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[Fe(TPP)(4-MePip)$_2$]: an axially compressed bis(secondary amine) complex of an iron(II) porphyrin

Orde Q. Munro* and Mthembeni M. Ntshangase

School of Chemical and Physical Sciences, University of Natal, Private Bag X01,
Scottsville 3209, Pietermaritzburg, South Africa
Correspondence e-mail: munroo@nu.ac.za

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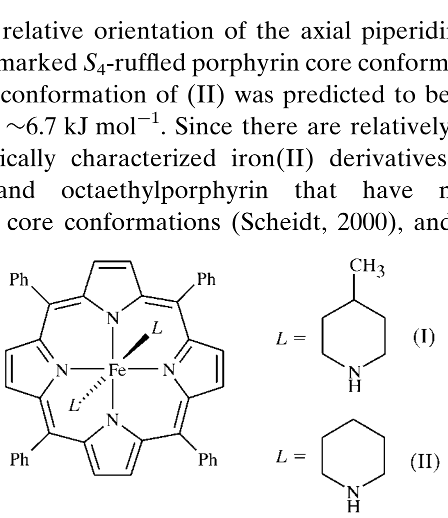
The low-spin iron(II) ion of bis(4-methylpiperidine)(5,10,15,-20-tetraphenylporphyrinato)iron(II), [Fe(TPP)(4-MePip)$_2$], where TPP is 5,10,15,20-tetraphenylporphyrinate ($C_{44}H_{28}N_4$) and 4-MePip is 4-methylpiperidine ($C_6H_{13}N$), is located at a center of inversion, and there is one molecule in the triclinic unit cell. The axial 4-MePip ligands adopt a chair conformation and the α-C atoms are oriented at angles of 21.2 (2) and 32.8 (2)° relative to the closest porphyrin N atoms. The equatorial Fe—N$_{\rm TPP}$ distances are 1.998 (2) and 1.990 (2) Å, while the axial Fe—N distance is 2.107 (2) Å. The relatively short axial coordination distance reflects compression of the molecule along its principal axis by intermolecular non-bonded interactions.

Comment

We have been investigating the structures, conformations, and electronic properties of bis(alkylamine) derivatives of low-spin iron(II) porphyrinates (Munro *et al.*, 1999) as part of an effort to understand the unusual coordination chemistry displayed by plant cytochrome f, in which one of the axial ligands is the N-terminal amino group of the protein (Martinez *et al.*, 1996). One of the objectives of the present investigation was to synthesize and structurally characterize a non-planar bis(amine) derivative of a ferrous porphyrin for two reasons: (i) the heme group in cytochrome f is non-planar and (ii) it is now widely recognized that non-planar conformations of porphyrins (Shelnutt, 2000) modulate the electronic structure (Barkigia *et al.*, 1999) of the heme iron and thus the reactivity of the metal center in heme proteins.

We previously used molecular mechanics (MM) simulations (Munro *et al.*, 1999) to show that [Fe(TPP)(Pip)$_2$] (Pip is piperidine), (II), could adopt three low-energy conformations: (i) a centrosymmetric structure with a planar porphyrin core conformation that matched the X-ray structure reported by Hoard's group in 1971 (Radonovich *et al.*, 1972), (ii) a non-centrosymmetric structure with a planar porphyrin core conformation, and (iii) a non-planar conformation in which a staggered relative orientation of the axial piperidine ligands leads to a marked S_4-ruffled porphyrin core conformation. The S_4-ruffled conformation of (II) was predicted to be lowest in energy by ~6.7 kJ mol^{-1}. Since there are relatively few crystallographically characterized iron(II) derivatives of tetraphenyl- and octaethylporphyrin that have non-planar porphyrin core conformations (Scheidt, 2000), and our MM simulations suggested that a non-planar conformation for (II) was in fact preferred on steric grounds, our strategy in this study was to build up some additional steric bulk on the axial ligands in the hope that crystal-packing constraints might favor crystallization of (I) in a non-centrosymmetric space group, or indeed at a general position in a centrosymmetric space group. Without crystallographically required inversion symmetry, the structure of (I) would, on conformational energy grounds, likely have an S_4-ruffled porphyrin core conformation. Unfortunately, as we show in this paper, a single 4-methyl substituent on the piperidine ring in the case of (I) is not sufficiently bulky to change the centrosymmetric crystal packing that was previously observed for (II). There are, however, crystallographic indicators that suggest an increase in molecular strain attends packing of the more bulky axial ligands of (I) in the triclinic lattice. Compound (I), in fact, experiences significant axial (ax) compression that leads to a rather short unique Fe—N$_{\rm ax}$ distance, a phenomenon that has probably been frequently overlooked as a significant cause



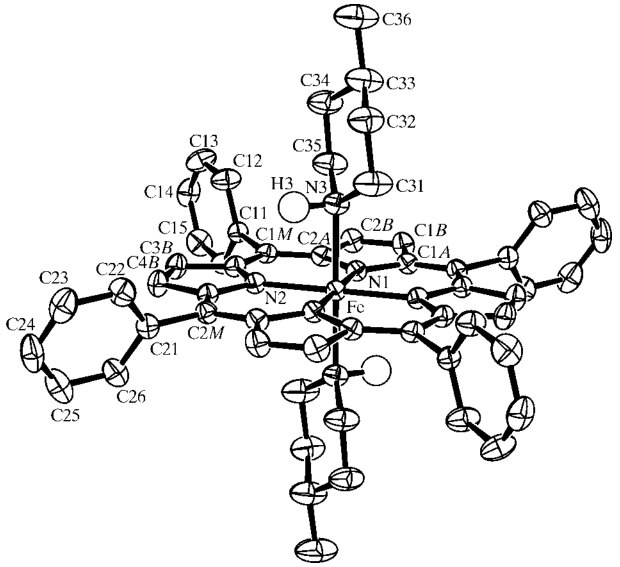


Figure 1

Selectively labeled view of (I), shown with ellipsoids at the 35% probability level. With the exception of the amine atom H3, all H atoms have been omitted for clarity (*ORTEP*-3; Farrugia, 1997).

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of coordination group structural variance in model heme systems.

The reaction of a ferric porphyrin with an excess of a primary or secondary amine in a non-aqueous solvent results in one-electron reduction of the metal to the Fe^{II} state by a mechanism which involves initial deprotonation of the metal-bound N—H group by excess ligand in solution (Del Gaudio & La Mar, 1978; Castro *et al.*, 1986). We previously made use of this redox process to synthesize and structurally characterize several $[Fe(TPP)L_2]$ derivatives, where L = butylamine, benzylamine, and 2-phenylethylamine (Munro *et al.*, 1999). In the present study, excess 4-MePip was reacted with a labile Fe^{III} complex, namely $[Fe(TPP)(OClO_3)]$, to ensure facile substitution of the anion by the secondary amine and thus complete reduction to the ferrous state. Reduction of the complex was confirmed by the dark-red color of the solution after the addition of the amine and the electronic spectrum of (I) under nitrogen, which was consistent with that reported for (II) (Del Gaudio & La Mar, 1978).

The X-ray crystal structure of (I) is shown in Fig. 1. The centrosymmetric structure exhibits an approximately planar porphyrin core conformation. The Fe^{II} state is confirmed by the absence of a counter-anion (ClO_4^-) in the lattice and the fact that atom H3 was cleanly located in a difference Fourier map. Importantly, this H atom refined well isotropically and its presence confirms that 4-MePip coordinates as the neutral amine. The axial 4-MePip ligands adopt a chair conformation and the mean planes taken through the 4-MePip rings are exactly eclipsed due to the crystallographically imposed symmetry. This is shown more clearly in Fig. 2, which is a view of the structure perpendicular to the N1—Fe—N2 plane. The $Fe—N_{TPP}$ distances differ by slightly more than 3σ [Fe—N1 = 1.998 (2) Å and Fe—N2 = 1.990 (2) Å]. We surmise that this in-plane coordination group asymmetry reflects the fact that the dihedral angles between each symmetry-unique porphyrin N atom and the closest 4-MePip α-C atom are non-equivalent [N1—Fe—N3—C35 = 21.2 (2)° and $N2^i$—Fe—N3—C31 = 32.8 (2)°; symmetry code: (i) $-x, -y, -z$]. Evidently, the smaller repulsive steric interaction between $N2^i$ and C31 allows for a slightly shorter $Fe—N_{TPP}$ coordination distance than is the case for N1. Interestingly, although not statistically significant, the average $Fe—N_{TPP}$ distance for (I) [1.994 (6) Å] is slightly shorter than that reported by Hoard for the bis(piperidine) analogue (II) [2.004 (4) Å]. Average values for all other chemically unique bonds and angles of (I) are summarized in Fig. 3; these are in good agreement with those reported for (II) (Radonovich *et al.*, 1972) and in even better agreement with those of the toluene solvate $[Fe(TPP)(Pip)_2]\cdot C_7H_8$ (Byrn *et al.*, 1991). The perpendicular displacements of each porphyrin core atom from the 24-atom mean plane of the macrocycle are also shown in Fig. 3. Since none of the displacements exceed 0.06 Å, the porphyrin conformation is essentially flat. Moreover, there is no real pattern or symmetry (*e.g.* D_{2d}-saddle or S_4-ruffle distortion) evident from the atomic displacements shown in Fig. 3.

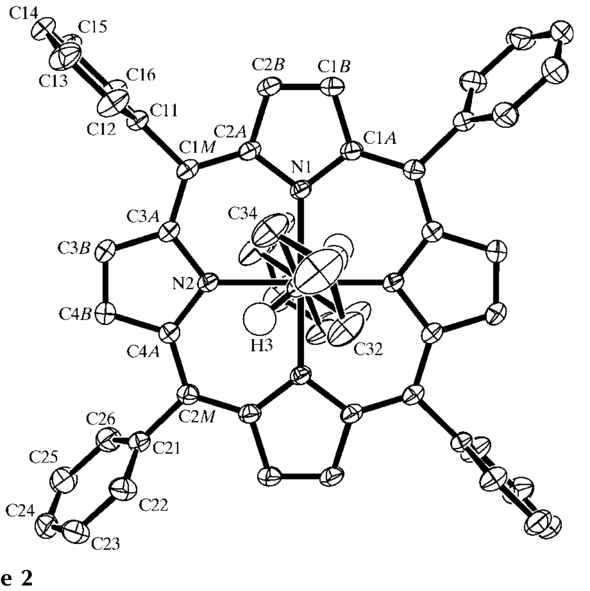

Figure 2
Selectively labeled view of (I), viewed perpendicular to the N1—Fe—N2 plane and shown with ellipsoids at the 35% probability level (*ORTEP*-3; Farrugia, 1997).

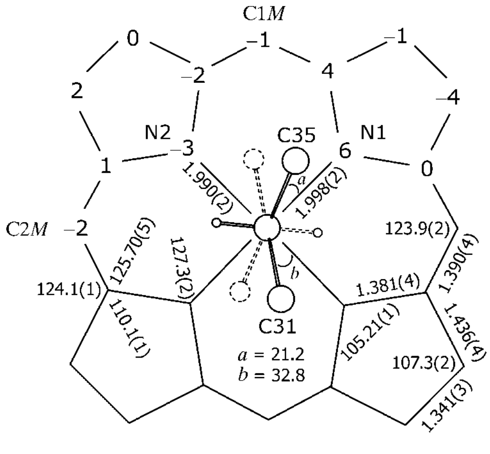

Figure 3
Formal diagram of (I), showing the perpendicular displacements (in units of 0.01 Å) of each atom from the 24-atom porphyrin mean plane, as well as the average structural parameters for each chemically unique class of bond (in Å) and angle (in °) in the porphyrin macrocycle. The Fe^{II} ion is located at the center of inversion (perpendicular displacement = 0 Å).

The unique axial coordination distance to the 4-MePip ligands, $Fe—N_{ax}$, measures 2.107 (2) Å in compound (I) and is considerably shorter than that reported for (II) [2.127 (3) Å]. The statistically significant difference between the axial coordination distances (> 6σ) observed for (I) and (II) is noteworthy. *AM*1 geometry optimizations (Dewar & Thiel, 1977) and calculations of the charge distributions for the free ligands Pip and 4-MePip show that the nitrogen donors are equivalent both geometrically and electronically (charge = −0.298 e) in these two compounds. If the electronic structures of the axial ligand donor atoms are the same, then the shorter axial coordination distance for (I) can only be attributed to crystal-packing constraints, particularly since the metal ions are located at the same (special) positions in the unit cell in both cases (space group $P\overline{1}$). In the case of (I), crystal packing (non-bonded contacts with the 4-Me groups of the axial ligands) would have to favor compression of the molecule

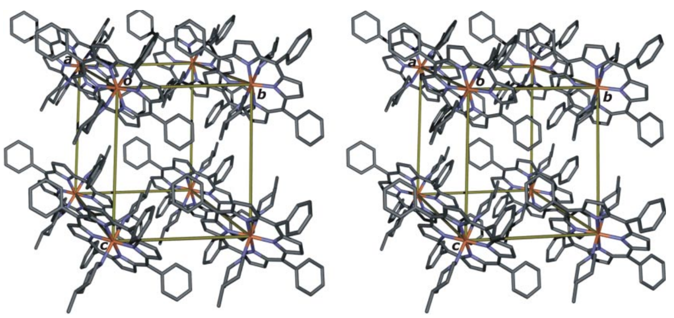

Figure 4
Stereoscopic view of the unit-cell contents of (I). H atoms have been omitted for clarity.

along its principal axis to bring about the observed ∼0.02 Å foreshortening of the Fe—N$_{\rm ax}$ bonds. Interestingly, although the structure of [Fe(TPP)(Pip)$_2$]·C_7H_8 is also centrosymmetric (space group *P*$\overline{1}$), it displays a somewhat different crystal packing symmetry to both (I) and (II) and, importantly, an even shorter Fe—N$_{\rm ax}$ bond distance of 2.092 Å (Byrn *et al.*, 1991).

The packing symmetry and interactions for (I) are shown more clearly in Fig. 4, which depicts a stereoview of the unit cell. Since the Fe$^{\rm II}$ ions are located on special positions, there is a full molecule positioned at each corner of the unit cell that projects into the neighboring unit cells. The crystal symmetry and occupancy of the asymmetric unit requires that the porphyrin rings are tilted equivalently with respect to each of the unit-cell axes such that the molecular packing places the molecule at [111] in close van der Waals contact with the molecule at [001] and those at the two flanking positions [101] and [011]. The crystal packing clearly demonstrates that, for example, the upper axial 4-MePip ligand of the molecule located at the cell origin [000] fits into a rather tight pocket created by the molecules at [110] and [00$\overline{1}$]. This is shown more clearly in the space-filling plot of Fig. 5. Although none of the intermolecular contacts is less than the sum of the van der Waals radii of the interacting atoms, there are several key contacts with the H atoms of the 4-MePip methyl group that are fully consistent with steric interactions being responsible for compression of the axial Fe—N distances in (I). Some of the more noteworthy contacts (Å) to pyrrole ring atoms include the following: C36$\cdots$H1*B*$^{\rm ii}$ 3.64, H36*A*$\cdots$C1*B*$^{\rm ii}$ 3.39, H36*A*$\cdots$H1*B*$^{\rm ii}$ 3.31, H36*B*$\cdots$C1*B*$^{\rm ii}$ 3.60, H36*B*$\cdots$H1*B*$^{\rm ii}$ 3.42 and H36*C*$\cdots$H1*B*$^{\rm ii}$ 3.61 [symmetry code: (ii) $-x+1$, $-y+1$, $-z$]. There are also several contacts (Å) with neighboring phenyl groups that add to the steric congestion around the 4-MePip methyl group: C36$\cdots$H22$^{\rm iii}$ 3.61, C36$\cdots$H23$^{\rm iii}$ 3.51, H36*B*$\cdots$C22$^{\rm iii}$ 3.36, H36*B*$\cdots$H22$^{\rm iii}$ 3.02, H36*B*$\cdots$C23$^{\rm iii}$ 3.12, H36*B*$\cdots$H23$^{\rm iii}$ 2.56 and H36*C*$\cdots$H22 3.33 [symmetry code: (iii) $-x$, $-y$, $-z-1$].

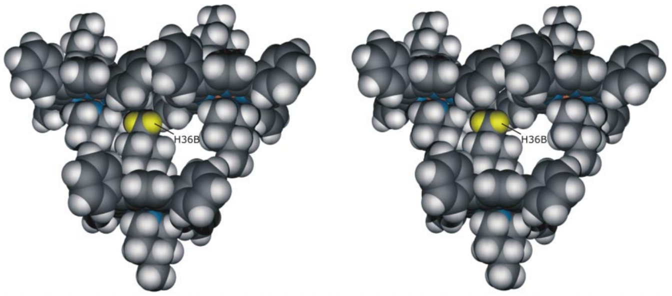

Figure 5
Space-filling plot (CPK model) of three neighboring molecules of (I) in the crystal lattice at the coordinates [000], [110], and [00$\overline{1}$]. Atom H36*B* of the uppermost 4-MePip ligand of the complex at the cell origin is labeled.

Finally, inspection of the crystal packing for [Fe(TPP)(Pip)$_2$]·C_7H_8 (Byrn *et al.*, 1991) shows that the equatorial H atom at the 4-position of the axial Pip ligand points directly between the *o*- and *m*-H atoms of one of the phenyl groups of the neighboring porphyrin. Two short H$\cdots$H contacts of 2.31 and 2.35 Å, respectively, are thus observed which may account for the marked compression of the Fe—N$_{\rm ax}$ bonds in this compound. Collectively, the structural evidence strongly supports the notion that the Fe—N$_{\rm ax}$ bond distances are critically dependent on the nature of the crystal packing in these ferrous porphyrin derivatives.

Experimental

All manipulations were carried out under nitrogen using a double manifold vacuum line, Schlenkware, and cannula techniques. Tetrahydrofuran (THF) and hexane were distilled over sodium/benzophenone and dichloromethane was distilled over over CaH_2. 4-Methylpiperidine (Aldrich) was freshly distilled over CaH_2 under nitrogen prior to use. H_2TPP was synthesized using published procedures (Barnett *et al.*, 1975). [Fe(TPP)Cl] was prepared by metallation of H_2TPP with anhydrous iron(II) chloride in refluxing dimethylformamide (Adler *et al.*, 1970). Silver perchlorate (Aldrich) was used as received. To [Fe(TPP)Cl] (156.3 mg, 0.222 mmol) and silver perchlorate (99.8 mg, 0.481 mmol) in a 100 ml two-necked round-bottomed flask under nitrogen was added 30 ml of freshly distilled THF. The solution was stirred for ∼12 h at room temperature. The solvent was removed *in vacuo* and the resulting red–brown solid redissolved in dichloromethane (*ca* 30 ml). The solution was cannula-filtered under nitrogen into a dry 100 ml two-necked round-bottomed flask containing 4-methylpiperidine (2.83 ml, 23.9 mmol). After swirling the solution for 10 min, the color changed from red–brown to deep red, consistent with reduction of the metal to the ferrous state (Castro *et al.*, 1986). The solution was transferred in ∼5 ml aliquots into Schlenk tubes and each aliquot layered with hexane; X-ray quality crystals were observed after 6 d. The deep-red crystals of (I) were collected by filtration and washed with 10% ethanol in hexane to remove colorless crystals of 4-methylpiperidine. Isolated yield: 28 mg (15%). Analysis calculated for $C_{56}H_{54}FeN_6$: C 77.59, H 6.28, N 9.69%; found: C 77.2, H 5.96, N 9.29%. *AM*1 geometry optimization calculations on Pip and 4-MePip were carried out with the default singlet-state parameters in *HyperChem* (Hypercube, 2000).

Crystal data

[Fe($C_{44}H_{28}N_4$)($C_6H_{13}N$)$_2$]
$M_r = 866.9$
Triclinic, *P*$\overline{1}$
$a = 10.3189$ (14) Å
$b = 11.2427$ (17) Å
$c = 11.8631$ (15) Å
$\alpha = 93.077$ (12)°
$\beta = 111.112$ (11)°
$\gamma = 113.483$ (12)°
$V = 1145.8$ (3) Å^3

$Z = 1$
$D_x = 1.256$ Mg m^{-3}
Mo *K*α radiation
Cell parameters from 25 reflections
$\theta = 2$–12°
$\mu = 0.37$ mm^{-1}
$T = 296$ (2) K
Rhomb, deep red
0.54 × 0.31 × 0.23 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
Non-profiled $\omega/2\theta$ scans
4719 measured reflections
3593 independent reflections
3317 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.010$

$\theta_{\max} = 24.0°$
$h = -2 \rightarrow 11$
$k = -12 \rightarrow 12$
$l = -13 \rightarrow 13$
3 standard reflections
frequency: 58 min
intensity decay: 2%

Refinement

Refinement on F^2
$R(F) = 0.038$
$wR(F^2) = 0.107$
$S = 1.06$
3593 reflections
290 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0561P)^2 + 0.6693P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.52$ e Å^{-3}
$\Delta\rho_{\min} = -0.41$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Fe—N2	1.9895 (17)	N3—C31	1.431 (3)
Fe—N1	1.9981 (17)	N3—C35	1.457 (3)
Fe—N3	2.1074 (19)		
N2—Fe—N1	90.02 (7)	C31—N3—C35	113.6 (2)
N2—Fe—N3^{i}	91.20 (7)	C31—N3—Fe	118.69 (16)
N1—Fe—N3^{i}	89.41 (7)	C35—N3—Fe	118.09 (15)
N3—Fe—N1—C1*A*	86.57 (18)	N1—Fe—N3—C31	−122.8 (2)
N3—Fe—N1—C2*A*	−84.56 (17)	N2—Fe—N3—C35	−68.8 (2)
N3—Fe—N2—C4*A*	−93.73 (18)	N1—Fe—N3—C35	21.2 (2)
N3—Fe—N2—C3*A*	86.69 (18)	Fe—N3—C31—C32	−172.0 (2)
N2—Fe—N3—C31	147.2 (2)	Fe—N3—C35—C34	174.6 (2)

Symmetry code: (i) $-x, -y, -z$.

Molecule (I) crystallized as deep-red rhombs in the triclinic crystal system (space group $P\overline{1}$). A difference Fourier calculation after anisotropic refinement of all non-H atoms located over 80% of the H atoms in the molecule, including the unique H atom appended to amine atom N3. This H atom (H3) was refined isotropically with H—N—C and H—N—Fe angle restraints (*SHELXL*97 DANG method; Sheldrick, 1997) and a distance restraint of 0.87 (2) Å (*SHELXL*97 DFIX method) to ensure chemically feasible values for these parameters (Byrn *et al.*, 1991). All other H atoms were refined using the standard riding model of *SHELXL*97.

Data collection: *CAD*-4-*PC Software* (Enraf–Nonius, 1992); cell refinement: *CAD*-4-*PC Software*; data reduction: *PROFIT* (Streltsov & Zavodnik, 1989); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 *for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1690). Services for accessing these data are described at the back of the journal.

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