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Supramolecular Assembly of Functionalized Metalloporphyrins. Porous Crystalline Networks of Zinc-Tetra(4-Carboxyphenyl)Porphyrin

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Two crystalline compounds based on the Zn-tetra(4-carboxyphenyl)porphyrin building block have been prepared and structurally analysed by x-ray diffraction in order to elucidate the characteristic supramolecular aggregation modes of this functionalized metalloporphyrin moiety. Crystals of the 1:1 complex with *sec*-phenethyl alcohol (**1**) are monoclinic, space group $I2/a$ (No. 15), $a = 14.420(1)$, $b = 24.678(2)$, $c = 33.688(2)$ Å, $\beta = 90.03(2)^\circ$, $D_c = 1.082$ g/cm³, $Z = 8$, $R = 0.080$ for 3053 data. Those of the 1:3 complex with dimethylsulphoxide (**2**) are monoclinic, space group $P2_1/n$ (No. 14), $a = 14.881(1)$, $b = 8.986(2)$, $c = 37.550(3)$ Å, $\beta = 94.21(1)^\circ$, $D_c = 1.444$ g/cm³, $Z = 4$, $R = 0.093$ for 4200 data. The two compounds consist of nearly square-pyramidal five-coordinate metalloporphyrin species, molecules of the *sec*-phenethyl alcohol (in **1**) and dimethylsulphoxide (in **2**) linking to the metal center at the axial site. In **2**, two additional molecules of dimethylsulphoxide associate through H-bonds to the terminal carboxylic substituents of the porphyrin framework. Incorporation of the carboxylic functionality into the tetraarylporphyrin unit leads to the formation of hollow hydrogen-bonded lattices in both crystals. Uniquely structured two-dimensional networks of the porphyrin building blocks with very large cavities (approximately 16×21 Å) are formed in **1**. These networks mutually interpenetrate each other in order to fill the empty voids, yielding a spectacular 'concatenated' arrangement.

One-dimensional polymeric patterns with smaller cavities (6.5×10 Å) are built in **2** by the interacting molecular components. In the condensed crystalline environment each such cavity is occupied by two dimethylsulphoxide molecules of adjacent chains. This study is part of an ongoing evaluation of the utility of functionalized metalloporphyrin building blocks in the designed construction of hollow lattices (with varying degree of rigidity and pore size) in molecular based solids. Correlation of current results to previous findings is also discussed.

INTRODUCTION

Rational design of molecular solids with specific properties is a challenging goal in modern molecular science, as such materials have diverse potential for scientific and technological applications. Within this context, assembly of the robust and chemically versatile metalloporphyrin and metallophthalocyanine building blocks into network structures or polymeric materials has drawn a considerable attention in recent years, in an effort to tailor crystalline solids with specific

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and useful electrical, optical, magnetic and chemical properties. Several different approaches turned out to be useful in the construction of structure-enforced assemblies of these metallo-macrocycles. Solid state condensation polymerization of the dihydroxy complex of planar metallophthalocyanine was found to be a particularly attractive pathway for the formation of electrically conductive crystalline rigid-rod polymers consisting of cofacially stacked molecular subunits.¹ Utilization of metal ions as chelating agents and of their coordination potential has led to successful self-assembly of two-dimensional and three-dimensional multiporphyrin arrays of pyridyl-substituted porphyrin molecules.^{2,3} This includes also formation of coordination polymers as well as of solids with large access channels of potential utility as microporous heterogeneous catalysts.^{4,5} Our own efforts over the last few years in crafting nanoporous lattices in molecular based solids are based on previous observations that the versatility of the tetraarylporphyrin compounds as crystalline hosts appears to be unequaled due to the large size, high symmetry, rigidity and thermal stability of the molecular framework.⁶ They focused on further exploration of the possible intermolecular architectures that can be designed from tetraarylporphyrin metallo-macrocycles by direct interaction, through non-covalent bonds, between the porphyrin building blocks. It has been demonstrated that a suitable functionalization of the rigid metalloporphyrin molecular framework with polarized aryl groups by deliberate synthesis can be used to affect in a pre-programmed way the spontaneous built-up of the porphyrin lattice by molecular recognition properties of the respective functional groups.⁷⁻¹⁰ Earlier preparative and crystallographic investigations in this laboratory have yielded several new classes of crystalline polymer-type aggregates, in which the functionalized porphyrin host units (by tetra-substitution of 4-hydroxyphenyl, 4-pyridyl and 4-halogenophenyl moieties on the metalloporphyrin core) are rigidly linked, through hydrogen bonds, metal-to-ligand coordination, and charge interactions into multidimensional porous polymeric patterns.⁷⁻¹⁰

The resulting nanostructures have a hollow cross-linked pseudo-rigid supramolecular architecture, readily incorporate guest components into the lattice, and thus provide novel types of potential solid state receptors for isolation, separation, transport, exchange and controlled release of molecular entities.

In order to study additional crystal engineering aspects of 'microporous' solids composed of tetraarylporphyrin building blocks, it was considered worthwhile to extend our interest to the tetra(4-carboxyphenyl)metalloporphyrin system, in which the COOH 'sensor' groups introduced in a symmetric manner into the tetraphenylporphyrin core might play an important role in steering the supramolecular architecture. Hydrogen bonding interactions are recognized as a powerful organizing force in molecular crystals,¹¹ as well as in self-assembling¹² and self-replicating processes,¹³ often leading to predictable architectures in the solid state as well as in solution. Most relevant to the present study is the typical intermolecular association in compounds containing the carboxylic function. Solids of monocarboxylic and dicarboxylic acids reveal the formation of cyclic dimeric and chain polymeric hydrogen-bond motifs, respectively.¹⁴ Planar trifunctional molecules such as benzene-1,3,5-tricarboxylic acid (trimesic acid) form porous two-dimensional nets of trimesic acid molecules held together by pairs of hydrogen bonds.¹⁵ Tetrahedral adamantane-tetracarboxylic acids are capable of forming hollow super-diamond architectures held together by pairwise H-bonds between the carboxylic groups.¹⁶ The solid structures in the latter examples consist of interpenetrating networks of the tri-acid and tetra-acid molecules, the formation of which is driven by the presence of large open spaces in the intermolecular organization directed by H-bonding. The square-shaped tetra-acid functionality of the title compound makes it a potentially excellent building block for the construction of a new class of microporous lattices. It has been anticipated that in environments lacking other

strong proton donors or proton acceptors the unique hydrogen-bonding potential of the COOH groups should dictate a formation of large, planar and rigid hollow networks by self-complementary H-bonded association. These lattices could serve as suitable "containers" for other molecular species. It has further been assumed that addition of a strong Lewis base to the crystallization mixture (e.g., dimethylsulphoxide which can simultaneously accept two protons) may influence the supramolecular organization by bridging between two carboxylic functions, and thus lead to networks of different dimensionality and pore size. Our continuous efforts over the last few years to generate from different environments crystalline inclusion solids based on the title host have been considerably less successful than with the other functionalized derivatives of the metalloporphyrin framework,⁷⁻¹⁰ although a similarly wide variety of solvents and potential guest components was applied. A rather small number of new compounds based on the tetra-acid porphyrin have been obtained thus far, and the supramolecular organization in only two of them could be reasonably well analysed by X-ray diffraction (although still with a considerable difficulty due to the large unit cell volumes, disorder of the included solvent and poorly diffracting crystals). In view of the potentially useful implications of the available results, we report here the first structural characterization of crystalline adducts of zinc-tetra(4-carboxyphenyl)porphyrin with racemic *sec*-phenethyl alcohol (DL- α -methylbenzyl alcohol, **1**) and with dimethylsulphoxide (**2**), relating to the unique interporphyrin architectures that are formed in these materials.

EXPERIMENTAL

Materials

The title compound (m.p. > 350°C) was obtained commercially from MidCentury Chemicals,

Posen, Illinois—standard literature methods for the preparation of tetraphenylporphyrin compounds are given in reference 17. Its crystalline complexes with dimethylsulphoxide, *sec*-phenethyl alcohol and benzyl alcohol were obtained by very slow recrystallization (over several weeks) from saturated solutions of the respective guest solvents; only very small crystals of **1** could be grown. Crystals of the benzyl alcohol adduct were characterized by a very broad mosaicity, and were not suitable for crystallographic analysis. Single crystals of the pure host could not be obtained.

Structure Determination

The analysed crystals of the inclusion compounds **1** and **2** were covered by an epoxy resin in order to avoid their possible deterioration during the diffraction experiments. Diffraction data were collected at room temperature on automated Picker (**1**) and CAD4 (**2**) diffractometers equipped with a graphite monochromator. Intensity data were collected by the ω -2 θ scan mode out to $2\theta_{\max} = 46^\circ$, using MoK α ($\lambda = 0.7107 \text{ \AA}$) radiation and a narrow scan range to avoid overlap between adjacent peaks in the diffraction pattern. Three standard reflections from different zones of the reciprocal space were measured periodically with no significant variation. No corrections for absorption and secondary extinction effects were applied; attempts to introduce empirical absorption corrections of the data sets did not improve the quality of the results. The structures were solved by direct methods using SHELXS-86,¹⁸ and then refined by least-squares using the SHELX-76 (**1**) and SHELXL-93 (**2**) programs.¹⁹ As in related studies of analogous materials, the precision of the detailed crystallographic determination is somewhat reduced by poor quality of the diffraction data resulting from the apparent structural disorder of the ligand/solvate species. The refinement calculations were based on F in structure **1** (analysed several years ago) and on F^2 in struc-

ture 2. The hydrogen atoms were introduced in calculated positions with isotropic U , the methyls being treated as rigid groups. Low number of 'observed' reflections and guest disorder required application of geometric constraints (the phenyl groups were usually treated as rigid hexagons) and restraints in the refinement calculations in order to facilitate convergence and prevent unreasonable distortion of the molecular structure of the disordered fragments. Nevertheless, the refinements converged at reasonably low R -values, allowing a reliable description of the atomic parameters and of the intermolecular organization and interaction scheme. The 1:3 porphyrin-DMSO composition of compound 2 was confirmed by thermal analysis (Figure 1). The DMSO ligand, which coordinates through the O-site to the metal center of the porphyrin, exhibits an orientational disorder about the axial Zn-O bond. This disorder could not be fully accounted for, and the final difference-Fourier map showed three relatively high residual peaks ($\leq 1.18 \text{ e}\text{\AA}^{-3}$) in the immediate vicinity of the S-atom of this species. Compound 1 consists of 1:1 five-coordinate complex of the porphyrin

with *sec*-phenethyl alcohol and some additional disordered solvent randomly distributed in the voids of the crystal lattice (most probably another molecule of phenethyl alcohol or a few molecules of water). The actual content of the latter could not be reliably determined either by the crystallographic refinement (no recognizable solvent fragments could be identified in the difference maps), or by thermal analyses (lacking sufficient amount of pure crystalline material). An effort was made to localize the molecules of the disordered solvent in 1 by collecting an additional set of diffraction data at low temperature (about -170°C), but it turned out to be unsuccessful and did not improve the structural results. Desorption of the phenethyl alcohol guest from 1 upon heating destabilizes the porphyrin lattice, yielding a polycrystalline material of unknown phase composition. Additional details of the routinely applied experimental procedures are reported in previous publications of this series.⁷⁻¹⁰

The crystal data and pertinent details of the experimental conditions for compounds 1 and 2 are summarized in Table I, and lists of the corre-

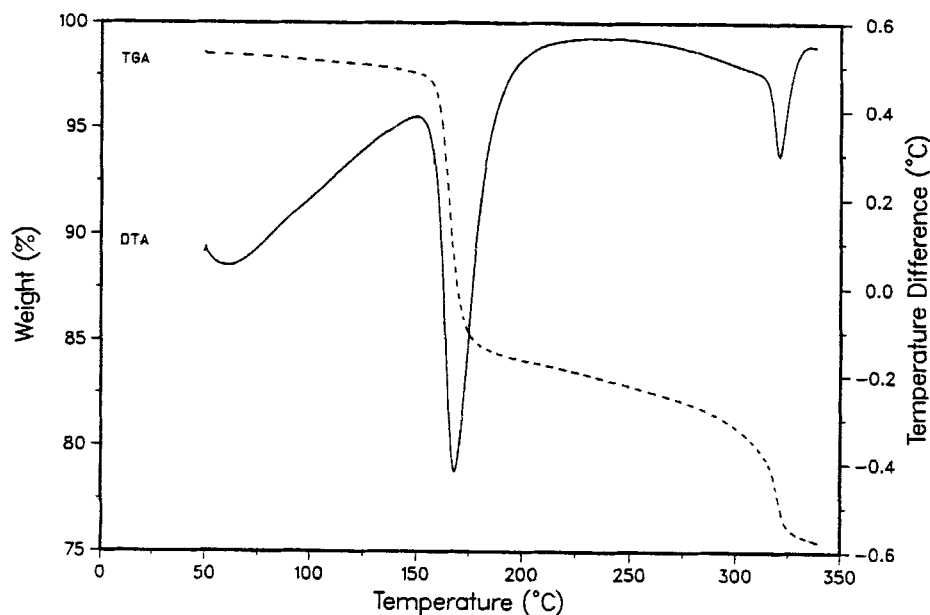


FIGURE 1 Thermal analysis data, TGA (dashed line) and DTA (heavy line), for 2. The onset temperatures of the two-step decomposition process are 159.2°C and 316.1°C . The observed TG weight loss during this process is 21.3% vs. the calculated value of 22.3% for a 1:3 composition of the porphyrin-DMSO complex.

TABLE I Summary of crystal data and experimental parameters for **1** and **2**

Compound	1	2
Formula	C ₄₈ H ₂₈ N ₄ O ₈ Zn· (C ₈ H ₁₀ O) ^a	C ₄₈ H ₂₈ N ₄ O ₈ Zn· (C ₂ H ₆ SO) ₃
F.W.	976.3	1088.5
Space group	I2/a (No. 15) ^b	P2 ₁ /n (No. 14)
Z	8	4
a, Å	14.420(1)	14.881(1)
b, Å	24.678(2)	8.986(2)
c, Å	33.688(2)	37.550(3)
α, deg	90.0	90.0
β, deg	90.03(2)	94.21(1)
γ, deg	90.0	90.0
V, Å ³	11988(2)	5008(1)
D _c , g cm ⁻³	1.082	1.444
F(000)	4032	2256
μ, cm ⁻¹	4.60	6.85
N (unique) > 0	6374	5984
N (observed) ^c	3053	4200
R _F (observed)	0.080	0.093
G.o.f.	2.08	1.35
Δρ _{max}	0.69	1.18

^aThe crystals of **1** include additional molecule(s) of disordered solvent (possibly another molecule of phenethyl alcohol or molecules of water) which could not be reliably identified. If a 1:2 porphyrin-phenethyl alcohol composition is assumed the calculated density becomes 1.217 g·cm⁻³ [F.W. = 1098.5, F(000) = 4032].

^bThe conventional space group of **1** is C2/c. We made the unconventional choice I2/a, instead, in order obtain a β-angle close to 90°, and thus minimize the correlation factors in the crystallographic refinement of the atomic parameters.

^c[I > 3σ(I)] for **1**, and [I > 2σ(I)] for **2**.

sponding fractional atomic coordinates are given in Tables II and III. The atom labeling scheme used for the metalloporphyrin framework is depicted in Figure 2. Lists of the structures factors, anisotropic thermal displacement coefficients of the nonhydrogen atoms, atomic coordinates of the hydrogen atoms, as well as of bond lengths and bond angles, have been deposited as supplementary material.

Thermal Analysis

Thermogravimetry (TGA) and differential analysis (DTA) of **2** were performed using TA Instruments module 910 and system controller 2100. Before analysis, crystals were removed from their mother liquor, blotted dry on filter paper,

and crushed. Sample weight 7.4 mg. A constant stream of argon (flow rate 55 mL per minute) was passed over the sample. The temperature range was 30–340°C at a heating rate of 10°C/min.

RESULTS

Molecular Structures

The Zn(II) complex of tetra(4-carboxyphenyl)porphyrin contains several potential ligating sites available for interporphyrin self-assembly or for association with other species. The 4-coordinate zinc, located in the center of the porphyrin core, can bind additional ligands at the axial sites above and below the molecular framework. Moreover, the peripherally oriented carboxylic groups also serve as effective recognition sites for binding to other entities with complementary functionality. Structures **1** and **2** are based on five-coordinate complexes of the metalloporphyrin, in which either the *sec*-phenethyl alcohol or the dimethylsulphoxide occupy the axial coordination site of the metal center and ligate to it through their O-nucleophile (Figure 3). The corresponding Zn-O distances are 2.217(15) Å in **1** and 2.133(5) Å in **2**, in accord with previous observations in related five-coordinate complexes of zinc-tetraarylporphyrins that >S=O nucleophiles form shorter bonds to the zinc than the OH group.¹⁰ The Zn-N equatorial coordination distances within the porphyrin core are within the normal range of 2.027(14)–2.072(14) Å in **1** and 2.056(5)–2.076(5) Å in **2**, and the respective deviations of the metal center from the mean plane of the pyrrole N-atoms towards the axial ligands are 0.236(1) and 0.309(1) Å. The porphyrin plane is slightly ruffled in the two structures, several atoms deviating from planarity of the porphyrinato ring by ≤0.17 Å in each case. These results conform well to previously reported experimental observations for differently substituted porphyrins,^{7–10} as well as to computa-

TABLE II Fractional atomic coordinates and thermal parameters for **1**

atom	x/a	y/b	z/c	$U_{eq}(\text{\AA}^2)$
N1	0.2406(11)	0.0724(6)	0.1252(4)	0.041(6)
N2	0.1539(10)	0.1374(6)	0.1864(3)	0.032(5)
N3	0.2388(10)	0.0717(6)	0.2458(4)	0.036(5)
N4	0.3195(10)	0.0023(6)	0.1863(4)	0.036(6)
C5	0.3521(14)	-0.0237(8)	0.1537(5)	0.043(8)
C6	0.3369(14)	-0.0097(8)	0.1139(5)	0.046(8)
C7	0.2870(14)	0.0356(8)	0.1008(5)	0.046(8)
C8	0.2694(16)	0.0504(9)	0.0606(5)	0.055(9)
C9	0.2177(16)	0.0952(11)	0.0603(5)	0.062(11)
C10	0.2004(14)	0.1097(8)	0.1013(5)	0.041(8)
C11	0.1453(14)	0.1541(8)	0.1137(5)	0.041(7)
C12	0.1276(13)	0.1675(8)	0.1529(5)	0.037(8)
C13	0.0780(15)	0.2140(8)	0.1664(6)	0.052(9)
C14	0.0788(14)	0.2145(8)	0.2072(5)	0.049(8)
C15	0.1281(13)	0.1674(7)	0.2192(5)	0.038(7)
C16	0.1502(13)	0.1551(7)	0.2580(5)	0.037(7)
C17	0.2023(15)	0.1105(9)	0.2697(5)	0.047(9)
C18	0.2248(16)	0.0987(9)	0.3105(5)	0.054(9)
C19	0.2740(17)	0.0539(9)	0.3104(5)	0.060(9)
C20	0.2846(14)	0.0351(7)	0.2698(5)	0.040(8)
C21	0.3357(14)	-0.0090(7)	0.2572(5)	0.043(7)
C22	0.3522(13)	-0.0246(8)	0.2178(5)	0.038(8)
C23	0.4067(13)	-0.0703(8)	0.2057(5)	0.044(8)
C24	0.4059(13)	-0.0701(8)	0.1660(5)	0.050(8)
C25	0.3726(16)	-0.0434(8)	0.0810(5)	0.047(8)
C26	0.4545(17)	-0.0311(8)	0.0634(6)	0.059(10)
C27	0.4845(15)	-0.0596(10)	0.0307(6)	0.064(10)
C28	0.4296(16)	-0.0985(10)	0.0144(6)	0.056(10)
C29	0.3492(17)	-0.1123(10)	0.0324(7)	0.069(11)
C30	0.3187(15)	-0.0850(11)	0.0664(6)	0.070(11)
C31	0.4569(22)	-0.1273(11)	-0.0239(7)	0.071(12)
O32	0.5366(14)	-0.1207(7)	-0.0359(5)	0.095(9)
O33	0.3986(12)	-0.1577(8)	-0.0402(4)	0.092(9)
C34	0.1147(16)	0.1931(8)	0.0826(5)	0.045(8)
C35	0.1773(16)	0.2251(11)	0.0632(7)	0.087(12)
C36	0.1532(20)	0.2590(14)	0.0341(8)	0.116(16)
C37	0.0630(23)	0.2620(10)	0.0228(6)	0.075(12)
C38	-0.0037(18)	0.2326(10)	0.0425(7)	0.072(11)
C39	0.0223(16)	0.1981(9)	0.0729(5)	0.060(9)
C40	0.0335(25)	0.2960(13)	-0.0131(9)	0.103(16)
O41	-0.0523(16)	0.2964(9)	-0.0220(5)	0.128(12)
O42	0.0936(16)	0.3214(10)	-0.0321(6)	0.134(11)
C43	0.1180(16)	0.1931(8)	0.2893(5)	0.048(9)
C44	0.1809(15)	0.2259(9)	0.3095(6)	0.055(9)
C45	0.1524(16)	0.2590(8)	0.3400(6)	0.056(9)
C46	0.0589(16)	0.2610(8)	0.3507(6)	0.050(9)
C47	-0.0040(16)	0.2311(10)	0.3304(6)	0.063(9)
C48	0.0256(16)	0.1989(9)	0.2996(6)	0.054(10)
C49	0.0299(19)	0.2945(9)	0.3858(6)	0.054(9)
O50	-0.0523(13)	0.2936(7)	0.3959(5)	0.090(9)
O51	0.0894(12)	0.3238(7)	0.4023(4)	0.087(8)
C52	0.3719(17)	-0.0432(8)	0.2906(5)	0.051(9)
C53	0.4624(17)	-0.0386(10)	0.3046(6)	0.072(10)

atom	x/a	y/b	z/c	$U_{eq}(\text{\AA}^2)$
C54	0.4936(17)	-0.0640(12)	0.3380(6)	0.076(11)
C55	0.4351(22)	-0.0981(11)	0.3584(7)	0.073(11)
C56	0.3451(22)	-0.1063(11)	0.3449(8)	0.094(13)
C57	0.3149(18)	-0.0782(11)	0.3104(7)	0.086(12)
C58	0.4645(28)	-0.1265(12)	0.3957(8)	0.091(15)
O59	0.5473(15)	-0.1225(8)	0.4059(5)	0.109(10)
O60	0.4044(17)	-0.1519(10)	0.4137(6)	0.132(12)
Zn61	0.2249(1)	0.0653(1)	0.1861(1)	0.037(1)
O62	0.1040(10)	0.0098(6)	0.1869(4)	0.063(6)
C63	0.1018(22)	-0.0462(13)	0.1786(9)	0.100(14)
C64	0.0529(23)	-0.0803(10)	0.2106(8)	0.087(13)
C65	-0.0222(24)	-0.1118(13)	0.2055(8)	0.095(15)
C66	-0.0585(22)	-0.1392(11)	0.2375(13)	0.106(16)
C67	-0.0193(38)	-0.1333(16)	0.2738(11)	0.134(23)
C68	0.0502(34)	-0.1028(18)	0.2795(13)	0.155(24)
C69	0.0889(22)	-0.0749(13)	0.2474(11)	0.109(17)
C70	0.0908(29)	-0.0632(16)	0.1381(11)	0.165(23)
X71	0.7292(137)	0.2378(70)	0.2381(54)	0.230(70)
X72	0.7642(81)	0.2317(47)	0.2171(37)	0.159(49)
X73	0.7946(57)	0.2430(36)	0.1299(25)	0.170(34)
X74	0.7770(46)	0.2225(26)	0.1764(21)	0.143(22)

U_{eq} is one third of the trace of the orthogonalized U_{ij} tensor. Atoms O62 through C70 represent the *sec*-phenethyl alcohol ligand. The coordinates of X71 through X74 are peaks apparent in difference-Fourier maps with heights between 1.2 e\AA^{-3} and 1.8 e\AA^{-3} . They were included in structure factor calculations as C-atoms with isotropic U and an occupancy factor of 0.5, as a partial representation of the disordered solvent. No recognizable solvent fragments could be, however, identified.

tional and experimental findings for unsubstituted tetraphenylmetalloporphyrins.^{20,21} The porphyrin molecules in the two structures differ significantly in the orientation of the peripheral phenyl substituents. In **1** the four phenyl rings are almost perpendicular to the porphyrin core, the dihedral angles between their planes and the mean plane of the central porphyrinato moiety ranging from 71.6(5) to 108.0(6)°. On the other hand, in **2** the phenyl groups deviate from a perpendicular orientation with respect to the central macroring by 31.6(1)–35.4(1)°. This twisting of the aryl rings represents, if fact, the softest mode of conformational freedom in the tetraarylporphyrin compounds. In both structures, each one of the carboxylic substituents is nearly coplanar with the phenyl ring to which it is bound. The corresponding torsion angles defining the conformation of the carboxylic groups with respect to the phenyl rings range from 4° to 14°. The

TABLE III Fractional atomic coordinates and thermal parameters of **2**

atom	x/a	y/b	z/c	$U_{eq}(\text{\AA}^2)$
N1	0.5105(3)	0.5214(6)	0.3026(1)	0.0420(20)
N2	0.3884(3)	0.4184(6)	0.2440(1)	0.0405(20)
N3	0.5167(3)	0.5064(6)	0.1941(1)	0.0388(19)
N4	0.6398(3)	0.6075(7)	0.2523(1)	0.0381(19)
C5	0.6862(4)	0.6584(7)	0.2832(1)	0.0370(23)
C6	0.6603(4)	0.6335(8)	0.3180(1)	0.0428(25)
C7	0.5779(4)	0.5741(8)	0.3265(1)	0.0426(25)
C8	0.5486(4)	0.5590(9)	0.3622(1)	0.0510(27)
C9	0.4656(5)	0.5003(8)	0.3590(1)	0.0515(31)
C10	0.4420(4)	0.4727(8)	0.3221(1)	0.0416(26)
C11	0.3629(4)	0.4054(8)	0.3084(1)	0.0384(23)
C12	0.3411(4)	0.3741(8)	0.2724(1)	0.0390(25)
C13	0.2663(4)	0.2801(9)	0.2580(2)	0.0522(30)
C14	0.2680(4)	0.2761(8)	0.2223(2)	0.0472(26)
C15	0.3447(4)	0.3638(8)	0.2133(1)	0.0409(25)
C16	0.3708(4)	0.3837(8)	0.1786(1)	0.0413(24)
C17	0.4516(4)	0.4507(8)	0.1699(1)	0.0419(24)
C18	0.4797(4)	0.4657(8)	0.1341(1)	0.0491(26)
C19	0.5612(4)	0.5306(8)	0.1372(1)	0.0486(26)
C20	0.5861(4)	0.5581(8)	0.1744(1)	0.0408(25)
C21	0.6657(4)	0.6256(7)	0.1884(1)	0.0370(21)
C22	0.6878(4)	0.6547(8)	0.2245(1)	0.0402(26)
C23	0.7647(4)	0.7422(8)	0.2387(2)	0.0442(26)
C24	0.7643(4)	0.7422(8)	0.2739(1)	0.0435(27)
C25	0.7281(2)	0.6753(4)	0.3482(1)	0.0440(25)
C26	0.8114(2)	0.6049(5)	0.3494(1)	0.0497(28)
C27	0.8748(2)	0.6317(6)	0.3777(1)	0.0592(32)
C28	0.8549(2)	0.7289(6)	0.4048(1)	0.0525(29)
C29	0.7715(3)	0.7993(5)	0.4036(1)	0.0522(29)
C30	0.7081(2)	0.7725(5)	0.3753(1)	0.0556(30)
C31	0.9248(5)	0.7469(10)	0.4357(2)	0.0634(34)
O32	0.8956(4)	0.8268(8)	0.4616(1)	0.0930(30)
O33	0.9998(4)	0.6956(8)	0.4361(1)	0.0915(32)
C34	0.2940(2)	0.3568(5)	0.3340(1)	0.0497(30)
C35	0.3177(2)	0.2677(5)	0.3635(1)	0.0611(31)
C36	0.2541(3)	0.2334(6)	0.3876(1)	0.0674(33)
C37	0.1668(3)	0.2881(6)	0.3821(1)	0.0709(33)
C38	0.1431(2)	0.3771(6)	0.3527(1)	0.0713(34)
C39	0.2067(2)	0.4115(5)	0.3286(1)	0.0606(31)
C40	0.0952(6)	0.2722(12)	0.4097(2)	0.0808(41)
O41	0.1266(5)	0.1883(9)	0.4351(1)	0.1065(36)
O42	0.0234(4)	0.3282(8)	0.4060(2)	0.1025(30)
C43	0.3076(2)	0.3314(5)	0.1481(1)	0.0487(28)
C44	0.2203(3)	0.3867(5)	0.1439(1)	0.0666(33)
C45	0.1629(2)	0.3410(7)	0.1151(1)	0.0868(41)
C46	0.1928(4)	0.2398(7)	0.0906(1)	0.0848(40)
C47	0.2801(4)	0.1845(6)	0.0948(1)	0.0806(36)
C48	0.3376(3)	0.2302(5)	0.1236(1)	0.0688(37)
C49	0.1374(7)	0.1894(13)	0.0553(2)	0.0973(44)
O50	0.0582(5)	0.2289(10)	0.0579(2)	0.1291(41)
O51	0.1719(5)	0.1306(10)	0.0316(2)	0.1336(39)
C52	0.7344(2)	0.6658(4)	0.1623(1)	0.0409(24)
C53	0.7117(2)	0.7564(5)	0.1329(1)	0.0492(28)

atom	x/a	y/b	z/c	$U_{eq}(\text{\AA}^2)$
C54	0.7740(3)	0.7824(5)	0.1078(1)	0.0545(31)
C55	0.8590(2)	0.7178(6)	0.1120(1)	0.0535(29)
C56	0.8817(2)	0.6273(6)	0.1413(1)	0.0556(30)
C57	0.8194(2)	0.6013(5)	0.1664(1)	0.0549(28)
C58	0.9261(5)	0.7309(11)	0.0844(2)	0.0685(36)
O59	0.8978(4)	0.8210(8)	0.0579(1)	0.0919(31)
O60	0.9970(3)	0.6694(8)	0.0861(1)	0.0851(26)
Zn61	0.5052(1)	0.5447(1)	0.2476(1)	0.0388(3)
S62	0.5140(1)	0.8968(3)	0.2591(1)	0.0576(8)
S62*	0.4405(12)	0.9117(23)	0.2446(4)	0.0969(63)
O63	0.4563(3)	0.7677(5)	0.2438(1)	0.0606(19)
C64	0.5241(9)	1.0155(18)	0.2249(4)	0.1554(56)
C65	0.4471(8)	1.0009(16)	0.2845(3)	0.1375(50)
S66	-0.1142(1)	0.2200(3)	-0.0214(1)	0.0855(10)
O67	-0.0188(3)	0.1848(8)	-0.0094(1)	0.0838(26)
C68	-0.1734(7)	0.1669(15)	0.0155(3)	0.1278(64)
C69	-0.1234(8)	0.4029(14)	-0.0183(3)	0.1501(77)
S70	0.6031(1)	0.7051(3)	0.0297(1)	0.0933(12)
O71	0.5073(3)	0.6686(8)	0.0198(1)	0.0893(27)
C72	0.6632(6)	0.6428(13)	-0.0050(3)	0.1120(59)
C73	0.6121(6)	0.8835(13)	0.0213(3)	0.1141(55)

U_{eq} is one third of the trace of the orthogonalized U_{ij} tensor. Atoms S62 through C65 represent the zinc coordinated orientationally disordered DMSO ligand; S62, S62*, C64 and C65 were assigned isotropic U . The S62 site with refined occupancy of 0.85(6) and the S62* site with occupancy of 0.15 represent two of the most probable positions of the sulphur atom. Atoms S66 through C69 and S70 through C73 represent two other DMSO species which are hydrogen bonded to the peripheral carboxy groups of the metalloporphyrin.

asymmetric unit in **2** contains two additional DMSO species, strongly linking to the carboxyphenyl arms through hydrogen bonds (Figure 3, Table IV).

Supramolecular Assembly into Porous Networks

The tetra(carboxyphenyl)porphyrin moieties in **1** are interlinked by pairwise hydrogen bonds between the terminal carboxylic functions, as shown in Figure 4a. Each molecule is H-bound to four neighboring species approaching along the equatorial directions of the molecular plane. This leads to the formation of a large central cavity of a rhombal shape (the approximate van der Waals dimensions of which are 18 Å along the edge, and 16 Å and 21 Å along the two diagonals), and yields a unique two-dimensional hy-

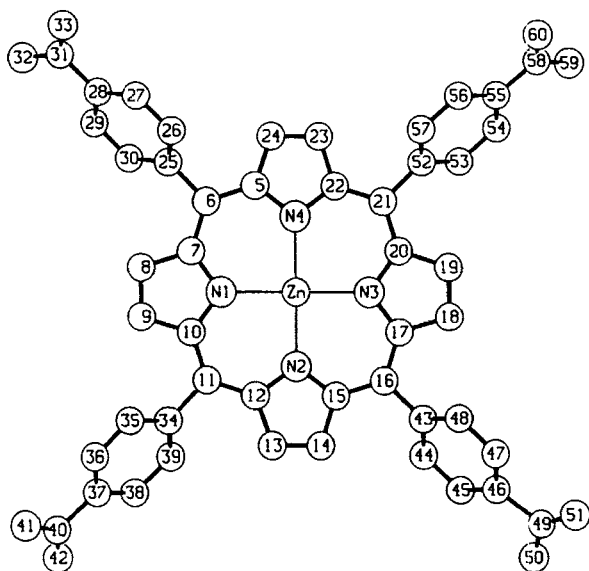


FIGURE 2 The atom labeling scheme used for Zn-tetra(4-carboxyphenyl)porphyrin.

drogen-bonded supramolecular network of the metalloporphyrin species. This network consists of molecules related to each other by transla-

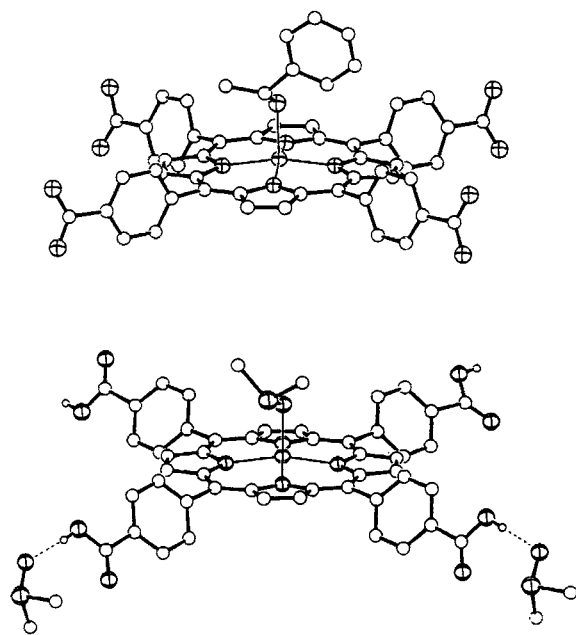


FIGURE 3 Perspective views of the molecular structures of: (top) compound **1** and (bottom) compound **2**. The N, O, S and Zn atoms are marked by crossed circles, and the hydrogen bonds in **2** are indicated by dashed lines.

TABLE IV Geometries of the hydrogen bonds in **1** and **2**

DH...A (symmetry code)	D...A (Å) ^a	H...A (Å) ^b	D-H...A (°) ^c
Compound 1			
O32...O51 ($x+\frac{1}{2}, y-\frac{1}{2}, z-\frac{1}{2}$)	2.60(2)	—	180
O33...O50 ($x+\frac{1}{2}, y-\frac{1}{2}, z-\frac{1}{2}$)	2.56(2)	—	180
O41...O60 ($x-\frac{1}{2}, y+\frac{1}{2}, z-\frac{1}{2}$)	2.59(3)	—	180
O42...O59 ($x-\frac{1}{2}, y+\frac{1}{2}, z-\frac{1}{2}$)	2.59(3)	—	180
O50...O33 ($x-\frac{1}{2}, y+\frac{1}{2}, z+\frac{1}{2}$)	2.56(2)	—	180
O51...O32 ($x-\frac{1}{2}, y+\frac{1}{2}, z+\frac{1}{2}$)	2.60(2)	—	180
O59...O42 ($x+\frac{1}{2}, y-\frac{1}{2}, z+\frac{1}{2}$)	2.59(3)	—	180
O60...O41 ($x+\frac{1}{2}, y-\frac{1}{2}, z+\frac{1}{2}$)	2.59(3)	—	180
Compound 2			
O32...O71 ($x+\frac{1}{2}, \frac{1}{2}-y, z+\frac{1}{2}$)	2.644(8)	1.72	167.3(5)
O41...O71 ($\frac{1}{2}-x, y-\frac{1}{2}, \frac{1}{2}-z$)	2.71(1)	1.78	173.1(5)
O50...O67 (x, y, z)	2.72(1)	1.81	164.2(6)
O59...O67 ($1-x, 1-y, -z$)	2.652(8)	1.72	173.5(5)

^aIt should be kept in mind that the observed values in **1** are affected by the orientational disorder of the carboxylic groups in this structure.

^bWith O-H bond lengths normalized to 0.938 Å.²⁴

^cThe O-H...O hydrogen bonds within the dicarboxylic pair are assumed to be linear.

tional symmetry (unit-cell and cell-centering displacements). At every H-bonding site, the carboxy groups are orientationally disordered. This is evident from the nearly equal C-O bond lengths (within 1.23–1.25 Å or 1.25–1.27 Å) observed in each group. Correspondingly, the positions of the H-atoms could not be defined. The hydrogen bonds appear to be quite strong as evidenced by the relatively short O...O distances between the interacting functions, ranging from 2.565 Å to 2.606 Å, which reflects on the rigidity of the interporphyrin network.

A different intermolecular architecture is characteristic to structure **2**. The metalloporphyrin units assemble here in one-dimensional arrays, linking to each other through the small DMSO bridges (Figure 5). The >S=O function of the bridging solvent molecules serves as an acceptor for the protons of two carboxyl groups of adjacent porphyrins approaching from opposite sides. Two molecules of DMSO are needed to bridge between the *cis*-related carboxyphenyl arms of two porphyrin molecules. The O-H...O=S hydrogen bonds thus formed are nearly linear with OH...O distances ranging

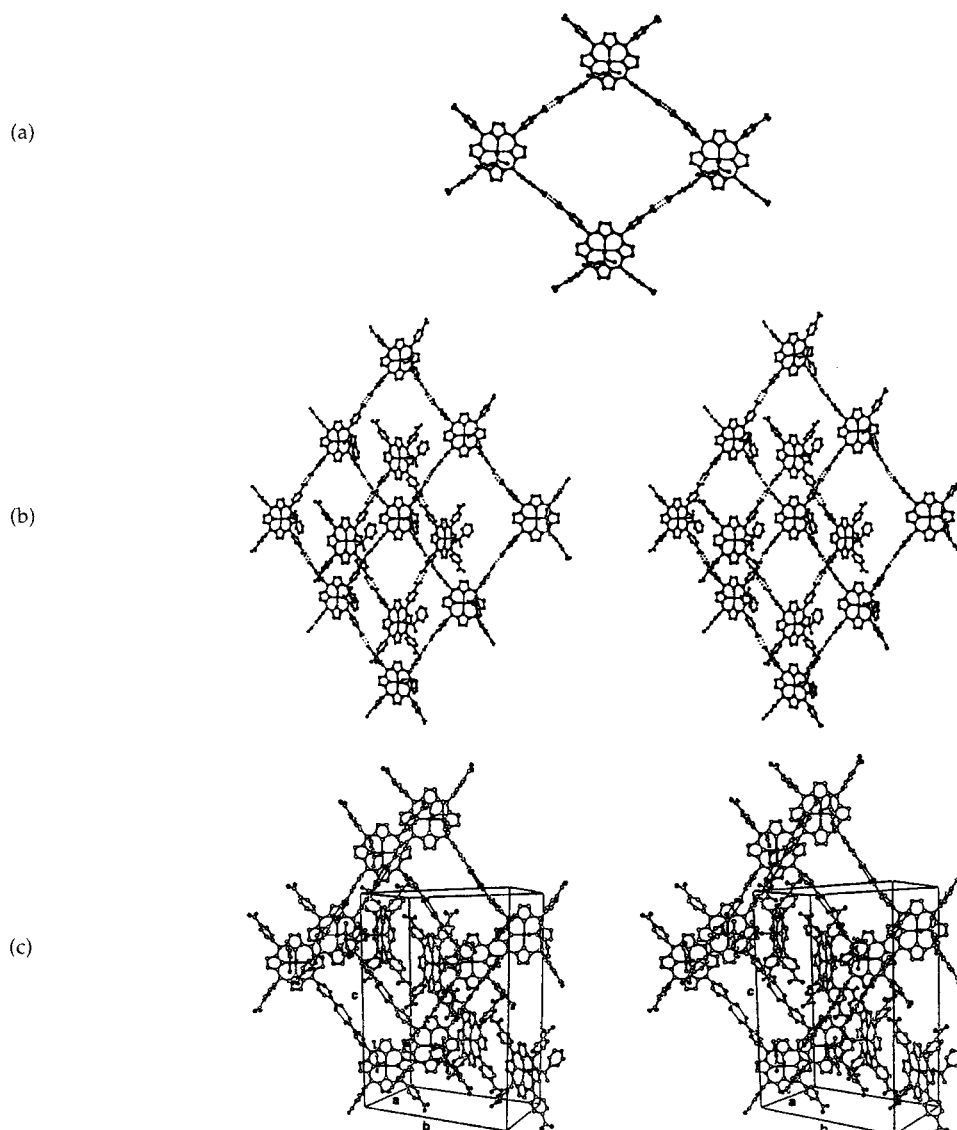


FIGURE 4 Illustration of the intermolecular arrangement in **1**. (a) The basic motif of the interporphyrin self-assembly through hydrogen bonding between the carboxylic groups. Note the large cavities associated with the formation of this pattern. (b) Stereoview of the two-dimensional metalloporphyrin lattices formed in this structure, and the interlocking mode between them. (c) Stereoview of the crystal packing showing the relative disposition of the four symmetry equivalent networks in the lattice.

from 2.644 to 2.727 Å. The basic structural motif thus consists of linear chains of nearly coplanar porphyrin species in which the COOH-ends of the *cis*-related carboxyphenyl arms of one molecule link through sulphoxide bridges to the peripheral COOH sites of adjacent molecules in the chain. This extended motif of hydrogen bonded moieties, although considerably different from

that observed in **1**, has also a hollow structure. The intermolecular cavities along the chain have an elliptical shape with van der Waals dimensions of about 6.5×10 Å. In this compound the C-O and C=O single and double bonds of the carboxylic residues are clearly distinguishable by the observed bond lengths, indicating an ordered arrangement. The carbonyl groups are ori-

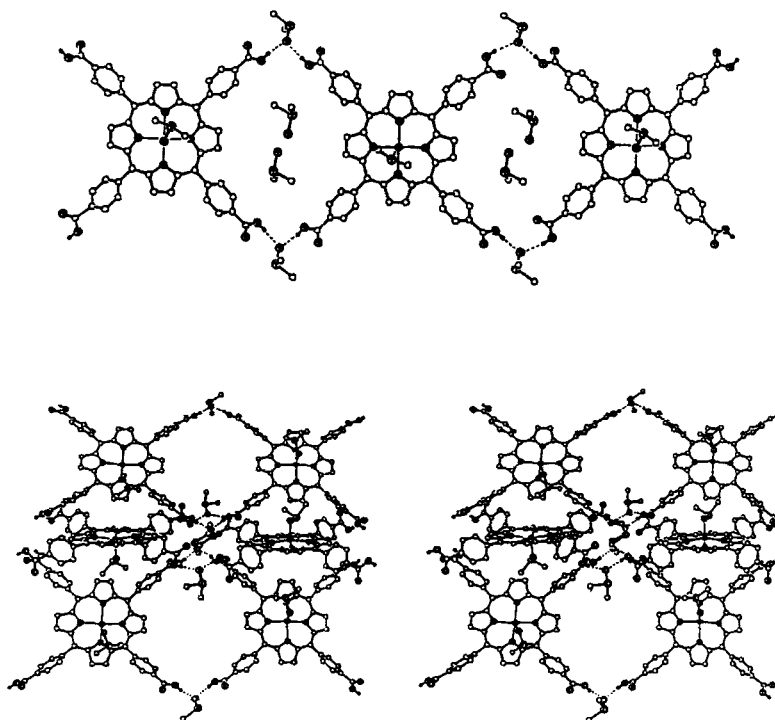


FIGURE 5 Structural features of crystalline **2**. (Top) The porous one-dimensional chain motifs consisting of H-bonded (dashed lines) metalloporphyrin and DMSO species. The latter bridge effectively between carboxyl substituents of successive porphyrins along the chain. The DMSO molecules accommodated within the elliptically shaped cavities belong to neighboring chain motifs which approach from both sides in a nearly perpendicular fashion, as shown below. (Bottom) Stereoview of the intermolecular arrangement, showing fragments of three adjacent hydrogen-bonded chains and the effective fit between them.

ented perpendicularly to the plane of the polymeric arrays, and are not involved in hydrogen bonding. Geometries of the hydrogen bonds in the 'polymeric' lattices of **1** and **2** are detailed in Table IV.

Three-Dimensional Architecture

The three-dimensional arrangement of the metalloporphyrin networks in **1** deserves a particular attention. In the absence of a sufficiently sizeable guest component which could fill effectively the interporphyrin voids, the two-dimensional networks formed by the five-coordinate molecular entities interlock into one another during the crystallization process. The unique crystal structure of this material is depicted in Figure 4. It consists of four equivalent layers related to each other by the crystallographic symmetry, their normals pointing ap-

proximately at either the $\mathbf{a}+\mathbf{b}$ or $\mathbf{a}-\mathbf{b}$ directions of the crystal. Networks related by inversion extend through the crystal in the same direction in an overlapping manner. Layers related by the glide symmetry are roughly perpendicular to one another (the dihedral angle between the two sets of planes is about 70°). The four two-dimensional lattices mutually interpenetrate each other in such a way that any interporphyrin pore in one set of parallel layers is accommodated by two metalloporphyrin species of the glide-related arrays. Clearly, this is facilitated by a distortion of the interporphyrin cavities from an idealized square shape in a constraint-free environment to a rhombal form in this structure, which allows enclosure of the large porphyrin framework within such cavity parallel to the long diagonal. Moreover, in the resulting arrangement the aromatic axial ligand of one layer lies roughly parallel, and in close proximity, to

the 'back side' of the porphyrin framework of another layer, thus possibly providing additional π - π stabilization^{22,23} to the interlocked structure (Figure 4c). The phenyl ring of the ligand is slightly inclined, by about 20°, with respect to the overlapped porphyrin core, its carbon atoms approaching the porphyrin plane at distances varying from 3.3 to 4.1 Å. The calculated density for the above described lattice is still relatively low, 1.08 g.cm⁻³, in comparison with related metalloporphyrin crystals, explaining the apparent inclusion of additional solvent in this structure (see above, Table I). Careful inspection of the overall packing confirms, in fact, the presence of narrow channels extending between, and parallel to, the interlocked porphyrin arrays along the *c* axis of the crystal at about $\frac{3}{4}$, $\frac{1}{4}$, *z* and $\frac{1}{4}$, $\frac{3}{4}$, *z*. The Zn-ligated molecules of phenethyl alcohol are lined on the channel walls as well.

The crystal packing of **2** is considerably simpler (Figure 5). Each of the hollow chains of hydrogen-bonded porphyrin and DMSO moieties is approached from above and below by two symmetry-equivalent chains with a roughly perpendicular orientation. The DMSO edges (which bridge between adjacent carboxylic functions along the chain) of the latter fit efficiently into the interporphyrin cavity of the central array. Thus, each one of these 'voids' is conveniently accommodated by two DMSO moieties, yielding a stable condensed arrangement. As in the previous structure, there are no H-bonding connections between the individual arrays. Rather, the three-dimensional organization in **2** is characterized by effective steric fit between the convex edges of one chain and the open cavities of another chain, the two arrays being related to each other by the glide symmetry. The somewhat loose packing around the metal-coordinated ligand allows an orientational disorder of the latter. Thermal analysis data show that the guest release process from this material takes place in two steps, which is consistent with the presence of two types of differently coordinated DMSO ligands in the crystalline lattice (Figure 1).

DISCUSSION

The self-assembly process of the zinc-tetra(4-carboxyphenyl)porphyrin utilizes, as expected, the hydrogen-bonding potential of the carboxylic functions. The observed aggregation modes are somewhat different, however, than in the structurally related functionalized porphyrin compounds analysed previously, due to the uniquely defined geometric and functional properties of the 4-carboxyphenyl substituent. Direct association between two porphyrin species requires coplanarity and head-to-head orientation of the interacting carboxylic functions, thus forcing each molecule to interact with four other species along the equatorial molecular axes. This leads to the formation of layered interporphyrin patterns with very large cavities—as in **1**. Pairwise interporphyrin binding through more than one functional group of each interacting unit, which is associated with the formation of relatively small intermolecular cavities, is thus possible only through additional bridging components—as in **2**. Apart from the solubility problems, these constraints and the cooperative nature of the crystallization process, in which the hydrogen bonding potential is utilized to optimal capacity, provide a plausible explanation of the considerable difficulty experienced in growing large single crystals of these compounds. It is evident that the type of the constructed network can be controlled by the crystallization environment according to the empirical hydrogen-bond rules recently formulated by Ether.^{11a,b} The typical carboxylic acid dimer pairing motif is retained in the presence of *sec*-phenethyl alcohol, as the OH group is a considerably weaker proton donor than the COOH group. Differently networked organization has been induced, however, by cocrystallizing the porphyrin host compound with dimethylsulphoxide. The latter aprotic component, being a rather strong bidentate proton acceptor, associates preferentially to the OH groups of the carboxylic sites and yields one-dimensional polymeric patterns with smaller cavities. In fact, the October 1995 release

of the Cambridge Structural Database²⁵ contains 28 structural references of compounds containing the carboxylic as well as sulphoxide functions (among them 11 solvates of dimethylsulphoxide), in which the $\text{COOH}\dots\text{O}=\text{S}(\text{CH}_3)_2$ intermolecular association is preferred over the $-\text{COOH}\dots\text{HOOC}$ -pairing. Most relevant illustration in the present context is provided by the structure of trimesic acid dimethylsulphoxide clathrate, in which formation of the common dicarboxylic acid dimer motif is similarly disrupted by the presence of DMSO.²⁶ Space-filling diagrams of the two observed open patterns of intermolecular association are shown in Figure 6.

The intermolecular organization in crystals based on the tetraphenylporphyrin building blocks can be readily tailored by functionalization of the rigid molecular framework by various functional groups. Moreover, due to the bulkiness, rigidity and high symmetry features, combined with the incorporated functionality, compounds substituted at the *para* positions of the phenyl rings reveal high propensity for assembling in the form of hollow polymeric networks.^{4,7-10} Consequently, they provide suitable building blocks for the formation of novel types of porphyrin-based inclusion solids consisting of coordination, hydrogen bonding, and dipolarly linked polymeric aggregates, with potential applications as solid state receptors. These materials also represent excellent models for the evaluation of noncovalent intermolecular forces as design elements in inclusion chemistry.

In this context it can be useful to summarize the structural features of the most common motifs of the porous interporphyrin organization in the various compounds. Figure 7 illustrates schematically the average cavity characteristics in planar polymeric networks observed in crystals of the differently functionalized porphyrin materials. Among these, the hydrogen-bonded networks occurring in 4-hydroxyphenyl and 4-carboxyphenyl derivatives in non-aqueous environments reveal interporphyrin cavities with

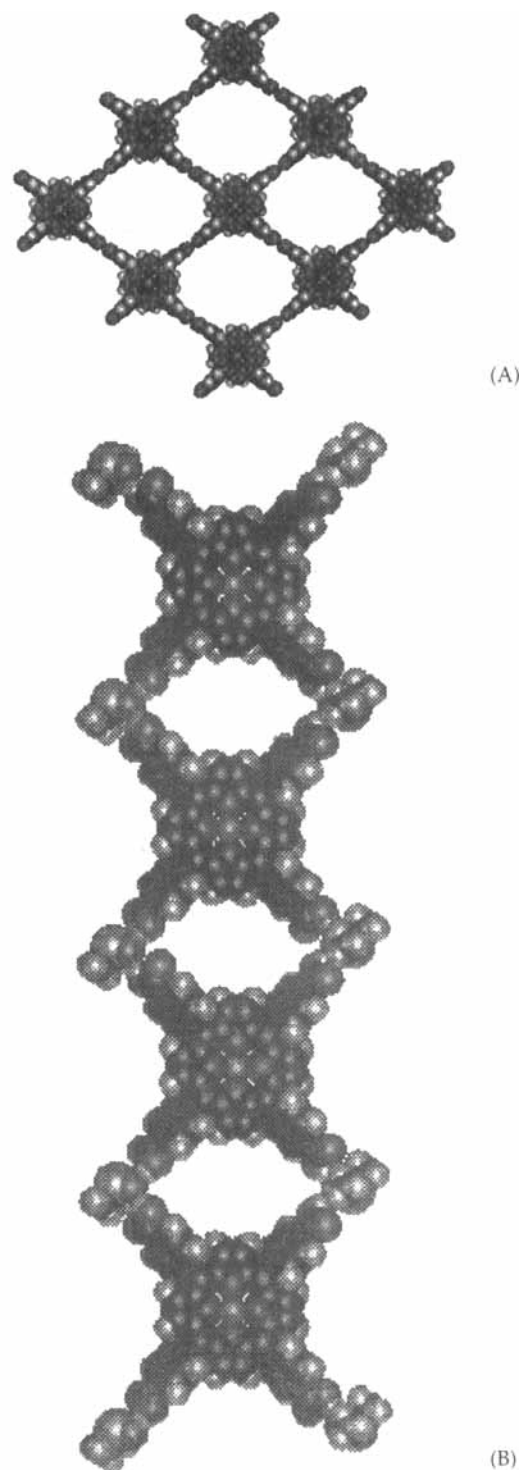


FIGURE 6 Space-filling illustration of the open patterns of intermolecular association found in structures (a) **1** and (b) **2**. (See color plate I).

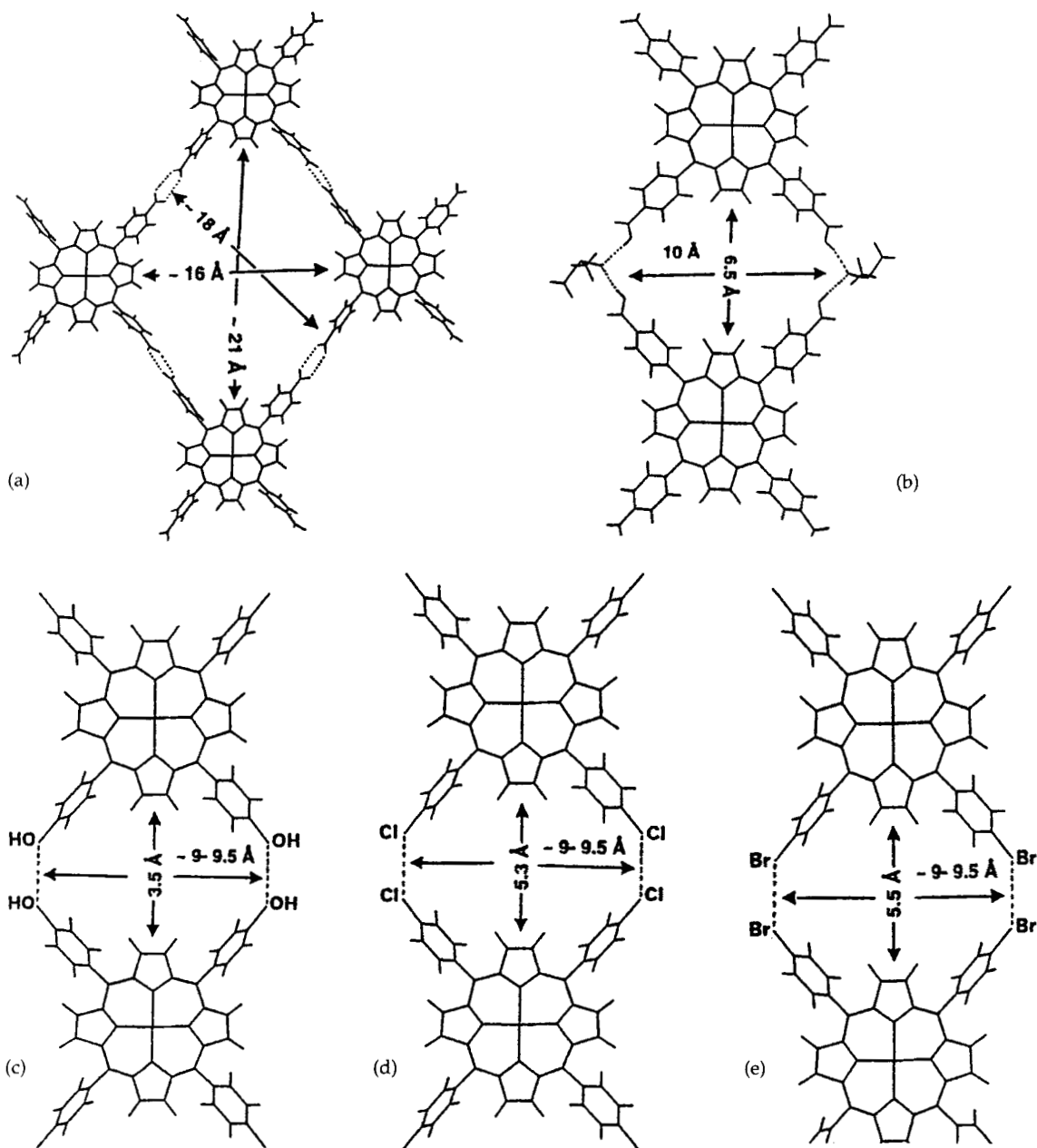


FIGURE 7 Schematic illustration of the characteristic interporphyrin voids formed in the crystal structures based on differently functionalized porphyrins: (a) Zn-tetra(4-carboxyphenyl)porphyrin in **1**, (b) Zn-tetra(4-carboxyphenyl)porphyrin in **2**, (c) Zn-tetra(4-hydroxyphenyl)porphyrin,⁸ (d) Zn-tetra(4-chlorophenyl)porphyrin,^{8,9} (e) Zn-tetra(4-bromophenyl)porphyrin.¹⁰ It demonstrates the high propensity of these porphyrin species to self-assemble in the form of hollow one-dimensional or two-dimensional networks. It also shows the effect of substitution of different functional groups on the geometric features of these cavities (the numbers indicated represent van der Waals dimensions of the open space).

best defined dimensions. Networks based on electrostatic interactions of longer range and lesser geometric constraint, as in the halogen-sub-

stituted porphyrins, are somewhat more flexible. Correspondingly, in the latter case other crystalline arrangements which resemble packing

modes in unsubstituted tetraphenylporphyrins are also possible.^{6,10} With the exception of structure 1 in this study, in all other materials the 'pores' within the interporphyrin networks are accommodated by readily absorbed and suitably sized guest components.⁷⁻¹⁰ Guest aromatic rings, for example, fit edge-on into the small cavities of porphyrin lattices based on the hydroxyphenyl derivative.⁸ The larger interporphyrin cavities in the chlorophenyl or bromophenyl materials can be occupied either by more flattened aryl groups or by (as in 2) two moieties of a smaller guest as DMSO.⁸⁻¹⁰ Finally, in structure 1 the cavities within the hollow networks are large enough to occlude two metalloporphyrin macrocycles oriented edge-on. In view of the above observations and the generally promising inclusion features of the porphyrin-based molecular solids, further studies are currently under way to explore on a more quantitative basis the selectivity features of these crystalline networks, as well as their potential in molecular transport and guest release applications.

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