A New Type of Infinite 3D Polymeric Network Containing 4-Connected, Peripherally Linked Metalloporphyrin Building Blocks

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New families of materials may be provided by interconnecting in various ways either rod-like[1] or slab-like units to form infinite framework structures. A simple example of such a slab-like unit is afforded by $Pt(CN)_4^{2-}$, which yields an infinite framework related to the PtS structure[2] when interconnected by tetrahedral Cu^I centers.[3] The stability and rigidity of metalloporphyrins, together with their potential for symmetrical 4-connection to other units, makes them especially attractive as slab-like components for the construction of new infinite structures. Linear polymeric structures based on metalloporphyrins and phthalocyanins linked together via axial bridges between metal centers have attracted considerable attention partly because of their anticipated unusual electrical behavior.[4] We report here the synthesis and X-ray crystal structure of a new geometrical and topological type of infinite 3D structure in which (5,10,15,20-tetra-4-pyridyl-21*H*,23*H*-porphinato)palladium (hereafter Pd·py·porph) units are interconnected by cadmium(II) centers.

Pd·py·porph (14.8×10^{-3} g, 0.020 mmol) was suspended in a solution of $Cd(NO_3)_2{\cdot}4H_2O$ (8.65 g, 0.028 mol) in methanol (12 mL) and water (12 mL) at its boiling point. Boiling ethanol was added in small portions to the boiling mixture until the suspended solid dissolved completely. The solution, after it had cooled to room temperature, was set aside in an open vessel to evaporate slowly. The dark red crystals that had grown after 4 days were collected, washed with ethanol, and dried in air: yield, 16.6×10^{-3} g. Anal. Calcd for $C_{40}H_{41.2}Cd_2N_{12}O_{20.6}Pd$ (i.e., (Pd·py·porph)·$2Cd(NO_3)_2{\cdot}8.6H_2O$): C, 35.6; H, 3.1; N, 12.4. Found: C, 35.9; H, 3.1; N, 12.1. The IR spectrum (KBr disk) showed a strong nitrate band at 1380 cm^{-1} and a pyridine ring vibration at 1605 cm^{-1}, significantly higher than that observed for Pd·py·porph itself (1590 cm^{-1}), indicative of coordination of the pyridyl nitrogens.

A crystal was mounted in air on a fine Lindemann glass fiber for X-ray crystallographic analysis.[5] Figure 1 shows a view[6] of the porphyrin ring and its immediate environment. Palladium centers are square planar. All porphyrin nuclei are equivalent. All four pyridyl units of the porphyrin are bound to essentially octahedral cadmium centers which are coordinated by two trans monodentate nitrate ligands, two water ligands, and two pyridyl ligands. Cd(2)'s are "linear" 2-connectors, having two trans pyridine ligands; Cd(1)'s are "bent" 2-connectors, having two cis pyridine ligands (N-Cd-N, 103 (1)°).

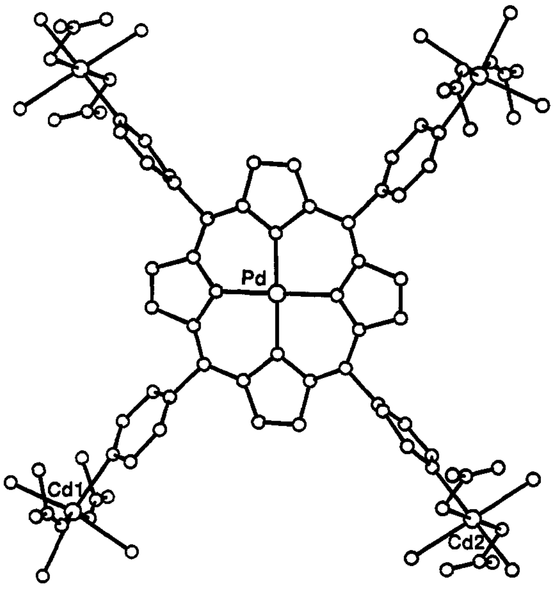

Figure 1. A view[6] of the porphyrin and the attached cadmium centers in (Pd·py·porph)·$2Cd(NO_3)_2$·hydrate. Cd(1) is coordinated by two cis pyridyl donors and Cd(2) by two trans pyridyl donors.

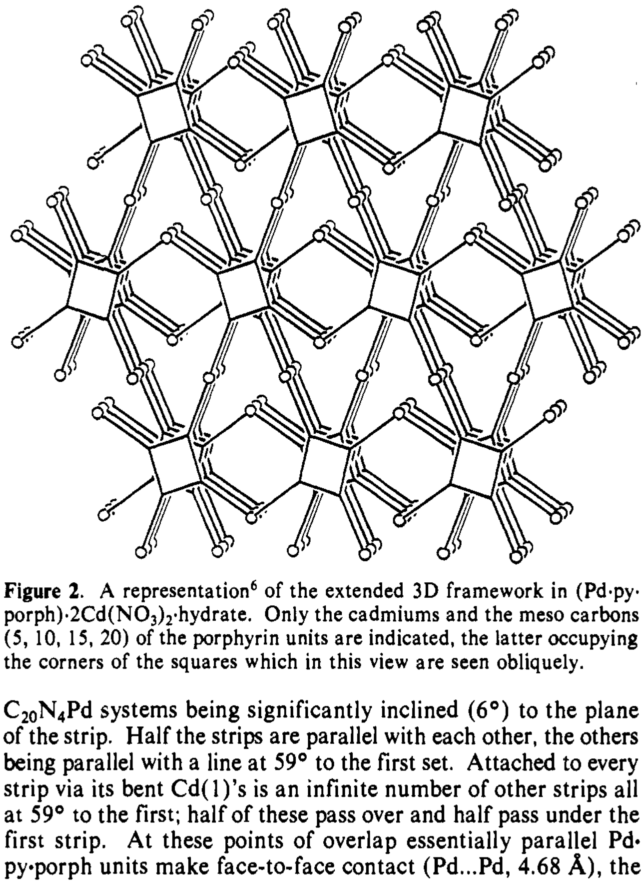

Figure 2. A representation[6] of the extended 3D framework in (Pd·py·porph)·$2Cd(NO_3)_2$·hydrate. Only the cadmiums and the meso carbons (5, 10, 15, 20) of the porphyrin units are indicated, the latter occupying the corners of the squares which in this view are seen obliquely.

As can be seen in Figure 2,[6] which represents the extended 3D arrangement, infinite linear strips are present, consisting of porphyrins interconnected by linear Cd's. All the Pd's, Cd(2)'s, and Cd(1)'s of one strip are coplanar, but deformations within each Cd_4–Pd·py·porph moiety lead to the individual macrocyclic $C_{20}N_4Pd$ systems being significantly inclined (6°) to the plane of the strip. Half the strips are parallel with each other, the others being parallel with a line at 59° to the first set. Attached to every strip via its bent Cd(1)'s is an infinite number of other strips all at 59° to the first; half of these pass over and half pass under the first strip. At these points of overlap essentially parallel Pd·py·porph units make face-to-face contact (Pd...Pd, 4.68 Å), the PdPd vector making an angle of 30° with the normal to the porphyrin planes; in this way stacks of porphyrins are generated with all Pd's collinear and parallel with *z*. As is common in 5,10,15,20-tetraaryl porphyrins, large dihedral angles between the planes of the pyridine rings and the macrocycle are observed (78° for the pyridines attached to Cd(2) and 53° for the others). Steric clashes between the pyridines of one porphyrin and those of its face-to-face neighbors are avoided by the extensive staggering apparent in Figure 2.

The preliminary result described here augurs well for future studies with frameworks constructed from various 4-connecting porphyrins linked to a variety of other connecting units from which

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(5) Crystal data for (Pd·py·porph)·$2Cd(NO_3)_2$·hydrate: monoclinic, space group *C*2/*c*, $a = 16.520$ (9) Å, $b = 34.60$ (1) Å, $c = 9.361$ (8) Å, $\beta = 112.40$ (6)°, $Z = 4$. Crystal structure analysis indicates ca. 9 H_2O/Pd atom consistent with the elemental analysis.

(6) Plots in this communication were obtained by using the ORTEP program.

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many new 3D (or 2D) nets may be anticipated.

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Supplementary Material Available: Crystal data and data collection, structure determination and refinement, numbering scheme, and tables of crystal data and structure determination, fractional atomic coordinates and isotropic thermal parameters, and interatomic distances and angles for (Pd·py·porph)·2Cd(NO_3)$_2$·hydrate (9 pages); listing of observed and calculated structure factors (5 pages). Ordering information is given on any current masthead page.

Urea Transport by Macrocyclic Carriers through a Supported Liquid Membrane

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Macrocyclic receptor molecules like crown ethers and calixarenes can be used for the selective transport of cations through bulk and supported liquid membranes.[1-7] In this communication we report the transport of urea in its neutral form through a supported liquid membrane assisted by macrocyclic receptor molecules. To the best of our knowledge this is the first example of transport of neutral molecules through supported liquid membranes by macrocyclic carriers. Only recently examples of assisted transport of neutral molecules through supported liquid membranes have been known.[8,9] Yoshikawa et al. have employed the formation of a covalent bond between the carrier and the guest to transport amines.[8] Pirkle and Doherty have used a lipophilic amino ester for the enantioselective transport of amino esters or amides across a swollen silicone rubber.[9]

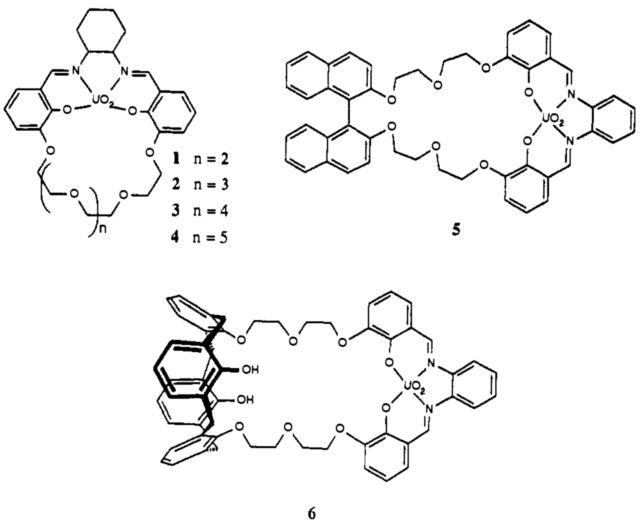

Figure 1. Structures of macrocyclic carriers used for urea transport.

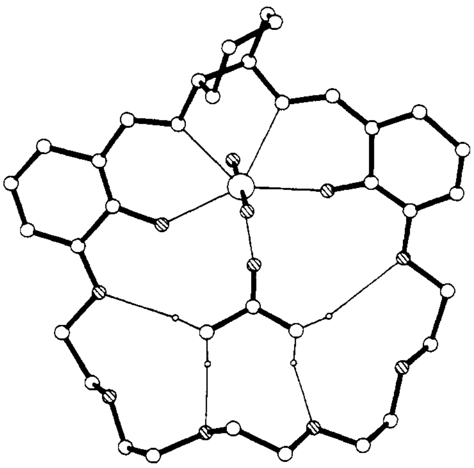

Figure 2. Crystal structure of **2**–urea.

Table I. Urea Fluxes[a] through a Supported Liquid Membrane Measured for Different Metallomacrocyclic Carriers

carrier	carrier concn, mM	flux 1	flux 2	flux 3
–	–	1.6		
1	6.9	2.3		
2	6.0	20.6	10.8	6.8
	2.8	12.0		
3	6.1	8.4		
4	2.8[b]	5.9		
5	6.0	22.2	22.7	23.0
6	6.3	20.0	20.2	20.5

[a] Initial fluxes (in units of 10^{-8} mol cm^{-2} h^{-1}) given after no replacements (flux 1), one replacement (flux 2) and two replacements (flux 3) of the receiving phase; source phase = 1 M urea; 298 K. [b] Saturated carrier solution.

Selective urea removal is of great importance in medicine. Crown ethers are known to form weak complexes with urea.[10,11] Searching for macrocyclic receptor molecules that complex urea well and can be used as selective carriers in supported liquid membranes, we have developed crown ethers with intraannular acidic groups (COOH, SO_3H) which result in a strong interaction with urea.[12,13] However, these receptor molecules have very low partition coefficients (log $P < 1$) and are therefore not suitable as carriers in supported liquid membranes.[6,7,14,15] To improve the lipophilicity, several metallomacrocycles containing a salophene moiety[16,17] have been prepared which complex urea well by coordination of the urea carbonyl to UO_2, which is complexed by

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