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Hydrogen-bonded assemblies of 20-(4-pyridyl)porphyrin-5^4,10^4,15^4-tribenzoic acid with dimethyl sulfoxide and 4-acetylpyridine in their dimethyl sulfoxide and tetrahydrofuran solvates

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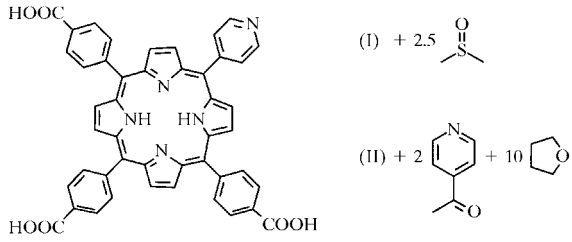
Crystals of the title compounds, 20-(4-pyridyl)porphyrin-5^4,10^4,15^4-tribenzoic acid–dimethyl sulfoxide (2/5), $C_{46}H_{29}N_5O_6\cdot2.5C_2H_6OS$, (I), and 20-(4-pyridyl)porphyrin-5^4,10^4,15^4-tribenzoic acid–4-acetylpyridine–tetrahydrofuran (1/2/10), $C_{46}H_{29}N_5O_6\cdot2C_7H_7NO\cdot10C_4H_8O$, (II), consist of hydrogen-bonded supramolecular chains of porphyrin units solvated by molecules of dimethyl sulfoxide [in (I)] and 4-acetylpyridine [in (II)]. In (I), these chains consist of heterogeneous arrays with alternating porphyrin and dimethyl sulfoxide species, being sustained by COOH$\cdots$O=S hydrogen bonds. They adopt a zigzag geometry and link on both sides to additional molecules of dimethyl sulfoxide. In (II), the chains consist of homogeneous linear supramolecular arrays of porphyrin units, which are directly connected to one another *via* COOH$\cdots$N(pyridyl) hydrogen bonds. As in the previous case, these arrays are solvated on both sides by molecules of the 4-acetylpyridine ligand *via* similar COOH(porphyrin)$\cdots$N(ligand) hydrogen bonds. The two crystal structures contain wide interporphyrin voids, which accommodate disordered/diffused solvent molecules, *viz.* dimethyl sulfoxide in (I) and tetrahydrofuran in (II).

Comment

Following our earlier studies on the designed construction of framework solids from symmetrically functionalized porphyrin building blocks of square-planar D_{4h} symmetry (Goldberg, 2005, and references therein), the supramolecular chemistry of porphyrin derivatives of reduced symmetry has also deserved considerable attention (Vinodu & Goldberg, 2003; George & Goldberg, 2006; George *et al.*, 2006). Within this context, porphyrin cores substituted with either four, three or two carboxylic acid functions of complementary hydrogen-bonding capacity have been investigated (Diskin-Posner & Goldberg, 1999; Vinodu & Goldberg, 2003, 2004). In most cases, the predominant propensity of such porphyrin species to associate directly *via* the cyclic dimeric $(COOH)_2$ hydrogen-bonding synthon into polymeric arrays has been demonstrated. However, disruption of this binding mode may occur in the presence of strong pyridyl- and sulfoxide-type Lewis base reagents, owing to competing solvation (Lipstman *et al.*, 2006; George *et al.*, 2006). Thus, lipophilic species, such as dimethyl sulfoxide (DMSO) or 4-acetylpyridine, reveal preferential affinity to associate to the carboxylic acid functions *via* hydrogen bonds, in competition with the alternative $(COOH)_2$ self-association of the porphyrin units. Furthermore, in porphyrins that bear both 3-pyridyl and 4-carboxyphenyl functions, intermolecular COOH$\cdots$pyridyl hydrogen bonding has been observed (Vinodu & Goldberg, 2005).



Within the above context, we report here on the synthesis of the title porphyrin compound, and the structures of its adducts with dimethyl sulfoxide, (I), and 4-acetylpyridine, (II), which crystallized as dimethyl sulfoxide and tetrahydrofuran solvates, respectively.

In agreement with previous results, the present study also reveals preferential formation of COOH$\cdots$O=S and COOH$\cdots$N(pyridyl) hydrogen bonds, rather than the $(COOH)_2$ interactions. Figs. 1 and 2 depict the molecular structures of adducts (I) and (II), respectively. The DMSO species is a strong acceptor of H atoms in hydrogen bonds, and

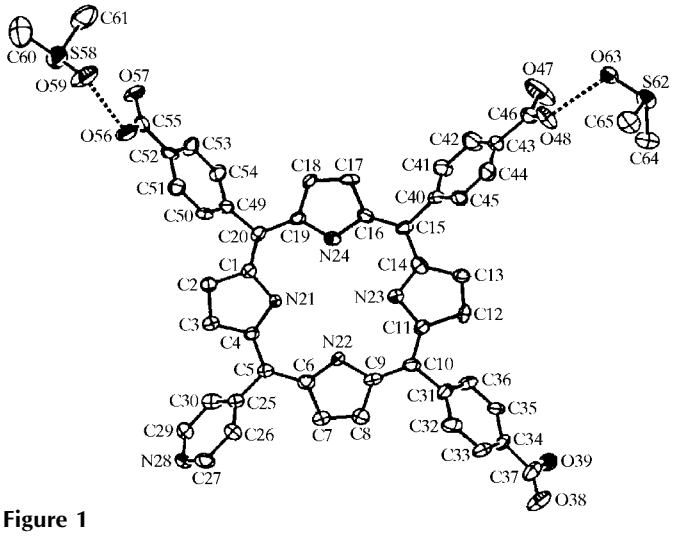


Figure 1
The molecular structure of (I), showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 50% probability level at *ca* 110 K. H atoms have been omitted. Hydrogen bonds between the component species within the asymmetric unit are marked by dashed lines.

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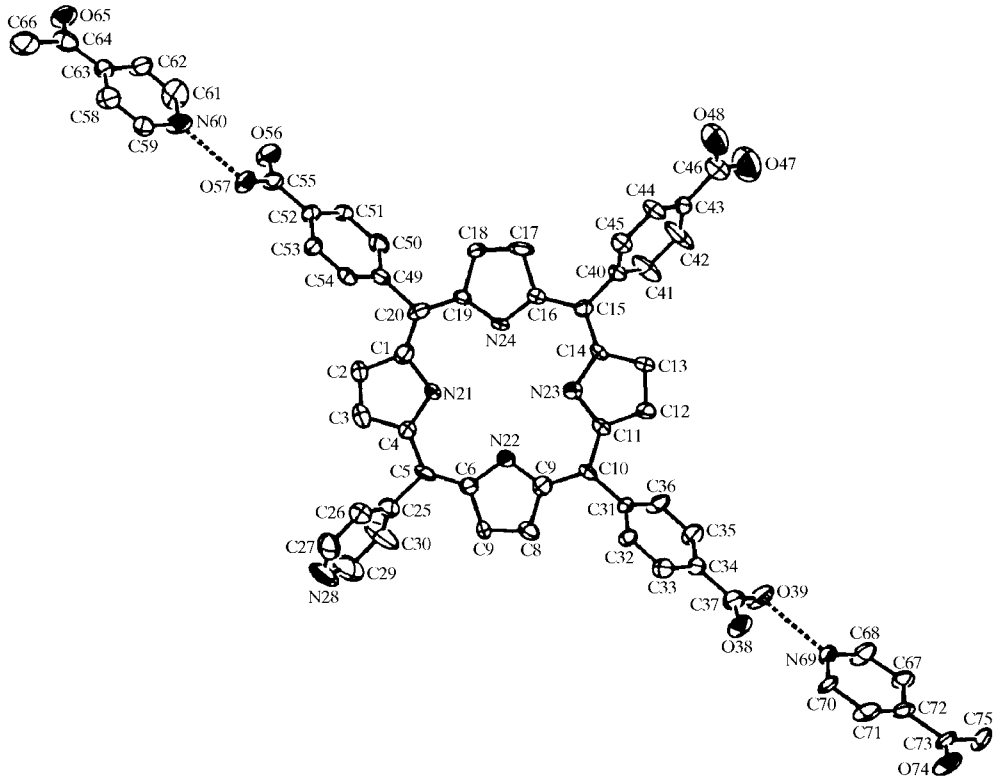

Figure 2
The molecular structure of (II), showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 40% probability level at *ca* 110 K. H atoms have been omitted. Hydrogen bonds between the component species within the asymmetric unit are marked by dashed lines.

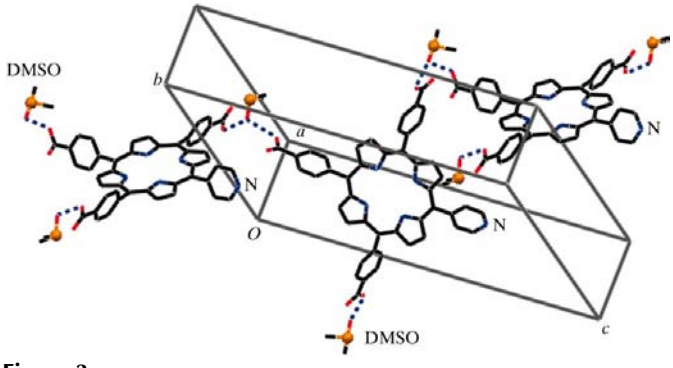

Figure 3
A stick illustration (except for the S atoms, which are marked by small spheres) of the hydrogen-bonding interaction scheme in (I). The hydrogen bonds between the carboxylic acid functions and the DMSO molecules are denoted by dashed lines (H atoms have been omitted).

can associate with either one or two COOH H-atom donors. In (I), they solvate completely the three carboxylic acid groups by relatively strong OH···O=S hydrogen bonds, with O···O distances ranging from 2.565 (6) to 2.624 (5) Å (Table 1). While one molecule of DMSO connects to a single COOH group, the other ligand bridges between two neighboring units, thus giving rise to the formation of heterogeneous porphyrin–DMSO hydrogen-bonded zigzag polymeric arrays (Fig. 3). The crystal packing of these chains is associated with occlusion of additional uncoordinated molecules of DMSO between these chains in a disordered manner. It is of further interest to note that in the presence of very strong hydrogen-bond acceptors, such as DMSO in excess, the pyridyl function of the porphyrin (a somewhat weaker acceptor) is not involved in inter-porphyrin hydrogen bonds with the carboxylic acid groups, as observed previously (Vinodu & Goldberg, 2004, 2003). Rather, it is involved in a weak C—H···N contact with a neighboring porphyrin unit (Table 1).

When the DMSO is replaced by a 4-acetylpyridine reagent in the crystallization mixture, a different intermolecular binding pattern emerges. Now the 4-acetylpyridine and the porphyrin-bound pyridyl groups have similar affinity, as hydrogen-bond acceptors, for the formation of COOH···N hydrogen bonds. This is well expressed in the observed structure of (II), crystallized from a 1:1 mixture of 4-acetylpyridine and tetrahydrofuran (THF, which is a very weak H-atom acceptor in hydrogen bonds). Thus, in order to optimally satisfy the hydrogen-bonding capacity of the porphyrin and the 4-acetylpyridine groups, one unit of the former associates with two units of the latter, wherein two of the carboxylic acid functions are solvated by two molecules of 4-acetylpyridine *via* COOH···N hydrogen bonds. In addition, the porphyrin scaffolds self-associate into homogeneous linear polymeric chains *via* COOH···N(pyridyl) hydrogen bonds (Fig. 4). The corresponding O···N distances range from 2.596 (5) to 2.653 (4) Å (Table 2). In this arrangement, the hydrogen-bonding potential of all COOH and pyridine/pyridyl N-atom sites is used optimally. Side packing of these chains creates open layers, which in turn stack one on top of the other, yielding a stable structure at room temperature. This stability may be attributed to attractive dispersion between the large

aromatic surfaces of adjacent layers, as well as to additional weak C—H···O interactions between the molecular entities (Table 2). The crystal packing of the supramolecular arrays creates very wide interporphyrin voids, which propagate parallel to the *a* axis, accommodating severely diffuse THF solvent molecules (Fig. 5). The van der Waals width of these canals is about 9–10 Å.

This study, along with our earlier observations, confirms the hierarchy of the hydrogen-bonding interactions expressed in the supramolecular assembly of the carboxyphenylporphyrin materials: the COOH···O=S synthon appears more stable than the COOH···N(pyridyl) synthon, while the $(COOH)_2$ interaction seems to be the least preferred among the three types (Lipstman *et al.*, 2006; George *et al.*, 2006; Etter, 1990, 1991). Owing to severe solubility problems, we have not been able so far to crystallize two-dimensionally hydrogen-bonded supramolecular arrays of the title porphyrin compound in the absence of the competing solvents, as was achieved successfully with the tetracarboxyphenyl (Diskin-Posner & Goldberg, 1999) and tris(4-carboxyphenyl)(3-pyridyl) (Vinodu & Goldberg, 2005) derivatives. Only one single-crystal structure of a compound containing 4-pyridyl and 4-carboxyphenyl functional substituents on the same porphyrin framework has ever been published before (Redman *et al.*, 2001).

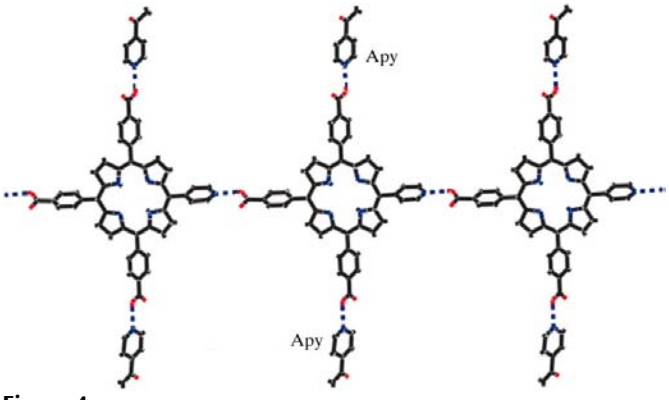

Figure 4
A stick illustration of the hydrogen-bonding scheme in (II) (dashed lines), showing direct connection between neighboring porphyrin entities and solvation of the thus formed chains by molecules of 4-acetylpyridine (indicated by 'Apy').

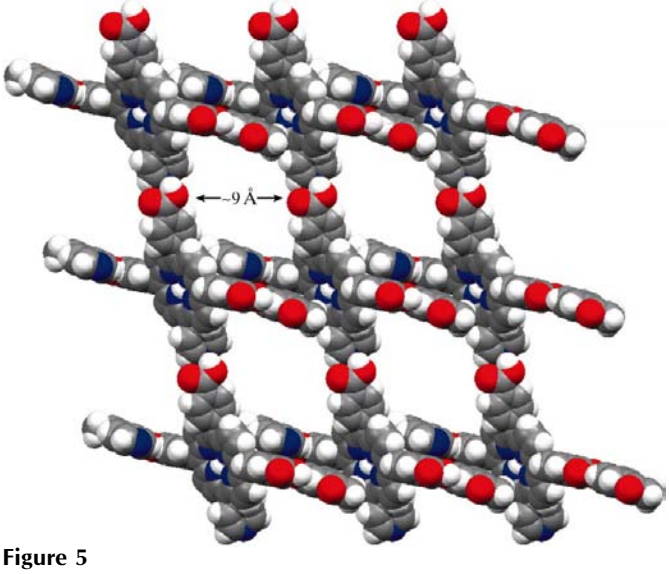

Figure 5
A space-filling illustration of the intermolecular organization of (II), as viewed down the *a* axis of the crystal, perforated by 9 Å-wide solvent-accessible channel voids.

Experimental

The free-base porphyrin species was synthesized by a two-step procedure. The first step is the synthesis of 10,15,20-tris(4-methoxycarbonylphenyl)-5-(4-pyridyl)porphyrin by Adler's method (Adler *et al.*, 1970). This involves the condensation of a 3:1 mixture of pyridine-4-carbaldehyde and 4-methoxycarbonylbenzaldehyde with distilled pyrrole in hot propionic acid, and separation of the product on a silica-gel column using chloroform as solvent and acetone–chloroform mixtures of gradually varying composition as eluants. The thus isolated 10,15,20-tris(4-methoxcarbonylphenyl)-5-(4-pyridyl)-porphyrin was then converted to the corresponding carboxylic acid derivative by alkaline hydrolysis with an aqueous solution of KOH. Spectroscopic data for the ester derivative: ^{1}H NMR ($CDCl_3$): δ 9.00 (*d*, *J* = 5.9 Hz, 2H), 8.79 (*m*, 8H), 8.43 (*d*, *J* = 8 Hz, 6H), 8.25 (*d*, *J* = 8.2 Hz, 6H), 8.12 (*d*, *J* = 5.9 Hz, 2H), 4.08 (*s*, 12H), −2.89 (*s*, 2H). UV–vis (in THF, nm): λ_{max} (logε) 417 (5.71), 513 (4.41), 547 (4.03), 590 (3.92), 649 (3.73). FAB–MS (*m*/*z*) for $C_{49}H_{35}N_5O_6$: found 790, calculated 789.85. Spectroscopic data for the acid derivative: ^{1}H NMR (DMSO-*d*): δ 13.30 (*s*, 3H), 9.07 (*d*, *J* = 4.8 Hz, 2H), 8.87 (*d*, *J* = 2 Hz, 6H), 8.47–8.25 (*m*, 16H), −2.97 (*s*, 2H). UV–vis (in THF, nm): λ_{max} (logε) 417 (5.65), 513 (4.30), 546 (3.84), 589 (3.60), 646 (3.14). FAB–MS (*m*/*z*) for $C_{46}H_{29}N_5O_6$: found 748, calculated 747.77. The carboxyphenylporphyrin was crystallized from a solution in dimethyl sulfoxide (by the solvothermal technique) as well as from a 4:1 mixture of THF and 4-acetylpyridine (by slow evaporation). The overall yield in both cases was within 5–10%. The content of the uncoordinated solvent in the two structures could not be reliably determined. Recently, the synthesis and isolation of a series of *meso*-(4-pyridyl)/(4-carboxyphenyl)porphyrins has been reported (Gianferrara *et al.*, 2007).

Compound (I)

Crystal data

$C_{46}H_{29}N_5O_6\cdot2.5C_2H_6OS$
M_r = 943.06
Monoclinic, *Cc*
a = 6.5978 (3) Å
b = 29.2458 (15) Å
c = 28.6630 (13) Å
β = 90.521 (2)°
V = 5530.5 (5) Å^3
Z = 4
Mo *K*α radiation
μ = 0.17 mm^{-1}
T = 110 (2) K
0.40 × 0.20 × 0.03 mm

Data collection

Nonius KappaCCD area-detector diffractometer
18496 measured reflections
11808 independent reflections
6211 reflections with $I > 2\sigma(I)$
R_{int} = 0.071

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.085
$wR(F^2)$ = 0.211
S = 1.06
11808 reflections
594 parameters
2 restraints
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.83 e Å^{-3}
$\Delta\rho_{min}$ = −0.31 e Å^{-3}
Absolute structure: Flack (1983), 5242 Friedel pairs
Flack parameter: 0.42 (12)

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

D—H···A	D—H	H···A	D···A	D—H···A
O56—H56···O59	0.84	1.78	2.565 (6)	154
O48—H48···O63	0.84	1.82	2.599 (5)	154
O39—H39···O63^{i}	0.84	1.79	2.624 (5)	169
C17—H17···N28^{ii}	0.95	2.55	3.387 (6)	147

Symmetry codes: (i) $x-1, -y+1, z-\frac{1}{2}$; (ii) $x+\frac{1}{2}, -y+\frac{3}{2}, z+\frac{1}{2}$.

Compound (II)

Crystal data

$C_{46}H_{29}N_5O_6\cdot 2C_7H_7NO\cdot 10C_4H_8O$
$M_r = 1711.05$
Triclinic, $P\overline{1}$
$a = 7.6005$ (3) Å
$b = 15.6609$ (10) Å
$c = 18.6149$ (12) Å
$\alpha = 77.718$ (3)°
$\beta = 89.630$ (4)°
$\gamma = 78.805$ (4)°
$V = 2122.4$ (2) Å^3
$Z = 1$
Mo $K\alpha$ radiation
$\mu = 0.09$ mm^{-1}
$T = 110$ (2) K
0.40 × 0.30 × 0.25 mm

Data collection

Nonius KappaCCD area-detector diffractometer
24317 measured reflections
10109 independent reflections
4725 reflections with $I > 2\sigma(I)$
$R_{int} = 0.060$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.052$
$wR(F^2) = 0.135$
$S = 0.80$
10109 reflections
669 parameters
8 restraints
H-atom parameters constrained
$\Delta\rho_{max} = 0.25$ e Å^{-3}
$\Delta\rho_{min} = -0.20$ e Å^{-3}

Table 2
Hydrogen-bond geometry (Å, °) for (II).

D—H···A	D—H	H···A	D···A	D—H···A
O39—H39···N69	0.84	1.82	2.653 (4)	172
O57—H57···N60	0.84	1.79	2.630 (5)	175
O48—H48···N28^{i}	0.84	1.77	2.596 (5)	167
C29—H29···O47^{ii}	0.95	2.68	3.273 (8)	121
C61—H61···O56	0.95	2.75	3.375 (7)	124
C70—H70···O38	0.95	2.61	3.221 (5)	123

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

Both crystals diffracted poorly, with a relatively low (<50%) percentage of observed intensities above the threshold of $2\sigma(I)$ within the 0–27.5° θ range. The crystal packing of the DMSO–porphyrin and acetylpyridine–porphyrin supramolecular arrays is associated in both cases with the formation of interporphyrin voids accessible to noncoordinated solvent molecules, which were found to be severely disordered in these voids. The noncoordinated solvent molecules could not be modeled by discrete atoms in either compound. Correspondingly, the contribution of the solvent to the diffraction pattern was subtracted using the SQUEEZE procedure of *PLATON* (Spek, 2003). In (I), these voids consist of about 27% percent of the crystal volume (1480 Å^3 per unit cell, equally distributed across four cavities). The residual electron-density count amounted to 68 e per unit cell, corresponding to nearly two molecules of DMSO (the content of each of the four cavities per unit cell being equivalent to one-half of a molecule of DMSO). Conventional least-squares refinement of the same solvent-excluded structural model against the original data set converged only at $R1 = 0.15$. Refinement calculations with the modified data converged at $R1 = 0.070$ for 5171 reflections with intensities above $3\sigma(I)$ and at $R1 = 0.085$ for 6211 reflections with intensities above the threshold of $2\sigma(I)$. The crystal structure of (I) represents a racemic twin in the space group *Cc*. The choice of the noncentrosymmetric space group was based on better intensity-statistics indicators, as well as on our inability to obtain and refine an alternative structure model in the space group *C*2/*c*. In (II), about 50% of the crystal volume comprises the solvent-accessible voids. The interporphyrin channels propagate parallel to the *a* axis of the crystal and appear to accommodate severely diffused molecules of the THF solvent. Conventional refinement of the ordered supramolecular fragments of the structure converged only at $R1 = 0.20$. The SQUEEZE procedure indicated that the single solvent-accessible void in the unit cell has a volume of 1051 Å^3 and that the residual electron-density count is 82 e per unit cell (which corresponds as a lower limit to at least two molecules of THF). This assessment seems to be very inaccurate, as independent thermogravimetric analysis indicated that on heating of this material about 42% weight loss occurs around 387 K, representing a markedly higher amount of the volatile THF solvent (about ten molecules per unit cell). As the crystals were out of the solvent for about the same time prior to the diffraction and thermogravimetric analysis experiments, the latter provided a better estimate of the actual solvent content. An additional 16% weight loss occurs around 422 K, which corresponds to the evaporation of the two molecules of the acetylpyridine component. Refinement calculations with the modified data converged smoothly at $R1 = 0.052$. Some orientational disorder of the aromatic substituents (that could not be reliably resolved) is also evident from the elongated atomic displacement parameters of the corresponding atoms. Assignment of the correct space group for this structure posed an additional problem. The distribution of the diffracted intensities suggested that the structure is centrosymmetric (space group $P\overline{1}$ with $Z = 1$), which would necessitate a twofold disorder of the porphyrin species associated with alternating orientations of the inter-porphyrin COOH···N hydrogen bond along the polymeric chain. Crystallographic refinement of the structural model in the space group $P1$ was characterized, however, by better convergence and a more coherent description of the hydrogen-bonding scheme, although the overall structure remains pseudocentrosymmetric. In the $P1$ model, the observed COOH(porphyrin)···N(porphyrin) hydrogen bond was found ordered and well defined, suggesting that the space group $P1$ represents the preferred choice for describing the supramolecular self-assembly in this structure.

All of the H atoms were placed in calculated positions and were constrained to ride on their parent atoms. For H atoms bound to C atoms, the C—H distances are in the range 0.95–0.98 Å, with U_{iso}(H) values set at $1.5U_{eq}$(C) for the methyl groups and at $1.2U_{eq}$(C) for other C-bound H atoms. For H atoms bound to O atoms, the O—H distances were set at 0.84 Å, with U_{iso}(H) values of $1.5U_{eq}$(O), and the positions of the H atoms were based on forming the 'best' hydrogen bond to a neighboring hydrogen-bond acceptor, *viz*. the O═S [in (I)] or pyridyl [in (II)] groups (Sheldrick, 1997). The two inner pyrrole H atoms bound to nitrogen could not be located in difference Fourier maps and were assumed to be disordered between the four N-atom sites in the two structures [N—H = 0.88 Å and U_{iso}(H) = $1.2U_{eq}$(N)]. In the refinement of (II), five bond-length restraints were applied to bonds C25—C30, C27—N28, C46—O48, C58—C63 and N69—C70.

For both compounds, data collection: *COLLECT* (Nonius, 1999); cell refinement: *DENZO* (Otwinowski & Minor, 1997); data reduction: *DENZO*; program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPIII* (Burnett & Johnson,

1996) and *Mercury* (Macrae *et al.*, 2006); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: LN3055). Services for accessing these data are described at the back of the journal.

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