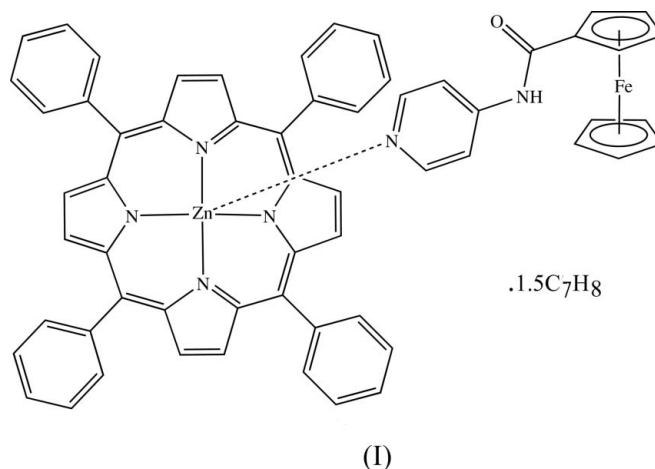


**[4-(Ferrocene-1-carboxamido)pyridine]-
(tetraphenylporphyrinato)zinc(II) toluene
sesquisolvate****Peter D. W. Boyd* and Ali
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pdw.boyd@auckland.ac.nz**Key indicators**Single-crystal X-ray study
 $T = 87\text{ K}$
Mean $\sigma(\text{C}-\text{C}) = 0.005\text{ \AA}$
Disorder in solvent or counterion
 R factor = 0.060
 wR factor = 0.152
Data-to-parameter ratio = 15.3For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.

The title compound is a five-coordinate square-pyramidal zinc–porphyrin complex, $[(\text{C}_{44}\text{H}_{28}\text{N}_4)\text{Zn}(\text{C}_{10}\text{H}_9\text{N}_2\text{O})\text{Fe}(\text{C}_5\text{H}_5)] \cdot 1.5\text{C}_7\text{H}_8$, with a 4-(ferrocene-1-carboxamido)pyridine apical ligand. The complexes assemble in the crystal structure by head-to-tail stacking of the 4-(ferrocene-1-carboxamido)pyridine groups, which interact through π – π stacking of the pyridine and cyclopentadienyl rings.

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The title complex, (I), was formed during a cocrystallization experiment with the fullerene C_{60} and a zinc porphyrin complex coordinated with ferrocenylamido-4-pyridine. Such fullerene–porphyrin assemblies (Boyd *et al.*, 2005) are of interest in the formation of multichromophoric photo-active materials with long-lived charge-separated states following photo-induced electron transfer. Crystals of (I) formed during the slow evaporation of an equimolar toluene solution of C_{60} , zinc tetraphenylporphyrin and ferrocenylamido-4-pyridine without the expected incorporation of C_{60} as is found for pyridine(tetraphenylporphyrinato)zinc(II) (Konarev *et al.* 2002).



The molecular structure of (I) is shown in Fig. 1. The porphyrin core is domed, with an r.m.s. deviation (rmsd) from the 24-atom porphyrin mean plane of 0.073 (3) Å. The Zn atom at the porphyrin centre lies out of the porphyrin plane by 0.425 (1) Å toward the apical N atom of the pyridine ligand. The Zn–N bond lengths are typical for five-coordinate zinc porphyrin complexes; see Table 1 (Byrn *et al.*, 1993; Lipstman *et al.*, 2006). The pyridine ring is aligned approximately parallel to the N1···N3 vector, centering the *ortho* pyridine H atoms asymmetrically over the N1/C6–C9 and N3/C16–C19

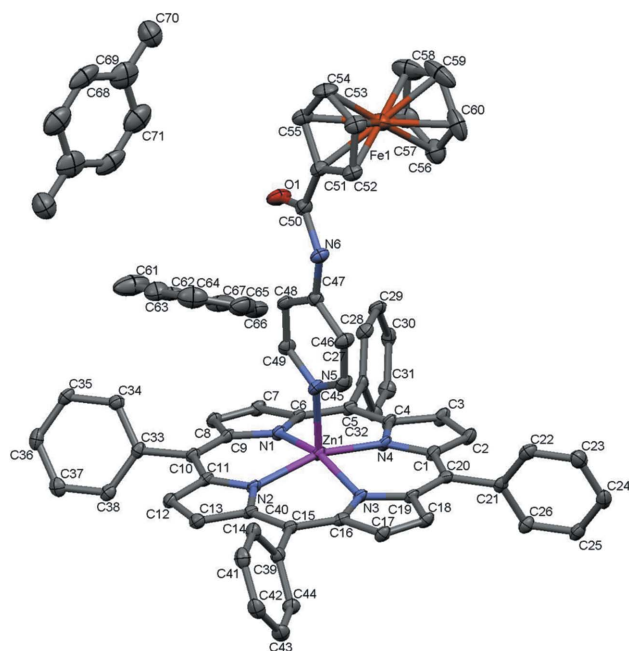


Figure 1
The structure of (I), showing 50% probability displacement ellipsoids. Atom C70 in the disordered toluene is disordered over two positions, both of which are shown. H atoms have been omitted. Unlabelled atoms on the disordered toluene are related to labelled atoms by symmetry code ($2 - x, 1 - y, -z$).

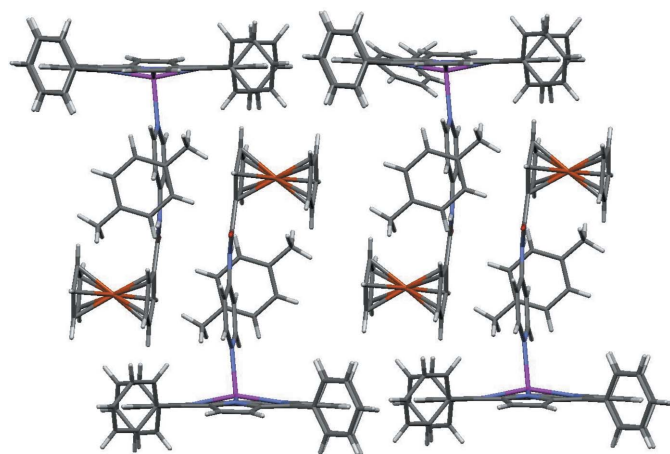


Figure 2
Stick illustration of the arrangement of the complex (I) in the crystal structure, showing the head-to-tail arrangement of the coordinated 4-(ferrocene-1-carboxamido)pyridine groups, the C–H... π interactions of the pyridine H to toluene solvent and the C–H... π interactions connecting the porphyrin pairs into a one-dimensional assembly.

pyrrole rings (H...centroids = 3.466 and 2.769 Å). This asymmetry appears to be associated with a strong C–H... π interaction from one *meta*-pyridine H atom to the centre of the disordered toluene solvent molecule (H46-centroid, 2.43 Å) (Nishio, 2004; Suezawa *et al.*, 2002). A ferrocene cyclopentadienyl ring and the pyridine amide groups are nearly coplanar [r.m.s.d. 0.098 (3) Å], with a slight bending at the amide N atom. The angle between the N5/C45–C40/N6 [rmsd = 0.023 (2) Å] and C50–C55/O1 planes [r.m.s.d. =

0.028 (3) Å] is 7.7 (2)°. The cyclopentadienyl rings have a staggered arrangement within the ferrocene group.

The porphyrin complexes assemble in the crystal structure *via* a head-to-tail alignment of ferrocenylamido-4-pyridine groups with π – π stacking of the pyridine and cyclopentadienyl rings (Fig. 2). The central amido groups are oriented with a close approach of the atoms C50 and N6 of the amide group [3.234 (5) Å]. These ‘pairs’ are then assembled in a linear fashion through C–H... π interactions of the porphyrin phenyl substituents (H36...C27–C32 centroid = 2.832 Å, H24...C39–C44 centroid = 2.863 Å) (see Fig. 2). The opposite face of the porphyrin has a toluene solvent molecule overlaying two pyrrole rings and two C–H... π interactions from the phenyl groups of neighbouring molecules to the other pyrrole rings (H29...N2/C11–C14 centroid = 2.865 Å and H35...N3/C16–C19 centroid = 2.738 Å).

Experimental

Crystals of (I) suitable for X-ray diffraction were grown by slow evaporation of a solution of zinc tetraphenylporphyrin, C₆₀ and 4-(ferrocene-1-carboxamido)pyridine (Kashiwagi *et al.*, 2003) (1:1:1) in toluene.

Crystal data

[FeZn(C₅H₅)(C₄₄H₂₈N₄)-
(C₁₀H₉N₂O)]·1.5C₇H₈
M_r = 1121.98
Triclinic, *P* $\bar{1}$
a = 11.0337 (1) Å
b = 11.2671 (1) Å
c = 22.8406 (1) Å
 α = 82.020 (1)°
 β = 89.865 (1)°

γ = 73.030 (1)°
V = 2687.45 (4) Å³
Z = 2
D_x = 1.387 Mg m⁻³
Mo K α radiation
 μ = 0.77 mm⁻¹
T = 87 (2) K
Lozenge, brown
0.28 × 0.18 × 0.1 mm

Data collection

Siemens SMART CCD
diffractometer
 ω scans
Absorption correction: multi-scan
(*SADABS*; Sheldrick, 1996)
T_{min} = 0.823, *T_{max}* = 0.926

26262 measured reflections
11093 independent reflections
8122 reflections with *I* > 2 σ (*I*)
R_{int} = 0.070
 θ_{\max} = 26.6°

Refinement

Refinement on *F*²
R [*F*² > 2 σ (*F*²)] = 0.060
wR(*F*²) = 0.152
S = 1.02
11093 reflections
724 parameters
H atoms treated by a mixture of
independent and constrained
refinement

$w = 1/[\sigma^2(F_o^2) + (0.0708P)^2 + 1.5528P]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.96 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.89 \text{ e \AA}^{-3}$

Table 1

Selected geometric parameters (Å, °).

Zn1–N2	2.059 (3)	Zn1–N3	2.076 (3)
Zn1–N4	2.061 (3)	Zn1–N5	2.129 (3)
Zn1–N1	2.064 (3)		
N2–Zn1–N5	96.52 (11)	N1–Zn1–N5	104.17 (10)
N4–Zn1–N5	103.50 (11)	N3–Zn1–N5	94.89 (10)

H atoms were placed in calculated positions and refined using the riding model (C–H = 0.93–0.97 Å), with $U_{\text{iso}}(\text{H}) = 1.2$ or 1.5 times $U_{\text{eq}}(\text{C})$, with the exception of the amide N6 where the H-atom position was refined. One toluene molecule, on an inversion centre, contains a disordered methyl group with half-occupancies and it was not possible to include the hydrogen in the position *para* to it. The large amplitude anisotropic displacement parameters of the atoms C56–C60 in the plane of the cyclopentadienide ring may be correlated with unresolved rotational disorder about the the ferrocene Fe–Cp centroid axis. This disorder could not be resolved.

Data collection: *SMART* (Siemens, 1995); cell refinement: *SAINT* (Siemens, 1995); data reduction: *SAINT*; program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *MERCURY* (Version 1.4.1; Bruno *et al.*, 2002); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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