Crystal Engineering

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A Phthalocyanine Clathrate of Cubic Symmetry Containing Interconnected Solvent-Filled Voids of Nanometer Dimensions**

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Dedicated to Professor Clifford C. Leznoff

Since the middle of the last century, the crystal structures of a vast number of organic inclusion compounds (namely, clathrates) have been determined.[1] In most cases, only one or two guest molecules reside at well-defined sites within the unit cell of the crystal; however, for a number of structures, such as those derived from urea,[2] thiourea,[2] or tris(*o*-phenylenedioxy)cyclotriphosphazene,[3] extended channels are formed within which the guest molecules, usually the solvent of recrystallization, are contained. Recent extensive research that involves rigid and extended organic components linked through hydrogen-bonding interactions[4] or by coordination to metal ions (namely, metal–organic frameworks (MOFs))[5] has resulted in structures in which solvent-filled channels occupy over 70% of the total volume of the crystal. Furthermore, there are now numerous examples of MOFs for which the removal of the included solvent does not result in loss of crystalline order, but instead gives microporous materials that resemble zeolites.[5,6] However, to offer practical advantages over conventional microporous materials, such as the zeolites and activated carbons, it is desirable that these organic-based microporous materials possess in-built functionalities for selective heterogeneous catalysis, adsorption, and separations. In this context, numerous crystalline porphyrin-based clathrates[7,8] and nanoporous coordination network polymers[8,9] have been reported which may ultimately allow the exploitation of the well-established homogeneous catalytic activity of metal-containing porphyrins in well-defined heterogeneous systems.[10]

Following on from the preparation of amorphous phthalocyanine-based microporous polymers,[11] we have become interested in the possibility of using the highly functional phthalocyanine macrocycle as a building block for the assembly of crystalline nanoporous materials. In analogy to the porphyrins, suitable transition-metal ions held in the central cavity of a phthalocyanine unit can induce catalytic behavior. Unlike porphyrins, for which large-scale production is unfeasible, the structurally related phthalocyanines are made routinely and cheaply by industry for use as stable blue colorants, photoconductors in xerography, and IR dyes, as well as for application to homogeneous oxidation catalysis in the removal of sulfurous compounds from crude petrochemicals (the Merox process).[12] Unfortunately, the extended planar shape of the phthalocyanine unit results in a strong tendency to form densely packed cofacial aggregates (e.g., stacked crystals,[13] columnar liquid crystals,[14] etc.), and this behavior must be prohibited to engineer open nanoporous structures that allow access to such active metal centers.

Our general strategy to avoid cofacial self-association involves the use of substituents that can introduce severe steric crowding adjacent to the phthalocyanine core.[15] Molecular modeling helped to identify that 2,6-diisophenoxy groups placed on the peripheral positions of the phthalocyanine ring would be perfectly suited for this purpose. Hence, a novel zinc 2,3,9,10,16,17,23,24-octa(2′,6′-diisopropylphenoxy)phthalocyanine (**1**) compound was prepared by using a simple two-step high-yielding synthesis from the commercially available 4,5-dichlorophthalonitrile and 2,6-diisopropylphenol via 4,5-di(2′,6′-disopropylphenoxy)phthalonitrile (**2**) by following a literature procedure (Scheme 1).[16]

Slow recrystallization by the diffusion of acetone into a solution of **1** in $CHCl_3$ gives large crystals (up to 1 mm^3) with a cubic morphology, for which a surprising molecular packing arrangement was revealed by single-crystal X-ray diffraction (XRD) analysis (Figure 1). The crystal structure is cubic and belongs to the exceptionally rare space group $Pn\bar{3}n$,[17] with 12 phthalocyanine molecules in the unit cell ($a = 3.77$ nm). The phthalocyanine core of **1** is a shallow cone-shape with the central Zn^{2+} ion and the oxygen atom of its axial ligand protruding from the molecular plane (probably from a water ligand as the acetone used for the recrystallization was not anhydrous). As predicted, the 2,6-diisopropylphenoxy substituents lie out of the plane of the macrocycle and thereby prohibit the formation of columnar stacks. Instead, the molecules pack to form cubes, with an equivalent of two per unit cell and a molecule of phthalocyanine comprises each of the six faces. The macrocycles are arranged so that their Zn^{2+} ion and its axial ligand point towards the center of the cube. Based upon the distance between the protruding Zn^{2+} ions on opposite sides of the cube, the minimum diameter of the cube is 2.33 nm, which gives a cavity volume of at least 8 nm^3, even if the width, calculated from the sum of the van der Waals radii, of the phthalocyanine unit (0.33 nm) is taken into account. In addition to the axial water ligand attached to the Zn^{2+} center of **1**, there are a further

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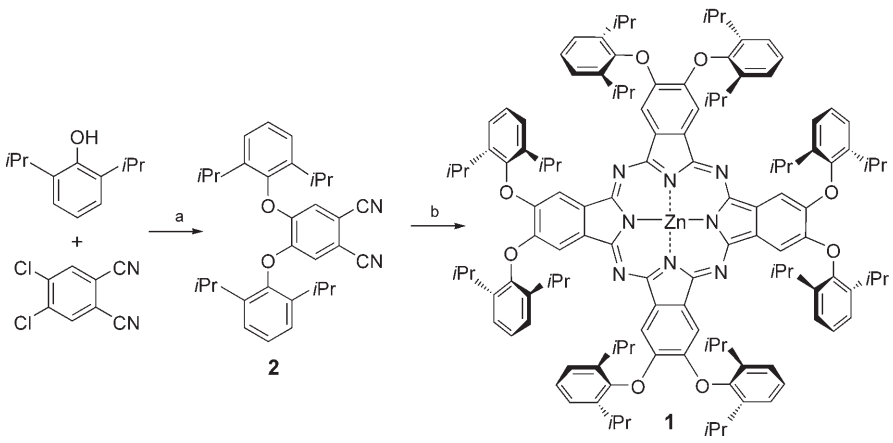

Scheme 1. The synthesis of phthalocyanine **1**. Reagents and conditions: a) K_2CO_3, DMF, 70 °C; b) $Zn(OAc)_2$, NMP, 150 °C. DMF = dimethylformamide, NMP = *N*-methylpyrrolidone.

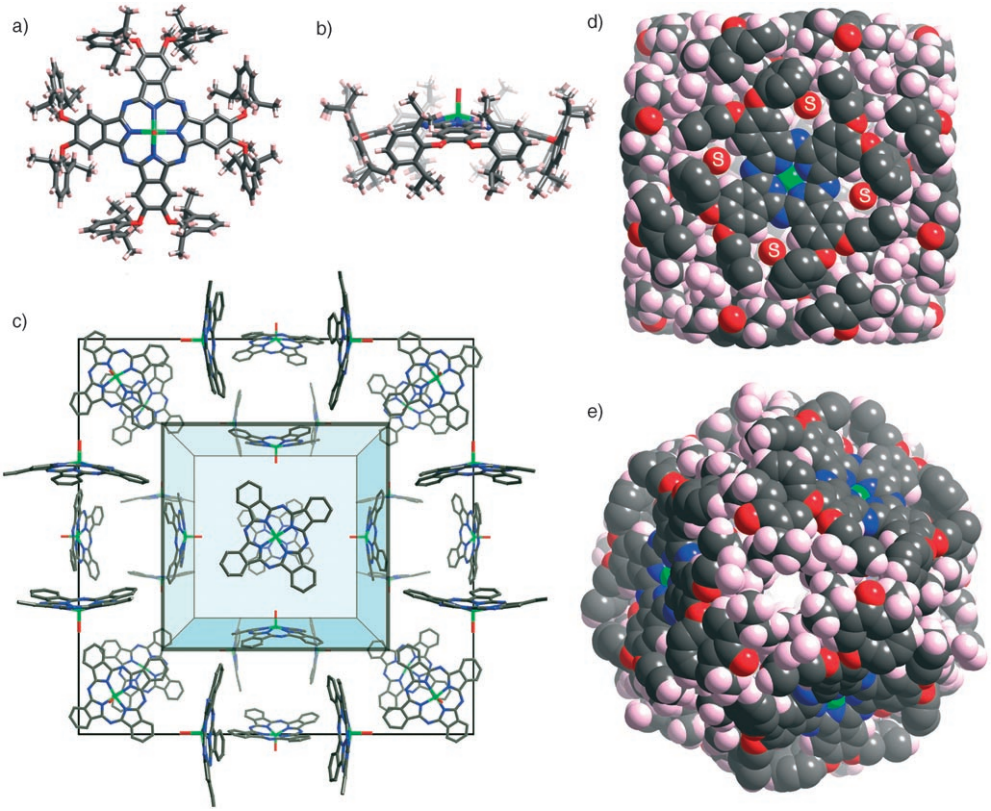

Figure 1. The molecular and crystal structure of **1**. a) Face-on and b) edge-on molecular views of **1** which show the orthogonal and square conformation of the eight peripheral 2′,6′-diisopropylphenoxy substituents relative to the phthalocyanine core, which prohibits cofacial molecular self-association. c) The cubic packing arrangement of **1** shown with the phenoxy substituents removed for clarity. The outer cube represents the unit cell, with dimensions of 3.77 nm, which contains 12 molecules of **1**. The inner cube represents one of the two voids of volume 8 nm^3 found in each unit cell. In this view, the second nanovoid is distributed at each corner of the unit cell in 8×1 nm^3 portions. d) Side-view of a space-filling representation of the central cubic subunit showing the location of the oxygen atoms (S) of the solvent (water or methanol) hydrogen bonded to the *meso* nitrogen atoms of the phthalocyanine unit. e) Corner view of the cubic subunit showing one of the 0.4-nm cylindrical openings, which interconnect the 8-nm^3 voids contained within the cubes.

24 water molecules per unit cell that appear to be associated through hydrogen-bonding interactions to the *meso* nitrogen atoms of the phthalocyanine ring (Figure 1d). No further solvent could be located within the crystal structure.

The calculated density of the crystal of **1** is only 0.75 $g\,mL^{-3}$, which when compared to that of the densely packed crystal of its phthalonitrile precursor **2** (approximately 1.15 $g\,mL^{-3}$), suggests a total void volume of 35% (namely, approximately 18 nm^3 per unit cell). Calculations with the PLATON program[18] indicate a solvent-accessible void volume of 20.5 nm^3 per unit cell (namely, 38.2% of the total volume). Thermal analysis of a freshly recrystallized sample of **1** with thermogravimetric analysis (TGA) shows a mass loss of 25.5% on heating up to 120 °C, for which the water of solvation observed in the crystal structure can account for only 1.6%. Assuming that the additional loss of mass observed by TGA is because of included, but disordered, solvent of recrystallization, it can be estimated that there is a molar ratio of **1**/acetone/H_2O of approximately 1:11:3. ^1H NMR spectroscopic analysis based on the peak integration for the clathrate dissolved in $CDCl_3$ provides a very similar molar ratio. This result is consistent with filling both of the two 8-nm^3 void spaces within the unit cell with approximately 132 molecules of acetone at a density of 0.77 $g\,mL^{-3}$ (density of acetone at 20 °C = 0.79 $g\,mL^{-3}$).

The crystal is not stable on removal from the crystallization solvent because of solvent loss, as indicated by XRD analysis, although the macroscopic appearance of the crystals is unchanged. Over half of the included solvent is lost within one hour (12% by mass remains, as determined by TGA) when placed in a dry stream of nitrogen at room temperature. A close inspection of the structure of each cubic subunit reveals that the void space appears almost fully

enclosed by the six phthalocyanine units and their 2,6-diisopropylphenoxy substituents (Figure 1 d). The largest apertures are situated at each corner of the cube, and these provide narrow cylindrical channels (approximately 0.4 nm in diameter) that connect the voids (Figure 1 e). Preliminary solvent-exchange experiments were performed by submergence of the clathrate crystals in [D_6]acetone, followed by NMR spectroscopic analysis of the crystals dissolved in $CDCl_3$. These experiments show that nearly all of the included acetone (approximately 98%) is exchanged within two hours. A similar experiment using methanol indicates that all of the included acetone can be replaced to give a crystal that contains a molar ratio of **1**/MeOH/H_2O of 1:20:2, thus giving approximately 120 molecules of methanol in each void at a calculated density of 0.8 g mL^{-3} (density of methanol at 20 °C = 0.79 g mL^{-3}). XRD analysis shows that the solvent exchange does not alter the basic crystal structure, although the water molecules hydrogen bonded to the *meso* nitrogen atoms of **1** (Figure 1 d) are replaced by methanol, and several other localized, but highly disordered, methanol molecules can be tentatively assigned within the crystal structure.

Remarkably, even water can be used to achieve almost complete exchange of acetone without loss of crystalline order. NMR spectroscopic analysis of the dissolved clathrate which had been previously submerged in water gives a molar ratio of **1**/acetone/H_2O of 1:0.5:30, which indicates each void is filled with approximately 180 water molecules at a calculated density of 0.65 g mL^{-3}. The apparent low density of the included water may be related to the predominately hydrophobic nature of the voids. It has been recognized that a narrow depletion layer, composed of water in the vapor phase, forms at the interface between a hydrophobic surface and water because of the disruption of hydrogen-bonding interactions.[19] At first sight, it seems surprising that water can gain access to the voids through the narrow interconnecting channels, which are lined with isopropyl groups (Figure 1 e). However, the recent observation of water transport through the extended hydrophobic channel of a carbon nanotube of similar diameter provides a close analogy.[20]

The cubic packing of **1** is clearly related to the fourfold symmetry of the phthalocyanine molecule and allows the number of weak intermolecular interactions to be maximized by the interleaved phenoxy substituents along each of the 12 vertices of the cubic subunit. Relative to reported hydrogen-bonded clathrate structures, the proportion of included solvent within the crystal structure of **1** is unremarkable; however, its distribution into such large well-defined cavities is unprecedented. Molecular enclosure on the subnanoscale may be achieved within the voids of discrete molecular cages,[21] crystalline clathrates,[4] and network coordination polymers;[22] however, only a few examples approach,[23] and fewer exceed,[24] an enclosed volume of 1 nm^3. Of interest, is the potential for the exploitation of the functionalities present in the phthalocyanine unit to provide catalytic sites that would be embedded in the wall of the cavities and accessible only through the narrow size-selective channels. Hence, we envisage a clathrate that exhibits similar size and shape selectivity to that of the channel inclusion complexes (e.g., urea) but with intrinsic catalytic activity. Studies on the preparation of similar clathrates that contain catalytically active transition-metal ions (e.g., Co^{2+}, Fe^{3+}, etc.) are in progress, as are attempts to stabilize the structure through the placement of polar and hydrogen-bonding substituents on the 2,6-diisopropylphenoxyl units. Furthermore, the unique crystal structure of **1** suggests an approach to novel inorganic or organic nanoparticles by their assembly within the enclosed voids.[25]

Experimental Section

1: A mixture of 4,5-di(2,6-diisopropylphenoxy)phthalonitrile (0.5 g, 1.04 mmol; prepared by using an adapted literature procedure)[16] and an excess of anhydrous zinc acetate (20 mg) in dry NMP (6 mL) was stirred at 150 °C under nitrogen for 24 h. The reaction mixture was added to stirred distilled water (200 mL) on cooling, and the solid product was collected by filtration and washed with water and MeOH. The crude product was purified by column chromatography on silica gel with dichloromethane as the eluent and recrystallized from acetone to afford a bright green crystalline solid. Yield: 0.32 g (65%). M.p. 286 °C, elemental analysis (%) calcd for $C_{128}H_{144}O_8N_8Zn$: C 77.33, H 7.30, N 5.63; found: C 76.98, H 7.14, N 5.44; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 1.35 (96 H, br s), 3.48 (16 H, sept), 7.51 (16 H, d), 7.62 (8 H, t), 8.20 ppm (8 H, s); IR (KBr disc): λ_{max} (CH_2Cl_2, nm): 680, 362, 280 cm^{-1}; MALDI-MS (*m*/*z*) 1988 ([M^++H$^+$]).

X-ray structural analysis: Data were collected at 150 K using synchrotron radiation at Daresbury SRS, UK (Station 9.8) with a Bruker-Nonius APEX11 CCD diffractometer (λ = 0.6934 Å), and the structure was solved by direct methods. All calculations were carried out using the SHELXTL package.

Crystal data for **1**·3 H_2O·11 C_3H_6O: crystal size 0.7 × 0.4 × 0.4 mm^3, cubic, space group $Pn\bar{3}n$, $a = b = c$ = 3.76973(2) nm, V = 53.571.1(5) nm^3, Z = 12, R_1 = 0.0915. The asymmetric unit contains a quarter of **1** together with half a water molecule. A number of the carbon atoms were disordered over two sites, whose occupancies were constrained to sum to unity. The components of the disordered phenyl group were constrained to be regular hexagons. Non-hydrogen atoms were refined anisotropically, with restraints on the thermal motion of the carbon atoms, except those that were disordered. Hydrogen atoms were included in calculated positions, except those bonded to the axial oxygen atoms, which were omitted. CCDC-279644 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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