conformational distortion observed in porphyrins.[8] Packing plots for H_2oetnp and [Ni(oetnp)] are given in the supplementary material. The free-base porphyrin forms two different layers of molecules, which are almost orthogonal to each other. The angle between the nitrogen plane of neighbouring molecules is 87.5°. This arrangement brings one nitro group in near proximity of the nitrogen core region of the neighbouring macrocycle. The closest contacts are 3.34 Å between O(5) and C(132) and 3.36 Å between O(5) and N(23). The latter might involve some weak H···O interaction. However, there are no indications of π-stacking. The centre-to-centre (defined as the geometrical middle of the 4N-plane) separation between molecules in layers of identical arrangement is 11.1 Å.

In [Ni(oetnp)] the molecules pack by the formation of parallel layers. The centre-to-centre distance within one layer is 10.6 Å, showing again the absence of π-interactions between neighbouring molecules. However, as for the free base, a nitro group of one molecule always lies above part of the macrocycle of a neighbouring ring. The closest contacts observed are 3.35 Å for Ni(1)···O(7) and 3.17 Å for Ni(2)···O(16). Nevertheless, the strong conformational distortion in both molecules, which is similar to that observed in related molecules, which show no short intermolecular interaction < 4 Å, and the absence of any π-stacking of the rings indicates that the non-planar conformations observed are not primarily due to intermolecular interactions.

The molecular packing of [Tl(oetnp)Cl] is rather similar to that described for [Ni(oetnp)]. The more planar macrocycle conformation is however reflected in more closely spaced layers. The axial chlorides in neighbouring layers point in opposite directions. The planes of the two independent molecules are related to each other by 5.2° and the Tl···Tl separation is 10.441 Å. Again, a number of close contacts are observed: Tl(2)···O(14) 3.464, O(7)···O(9) 2.916 and C(13)···C(15) 3.519 Å. Evidence for π-stacking was not found.

Solution Structure.—The question of the solution structure of these compounds has been addressed in some detail by Shelnutt *et al.*[14] On the basis of resonance-Raman data a very non-planar conformation was predicted for [Ni(oetnp)] in solution, while the 5-nitrooctaethyl nickel(II) derivative showed spectroscopic characteristics similar to planar [Ni(oep)].[31] Similar indications can be found on the basis of the relevant UV/VIS spectroscopic data. While the nickel(II) complex and the free base show considerably bathochromic shifted absorption bands compared to oep, these shifts are much smaller for [Tl(oetnp)Cl] and are only slightly different from those of [Tl(tpp)Cl].[32] This indicates a lesser degree of distortion in solution for [Tl(oetnp)Cl] compared to the nickel(II) complex or the free base. A detailed analysis of the effect of successive introduction of nitro groups on the degree of distortion in solution has been given by Gong and Dolphin.[20b] The non-planar conformations of [Ni(oetnp)] have also been predicted on the basis of molecular-mechanics calculations.[14]

On the basis of these and other reports it becomes evident that, for example, the 5,10,15,20-tetrachlorooctaethylporphyrins must have non-planar conformations. They exhibit absorption maxima red-shifted by 94 nm when compared with H_2oep,[17] while the related 5,10,15,20-tetrafluorooctaethylporphyrins show only a bathochromic shift of 24 nm.[33] Thus the chloride substituents are large enough to induce some conformational distortion while the shifts observed in the fluoro derivative are likely owing only to an electronic effect. The tetra-*meso*-halogenated and nitrated porphyrins are easily prepared and allow more detailed studies on the conformational flexibility of tetrapyrroles.

Conclusions

The present study clearly shows the non-planar conformation of H_2oetnp and its nickel(II) complex in the solid state and shows that strongly non-planar conformations can be prevented by large metals like thallium. The structure of the thallium complex presents a unique example of a dodecasubstituted porphyrin, which relieves steric strain from the peripheral substituents by in-plane rather than out-of-plane distortion. A comparison of the results in the present series with those of the octaethyltetraphenylporphyrin series shows that, depending on the ligand system, considerable differences in type and degree of distortion can occur. This indicates the necessity for further studies on metal and axial ligand effects in different dodecasubstituted porphyrins.

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References

1 (*a*) J.-H. Fuhrhop, L. Witte and W. S. Sheldrick, *Liebigs Ann. Chem.*, 1976, 1537; (*b*) J. Fajer, K. M. Barkigia, E. Fujita, D. A. Goff, L. K. Hanson, J. D. Head, T. Horning, K. M. Smith and M. C. Zerner, in *Antennas and Reaction Centers of Photosynthetic Bacteria*, ed. M. E. Michel-Beyerle, Springer, Berlin, 1985, p. 324; J. Fajer, K. M. Barkigia, K. M. Smith and D. A. Goff, *ACS Symp. Ser.*, 1986, **321**, 51; (*c*) K. M. Barkigia, L. Chantranupong, K. M. Smith, and J. Fajer, *J. Am. Chem. Soc.*, 1988, **110**, 7566.

2 R. Huber, *Eur. J. Biochem.*, 1990, **187**, 283; J. Fajer, *Chem. Ind. (London)*, 1991, 869; M. O. Senge, *J. Photochem. Photobiol. B*, 1992, **16**, 3.

3 D. E. Tronrud, M. F. Schmid and B. W. Matthews, *J. Mol. Biol.*, 1986, **188**, 443; J. Deisenhofer and H. Michel, *Angew. Chem., Int. Ed. Engl.*, 1989, **28**, 829; T. O. Yeates, H. Komiya, A. Chirino and R. C. Rees, *Proc. Natl. Acad. Sci. USA*, 1988, **85**, 7993.

4 K. Moffat, R. S. Loe and B. M. Hoffman, *J. Mol. Biol.*, 1976, **104**, 707; R. Takano, *J. Mol. Biol.*, 1977, **110**, 537.

5 W. Hoppe, H. Will, J. Gassmann and H. Weichselgartner, *Z. Kristallogr.*, 1969, **128**, 18; H. C. Chow, R. Serlin and C. E. Strouse, *J. Am. Chem. Soc.*, 1975, **97**, 7230; R. Serlin, H. C. Chow and C. E. Strouse, *J. Am. Chem. Soc.*, 1975, **97**, 7237; C. Kratky and J. D. Dunitz, *Acta Crystallogr., Sect. B*, 1975, **32**, 1586; 1977, **33**, 545; *J. Mol. Biol.*, 1977, **113**, 431; C. Kratky, H. P. Isenring and J. D. Dunitz, *Acta Crystallogr., Sect. B*, 1977, **33**, 547; K. M. Smith, D. A. Goff, J. Fajer and K. M. Barkigia, *J. Am. Chem. Soc.*, 1982, **104**, 3747; 1983, **105**, 1674; K. M. Barkigia, D. S. Gottfried, S. G. Boxer and J. Fajer, *J. Am. Chem. Soc.*, 1989, **111**, 6444; M. O. Senge and K. M. Smith, *Photochem. Photobiol.*, 1991, **54**, 841; *Z. Kristallogr.*, 1992, **199**, 239; M. O. Senge, F. W. Bobe, M. S. Huster and K. M. Smith, *Liebigs Ann. Chem.*, 1991, 871.

6 L. D. Spaulding, L. C. Andrews and G. J. B. Williams, *J. Am. Chem. Soc.*, 1977, **99**, 6918; A. Ulmann, J. Gallucci, D. Fisher and J. A. Ibers, *J. Am. Chem. Soc.*, 1980, **102**, 6852; W. B. T. Cruse, P. J. Harrison and O. Kennard, *J. Am. Chem. Soc.*, 1982, **104**, 2376; K. M. Barkigia, J. Fajer, C. K. Chang and G. J. B. Williams, *J. Am. Chem. Soc.*, 1982, **104**, 315; M. P. Suh, P. N. Swepston and J. A. Ibers, *J. Am. Chem. Soc.*, 1984, **106**, 5164; S. H. Strauss, M. E. Silver, K. M. Long, R. G. Thompson, R. A. Hudgens, K. Spartalian and J. A. Ibers, *J. Am. Chem. Soc.*, 1985, **107**, 4207; A. M. Stolzenberg, P. A. Glazer and B. M. Foxman, *Inorg. Chem.*, 1987, **27**, 1970; K. M. Barkigia, C. K. Chang and J. Fajer, *J. Am. Chem. Soc.*, 1991, **113**, 7445; K. M. Barkigia, C. K. Chang, J. Fajer and M. W. Renner, *J. Am. Chem. Soc.*, 1992, **114**, 1701; M. O. Senge, K. Ruhlandt-Senge and K. M. Smith, *Acta Crystallogr., Sect. C*, 1992, **48**, 1810; M. O. Senge, H. Hope and K. M. Smith, *J. Chem. Soc., Perkin Trans. 2*, 1993, 11; K. M. Barkigia, M. A. Thompson, J. Fajer, R. K. Pandey, K. M. Smith and M. G. H. Vicente, *New J. Chem.*, 1992, **16**, 599.

7 A. Eschenmoser, *Ann. N.Y. Acad. Sci.*, 1986, **471**, 108; C. Kratky, R. Waditschatka, C. Angst, P. E. Johansen, J. C. Plaquevent, J. Schreiber and A. Eschenmoser, *Helv. Chim. Acta*, 1985, **68**, 1312 and refs. therein.

8 W. R. Scheidt and Y. J. Lee, *Struct. Bonding (Berlin)*, 1987, **64**, 1 and refs. therein.

9 K. Maruyama, T. Nagata and A. Osuka, *J. Phys. Org. Chem.*, 1988, **1**, 63; H. K. Hombrecher and G. Horter, *Liebigs Ann. Chem.*, 1991, 219; M. O. Senge, M. G. H. Vicente, S. R. Parkin, H. Hope and K. M. Smith, *Z. Naturforsch, Teil B*, 1992, **47**, 1189.

10 K. M. Barkigia, M. D. Berber, J. Fajer, C. J. Medforth, M. W. Renner and K. M. Smith, *J. Am. Chem. Soc.*, 1990, **112**, 8851.

11 C. J. Medforth, M. O. Senge, K. M. Smith, L. D. Sparks and J. A. Shelnutt, *J. Am. Chem. Soc.*, 1992, **114**, 9859.

12 S. Tsuchiya, *Chem. Phys. Lett.*, 1990, **169**, 608; *J. Chem. Soc., Chem. Commun.*, 1991, 716; 1992, 1475; J. Takeda, T. Ohya and M. Sato, *Chem. Phys. Lett.*, 1991, **183**, 384; *Inorg. Chem.*, 1992, **31**, 2877.

13 C. J. Medforth, M. D. Berber, K. M. Smith and J. A. Shelnutt, *Tetrahedron Lett.*, 1990, **31**, 3719; J. A. Shelnutt, C. J. Medforth, M. D. Berber, K. M. Barkigia and K. M. Smith, *J. Am. Chem. Soc.*, 1991, **113**, 4077.

14 J. A. Shelnutt, S. A. Majumder, L. D. Sparks, J. D. Hobbs, C. J. Medforth, M. O. Senge, K. M. Smith, M. Miura, L. Luo and J. M. E. Quirke, *J. Raman Spectrosc.*, 1992, **23**, 523.

15 L. D. Sparks, C. J. Medforth, M.-S. Park, J. R. Chamberlain, M. R. Ondrias, M. O. Senge, K. M. Smith and J. A. Shelnutt, *J. Am. Chem. Soc.*, 1993, **115**, 581.

16 (*a*) P. Bhyrappa and V. Krishnan, *Inorg. Chem.*, 1991, **30**, 239; (*b*) D. Mandon, P. Ochsenbein, J. Fischer, R. Weiss, K. Jayarai, R. N. Austin, A. Gold, P. S. White, O. Brigaud, P. Mattioni and D. Mansuy, *Inorg. Chem.*, 1992, **31**, 2044.

17 B. Evans and K. M. Smith, *Tetrahedron Lett.*, 1977, **18**, 3079; Y. Naruta, F. Tani and K. Maruyama, *Tetrahedron Lett.*, 1992, **33**, 1069.

18 R. Bonnett, I. A. D. Gale and G. F. Stephenson, *J. Chem. Soc. C*, 1966, 1600.

19 (*a*) G.-Z. Wu, W.-X. Gan and H.-K. Leung, *J. Chem. Soc., Faraday Trans.*, 1991, **87**, 2933; (*b*) N.-J. Zhu, Y. Li, G.-Z. Wu and X.-G. Liang, *Acta Chim. Sin.*, 1992, **50**, 249.

20 (*a*) E. Watanabe, S. Nishimura and H. Ogoshi, *Tetrahedron*, 1975, **31**, 1385; (*b*) L.-C. Gong and D. Dolphin, *Can. J. Chem.*, 1985, **63**, 401.

21 H. Hope, *ACS Symp. Ser.*, 1987, **357**, 357.

22 H. Hope and B. Moezzi, Program XABS, University of California, Davis, CA, 1987.

23 G. M. Sheldrick, SHELXTL PLUS, Program for crystal structure solution. Universität Göttingen, Germany, 1990.

24 M. O. Senge, C. W. Eigenbrot, T. D. Brennan, J. Shusta, W. R. Scheidt and K. M. Smith, *Inorg. Chem.*, 1993, **32**, 3134.

25 R. Bonnett, M. B. Hursthouse, P. A. Scourides and J. Trotter, *J. Chem. Soc., Perkin Trans. 1*, 1980, 490.

26 J. L. Hoard, in *Porphyrins and Metalloporphyrins*, ed. K. M. Smith, Elsevier, Amsterdam, 1975, p. 325.

27 E. F. Meyer, jun., *Acta Crystallogr., Sect. B*, 1972, **28**, 2162; D. L. Cullen and E. F. Meyer, jun., *J. Am. Chem. Soc.*, 1974, **96**, 2095.

28 (*a*) D. L. Cullen, E. F. Meyer, jun. and K. M. Smith, *Inorg. Chem.*, 1977, **16**, 1179; (*b*) K. Henrick, R. W. Matthews and P. A. Tasker, *Inorg. Chem.*, 1977, **16**, 3293.

29 F. Brady, K. Henrick and R. W. Matthews, *J. Organomet. Chem.*, 1981, **210**, 281; A. G. Coutsolelos, M. Orfanopoulos and D. L. Ward, *Polyhedron*, 1981, **10**, 885; A. G. Coutsolelos, A. Tsapara, D. Daphnomili and D. L. Ward, *J. Chem. Soc., Dalton Trans.*, 1991, 3319; M. O. Senge and K. M. Smith, *Z. Naturforsch., Teil B*, 1992, **47**, 837; M. O. Senge, K. Ruhlandt-Senge, K. J. Regli and K. M. Smith, preceding paper.

30 M. O. Senge, C. J. Medforth, L. D. Sparks, J. A. Shelnutt and K. M. Smith, *Inorg. Chem.*, 1993, **32**, 1716.

31 T. D. Brennan, W. R. Scheidt and J. A. Shelnutt, *J. Am. Chem. Soc.*, 1988, **110**, 3919.

32 K. M. Kadish, A. Tabard, A. Zrineh, M. Ferhat and R. Guilard, *Inorg. Chem.*, 1987, **26**, 2459.

33 L. A. Andrews, R. Bonnett, A. N. Kozyrey and E. H. Appelman, *J. Chem. Soc., Perkin Trans. 1*, 1988, 1735.

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