$S = 1.008$
3868 reflections
276 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0355P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
Extinction correction: *SHELXL*93
Extinction coefficient: 0.0028 (2)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

Zn—O4	2.083 (2)	Zn—N2	2.156 (3)
Zn—O2	2.096 (2)	S—O8	1.465 (2)
Zn—O3	2.128 (2)	S—O7	1.466 (2)
Zn—O1	2.130 (2)	S—O5	1.468 (2)
Zn—N1	2.136 (3)	S—O6	1.478 (2)
O4—Zn—O2	89.0 (1)	O1—Zn—N2	100.5 (1)
O4—Zn—O3	93.0 (1)	N1—Zn—N2	77.4 (1)
O2—Zn—O3	87.4 (1)	O8—S—O7	109.3 (1)
O4—Zn—O1	86.1 (1)	O8—S—O5	109.6 (1)
O2—Zn—O1	171.2 (1)	O7—S—O5	109.8 (1)
O3—Zn—O1	85.5 (1)	O8—S—O6	109.5 (2)
O4—Zn—N1	167.1 (1)	O7—S—O6	109.7 (1)
O2—Zn—N1	98.89 (9)	O5—S—O6	108.9 (1)
O3—Zn—N1	97.6 (1)	C1—N1—Zn	127.6 (2)
O1—Zn—N1	87.3 (1)	C12—N1—Zn	113.9 (2)
O4—Zn—N2	92.9 (1)	C10—N2—Zn	128.3 (2)
O2—Zn—N2	87.0 (1)	C11—N2—Zn	113.6 (2)
O3—Zn—N2	171.8 (1)		

The phen H atoms were placed using a riding model. Water H atoms were found from a difference Fourier synthesis, except for those on O10, which could not be modelled.

Data collection: *XSCANS* (Siemens, 1991). Cell refinement: *XSCANS*. Data reduction: *SHELXTL-Plus* (Sheldrick, 1990*a*). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990*b*). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *XP* (Siemens, 1990). Software used to prepare material for publication: *SHELXTL-Plus* (Sheldrick, 1990*a*).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: JA1003). Services for accessing these data are described at the back of the journal.

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Chloro(*meso*-tetrapropylporphyrinato)iron(III)

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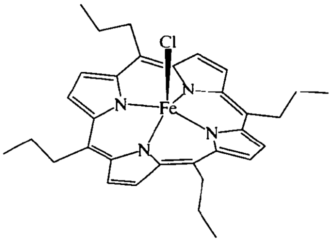
Abstract

In the chloroiron(III) complex of *meso*-tetrapropylporphyrin, $[Fe(C_{32}H_{36}N_4)Cl]$, the Fe^{III} atom has slightly distorted square-pyramidal coordination. The porphyrin ring shows a typical S_4-ruffled structure in addition to a normally observed domed core; the deviations of the *meso*-C and Fe atoms from the least-squares plane of the $C_{20}N_4$ core are 0.366 (4) (maximum) and 0.578 (1) Å, respectively. The average Fe—N_p bond distance is 2.063 (4) Å.

Comment

Non-planar distortions of porphyrin macrocycles are found frequently in haemoproteins and are expected to play important roles in biological functions (Finzel *et al.*, 1984; Hobbs & Shelnutt, 1995). Through extensive studies using non-planar haem model complexes, it is now clear that non-planarity of the porphyrin influences various physicochemical properties (Barkigia *et al.*, 1990; Jentzen *et al.*, 1995; Nakamura *et al.*, 1996; Senge *et al.*, 1995). Recent X-ray crystallographic analyses, as well as molecular-mechanics calculations, have revealed the existence of several deformation modes in porphyrin rings such as waving, doming, saddling and ruffling. In order to understand the effects of the deformation mode on the physicochemical properties, complexes with various types of deformed porphyrin rings have been prepared and examined by various spectroscopic techniques, *e.g.* NMR, EPR and resonance Raman, and X-ray crystallography and theoretical calculations (Munro *et al.*, 1995; Nakamura *et al.*, 1997, 1998; Prendergast & Spiro, 1992; Saitoh *et al.*, 1997; Wolowiec *et al.*, 1998). Authors have approached this problem by using a series of (*meso*-tetraalkylporphyrinato)iron(III) complexes, [Fe(T*R*P)]$^+$, where *R* is H, Me, Et, ^{n}Pr, ^{c}Pr or ^{i}Pr. The magnitude of porphyrin deformation depends on the bulkiness of the *meso*-alkyl substituents.



(I)

The molecular structure of the title compound, (I), is shown in Fig. 1. There is a pseudo-twofold axis parallel to the *b* axis along the Fe—Cl1 bond, which is just local symmetry in the crystal. The structure of the core is essentially an S_4-ruffle incorporating some doming. Peripheral alkyl groups take the $\alpha\beta\alpha\beta$ conformation, which is reasonable to alleviate the strain energy due to the interaction between the *meso*-α [$H_{meso(\alpha)}$] and pyrrole-β protons [$H_{py(\beta)}$] in the S_4-ruffled structure. The average spatial distance between $H_{meso(\alpha)}$ and $H_{py(\beta)}$ is 2.20 Å. The deviations of the *meso*-C atoms C5, C10, C15 and C20 from the least-square plane of the $C_{20}N_4$ porphyrinato core are −0.326 (3), 0.366 (4), −0.324 (4) and 0.305 (4) Å, respectively. The Fe atom is out of the mean plane by 0.578 (1) Å. The ruffling dihedral angles of the two pairs of diagonal pyrroles are 22.3 (1) and 21.2 (1)°, whereas those of [Fe(T^{i}PrP)Cl] are 42.8 and 33.5° (Ikeue *et al.*, 1999). The ruffling dihedral angle is one of the indices used to represent a magnitude of non-planarity in an S_4-ruffled structure, so that the porphyrin deformation of (I) is much smaller than that of the ^{i}Pr complex. Another index is Fe—N_p bond distances. Planar porphyrin complexes generally show longer Fe—N_p distances than those of the deformed porphyrin complexes; the average Fe—N_p distance is 2.070 (3) Å in nearly planar [Fe(TPP)Cl] (TPP is *meso*-tetraphenylporphyrin; Scheidt & Finnegan, 1989), compared with 2.037 (2) Å in highly deformed [Fe(T^{i}PrP)Cl]. The average Fe—N_p distance in (I) [2.063 (4) Å] also indicates much smaller deformation than in [Fe(T^{i}PrP)Cl].

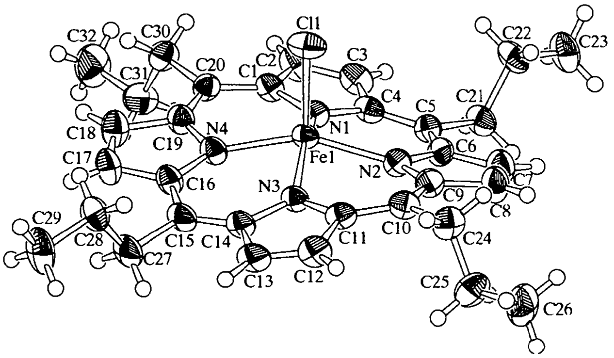


Fig. 1. The molecular structure (*ORTEP*; Johnson, 1965) of the title complex with the atom-numbering scheme. Displacement ellipsoids are shown at the 50% probability level.

In conclusion, the present study has revealed that the type of *meso*-alkyl substituents determines the deformation mode of the porphyrin ring in high-spin [Fe(T*R*P)Cl]; while the ^{n}Pr groups lead to the typical S_4-ruffled structure for the porphyrin core, ^{i}Pr groups form the unique S_4-ruffled structure incorporating some saddled character.

Experimental

meso-Tetrapropylporphyrin was prepared according to the literature method of Neya & Funasaki (1997). Insertion of iron was carried out in refluxing methanol–chloroform (1:3) with $FeCl_2 \cdot 4H_2O$. The crystal used for analysis was obtained by slow evaporation from chloroform solution.

Crystal data

[Fe($C_{32}H_{36}N_4$)Cl]
$M_r = 567.96$
Monoclinic
$P2_1/n$
$a = 13.142\,(10)$ Å
$b = 15.479\,(8)$ Å
$c = 14.712\,(6)$ Å
$\beta = 109.83\,(4)^\circ$
$V = 2815\,(3)$ Å^3
$Z = 4$
$D_x = 1.340$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 23 reflections
$\theta = 14.9$–15.0°
$\mu = 0.659$ mm^{-1}
$T = 298$ K
Prismatic
0.5 × 0.5 × 0.5 mm
Black

Data collection

Rigaku AFC-5 diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{min} = 0.686$, $T_{max} = 0.719$
6637 measured reflections
6407 independent reflections
3977 reflections with $I > 2\sigma(I)$

$R_{int} = 0.020$
$\theta_{max} = 27.5^\circ$
$h = 0 \rightarrow 17$
$k = 0 \rightarrow 20$
$l = -19 \rightarrow 17$
3 standard reflections every 100 reflections frequency: 50 min intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.052$
$wR(F^2) = 0.208$
$S = 1.11$
6407 reflections
355 parameters
H atoms constrained
$w = 1/[\sigma^2(F_o^2) + (0.1255P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.51$ e Å^{-3}
$\Delta\rho_{\min} = -0.86$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

Fe1—N2	2.059 (3)	Fe1—N4	2.066 (3)
Fe1—N1	2.061 (3)	Fe1—Cl1	2.233 (2)
Fe1—N3	2.063 (3)		
N2—Fe1—N1	87.1 (1)	N4—Fe1—Cl1	104.1 (1)
N2—Fe1—N3	86.6 (1)	C4—N1—Fe1	127.8 (2)
N1—Fe1—N3	152.3 (1)	C1—N1—Fe1	124.8 (2)
N2—Fe1—N4	152.0 (1)	C6—N2—Fe1	128.2 (2)
N1—Fe1—N4	86.3 (1)	C9—N2—Fe1	124.2 (2)
N3—Fe1—N4	86.8 (1)	C14—N3—Fe1	128.5 (2)
N2—Fe1—Cl1	103.9 (1)	C11—N3—Fe1	124.6 (2)
N1—Fe1—Cl1	103.7 (1)	C16—N4—Fe1	128.2 (2)
N3—Fe1—Cl1	104.0 (1)	C19—N4—Fe1	124.2 (2)

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1992*a*). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1992*b*). Program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1994). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997). Molecular graphics: *ORTEP* (Johnson, 1965). Software used to prepare material for publication: *SHELXL*97.

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N-(Tropon-2-yl)-1,4,7,10-tetraoxa-13-aza-cyclopentadecane with calcium thiocyanate

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Abstract

In the title complex, [*N*-(7-oxocyclohepta-1,3,5-trien-1-yl)-1,4,7,10-tetraoxa-13-azacyclopentadecane]bis(thiocyanato-*N*)calcium, $[Ca(NCS)_2(C_{17}H_{25}NO_5)]$, the calcium ion has irregular eight coordination involving four ether O atoms, one tropone O atom, one aza-crown N atom and two thiocyanate N atoms.

Comment

Recently, we have prepared several mercurophilic dithio-crown derivatives having a tropone system and their mercury(II) salt complexes (Kato *et al.*, 1995; Mori