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5,10,15,20-Tetrakis(4-pyridyl)porphyrin tris(acetic acid) clathrate

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Key indicators

Single-crystal X-ray study
T = 110 K
Mean σ(C–C) = 0.002 Å
R factor = 0.047
wR factor = 0.134
Data-to-parameter ratio = 16.0

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

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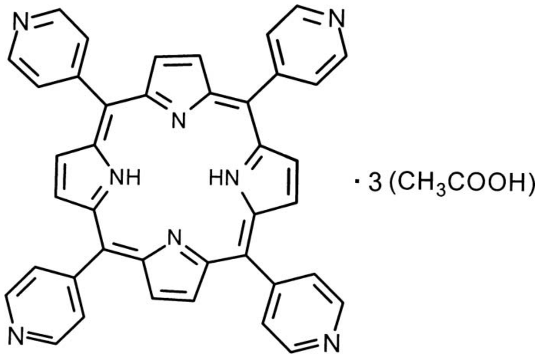
The crystal structure of the title compound, $C_{40}H_{26}N_8 \cdot 3CH_3COOH$, has been determined at *ca* 110 K. The compound crystallizes as an acetic acid clathrate in which three guest molecules are intercalated between layered zones of offset stacked porphyrins. Two of the pyridyl groups of the latter are involved in hydrogen bonds with the acetic acid.

Comment

The tetrapyridylporphyrin (TPyP) scaffold reveals unique modes of aggregation in solution and in crystalline solids (Fleischer & Shachter, 1991; Krupitsky *et al.*, 1994; Abrahams *et al.*, 1994), and has been widely used in the construction of supramolecular architectures mainly *via* coordination polymerization with the aid of metal ion centers (*e.g.* Krishna Kumar & Goldberg, 1998; Sharma *et al.*, 1999; Carlucci *et al.*, 2003). More recently, pyridyl and quinolyl porphyrins have been employed in supramolecular self-assembly processes *via* hydrogen bonding (Vinodu & Goldberg, 2003, 2005). In the latter context we reacted the TPyP building block dissolved in glacial acetic acid with the bidentate terephthalic (benzene 1,4-dicarboxylic) acid in an attempt to create continuous supramolecular arrays sustained by hydrogen bonds between the pyridyl and carboxylic acid molecular recognition sites of the TPyP and terephthalic acid components. Instead, in the given experimental conditions, the porphyrin units were preferentially associated with the competing molecules of the acetic acid solvent, affording a simple 1:3 TPyP–acetic acid clathrate compound, (I), rather than the anticipated hydrogen-bonded chains of alternating porphyrin and terephthalic acid molecules. The molecular structure of (I) has been determined with relatively high precision at *ca* 110 K and is illustrated in Fig. 1.



(I)

The porphyrin macrocycle is slightly saddled in order to avoid steric hindrance between the two inner pyrrole H atoms;

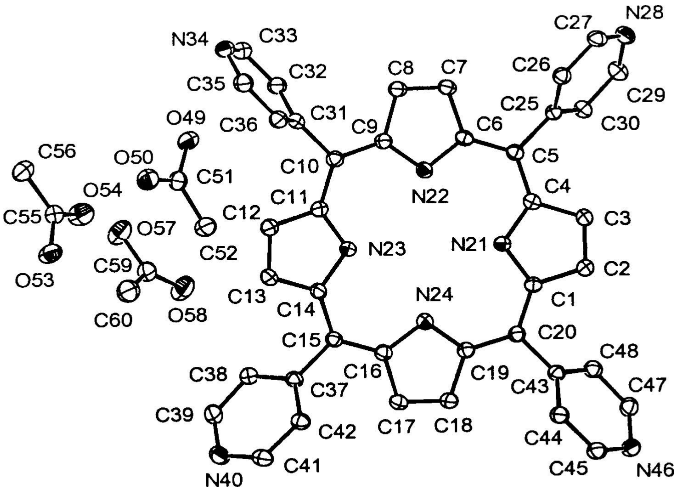


Figure 1
The molecular structure of (I), showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 50% probability level at *ca* 110 K. H atoms have been omitted for clarity.

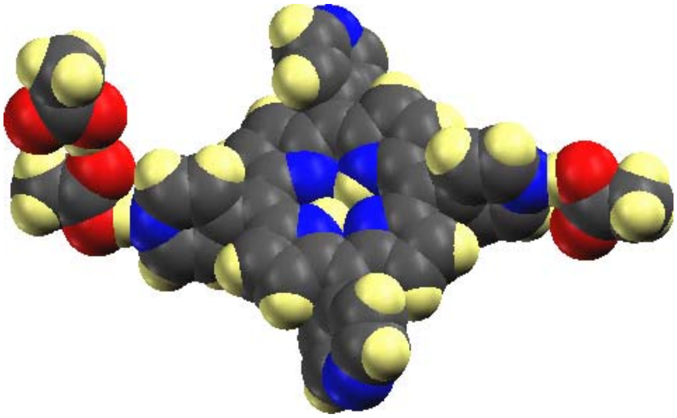


Figure 2
Space-filling illustration of the asymmetric unit, showing the hydrogen-bonding scheme. Color code: C: gray; N: blue; O: red; H: yellow.

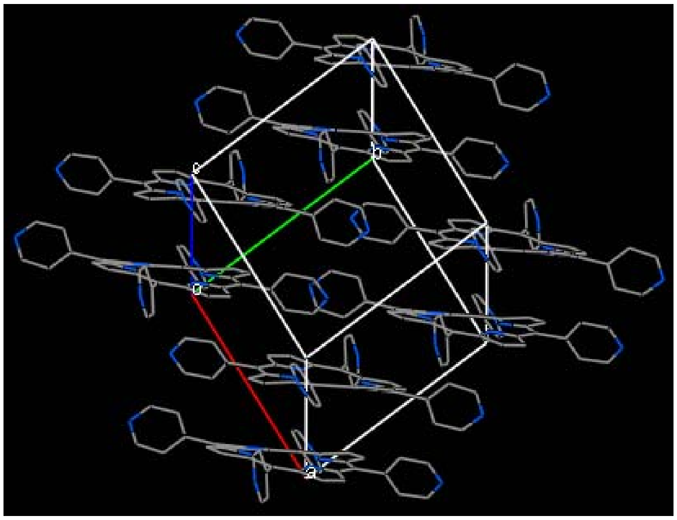


Figure 3
View of the TPyP organization within layers parallel to the *ab* plane of the crystal. Note the offset stacking of the porphyrins along the *b* direction, and the aryl–aryl interaction between the pyridyl rings within the layer. The pyridyl rings oriented roughly perpendicular to the projection shown are those that hydrogen bond to the acetic acid guest.

in the observed conformation, the non-bonding distance between these atoms, H21···H23, is 2.201 Å, conforming to the expected van der Waals distance. Two *trans*-related pyridyl substituents of the porphyrin hydrogen bond effectively to two corresponding molecules of acetic acid, one of which hydrogen bonds further to the third molecule of the acid (Table 1 and Fig. 2). Similarly to the other clathrates of TPyP, the crystal structure consists of tightly packed layers of the porphyrin molecules extending parallel to the *ab* plane of the unit cell and centered at $z = \frac{1}{2}$ (Krupitsky *et al.*, 1994). The porphyrins are stacked, as expected, in an offset manner (Krishna Kumar *et al.*, 1998), the mean planes of the porphyrin cores being roughly parallel to each other and roughly perpendicular to the layer. The pyridyl arms directed perpendicular to the layer are those that associate to the guest acetic acid species and intercalate them between neighboring layers. The two other pyridyl groups, embedded within the porphyrin layer, partly overlap the pyridyl substituents of adjacent species, thus contributing to favorable dipolar and dispersive intermolecular interactions (Fig. 3). The resulting structure thus consists of alternating zones of TPyP centered at $z = \frac{1}{2}$ and the acetic acid molecules centered at $z = 0$ (Fig. 4).

Experimental

Tetra(4-pyridyl)porphyrin (MidCentury Chemicals) was dissolved in glacial acetic acid and reacted with terephthalic acid (Aldrich) in a 1:2 ratio. The solution was kept for crystallization at room temperature, yielding after several days violet-colored crystals suitable for X-ray diffraction analysis.

Crystal data

$C_{40}H_{26}N_8 \cdot 3C_2H_4O_2$
$M_r = 798.84$
Triclinic, $P\overline{1}$
$a = 10.4672$ (2) Å
$b = 11.2549$ (2) Å
$c = 17.1109$ (4) Å
$\alpha = 92.2350$ (12)°
$\beta = 106.5621$ (10)°
$\gamma = 94.8600$ (12)°
$V = 1921.00$ (7) Å^3

$Z = 2$
$D_x = 1.381$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 6720 reflections
$\theta = 2.0$–$27.5°$
$\mu = 0.09$ mm^{-1}
$T = 110$ (2) K
Chunk, violet
0.40 × 0.35 × 0.20 mm

Data collection

Nonius KappaCCD diffractometer
1° φ and ω scans
Absorption correction: none
20904 measured reflections
8806 independent reflections
6790 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.027$
$\theta_{\rm max} = 27.5°$
$h = -13 \rightarrow 13$
$k = -14 \rightarrow 14$
$l = -22 \rightarrow 21$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.047$
$wR(F^2) = 0.134$
$S = 1.04$
8806 reflections
549 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0724P)^2 + 0.4868P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.041$
$\Delta\rho_{\rm max} = 0.28$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.33$ e Å^{-3}

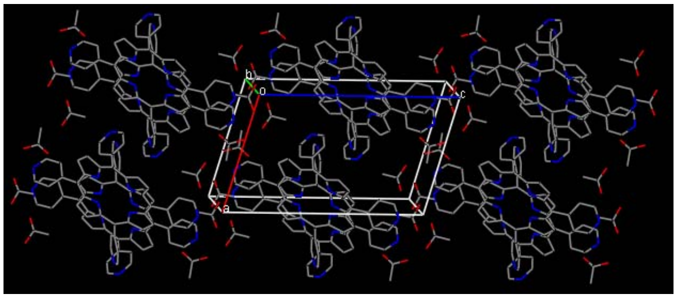


Figure 4
The crystal packing of (I), viewed approximately down the *b* axis, illustrating the stacking of the TPyP units and the alternating zones of the porphyrin and acetic acid components.

Table 1
Hydrogen-bond geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O49—H49$\cdots$N46^{i}	1.06	1.60	2.6572 (17)	176
O53—H53$\cdots$N34^{ii}	1.03	1.66	2.6733 (18)	167
O57—H57$\cdots$O50	1.00	1.73	2.6367 (18)	149

Symmetry codes: (i) $x, y, z - 1$; (ii) $x, y - 1, z$.

H atoms bound to C atoms were positioned geometrically and refined as riding on their carrier atoms, with C—H distances of 0.95–0.98 Å and $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C). H atoms bound to the pyrrole N atoms and the acetic acid O atoms were located in difference Fourier maps and refined as riding in their as-found positions (N—H = 0.99 Å and O—H = 1.00–1.06 Å), with $U_{\rm iso}$ = 0.050 Å^2.

Data collection: *COLLECT* (Nonius, 1999); cell refinement: *DENZO* (Otwinowski & Minor, 1997); data reduction: *DENZO*; program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPIII* (Burnett & Johnson, 1996) and *MERCURY* (Bruno *et al.*, 2002); software used to prepare material for publication: *SHELXL97*.

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