

Andrew D. Bond,^{a*†} Neil Feeder,^{a‡} James E. Redman,^a Simon J. Teat^b and Jeremy K. M. Sanders^a

^aUniversity of Cambridge, Department of Chemistry, Lensfield Road, Cambridge CB2 1EW, England, and ^bCLRC Daresbury Laboratory, Warrington, Cheshire WA4 4AD, England

† Present address: University of Southern Denmark, Department of Chemistry, Campusvej 55, 5230 Odense M, Denmark

‡ Present address: Pfizer Global R & D, Ramsgate Road, Sandwich, Kent CT13 9NJ, England

Correspondence e-mail: adb@chem.sdu.dk

Key indicators

Single-crystal synchrotron study
T = 150 K
Mean $\sigma(\text{C}-\text{C}) = 0.003 \text{ \AA}$
R factor = 0.052
wR factor = 0.129
Data-to-parameter ratio = 23.4

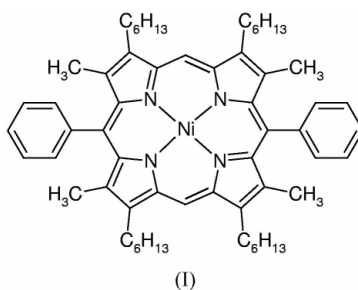
For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

Synchrotron X-ray study of [5,15-diphenyl-2,8,12,18-tetra-*n*-hexyl-3,7,13,17-tetramethylporphyrinato]nickel(II)

The crystal structure of the title compound, $[\text{Ni}(\text{C}_{60}\text{H}_{76}\text{N}_4)]$, has been determined at 150 K by a synchrotron single-crystal X-ray diffraction study. The asymmetric unit contains two independent molecules of the porphyrinatonicel complex which display distorted saddle conformations. The porphyrins are arranged into layers, with the *n*-hexyl substituents extending above and below the plane of these layers, and interdigitating between them.

Comment

[5,15-Diphenyl-2,8,12,18-tetra-*n*-hexyl-3,7,13,17-tetramethylporphyrinato]nickel(II), (I) (Fig. 1), crystallizes in space group $P2_1/n$ with two independent molecules in the asymmetric unit. The porphyrin cores of both molecules display comparable saddle conformations in which the phenyl substituents at the 5- and 15-positions of the porphyrin adopt a *syn* conformation with respect to the porphyrin plane. The *n*-hexyl substituents adopt extended conformations lying approximately in the plane of the porphyrin, and are well ordered. The deviation of the porphyrin core from planarity is considerably greater than that in the comparable nickel(II) porphyrins [5,15-diphenyl-2,8,12,18-tetraethyl-3,7,13,17-tetramethylporphyrinato]nickel(II) and [5,15-di(2,5-methoxyphenyl)-2,8,12,18-tetraethyl-3,7,13,17-tetramethylporphyrinato]nickel(II) (Senge *et al.*, 1997).



The molecules may be considered to be arranged into layers parallel to (001), in which the porphyrin planes lie orthogonal to the planes of the layers. The least-squares planes through the porphyrin moieties are approximately parallel and adopt alternate perpendicular separations of *ca* 5.2 Å (between molecules *A* and *B* in the same asymmetric unit) and 3.2 Å [between molecule *B* and molecule *A* at $(\frac{3}{2} - x, y - \frac{1}{2}, \frac{3}{2} - z)$]. Projection on to the plane of a single layer (approximately along the *c* direction, Fig. 2) reveals a rectangular packing arrangement with repeat dimensions (*a*, 0.5*b*) in projection. The central porphyrin moiety in this arrangement is inverted

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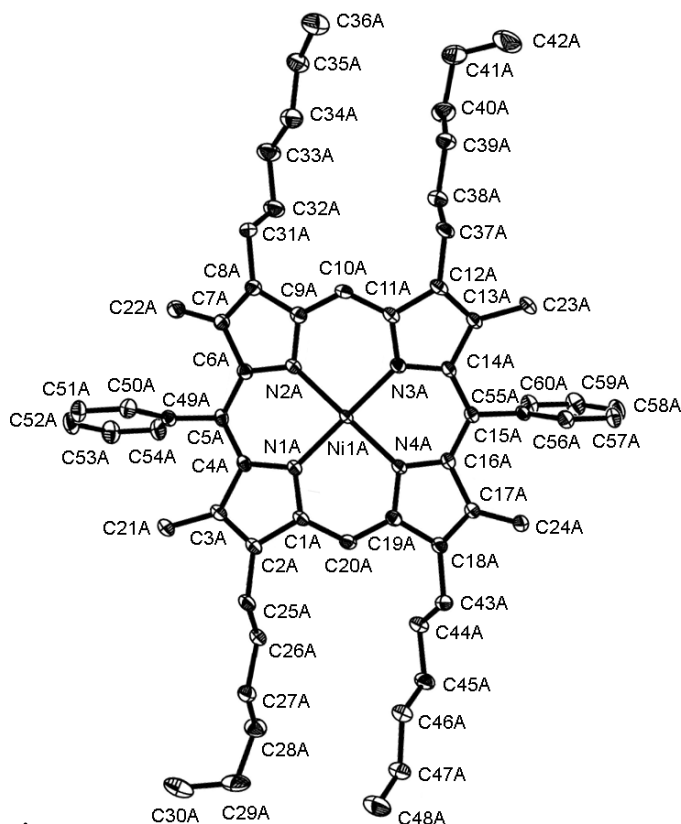


Figure 1
One of the independent molecules of (I), with displacement ellipsoids at the 50% probability level (H atoms omitted). The second independent molecule is comparable.

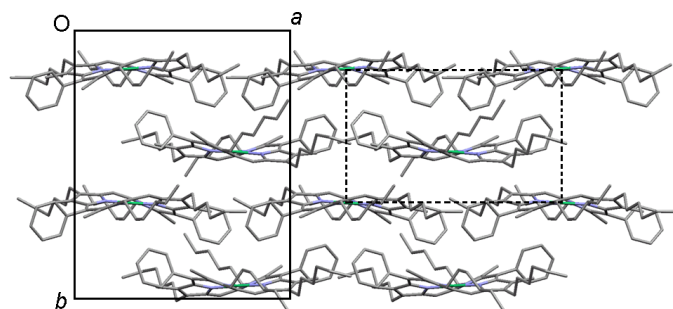


Figure 2
Projection of a single layer on to the (001) plane, illustrating the rectangular packing arrangement as dotted lines (H atoms omitted).

with respect to its neighbours, so that the phenyl substituents are directed into the hollow formed in the neighbouring saddled porphyrin. The phenyl substituents adopt edge-on contacts with the adjacent porphyrin faces, making several short C—H...N and C—H...C contacts: C59A—H59A...N4B = 2.67 Å, C59A—H59A...N1B = 2.79 Å, C60A—H60A...C4B = 2.85 Å, C53B—H53B...N3A = 2.87 Å, C53B—H53B...N2A = 2.89 Å and C54B—H54B...C14A = 2.80 Å. The *n*-hexyl substituents extend above and below the plane of the porphyrin layers and interdigitate between layers stacked along the *c* direction (Fig. 3), in a manner similar to that observed in the comparable free-base derivative (Bond *et al.*, 2002).

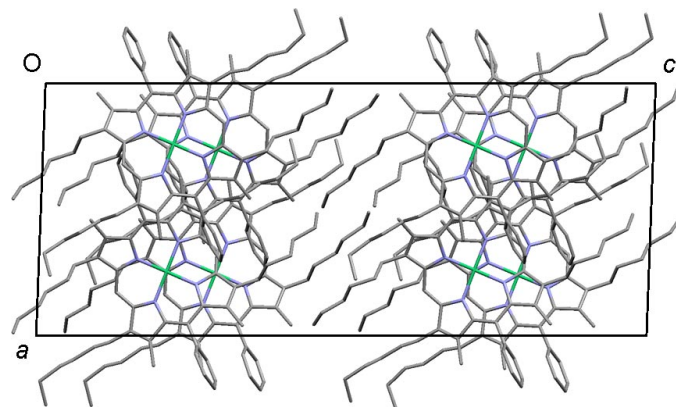


Figure 3
Projection along *b*, showing interdigitation of the *n*-hexyl substituents between adjacent porphyrin layers stacked along *c*.

Experimental

The free-base derivative of the title compound was prepared according to the method of Anderson & Sanders (1995). Formation of the nickel(II) complex was effected in quantitative yield by reflux of the free-base porphyrin with nickel(II) acetate in chloroform/methanol solution. Single crystals suitable for diffraction analysis were obtained from a toluene solution layered with methanol.

Crystal data

[Ni(C₆₀H₇₆N₄)]
M_r = 911.96
 Monoclinic, *P*2₁/*n*
a = 14.964 (1) Å
b = 18.492 (1) Å
c = 36.260 (2) Å
 β = 92.04 (1)°
V = 10027.3 (10) Å³
Z = 8
D_x = 1.208 Mg m⁻³

Synchrotron radiation
 λ = 0.6891 Å
 Cell parameters from 35312 reflections
 θ = 2.9–29.5°
 μ = 0.43 mm⁻¹
T = 150 (2) K
 Block, red
 0.12 × 0.06 × 0.04 mm

Data collection

Bruker SMART CCD diffractometer
 Thin-slice ω scans
 Absorption correction: multi-scan (SADABS; Sheldrick, 1996).
T_{min} = 0.950, *T_{max}* = 0.983
 69934 measured reflections

27810 independent reflections
 17657 reflections with *I* > 2σ(*I*)
R_{int} = 0.053
 θ_{\max} = 29.5°
h = -21 → 19
k = -20 → 25
l = -49 → 48

Refinement

Refinement on *F*²
R [*F*² > 2σ(*F*²)] = 0.052
wR (*F*²) = 0.129
S = 0.95
 27810 reflections
 1187 parameters

H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0702P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.003$
 $\Delta\rho_{\max} = 0.71 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.74 \text{ e \AA}^{-3}$

H atoms were placed geometrically (C—H = 0.95–0.99 Å) and refined using a riding model, with *U*_{iso}(H) = 1.5*U*_{eq}(C) for methyl groups and *U*_{iso}(H) = 1.2*U*_{eq}(C) otherwise. Methyl groups were allowed to rotate about their local threefold axes. The *n*-hexyl chains were refined without restraint.

Data collection: SMART (Siemens, 1994); cell refinement: LSCCELL (Clegg, 1995); data reduction: SAINT (Siemens, 1994); program(s) used to solve structure: SHELXTL (Sheldrick, 2000); program(s) used to refine structure: SHELXTL; molecular graphics:

SHELXTL; software used to prepare material for publication:
SHELXTL.

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