



Solid-State Supramolecular Chemistry of Porphyrins. Ligand-Bridged Tetraphenylmetalloporphyrin Dimers

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Abstract. Eight new crystalline materials based on ligand-bridged dimers of either Zn(II)- or Co(II)-tetraphenylporphyrins have been prepared and characterized by X-ray diffraction analysis. These supramolecular entities have a “wheel-and-axle” type shape, the elongated bidentate ligands 1,3-diaminopropane, 1,4-diaminobutane, 4,4'-bipyridyl, 1,2-*bis*(4-pyridyl)ethene or 1,2-*bis*(4-pyridyl)ethane coordinating axially on both sides to the metal centers of the porphyrin species. They vary from one another by the length of the ligand spacer, the distance between the two porphyrin components ranging from 9.4 Å to 14.0 Å. The intermolecular organization in these structures is characterized by a similar chain motif in which adjacent oligomeric units interlock into one another. In spite of the steric constraint imposed by the bridging ligand, this packing preserves the typical corrugated stacked arrangement of the porphyrin frameworks which has been commonly observed in clathrates of monomeric tetraarylporphyrins. It also induces in most cases large voids between the interlocked motifs, causing enclathration of solvent molecules in the crystal lattice. The experimentally established geometries of these oligomers and their crystal packing modes provide useful information for further crystal engineering efforts of polymeric multiporphyrin domains.

Key words: porphyrin complexes and clathrates, coordination oligomers, supramolecular chemistry, crystal structure.

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1. Introduction

In light of the tremendous versatility of porphyrins and metalloporphyrins in mediating electron and energy transfer, their utility as redox catalysts, and their dynamic photophysical properties, there has been a widespread interest in the design and synthesis of multiporphyrin architectures. Earlier studies of a large number of tetraarylporphyrin-based lattice clathrates have shown that the organization of the porphyrin building blocks is strongly conserved [1]. More recent investigations by us, among many others, have shown also that a variety of crystalline oligomers

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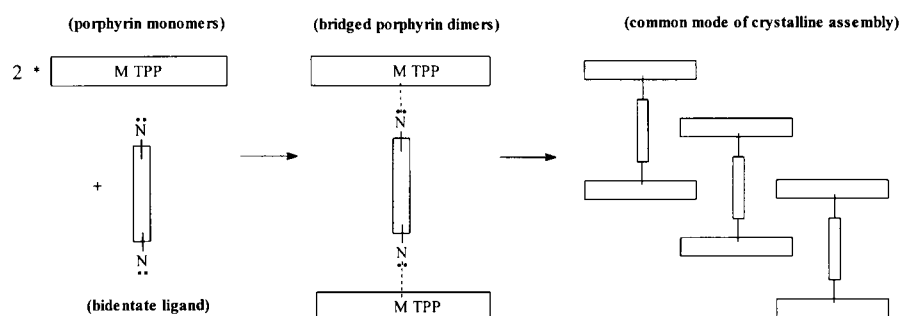


Figure 1. A schematic illustration of the supramolecular metalloporphyrin dimer system bridged by a linear bidentate ligand (center), and its conserved packing motif in the analysed crystals (right).

and polymers of different structural characteristics can be rationally designed from these metallomacrocycles by selection of the coordination geometry of metals, suitable functionalization of the porphyrin framework, and the geometry of multitopic ligands involved in the supramolecular synthesis. Relevant examples of successful attempts to assemble multiporphyrin domains in the solid as well as in solution include: (i) the generation of polymeric patterns sustained by external metal centers [2–4], (ii) the formation of large molecular network arrays with hollow architectures [5–8], (iii) the construction of homogeneous as well as heterogeneous coordination polymers of varying dimensionality and crystalline porosity, propagated by metal-to-ligand interactions [9], and (iv) assembly of columnar porphyrin arrays with an easy access to the metal cores enforced by hydrogen bonds [10–12]. Current efforts are directed at the formulation of structurally robust porous molecular crystals, and assessment of the potential utility of such structures as zeolite mimics (e.g., molecular sensors and solid state catalysts). The ability to fine-tune the supramolecular organization of the porphyrin entities by noncovalent interactions is a crucial step on the road to achieving this goal.

Laterally functionalized tetraphenylporphyrin frameworks have a strong propensity to self-assemble in the form of flat β -molecular networks [5, 8]. The interlayer distance between such porphyrin networks can be controlled by a suitable multidentate spacer ligand used to bridge between adjacent metalloporphyrin cores along the axial direction. In the above context, we evaluate in this paper, as structural probes, the geometrical features of a series of Zn(II)- and Co(II)-tetraphenylporphyrin (ZnTPP and CoTPP, respectively) dimers bridged by bidentate ligands of varying dimensions (Figure 1) [13]. The structural aspects of such systems have not been studied systematically before, and only a few isolated examples have been reported [1]. The solvent inclusion characteristics of the corresponding crystals are related to the general tendency of the TPP building blocks to form clathrates.

2. Experimental and Crystal Data

The ligand-bridged porphyrin dimers were obtained by adding stoichiometric amounts of ZnTPP or CoTPP to a solution of the respective ligand in chloroform or in nitrobenzene. Single crystals suitable for X-ray diffraction analysis were obtained by recrystallization of the composite materials under controlled conditions. The crystalline solids thus obtained include metalloporphyrin dimers bridged by 1,3-diaminopropane (**1** and **2**), 1,4-diaminobutane (**3** and **4**), 4,4'-bipyridyl (**5** and **6**), 1,2-*bis*(4-pyridyl)ethene (**7**) or 1,2-*bis*(4-pyridyl)ethane (**8**) with varying solvent content (see crystal data below). The X-ray diffraction measurements of these crystals were carried out on either a CAD4 (**1–2** and **6–8**, ω - 2θ scan mode) or a KappaCCD (**3–5**, 1° ϕ -scans) Nonius diffractometer equipped with a graphite monochromator, using MoK_α ($\lambda = 0.7107 \text{ \AA}$) radiation. The structures were solved by Patterson and direct methods (SHELXS-86 [14], SIR-92 [15] or DIRDIF-96 [16]) and refined by full-matrix least-squares based on F^2 (SHELXL-97, [17]). Non-hydrogen atoms were treated anisotropically (except for those in the disordered fragments or solvates of some of the structures). The hydrogen atoms were located in calculated positions to correspond to standard bond lengths and angles. The crystallographic data for the corresponding compounds are:

1, $(\text{C}_{44}\text{H}_{28}\text{N}_4\text{Zn})_2(\text{C}_3\text{H}_{10}\text{N}_2) \cdot (\text{CHCl}_3)_2$: formula weight 1658.9, triclinic, space group $P\bar{1}$, $a = 9.028(4)$, $b = 11.906(5)$, $c = 19.214(7) \text{ \AA}$, $\alpha = 87.64(2)$, $\beta = 80.57(2)$, $\gamma = 78.40(3)^\circ$, $V = 1995.7 \text{ \AA}^3$, $Z = 1$, $D_{\text{calc}} = 1.380 \text{ g cm}^{-3}$, $F(000) = 848$, $\mu(\text{MoK}_\alpha) = 0.85 \text{ mm}^{-1}$, crystal size $\sim 0.35 \times 0.20 \times 0.10 \text{ mm}$, $2\theta_{\text{max}} = 46.0^\circ$, 5078 unique reflections, $R_1 = 0.057$ for 4088 observations with $F_o > 4\sigma(F_o)$, $R_1 = 0.074$ ($wR_2 = 0.170$) for all unique data, $|\Delta\rho| \leq 0.54 \text{ e \AA}^{-3}$. Refinement calculations were carried out in $P1$ as well as in $P\bar{1}$ space group, and the diamino-propane bridge was found to be conformationally disordered in both. Based on additional indications from intensity statistics (which clearly suggested a centric distribution), the final structural model was thus refined in the centrosymmetric space group $P\bar{1}$, with inversion at the geometric center of the dimeric complex, thus assuming two disordered inversion-related orientations of the diamino-propane bridge. The chloroform molecules included in the crystal lattice were found to be partially disordered as well, as indicated by their relatively large thermal displacement parameters.

2, $(\text{C}_{44}\text{H}_{28}\text{N}_4\text{Zn})_2(\text{C}_3\text{H}_{10}\text{N}_2) \cdot (\text{C}_6\text{H}_5\text{NO}_2)_2$: formula weight 1676.5, triclinic, space group $P\bar{1}$, $a = 11.460(2)$, $b = 11.795(3)$, $c = 16.469(7) \text{ \AA}$, $\alpha = 108.81(2)$, $\beta = 95.64(2)$, $\gamma = 99.16(3)^\circ$, $V = 2053.5 \text{ \AA}^3$, $Z = 1$, $D_{\text{calc}} = 1.356 \text{ g cm}^{-3}$, $F(000) = 870$, $\mu(\text{MoK}_\alpha) = 0.65 \text{ mm}^{-1}$, crystal size $\sim 0.35 \times 0.30 \times 0.20 \text{ mm}$, $2\theta_{\text{max}} = 50.0^\circ$, 6224 unique reflections, $R_1 = 0.070$ for 3908 observations with $F_o > 4\sigma(F_o)$, $R_1 = 0.108$ ($wR_2 = 0.184$) for all unique data, $|\Delta\rho| \leq 0.34 \text{ e \AA}^{-3}$. Similar disorder of the diamino-propane bridge as in **1** was observed also in this structure, irrespective of whether the crystallographic refinement was carried out in $P1$ or in $P\bar{1}$ space groups. The latter was thus assumed, with the porphyrin dimers centered at 0,

0, 0. The two nitrobenzene molecules appeared to be disordered near $\frac{1}{2}, 0, \frac{1}{2}$, as indicated by a wide distribution of relatively high difference electron-density peaks around this site. Their atomic positions could not be reliably determined, and without accounting for them the least-squares refinement converged only at $R_1 = 0.16$. Correspondingly, the contribution of this solvent was subtracted from the diffraction pattern by the 'Bypass' procedure [18]. The volume occupied by the solvent and the residual electron density in it were assessed by the PLATON computer program to be about 359 \AA^3 (i.e., 17.5% of the unit cell volume) and 121 e, respectively [19], matching reasonably well the assumed crystal composition. The refinement of the reduced data converged smoothly at $R_1 = 0.07$ (as indicated above), yielding an acceptable structural model of the main structure.

3, $(\text{C}_{44}\text{H}_{28}\text{N}_4\text{Zn})_2(\text{C}_4\text{H}_{12}\text{N}_2)$: formula weight 1444.3, triclinic, space group $P\bar{1}$, $a = 11.905(1)$, $b = 12.165(1)$, $c = 14.515(1) \text{ \AA}$, $\alpha = 68.98(1)$, $\beta = 79.81(1)$, $\gamma = 67.58(1)^\circ$, $V = 1812.0 \text{ \AA}^3$, $Z = 1$, $D_{\text{calc}} = 1.324 \text{ g cm}^{-3}$, $F(000) = 750$, $\mu(\text{MoK}\alpha) = 0.72 \text{ mm}^{-1}$, crystal size $\sim 0.30 \times 0.05 \times 0.05 \text{ mm}$, $2\theta_{\text{max}} = 52.6^\circ$, 241 detector frames, 7313 unique reflections, $R_1 = 0.071$ for 3290 observations with $F_o > 4\sigma(F_o)$, $R_1 = 0.194$ ($wR_2 = 0.183$) for all unique data, $|\Delta\rho| \leq 0.40 \text{ e \AA}^{-3}$. The molecular units of the complex are located on crystallographic inversion. The crystals of this compound diffracted poorly, due to the loose packing of the ligand-bridged dimers along one crystal direction which is exhibited by high thermal displacement parameters associated with the peripheral atoms of two out of the four phenyl substituents of the porphyrin unit.

4, $(\text{C}_{44}\text{H}_{28}\text{N}_4\text{Zn})_2(\text{C}_4\text{H}_{12}\text{N}_2) \cdot (\text{C}_6\text{H}_5\text{NO}_2)_2$: formula weight 1690.5, triclinic, space group $P\bar{1}$, $a = 11.966(1)$, $b = 12.242(1)$, $c = 15.836(1) \text{ \AA}$, $\alpha = 112.61(1)$, $\beta = 90.36(1)$, $\gamma = 102.42(1)^\circ$, $V = 2081.2 \text{ \AA}^3$, $Z = 1$, $D_{\text{calc}} = 1.349 \text{ g cm}^{-3}$, $F(000) = 878$, $\mu(\text{MoK}\alpha) = 0.64 \text{ mm}^{-1}$, crystal size $\sim 0.25 \times 0.25 \times 0.20 \text{ mm}$, $2\theta_{\text{max}} = 56.5^\circ$, 424 detector frames, 9454 unique reflections, $R_1 = 0.054$ for 7063 observations with $F_o = 4\sigma(F_o)$, $R_1 = 0.080$ ($wR_2 = 0.159$) for all unique data, $|\Delta\rho| \leq 1.04 \text{ e \AA}^{-3}$. The molecular units of the complex are located on crystallographic inversion. The nitrobenzene solvent was found to be orientationally disordered about its center of mass, which was modeled by two major orientations of the nitrobenzene molecule with refined occupancies of 0.58 and 0.42, respectively.

5, $(\text{C}_{44}\text{H}_{28}\text{N}_4\text{Co})_2(\text{C}_{10}\text{H}_8\text{N}_2) \cdot (\text{C}_6\text{H}_5\text{NO}_2)_4$: formula weight 1991.9, monoclinic, space group $C2/c$, $a = 18.554(1)$, $b = 13.458(1)$, $c = 39.706(1) \text{ \AA}$, $\beta = 99.73(1)^\circ$, $V = 9771.9 \text{ \AA}^3$, $Z = 4$, $D_{\text{calc}} = 1.354 \text{ g cm}^{-3}$, $F(000) = 4128$, $\mu(\text{MoK}\alpha) = 0.41 \text{ mm}^{-1}$, crystal size $\sim 0.20 \times 0.20 \times 0.07 \text{ mm}$, $2\theta_{\text{max}} = 52.7^\circ$, 385 detector frames, 9588 unique reflections, $R_1 = 0.067$ for 4411 observations with $F_o > 4\sigma(F_o)$ and $R_1 = 0.172$ ($wR_2 = 0.193$) for all unique data, $|\Delta\rho| \leq 0.38 \text{ e \AA}^{-3}$. The molecular entities are located on symmetry elements of twofold rotation. The nitrobenzene solvent included in the crystal lattice is partly disordered.

6, $(\text{C}_{44}\text{H}_{28}\text{N}_4\text{Zn})_2(\text{C}_{10}\text{H}_8\text{N}_2) \cdot (\text{C}_6\text{H}_5\text{NO}_2)_4$: formula weight 2004.8, monoclinic, space group $C2/c$, $a = 18.379(5)$, $b = 13.517(2)$, $c = 40.281(5) \text{ \AA}$, $\beta = 99.36(2)^\circ$, V

= 9874 Å³, $Z = 4$, $D_{\text{calc}} = 1.349 \text{ g cm}^{-3}$, $F(000) = 4152$, $\mu(\text{MoK}\alpha) = 0.55 \text{ mm}^{-1}$, crystal size $\sim 0.40 \times 0.30 \times 0.20 \text{ mm}$, $2\theta_{\text{max}} = 50.0^\circ$, 7376 unique reflections, $R_1 = 0.084$ for 4666 observations with $F_o > 4\sigma(F_o)$ and $R_1 = 0.129$ ($wR2 = 0.241$) for all unique data, $|\Delta\rho| \leq 0.76 \text{ e \AA}^{-3}$. This structure is isomorphous with **5**.

7. $(\text{C}_{44}\text{H}_{28}\text{N}_4\text{Zn})_2(\text{C}_{12}\text{H}_{10}\text{N}_2) \cdot (\text{C}_6\text{H}_5\text{NO}_2)_3$: formula weight 1907.7, triclinic, space group $P\bar{1}$, $a = 11.489(4)$, $b = 11.688(5)$, $c = 17.966(5) \text{ \AA}$, $\alpha = 86.85(3)$, $\beta = 83.16(3)$, $\gamma = 81.68(3)^\circ$, $V = 2368.4 \text{ \AA}^3$, $Z = 1$, $D_{\text{calc}} = 1.338 \text{ g cm}^{-3}$, $F(000) = 988$, $\mu(\text{MoK}\alpha) = 0.57 \text{ mm}^{-1}$, crystal size $\sim 0.40 \times 0.35 \times 0.30 \text{ mm}$, $2\theta_{\text{max}} = 42.0^\circ$, 4436 unique reflections, $R_1 = 0.078$ for 3020 observations with $F_o > 4\sigma(F_o)$, $R_1 = 0.107$ ($wR2 = 0.204$) for all unique data, $|\Delta\rho| \leq 0.58 \text{ e \AA}^{-3}$. The molecular units of the complex are located on centers of inversion. The atomic positions of the two out of the three disordered nitrobenzene molecules in the unit-cell (near $\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$) could be approximately located in difference-Fourier maps, but not refined with satisfactory precision ($R_1 = 0.13$). Correspondingly, the contribution of this solvent was subtracted from the diffraction pattern [18]; the volumes occupied by the solvent (centered at $0, \frac{1}{2}, 0$ and $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$) and the residual electron density in them were assessed to total about 692 \AA^3 (i.e., $\sim 29\%$ of the unit cell volume) and 171 e , respectively [19], matching reasonably well the assumed crystal composition. The refinement of the reduced data yielded an acceptable structural model of the main structure.

8. $(\text{C}_{44}\text{H}_{28}\text{N}_4\text{Zn})_2(\text{C}_{12}\text{H}_{12}\text{N}_2) \cdot (\text{C}_6\text{H}_5\text{NO}_2)_{3.5}$: formula weight 1971.3, triclinic, space group $P\bar{1}$, $a = 15.291(6)$, $b = 17.292(3)$, $c = 20.669(8) \text{ \AA}$, $\alpha = 106.67(2)$, $\beta = 110.94(4)$, $\gamma = 91.32(2)^\circ$, $V = 4841 \text{ \AA}^3$, $Z = 2$, $D_{\text{calc}} = 1.352 \text{ g cm}^{-3}$, $F(000) = 2044$, $\mu(\text{MoK}\alpha) = 0.56 \text{ mm}^{-1}$, crystal size $\sim 0.45 \times 0.25 \times 0.15 \text{ mm}$, $2\theta_{\text{max}} = 42.0^\circ$, 9066 unique reflections, $R_1 = 0.060$ for 6493 observations with $F_o > 4\sigma(F_o)$, $R_1 = 0.090$ ($wR2 = 0.156$) for all unique data, $|\Delta\rho| \leq 0.58 \text{ e \AA}^{-3}$. The molecular units of the complex are located at general positions. Only three molecules of nitrobenzene solvent could be reliably located and included in the structural refinement ($R_1 = 0.09$). Another nitrobenzene was found to be disordered around the $0, \frac{1}{2}, 0$ inversion, and its contribution was subtracted from the diffraction pattern [18]. The volume occupied by this species and the residual electron density in it were assessed to be about 240 \AA^3 and 56 e , respectively [19]. The refinement of the reduced data converged smoothly at $R_1 = 0.060$.

Despite the apparent solvent disorder in most of these structures, as well as the disorder of the diaminopropane bridge in **1** and **2**, the structural features of the ligand-bridged dimers in question have been determined with good precision. The resulting bond distances and angles of the porphyrin complexes conform to normally observed values documented in the literature, including the coordination geometries around the metal centers. The discussion which follows focuses, therefore, mainly on aspects of the supramolecular coordination and intermolecular organization. The crystallographic data have been deposited in the Cambridge Crystallographic Database.

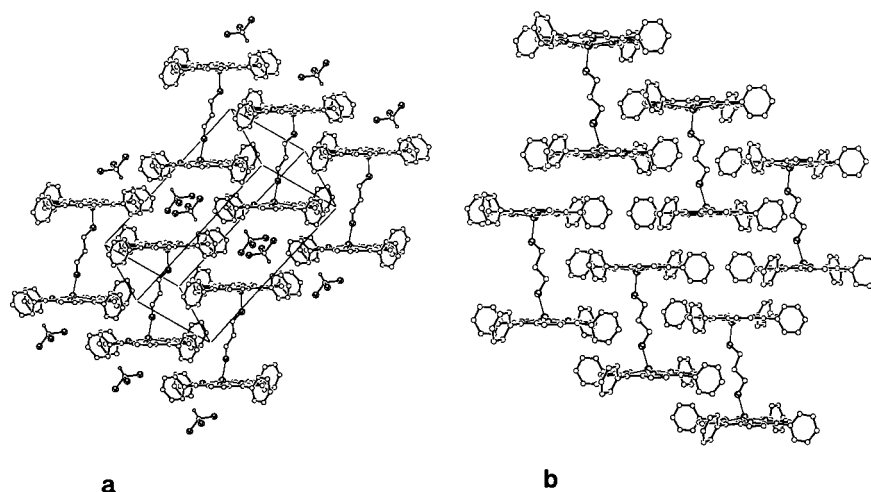


Figure 2. Coordination oligomers bridged by 1,3-diaminopropane. (a) Crystal packing in **1**, showing the interlocking chain motif of the TPP-dimers, and inclusion of chloroform solvent in voids between adjacent chains. (b) Crystal packing of two chains of TPP-dimers in **2**, illustrating also the resulting layered organization of the porphyrin components. The disordered nitrobenzene solvent included in intermolecular cavities along a direction perpendicular to the plane of this drawing is omitted for clarity. The Zn and N coordinating sites are marked by crossed circles.

3. Results and Discussion

The ligand-bridged dimers of TPP (referred to below as TPP-dimers) with a variety of spacer ligands are readily available. They thus provide excellent means for structural elucidation of the porphyrin-ligand-porphyrin assembly unit, an essential element in the design and regulation of porphyrin-based coordination polymers and networks. Formation of such oligomers was facilitated by metallation of the porphyrin core with Zn(II) and Co(II) (ions with a considerable preference for five-coordinate square-pyramidal geometry), as well as by the use of ‘linear’ bidentate ligands. In these compounds the metal ions which coordinate to the central ligand typically deviate from the corresponding porphyrin plane towards the axial ligand (the deviations of the metal ions from the planes defined by the four N-pyrrole atoms of the corresponding porphyrin core are 0.11 Å for Co and within 0.28–0.33 Å for Zn, Table I).

Figure 2 illustrates the crystal structures of TPP-dimers **1** and **2**, which involve the aliphatic diaminopropane ligand. They represent “wheel-and-axle”-type entities which interlock into one another in order to yield the most effective packing in the lateral direction (i.e., parallel to the porphyrin plane). In the resulting self-assembled structures the aliphatic ligand of each unit is enclosed by four phenyl groups of two adjacent complexes. The chloroform (in **1**) or nitrobenzene (in **2**) solvent is incorporated into the crystal between chains of the interlocked units, being sandwiched between the concave surfaces of the top porphyrin “wheel” of

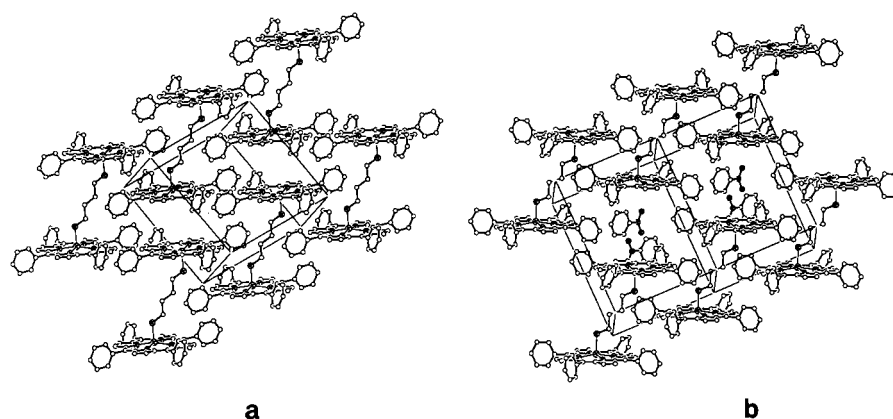


Figure 3. Coordination oligomers bridged by 1,4-diaminobutane. Crystal structures of (a) the solvent free **3**, and (b) the nitrobenzene clathrate **4**. Notable is the conservation of the interlocked motif of the TPP-dimers in both structures, as well as the expansion mode of this motif to form a clathrate.

the lower chain and the bottom porphyrin “wheel” of the upper chain (as clearly shown for **1** in Figure 2a). Although in a TPP-dimer the linear ligand imposes a structural constraint on the relative dispositions of the two porphyrins bound to it, these structures maintain the characteristic pattern of the porphyrin organization observed in clathrates of *monomeric* tetraphenylporphyrins, i.e., formation of corrugated sheets of offset-stacked TPP entities [1]. As in the other porphyrin crystals, side packing of adjacent chains is also stabilized by π - π stacking and edge-to-face interaction modes between the peripheral phenyl rings substituted on the porphyrin periphery [1, 6].

The chain arrangement of the interlocked trimeric TPP-dimers is preserved also in compounds **3** and **4**, with fully stretched diaminobutane as the spacer ligand (Figure 3). Structure **3** does not show sizeable intermolecular voids between the dimers, and does not contain solvent in the lattice. The porphyrin frameworks compose a layered arrangement interspaced by the bridging ligand (Figure 3a). Such layers are stacked one on top of the other in a typical offset manner at regular intervals of about 4.9 Å (half the spacing between the porphyrins in each TPP-dimer unit), as in the structures of ZnTPP clathrates [6]. The known high propensity of TPP derivatives to form lattice intercalates (“porphyrin sponges” [1]) is also well manifested in the structure of **4**. Here, the crystal lattice expands by intercalation of nitrobenzene between adjacent chains of the TPP-dimers, yet still preserving the same interlocking motif of these entities (Figure 3b).

Structures **5** and **6** are isomorphous. Although these compounds crystallize in a monoclinic rather than triclinic form, and involve a larger ligand, they still maintain similar packing characteristics as in **1** and **4** (Figure 4). In order to do so all the TPP-dimer units are aligned in the same direction in the lattice, and are more inclined with respect to the main axis of the interlocked chain motif. This larger tilt gives

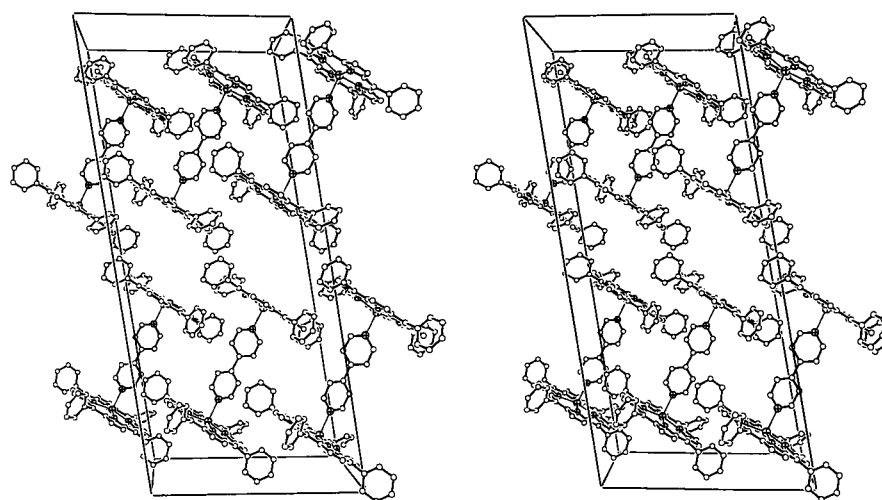


Figure 4. Metalloporphyrins bridged by 4,4'-bipyridyl. Stereoview of the crystal packing in **6**, approximately down the *b* crystal axis. The nitrobenzene solvent enclathrated between the TPP-dimers is omitted for clarity. Compound **5** forms an isomorphous structure.

rise to an increased interporphyrin spacing between adjacent chains. As a result, the TPP-dimer:solvent stoichiometry changes from 1 : 2 in the previous examples to 1 : 4 in the present case. Replacement of the aliphatic ligand (as in **1–4**) by the aromatic bipyridyl bridge adds another important element of intermolecular stabilization. It involves attractive π - π stacking interactions between the pyridyl rings of the bridging ligand in one complex and the surrounding phenyl arms (which overlap the pyridyls) of adjacent TPP-dimers (Figure 4), thus further stabilizing their observed interlocked arrangement.

Similar features are apparent in compounds **7** and **8**, which involve more elongated ligands containing an additional CH=CH or CH₂—CH₂ element between the two pyridyl rings. In **7**, the increased spacing between the two porphyrin components of about 14 Å (Table I) allows each ligand to be approached by the porphyrin fragments of adjacent assemblies which are differently displaced with respect to the axial direction (Figure 5). Each TPP-dimer in this structure spans over four layered zones composed of the porphyrin entities, which facilitates efficient packing of these units in two dimensions perpendicular to the ligand “axle”. The nitrobenzene solvent in this structure is accommodated in a disordered manner in channels formed between such adjacent arrays. A somewhat different packing occurs in **8**. In the latter, one of the ligand pyridyls interacts with the aromatic periphery of the surrounding assemblies along one direction (as in the previous examples), but the other pyridyl ring is overlapped by nitrobenzene species incorporated into the crystal lattice (Figure 6). The π - π interactions associated with the latter arrangement appear to prevent a significant disorder of these nitrobenzene species.

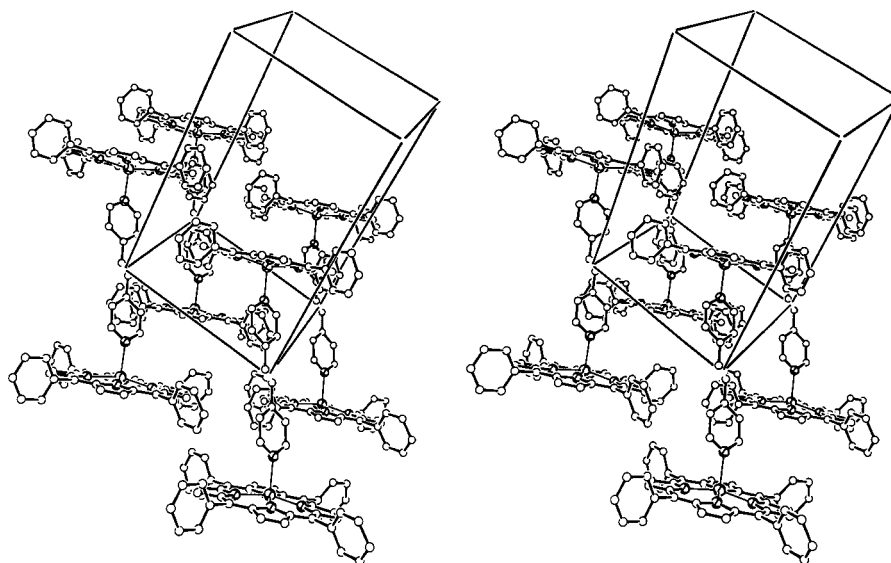


Figure 5. Stereoview of structure **7**, involving the 1,2-*bis*(4-pyridyl)ethene bridging ligand (solvent is excluded). Each TPP-dimer in this structure spans over four layered zones composed of the porphyrin components.

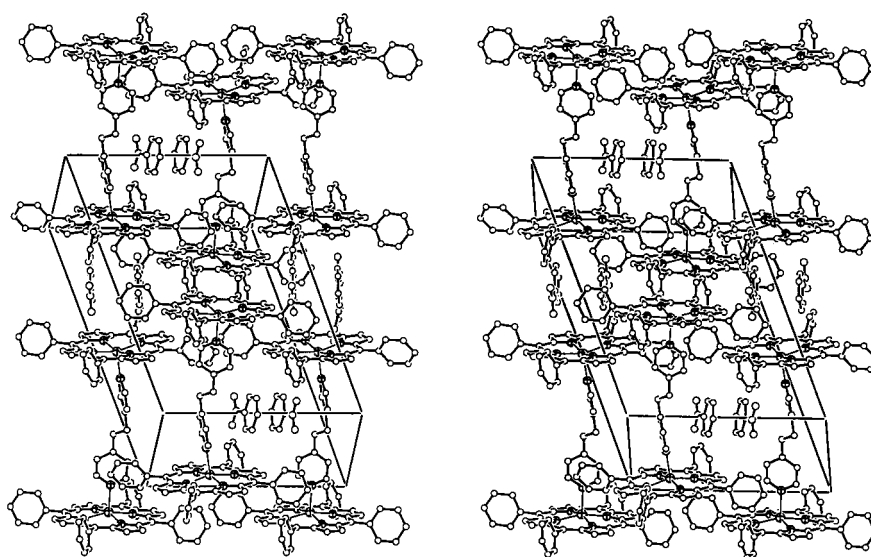


Figure 6. Stereoview of clathrate **8**, involving 1,2-*bis*(4-pyridyl)ethane as the bridging ligand. The stacked arrangement at close proximity of the different aryl groups (porphyrin phenyls, ligand pyridyls, molecules of nitrobenzene), which contribute to the stability of this structure through diverse π - π interactions, is illustrated.

Table I. Selected bonding and coordination distances within the TPP-dimers **1–8**

Compound	Interporphyrin spacing ^a (Å)	$M^b - N(\text{porphyrin})$ bond length range (Å)	$M^b - N(\text{ligand})$ distance range (Å) ^c	M^b deviation from the porphyrin plane ^a (Å)
1	9.54	2.063–2.067(5)	2.17(1)	0.305(1)
2	9.41	2.064–2.076(5)	2.18(1)	0.334(1)
3	9.79	2.060–2.065(5)	2.148(5)	0.277(1)
4	9.73	2.057–2.070(4)	2.140(3)	0.314(1)
5	11.75	1.983–1.988(3)	2.223(3)	0.114(1)
6	11.96	2.060–2.072(6)	2.196(5)	0.288(1)
7	13.90	2.075–2.088(7)	2.178(7)	0.335(1)
8	14.00	2.057–2.097(7)	2.179(6)	0.334(1)

^a Reference was made to distances from the mean plane(s) defined by the four $N(\text{porphyrin})$ atoms in each porphyrin entity.

^b M refers to Zn(II), except for **6** where it is Co(II).

^c For cases with two crystallographically independent distances, a mean value is shown.

Table I summarizes selected structural parameters of the TPP-dimers. Of particular interest is the observed distance between the top and bottom porphyrin components in these units. This dimension varies from an average of 9.47 Å for the diamino propane bridge, through 9.76 Å for the diamino butane, 11.85 Å for the bipyridyl and 13.95 Å for the two extended bipyridyl ligands, illustrating the extent of structural variation that can be readily introduced in order to crosslink between the flat porphyrin entities without distorting the characteristic tendency of these relatively large and rigid frameworks to form layered patterns. Indeed, the examples described above preserve the characteristic modes of intermolecular architecture previously observed in crystalline solids of monomeric metallated TPPs [1], in spite of the added constraint in the form of the bridging ligands. The dominant structural motif in these structures is presented by the interlocked chain of the TPP-dimers (schematically depicted in Figure 1) which is characterized by a corrugated arrangement of offset-stacked TPP components which optimizes the porphyrin-porphyrin interaction [20]. Moreover, all TPP-dimer moieties in the observed structures are oriented in the same direction, and the roughly flat porphyrin species form a layered arrangement in two dimensions parallel to the porphyrin plane with regular intervals of 4.5–5.0 Å between the layers. A particularly effective illustration of the latter feature is provided by comparison between structures **1–4** and structure **7**. In the former examples the distance between the top and bottom TPPs in each unit is less than 10 Å, and thus only a single porphyrin layer (composed of TPP components from adjacent dimer units) may interpenetrate into it (Figures 2 and 3). On the other hand, the TPP-dimers in **7** (which are about 14 Å long) are conveniently interspaced by two porphyrin layers (Figure 5).

Further studies are currently under way to incorporate similar axial bridging ligands, as cross linking elements, to structures based on stable β -molecular networks of peripherally functionalized porphyrins [5]. Our long range target in this series of investigations is to crystal-engineer stable molecular solids consisting of open three-dimensional networks of multiporphyrin aggregates sustained by non-covalent interactions, which provide a promising perspective for new materials with interesting and useful properties.

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