A calcium-bridged porphyrin coordination network

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ABSTRACT: The hydrothermal assembly of a very stable porphyrin network with nanoscale cavities is described. A tightly packed and interpenetrated, linear polymeric framework was observed in the solid-state X-ray structure of freebase 5,10,15,20-*tetrakis*-(4-carboxyphenyl)porphyrin coordinated to calcium(II) ions. Strong hydrogen-bonding interactions between the coordination polymers form a two-dimensional network. Perpendicular bands interpenetrate generating an unusual three-dimensional box that clathrates a pyridine molecule. Copyright © 2002 Society of Porphyrins & Phthalocyanines.

KEYWORDS: carboxylate compounds, clathrates, crystal engineering, para-carboxylate phenyl porphyrin, solid-state structures.

INTRODUCTION

Porphyrins and related macrocycles provide an extremely versatile synthetic component for a variety of materials applications. The exploration of metalloporphyrin molecules as building blocks for tailored materials has found rapid growth during the past decade. Diverse synthetic strategies for the construction of porphyrinic solids that contain molecularly-sized cavities or channels have been pursued by a number of researchers. In the last decade, significant progress toward the rational construction of three-dimensional solids assembled from metal cations and organic molecules has been described [1-3]. While porphyrins should be useful building blocks in such efforts, porphyrinic solids have usually also contained space-filling counterions or solvates without which the structures are not stable [4-11]. We have borrowed from the geological formation of natural network materials (e.g., zeolites) a hydrothermal methodology for the synthesis of novel porphyrinic network materials. Specifically, we report the synthesis and X-ray crystal structure of a clathrate solid made from a highly interpenetrated network solid that utilizes the coordination bonding of a porphyrin with carboxylate substituents to calcium(II) ions.

5,10,15,20-*tetrakis*-(4-carboxyphenyl)porphyrin, $H_2(p\text{-COOH})TPP$, was chosen because its carboxylic acid substituents provide water solubility and anionic sites for metal ion coordinative bonding to a cationic metal atom, thereby circumventing the counterion problems associated with a charged framework. Porphyrin macrocycles can be envisioned as flat, geometrically square building blocks approximately 1 nm wide. The alkaline earth metals were initially selected as the coordinate bridging ions to pursue with the building block *p*-carboxy porphyrins.

EXPERIMENTAL

$H_2(p\text{-COOH})TPP$ was prepared according to literature [12]. The pyridine adduct was obtained upon recrystallization from 50/50 pyridine/EtOH saturated solution. A basic solution (0.01M NaOH) of $H_2(p\text{-COOH})TPP \cdot C_5H_5N$ (5.0 mM, 2.5 mL) was added to $Ca(OH)_2$ (9.35 mg, 1.25×10^{-3} mmol) in a 5 mL borosilicate vial fitted with Teflon-lined septum and heated to 150 °C for 24 h in a Parr thermal reaction bomb (5 atm maximum observed internal pressure of bomb). Bomb was allowed to cool at a rate of 3.0 °C.min^{-1}. Solids were isolated

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from mother liquor on Millipore 0.22 μm Durapore centrifuge filters and washed five times with 2 mL aliquots of water. Elemental Analysis cald for $H_2(p$-$CO_2)PPCa_2(H_2O)_8 \cdot C_5H_5N$: C 58.39, H 4.35, N 6.42 Ca 7.35; found: C 58.20, H 4.25, N 6.54, Ca 7.49.

Crystallography: Single crystals ($0.20 \times 0.12 \times 0.08$ mm^3) of the porphyrin-Ca network clathrate material were stored in the mother liquor, quick-mounted to a thin glass fiber under oil (paratone-N, Exxon) and immediately cooled to 198(2) K. Collected on a Siemens 3-circle platform diffractometer equipped with a graphite monochromated Mo-Kα radiation source (λ = 0.71073 Å) and with a CCD area detector, the crystal data for the compound: orthorhombic, Cmca (No. 64), a = 37.647(1) Å, b = 11.0621(4) Å, c = 11.4149(1) Å, $\alpha = \beta = \gamma = 90°$, Z = 4, V = 4753.8(2) Å^3, density (calculated) = 1.523 mg/m^3. The structure was solved by direct methods [13]. The pyridine solvate molecule was disordered about the 2/m site and refined as a rigid idealized group. Crystallographic 2/m symmetry was imposed on the host porphyrin molecule. Atom H(2) was restrained to remain within 0.95 Å of N(2) with an effective standard deviation of 0.01 Å. Positions for the remaining ordered H atoms were independently refined. The structure was refined by using 1593 independent reflections collected in the range $2.16° \leq \theta \leq 22.56°$. Final values of conventional indices, by successful convergence of the full-matrix least-squares refinement, for the model were R_1 = 8.45 and wR_2 = 21.75. R(int) = 0.1550 and percentage of observed data was 65%. The largest remaining peak and hole in the electron difference Fourier map were 0.649 and -0.561 e.Å^{-3} The highest peak was located on the 2/m site at the center of the host molecule; the final map had no other significant features. The unit cell contents are $C_{212}H_{188}N_{20}O_{64}Ca_8$.

RESULTS AND DISCUSSION

Small dark red crystals suitable for single crystal X-ray diffraction were obtained from the hydrothermal reaction of $H_2(p$-COOH)TPP$\cdot C_5H_5N$ with Ca(OH)$_2$ in a 0.01M aqueous solution of sodium hydroxide. The unit cell [space group *Cmca*, a = 37.647(1) Å, b = 11.0621(4) Å, c = 11.4149(1) Å, $\alpha = \beta = \gamma = 90.0°$] consists of four porphyrin entities, eight calcium(II) centers, sixteen calcium-bound water ligands, and four disordered pyridine molecules, generating the stoichiometry $C_{48}H_{26}N_4O_8Ca_2 \cdot 4H_2O \cdot C_5H_5N$. The materials were completely insoluble (<< μM) in common organic solvents and neutral water and exhibited only very limited solubility in concentrated aqueous tetraethylammonium hydroxide.

The carboxylate groups coordinate calcium ions in an asymmetric bis-chelation mode; key distances are

Ca-O$_{carboxylate}$ = 2.451(5) and 2.515(5) Å. The average Ca-O interatomic distance in bischelate motifs, 2.53(7) Å, is longer than that observed for the more common unidentate complexes, 2.38(7) Å [14]. Each calcium ion interacts with two carboxylate groups from two linearly aligned porphyrins of an infinite band (Fig. 1). The porphyrin units act as a tetrakis-bidentate species coordinating four calcium ions. The bidentate carboxylate O-Ca-O angle is 52.5(2)°, and the Ca(II) coordination sphere is a distorted square antiprism. The O-C-O angle of 122.1(7)° compares favorably to the average angle (122°) determined from a survey of calcium-bischelation carboxylate coordination complexes [14]. Precedence for this type of coordination in Ca^{+2} carboxylate compounds includes the salts of terephthalic acid [15], 1,4,5,8-naphthalenetetracarboxylic acid [16], salicylic acid
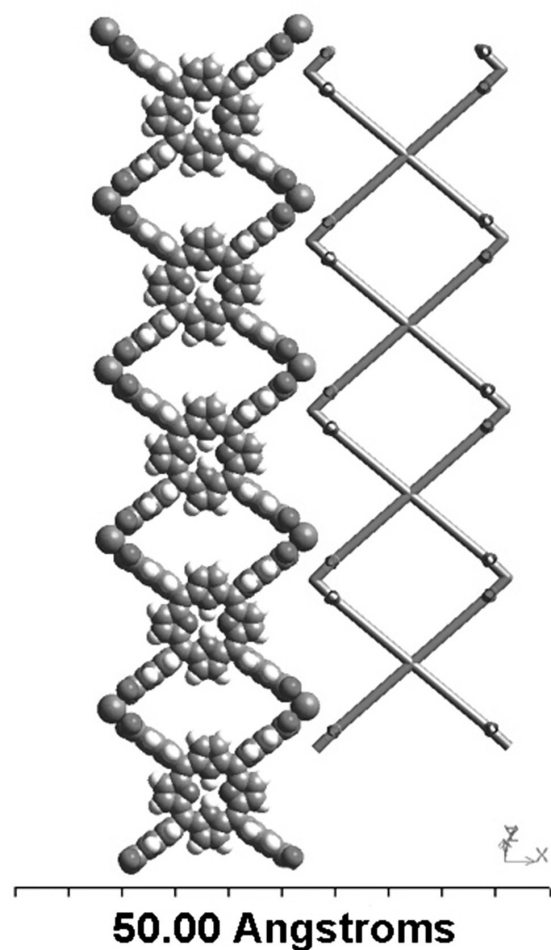

50.00 Angstroms

Fig. 1. Two parallel polymeric porphyrin bands showing the coordinative bonding between tetrakis-bidentate porphyrin carboxylate and calcium ions (large gray spheres) both as space-filling model and as a schematic model in which the tetraphenylporphyrin macrocycles have been replaced by cylinders that intersect at the center of the porphyrin. The orientation of the bands accurately depicts packing in the crystal, Ca-O (carboxylate) = 2.451(5) & 2.515(5) Å, bond angle O-Ca-O = 52.6°; Ca-OH$_2$ = 2.388(6) and 2.454(6) Å

[17], and succinic acid [18]. The summation of the angles surrounding the carbonyl carbon is 360.0° confirming the planarity of the carboxylate unit. The experimental Ca-O-C angles [94.2(5)° and 90.8(4)°] are within the range observed for Ca^{+2} bidentate carboxylate complexes (80-100°), whereas examples of the unidentate coordination mode showed larger angles (110-140°). The other four ligands are coordinated water ligands: Ca-O(3) = 2.388(6) Å and Ca-O(4) = 2.454(6) Å. For a Ca(II) ion with coordination number of eight, the average Ca-OH$_2$ distance is 2.42 Å [19].

In crystalline calcium-carboxylate complexes, the calcium coordination sphere typically includes multiple carboxylate groups; the most commonly observed number is three [20]. The preferred coordination mode is unidentate, corresponding to approximately two-thirds of the structurally characterized calcium-carboxylate interactions [14]. Water molecules frequently coordinate to the calcium(II) ion along with ligated carboxylate groups. The most commonly reported coordination number is eight, although approximately 40% of structurally characterized calcium carboxylate complexes display coordination spheres with six or seven ligands [14-24]. The average Ca-O$_{carboxylate}$ interatomic distance is 2.44 Å; bond lengths for complexes with fewer ligands were shorter (2.32 Å and 2.41 Å for coordination numbers six and seven, respectively) than the higher coordination compounds (2.47 Å, for coordination number eight). The calcium ions are commonly observed to be located significantly out of the plane of the carboxylate group. A common geometric pattern encountered is the lamellar segregation of calcium ions between the organic carboxylate species [15, 21, 22].

The calcium layer is held together by hydrogen bonds (2.791-3.132 Å as measured from donor oxygen to acceptor oxygen atom) between carboxylate and aqua ligands (Fig. 2) to yield a tightly held three-dimensional solid with a total of seventy-two hydrogen bonding interactions per formula unit (i.e., nine per calcium tetra-aqua center). There are no coordinative bonding interactions between layers of porphyrin bands. Hydrogen bonding between coordinated water and carboxylate ligands within the calcium layers is observed to stabilize the three-dimensional structure.

Strong interlayer hydrogen bonds between water ligands and carboxylate groups of different coordination polyhedra have been observed to construct two- and three-dimensional networks in other calcium-carboxylate coordination polymers. Such networks include the complexes of the terephthalate (2.732-2.944 Å, O···O interatomic distances) [15], succinate (2.761-3.058 Å) [18], napthalenetetracarboxylate [16], phthalate
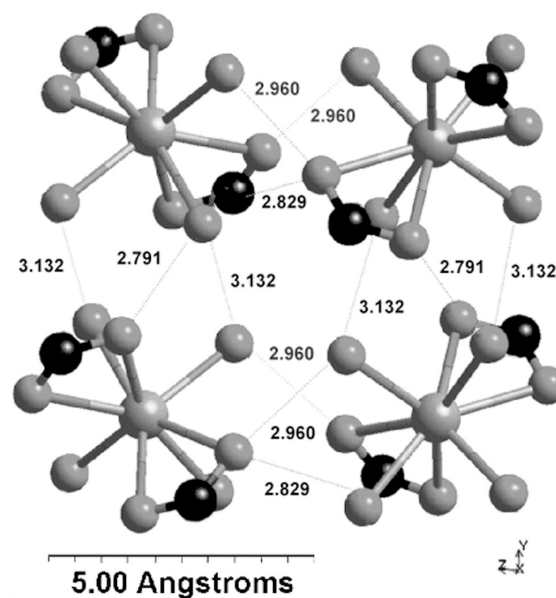

Fig. 2. Coordination of calcium ions (largest central spheres) with hydrogen-bonding between water and carboxylate ligands (carbon atoms in black) indicated by dashed lines between oxygen atoms

(2.897-2.951 Å) [22], glycerate (2.689-2.904 Å) [23], glutamate (2.683-2.942 Å) [24], and 1,3,5-benzenetricarboxylate [25] ions. Many of these structures also exhibit the general motif consisting of layers of organic-carboxylate groups alternating with layers of calcium ions and water molecules.

A similar structural motif was elucidated by Noll and Wang using H$_2$(TPyP) in which the pyridine nitrogen atoms coordinate HgBr$_2$ moieties [9]. The independent linear polymers are also geometrically similar to those observed for the T(p-OH)PP hydrogen bonded networks found by Strouse and coworkers [5].

Parallel layers of porphyrin bands are segregated in a pillar-like fashion by rows of calcium(II) ions and coordinated water molecules. The interfacial separation between the parallel porphyrin bands is 4.1 Å and 5.1 Å. Another infinite set of parallel porphyrin bands interpenetrates the first, thereby creating a three-dimensional network (Fig. 3). Successive parallel porphyrin bands are offset by half a porphyrin unit. This forms an intricate weave-like three-dimensional interpenetrating structure (Fig. 4). The stacking of the orthogonal porphyrin bands and the calcium-water layer forms a clathrate structure in which a pyridine molecule is included (Fig. 5). The size of the interstices within the host compound was determined to be 4.1 Å × 5.1 Å × 13.9 Å, based on Van der Waals radii of bordering atoms. The pyridine molecule (linear dimensions: 3.4 Å × 7.1 Å × 6.4 Å) is canted toward the corners of the clathrate "box" in order to fit into the constrained space.

The freebase porphyrin in the Ca-clathrate network

is nearly planar. The tilt angles of the porphyrin phenyl rings relative to the nitrogen plane of the porphyrin (φ_{ar}) were found to be 83.1°. The pyrrole tilt angles (φ_{pyr}) were measured to alternate values of 2.9° and 0.4°.

Thermogravimetric analysis showed (Perkin-Elmer 7 Series Thermal Analyzer under N_2) an initial weight loss below 50 °C of 5.72%, which was attributed to loosely adsorbed water vapor from

Fig. 3. Schematic of porphyrin bands showing interpenetration of orthogonal bands. Outside vertices of the diamond correspond to location of the calcium ions within solid-state packing model; crossing of cylinders corresponds to the center of the porphyrin macrocyclic plane. The primary building unit of the extended solid-state structure, the bands interpenetrate at half-porphyrin unit intervals in both directions
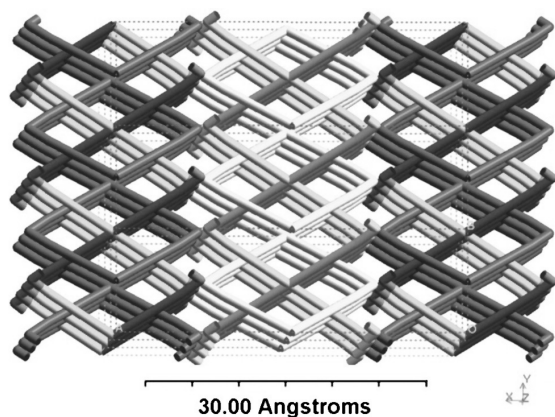

Fig. 4. The extended 3-D structure of ($H_2T(p$-$CO_2)PPCa_2)(H_2O)_4 \cdot C_5H_5N$ depicting the weaving of Ca-carboxylate porphyrin bands. Shading differentiates interpenetrating coordination polymer layers. Bands within layers are orthogonal
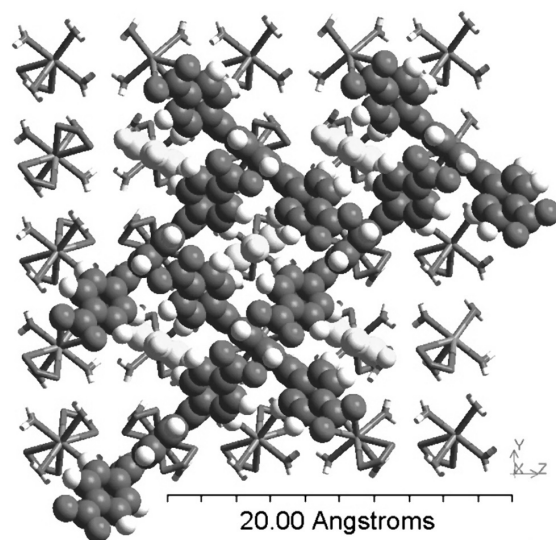

Fig. 5. Cut-away projection down the *a*-axis delineating the clathrate cavity formed by 4 porphyrin moieties (edge on view in dark gray space-filling model) and the calcium-water layers (cylinders) around the included pyridine (very light gray space-filling model). The "top" of the box is formed by the next calcium-water layer (removed for clarity). The cavity dimensions are 4.1 Å and 5.1 Å across from porphyrin to porphyrin face and 13.9 Å between Ca-layers

exposure to ambient atmosphere. Upon continued heating to 200 °C, there is an additional 6.57% weight loss corresponding to the loss of pyridine guest molecules (theoretical 6.76%) as the hydrogen bonded layers separate. Above 400 °C, decomposition of the porphyrin is observed.

These results suggest further exploration of the material's potential as an intercalation compound. Expansion and fine-tuning of the size of the clathrate cavity should be possible by the use of larger nitrogenous base template molecules, such as aniline, 2,4,6-collidine, 4,4'-bipyridine, dicyclohexylamine, or adamantylamine.

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