

**(5-*tert*-Butylporphyrinato)copper(II),
a nonplanar porphyrin with only one
sterically demanding *meso* residue**

Mathias O. Senge

SFI Tetrapyrrole Laboratory, School of Chemistry, Trinity College Dublin, Dublin 2,
Ireland

Correspondence e-mail: sengem@tcd.ie

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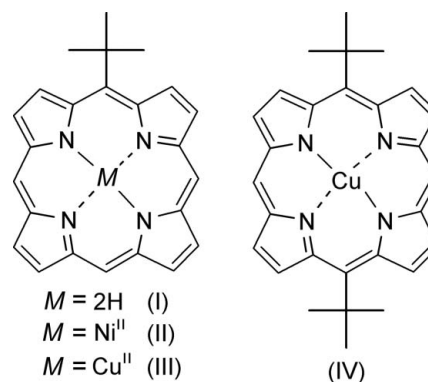
The title compound, [Cu(C₂₄H₂₀N₄)], is a rare example of a porphyrin carrying only one substituent. Its crystal structure exhibits two molecules in the asymmetric unit. The bulky *meso tert*-butyl residue gives rise to a nonplanar macrocycle with significant *ruf* and *sad* distortions. As a result of the position of the substituent, the conformational effects are unsymmetric and to a significant extent localized in the affected quadrant of the macrocycle. In line with results for highly substituted nonplanar porphyrins, comparison with a free base and a nickel(II) complex shows that the conformation of the macrocycle is modulated *via* additional metal effects.

Comment

Porphyrins are conformationally very flexible compounds and, depending on steric strain, packing or metal effects, can have a wide range of different macrocycle conformations (Hoard, 1973; Scheidt & Lee, 1987; Senge, 2006). Highly substituted porphyrins, where peripheral *peri* interactions give rise to nonplanar conformations, have elicited wide interest (Senge, 2006). They exhibit photophysical and chemical properties quite distinct from planar porphyrins and they have served as models for the modulation of porphyrin cofactors *in vivo* through apoprotein–chromophore interactions (Barkigia *et al.*, 1988, 2004; Senge, 1992). Nevertheless, these studies have almost exclusively addressed the structure and conformation of sterically ‘overloaded’ porphyrins, *e.g.* dodeca-substituted porphyrins (Barkigia *et al.*, 1990; Senge *et al.*, 2000) where numerous peripheral steric interactions give rise to very nonplanar tetrapyrroles.

Much less attention has been given to sterically strained porphyrins with as few substituents as possible (Senge *et al.*, 1996; Song, Jaquinod *et al.*, 1998). The simplest and most interesting systems would be porphyrins with only one sterically demanding residue and no other *meso* or β substituents. The first such structure, (II), was obtained from a low-yield condensation some time ago (Song, Jentzen *et al.*, 1998).

However, a general entry into these systems has only recently become available through new synthetic developments and now allows more detailed structural comparisons (Wiehe *et al.*, 2002; Ryppa *et al.*, 2005). We describe here the conformation of the related copper(II) complex, (III), which carries one *tert*-butyl residue in a *meso* position of the porphyrin ring system. Only a few structures of *tert*-butylporphyrins have been reported (Ema *et al.*, 1994; Senge *et al.*, 1995; Song *et al.*, 1996).



The molecular structure of one of the two symmetry-independent molecules (molecule 1) of the title compound, (III), is shown in Fig. 1. Dimensions are available in the archived CIF. The compound was prepared *via* standard insertion of copper(II) into the corresponding free base, (I). The two molecules form π -stacked dimers with the *tert*-butyl groups pointing in opposite directions (Fig. 2). This is in line with the general characteristics for the crystal packing of unsymmetrical porphyrins (Senge *et al.*, 1993). According to the definitions given by Scheidt & Lee (1987) these aggregates in (III) are characterized by a mean-plane separation of 3.396 Å, a centre-to-centre distance of 4.969 Å and a slip angle of 45.6°, giving a lateral shift of 3.55 Å. These ‘dimers’ in turn form slightly closer packed face-to-face-stacked dimers, with a mean-plane separation of the two N₄ planes of 3.329 Å, a

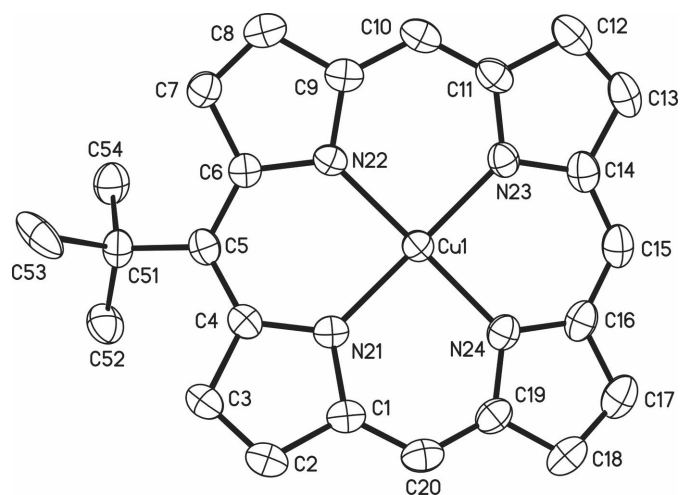
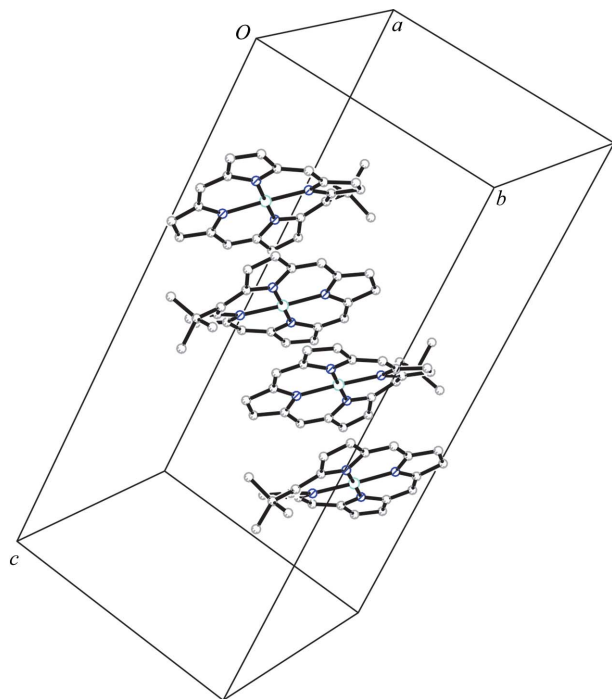


Figure 1
A view of the molecular structure of one of the two independent molecules of (III) in the crystal; a view of the second molecule is available in the *Supplementary material*. Displacement ellipsoids are drawn at the 50% probability level and H atoms have been omitted for clarity.

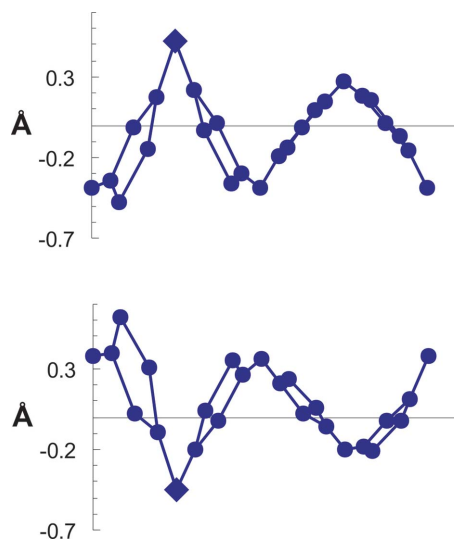

Figure 2

A view of the π -stacks formed in the crystal structure of (III). H atoms have been omitted for clarity.

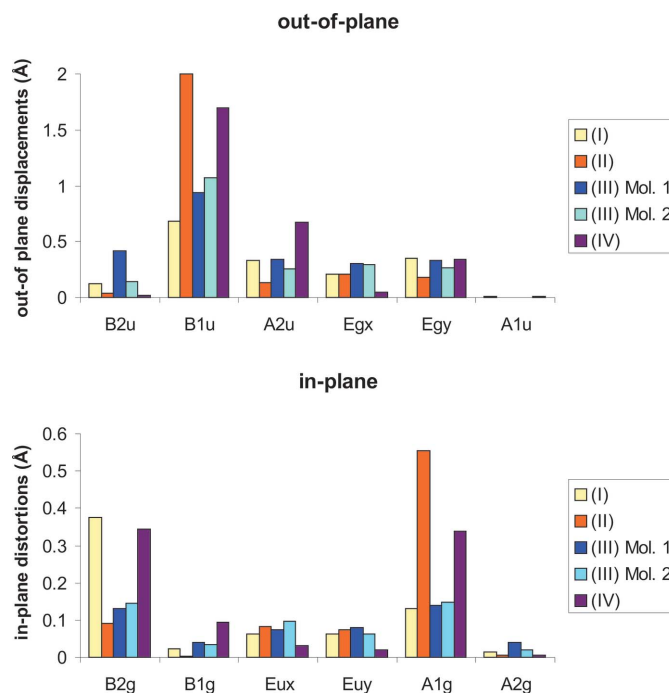
centre-to-centre distance of 4.461 Å, a slip angle of 43.3° and a lateral shift of 3.059 Å. Both types of dimers belong to group 'I' (Scheidt & Lee, 1987). Thus, the packing is characterized by the formation of tetrameric units (Cu1...Cu2...Cu2...Cu1) through edge-to-edge contacts.

Table 1 compiles selected structural data for the three available mono-*tert*-butylporphyrins. These include the free base, (I) (Ryppa *et al.*, 2005), the nickel(II) complex, (II) (Song, Jentzen *et al.*, 1998), and the copper(II) complex, (III). In addition, we include the structure of the related (5,15-di-*tert*-butylporphyrinato)copper(II), (IV) (Song, Jaquinod *et al.*, 1998). Visual inspection of the crystal structure of (III) reveals a 'folded' macrocycle conformation with a localized influence of the *tert*-butyl substituents, as indicated in the skeletal deviation plot shown in Fig. 3. Clearly, the deformation is more pronounced in the two quadrants involving the substituent than the others. For example, the tilt angles of individual pyrrole rings against the 24-atom plane are 17.9 (2), 14.3 (2), 7.6 (2) and 8.4 (2)° for the pyrrole rings including atoms N21, N22, N23 and N24, respectively, in molecule 1. This localized effect of the bulky residue is also evidenced in the displacements of the individual *meso* C atoms from the N_4 plane and the widening of the respective $C_a-C_m-C_a$ angles. In (III), the substituted position is displaced by about 0.6 Å from the N_4 plane compared to 0.21–0.34 Å for the unsubstituted *meso* positions. The 5,15-disubstituted derivative, (IV), exhibits similar trends along the 5,15-axis, albeit in a much more symmetrical fashion.

Metal effects established for other nonplanar porphyrins are retained in this series. Thus, the core size of the free base, (I), is larger and that of the nickel(II) complex, (II), is smaller


Figure 3

A skeletal deviation plot with respect to the plane of the 24 macrocycle atoms for (III). The *tert*-butyl-substituted *meso* C atom is highlighted with a diamond, the x axis is not to scale and the sequence of pyrrole rings follows the IUPAC nomenclature from left to right (N21, N22, N23, N24).


Figure 4

A graphical representation of the displacements along the lowest-frequency coordinates that best simulate the structures.

compared to (III). As expected, no significant in-plane distortion is evident from the core size elongation parameter in (III). The overall degree of nonplanarity (Δ_{24}) is significantly larger (0.19 Å) compared to the free base (0.14 Å) but smaller than in the nickel(II) complex (0.34 Å).

A normal-coordinate structural decomposition analysis as developed by Shelnutz and coworkers (Jentzen *et al.*, 1997) gives further details on the mix of distortion modes present in this type of porphyrin. This method classifies the distortions in

terms of equivalent displacements along the normal coordinates. As shown in Fig. 4, the main contributors to the out-of-plane distortions are *ruf* (B_{1u}), *dom* (A_{2u}), *wav*(x) (E_{gx}) and *wav*(y) (E_{gy}) and a minor contribution of *sad* (B_{2u}) distortion, which differs significantly in the two independent molecules. For the in-plane distortions, the main contributors are *m-str* (B_{2g}) and A_{1g} . The nickel(II) complex clearly shows a significantly larger *ruf* distortion, as a result of $M-N$ bond shortening. For the in-plane distortions *m-str* is larger in the free base and the disubstituted copper(II) complex, while the A_{1g} contribution is larger in the nickel(II) complex and in compound (IV). Thus, the central metal atom exerts a significant influence on the overall conformation and the mix of individual distortion modes, and can mask the steric influence of the individual *meso* substituent to some extent.

Experimental

Compound (III) was prepared *via* metallation of the respective free base porphyrin, (I). 5-*tert*-Butylporphyrin (58 mg, 0.16 mmol) was dissolved in dimethylformamide (50 ml) and heated under reflux with copper(II) acetate (10 equivalents) for 10 h. The residue was dissolved in CH_2Cl_2 and the mixture filtered through silica gel, eluting with CH_2Cl_2 . Finally, the solvent was removed under reduced pressure and the product recrystallized from CH_2Cl_2 -MeOH (1:1 *v/v*) [yield: 49 mg (0.11 mmol, 72%) of purple crystals; m.p. 547 K]. R_F = 0.73 (CH_2Cl_2 -*n*-hexane = 2:1 *v/v*, silica gel, 6×3 cm). UV/vis (CH_2Cl_2) [λ_{max} , nm (lg ϵ): 404 (5.44), 534 (4.00), 575 (3.65)]. MS (EI, 493 K, 70 eV) *m/z*: 427 (89%, $[M]^+$), 412 (100%, $[M-CH_3]^+$), 397 (18%, $[M-C_2H_6]^+$), 371 (69%, $[C_{20}H_{12}N_4Cu]^+$), 214 (6%, $[M]^{2+}$). HRMS (EI): *m/z* = 427.0977 (427.0984 for $C_{24}H_{20}CuN_4$).

The compound was crystallized *via* liquid diffusion of methanol into a solution of the porphyrin in methylene chloride. Crystals were handled as described by Hope (1994).

Crystal data

$[Cu(C_{24}H_{20}N_4)]$	$V = 3745.1 (5) \text{ \AA}^3$
$M_r = 427.98$	$Z = 8$
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
$a = 11.6765 (10) \text{ \AA}$	$\mu = 1.19 \text{ mm}^{-1}$
$b = 12.4744 (8) \text{ \AA}$	$T = 213 \text{ K}$
$c = 26.024 (2) \text{ \AA}$	$0.38 \times 0.27 \times 0.21 \text{ mm}$
$\beta = 98.892 (7)^\circ$	

Data collection

Bruker SMART 1000 CCD area-detector diffractometer	23765 measured reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 2008)	6481 independent reflections
$T_{min} = 0.662$, $T_{max} = 0.789$	4741 reflections with $I > 2\sigma(I)$
	$R_{int} = 0.047$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.048$	529 parameters
$wR(F^2) = 0.123$	H-atom parameters constrained
$S = 0.96$	$\Delta\rho_{max} = 1.82 \text{ e \AA}^{-3}$
6481 reflections	$\Delta\rho_{min} = -0.66 \text{ e \AA}^{-3}$

H atoms were located in difference maps and refined using a standard riding model, with $C-H = 0.94 \text{ \AA}$ and $U_{iso}(H) = 1.2U_{eq}(C)$ for aromatic H atoms, and $C-H = 0.97 \text{ \AA}$ and $U_{iso}(H) = 1.5U_{eq}(C)$ for methyl H atoms. The largest residual electron-density peak is located in the *tert*-butyl residue at C25. Together with some elongated

Table 1

Selected structural parameters (\AA , $^\circ$) for *tert*-butylporphyrins.

	(I)	(II)	(III)	(III)	(IV)
			Molecule 1	Molecule 2	
Metal	2H	Ni ^{II}	Cu ^{II}	Cu ^{II}	Cu ^{II}
Ct-N ^a	2.052	1.902	1.988 (3)	1.985 (3)	1.973
M-N21		1.907	1.980 (3)	1.983 (3)	1.978
M-N22		1.894	1.984 (3)	1.983 (4)	1.969
M-N23		1.902	1.988 (3)	1.988 (4)	1.973
M-N24		1.904	2.000 (3)	1.988 (3)	1.976
C4-C5-C6	120.8	119.3	119.6 (3)	119.2 (4)	119.1
C9-C10-C11	129.2	123.3	125.7 (4)	126.5 (4)	126.1
C14-C15-C16	125.3	122.4	125.4 (4)	125.9 (4)	119.3
C19-C20-C1	129.0	122.5	126.3 (4)	126.3 (4)	126.4
Θ (\AA) ^b	0.25	0.068	0.051 (4)	0.073 (4)	0.131
$\Delta 24$ (\AA) ^c	0.14	0.34	0.197 (4)	0.195 (4)	0.319
$\delta C5$ (\AA) ^d	0.47	0.88	0.60 (2)	0.63 (2)	0.74
$\delta C10$ (\AA) ^d	-0.17	-0.68	-0.28 (2)	-0.34 (2)	-0.49
$\delta C15$ (\AA) ^d	0.14	0.63	0.21 (2)	0.26 (2)	0.72
$\delta C20$ (\AA) ^d	-0.23	-0.67	-0.30 (2)	-0.33 (2)	-0.55

Notes: (a) core size; (b) core elongation parameter = difference in $N \cdots N$ vector lengths: $[(N21-N22) + (N23-N24)] - [(N21-N24) + (N22-N23)]$; (c) average deviation from the least-squares plane of the 24 macrocycle atoms; (d) displacement of the atom from the N_4 plane.

displacement ellipsoids, this indicates a minor unresolved disorder of the *tert*-butyl group.

Data collection: SMART (Bruker, 2000); cell refinement: SAINT (Bruker, 2000); data reduction: XPREP (Sheldrick, 2008); program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: XP within SHELXTL (Sheldrick, 2008); software used to prepare material for publication: SHELXTL.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: DN3156). Services for accessing these data are described at the back of the journal.

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