metal-organic papers

(1,4:8,11:15,18:22,25-Tetraethanotetra-benzo[b,g,l,q]porphyrinato)nickel(II) chloroform disolvate

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In the title compound, [Ni($C_{44}H_{36}N_4$)]·2CHCl$_3$, the porphyrin macrocycle adopts a ruffle conformation. The Ni^{II} atom is coordinated by four N atoms of the porphyrin in a slightly distorted square-planar geometry. The bicyclic groups show disorder of the single and double bonds. The porphyrin planes form two columnar arrays along the b-axis direction through π–π stacking interactions.

Comment

Metal porphyrin complexes play an important role in biological redox processes such as photosynthesis and respiration (Senge, 2000). Although the porphyrin ring is aromatic, steric crowding of the peripheral substituents can cause conformational distortions of the porphyrin macrocycle, resulting in new functions and properties (Haddad *et al.*, 2003). The size of the peripheral substituents and the central metal atom can cause different conformational distortions, such as saddle, wave, ruffle and dome. In particular, ruffle and saddle deformations are known to result in significant changes in the chemical and spectroscopic properties of the porphyrin macrocycle (Shelnutt *et al.*, 1998). The structure of a metal-free bicyclic ring-fused porphyrin has been reported previously (Aramaki, Sakai, Yanagisawa & Mizuguchi, 2005). We present here the structure of the title nickel(II) complex of a bicyclic ring-fused porphyrin, (I).
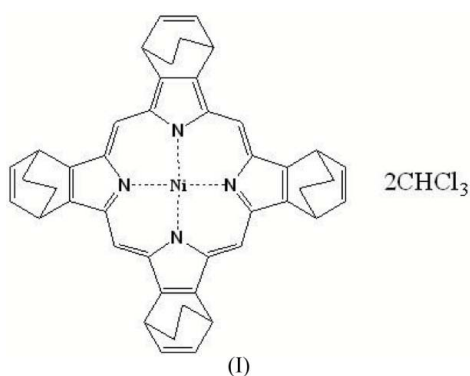
As shown in Fig.1, the Ni^{II} atom of (I) is coordinated by four N atoms of the porphyrin macrocycle in a slightly distorted square-planar geometry. The central porphyrin ring adopts a ruffle conformation, with the maximum displacement of the β-pyrrole C atoms from the mean plane being 0.3815 Å for atom C18. The isoindole units are almost planar, with mean deviations in the range 0.0106–0.0158 Å.

It is interesting to note that bond localization of the porphyrin skeleton is observed: the bonds C1—C2, C5—C6,
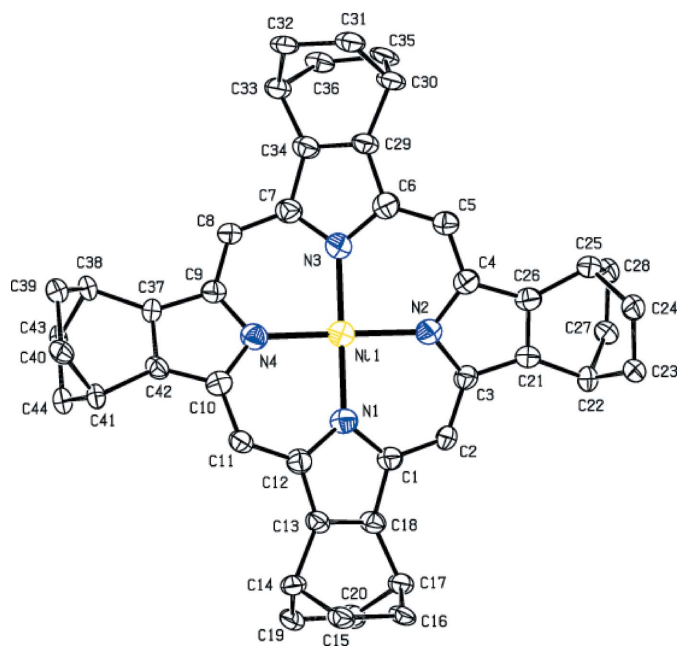
Figure 1
A view of the molecular structure of (I), with displacement ellipsoids drawn at the 50% probability level. The chloroform solvent molecules and H atoms have been omitted for clarity.
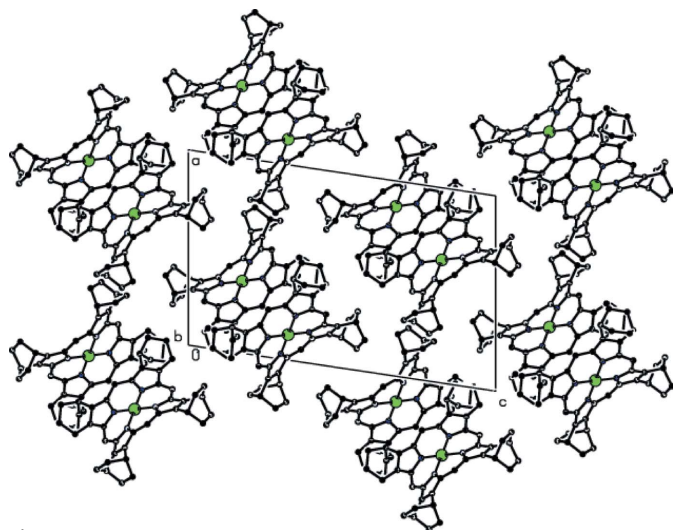

Figure 2
The crystal structure, viewed along the *b* axis. The chloroform solvent molecules and H atoms have been omitted.

C8—C9, C10—C11, C13—C18, C21—C26, C29—C34, C37—C42, N1—C1, N2—C3, N3—C6 and N4—C10 are shortened, the average C—C bond distance being 1.365 Å and the average N—C bond distance being 1.368 Å. On the other hand, the bonds C1—C18, C2—C3, C3—C21, C4—C5, C4—C26, C6—C29, C7—C34, C7—C8, C9—C37, C10—C42, C11—C12 and C12—C13 are elongated, with an average value of 1.412 Å.

The tilt angles of the pyrrole planes to the mean plane of the porphyrin are 20.5 (2), −21 (2), 21.4 (2) and 20.8 (2)°. This is typical of the ring distortion of metalloporphyrins in the crystalline state (Shen *et al.*, 2004).

According to the scheme, there should be one C—C single bond and one double bond in the bicyclic ring system at the periphery of the porphyrin skeleton. However, the bond lengths of C15—C16, C19—C20, C23—C24, C27—C28, C31—C32, C35—C36, C39—C40 and C43—C44 are in the range 1.440 (6)–1.505 (5) Å, intermediate between single and double bonds. This may be due to disorder of the saturated and unsaturated limbs of the bicyclic units, which generates a crystallographically averaged bond length (Aramaki, Sakai, Yanagisawa, Senju & Mizuguchi, 2005).

Fig. 2 shows the packing arrangement of (I). The porphyrin planes form columnar arrays along the *b*-axis direction through π–π stacking interactions. The angle between porphyrins in adjacent symmetry-related arrays is 73.9 (2)°.

Experimental

All manipulations were carried out in the air. A solution of nickel(II) acetate (177 mg, 1 mmol) in methanol (5 ml) was added dropwise to a solution of the metal-free porphyrin (63 mg, 0.1 mmol), prepared according to the published procedure of Ito *et al.* (1998), in chloroform (20 ml). The reaction mixture was stirred for 48 h at room temperature in the dark. The combined organic solutions were washed three times with water and once with saturated brine. The organic layer was dried over sodium sulfate and the solvent evaporated under reduced pressure to give the title compound, (I), in 90% yield. Green single crystals of (I) were obtained from a chloroform solution.

Crystal data

[Ni(C$_{44}$H$_{36}$N$_4$)]·2CHCl$_3$	$D_x = 1.497$ Mg m^{-3}
$M_r = 918.21$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 1420
$a = 14.9772$ (19) Å	reflections
$b = 11.5479$ (16) Å	$\theta = 2.3$–17.8°
$c = 23.822$ (3) Å	$\mu = 0.91$ mm^{-1}
$\beta = 98.507$ (3)°	$T = 293$ (2) K
$V = 4074.8$ (9) Å^3	Block, green
$Z = 4$	$0.30 \times 0.24 \times 0.22$ mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer	8015 independent reflections
	6118 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{int} = 0.030$
Absorption correction: multi-scan (*SADABS*; Bruker, 2000)	$\theta_{max} = 26.0°$
	$h = -11 \rightarrow 18$
$T_{min} = 0.72$, $T_{max} = 0.81$	$k = -14 \rightarrow 14$
21446 measured reflections	$l = -28 \rightarrow 29$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.07P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.057$	$+ 1.55P]$
$wR(F^2) = 0.136$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.08$	$(\Delta/\sigma)_{max} < 0.001$
8015 reflections	$\Delta\rho_{max} = 0.67$ e Å^{-3}
514 parameters	$\Delta\rho_{min} = -0.60$ e Å^{-3}
H-atom parameters constrained	

All H atoms were placed in calculated positions and included as part of a riding model, with C—H distances in the range 0.93–0.98 Å and with $U_{iso}(H) = 1.2U_{eq}(C)$.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Bruker, 2000); program(s) used to refine

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