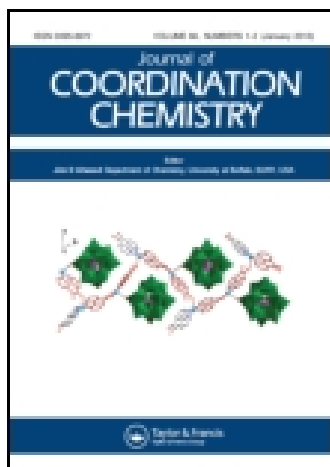


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Journal of Coordination Chemistry

Publication details, including instructions for authors and subscription information:

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Accepted author version posted online: 01 Aug 2013. Published online: 02 Sep 2013.

To cite this article: Venkata S. Pavan K. Neti, Alejandro J. Metta-Magaña & Luis Echegoyen (2013) Solvothermal synthesis and crystal structure of a 3-D hexagonal metal-porphyrin coordination network, *Journal of Coordination Chemistry*, 66:18, 3193-3198, DOI: [10.1080/00958972.2013.830715](https://doi.org/10.1080/00958972.2013.830715)

To link to this article: <http://dx.doi.org/10.1080/00958972.2013.830715>

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Solvothermal synthesis and crystal structure of a 3-D hexagonal metal-porphyrin coordination network

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(Received 3 September 2012; accepted 12 July 2013)

A hexagonal-shaped hybrid metal-porphyrin coordination framework containing 5,15-di(4-pyridyl)-10,20-diphenylporphyrin (trans-H₂DPyP) and Zn(NO₃)₂·6H₂O in DMF has been self-assembled solvothermally. The solvothermal reaction of Zn(II) with conformationally versatile 5,15-di(4-pyridyl)-10,20-diphenylporphyrin, which can coordinate axially to two ligands, resulted in metallation of the porphyrin core and then self-coordination of the metallated porphyrin produced single crystals of 3-D polymeric arrays. The trans-ZnDPyP framework is thermally stable at 450 °C and allows solvent exchange without losing the crystal structure.

Keywords: Solvothermal synthesis; Porphyrin; Coordination network

Introduction

Self-assembly of inorganic/organic hybrid materials that lead to coordination polymers or networks has been a central theme in materials chemistry [1]. Syntheses of highly organized multiporphyrin-based materials are very attractive due to their photochemical, electron transfer, and catalytic properties [2]. Solvothermal synthetic methods of microporous and mesoporous 1-D, 2-D, and 3-D porphyrin metal-organic frameworks (MOFs) offer a strategy to synthesize tailor made nanostructured materials having high surface areas, large pore volumes, and thermal and chemical stabilities [3]. Advantages of the solvothermal synthetic method over others are short reaction times and simplicity, which allow the preparation of large quantities of samples with high crystallinity. Many investigations have been made using porphyrins materials in MOFs and coordination networks [4]. The 5,15-di(4-pyridyl)-10,20-diphenylporphyrin (trans-H₂DPyP)-based metal-porphyrin 3-D coordination network was reported [5] using diffusion methods by Hosseini *et al.* For this system, a single-crystal-to-single-crystal transformation resulting from solvent molecule exchange shows that the framework is highly robust. Here, we report a solvothermal synthesis of the same framework using DMF as a solvent under solvothermal conditions which yields the same single crystal structure (figure 1). Additionally, we determined the thermal stability and

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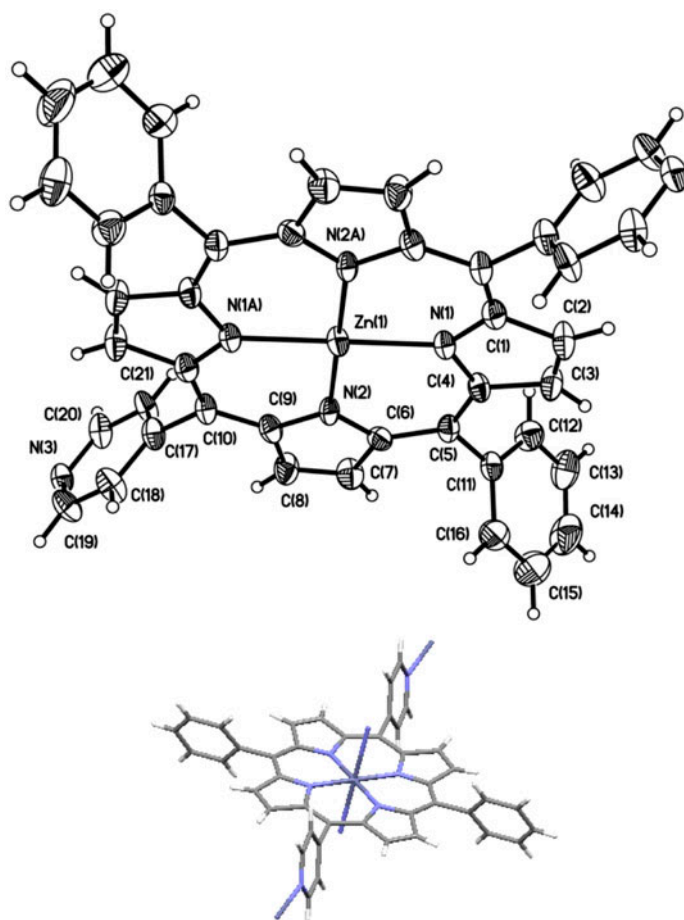


Figure 1. Ellipsoids of trans-ZnDPyP are drawn at 35% probability. Only the asymmetric part is numbered (above). Octahedral geometry of Zn (blue) in the trans-ZnDPyP framework (below) (see <http://dx.doi.org/10.1080/00958972.2013.830715> for color version).

obtained powder X-ray diffraction (PXRD) of trans-H₂DPyP primarily to establish the material's overall crystalline phase purity (figure 2).

Experimental

Zinc nitrate hexahydrate, dimethylformamide, 4-pyridinecarboxaldehyde, benzaldehyde, and pyrrole were purchased from Aldrich and used as received. 5,15-Bispyridyl-10,20-dibenzylporphyrin was synthesized according to a previously reported procedure [6].

Synthesis of porphyrin coordination network

Zn(NO₃)₂·6H₂O (35.6 mg, 0.12 mM), 5,15-bispyridyl-10,20-dibenzylporphyrin (36.9 mg, 0.06 mM) and 8 ml of DMF were combined in an ampoule (20 ml), sonicated for 2 min,

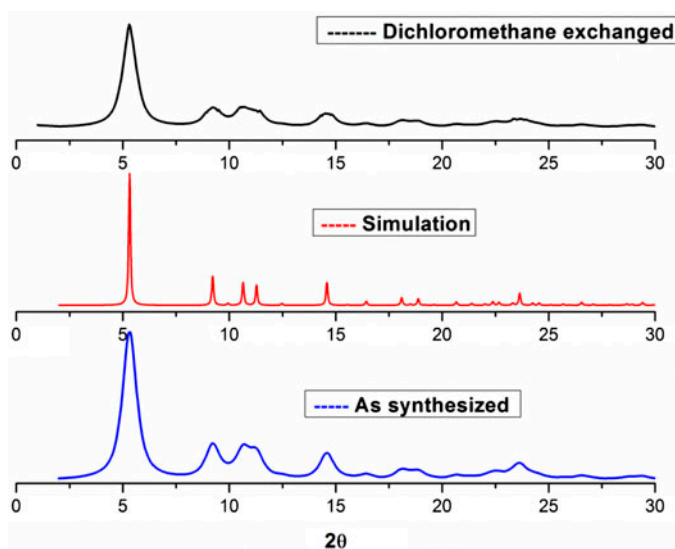


Figure 2. PXRD of (trans-DPyP)Zn.

sealed under vacuum, and then heated to 100 °C for 10 h. The mixture was allowed to cool, filtered, and stored over fresh DMF (4 ml). Single crystals suitable for XRD were formed in the filtered mixture. Yield: 45% (18.2 mg) based on porphyrin. Elemental analysis (%) Calcd for trans-ZnDPyP ($C_{42}H_{26}N_6Zn \cdot 1.6$ DMF). Theory: C, 69.57; H, 4.60; N, 13.82. Found: C, 68.74; H, 4.20; N, 13.97, respectively.

X-ray crystallography. Suitable single crystals were mounted on a Bruker Smart Apex CCD diffractometer equipped with graphite-monochromated Mo-K α radiation ($\lambda = 0.71073$ Å)

Table 1. Crystal data and structure refinement.

Empirical formula	$C_{42}H_{26}N_6Zn$
Formula weight	680.06
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal system	Rhombohedral
Space group	$R\bar{3}$
Unit cell dimensions	$a = 33.198(5)$ Å $\alpha = 90^\circ$ $b = 33.198(5)$ Å $\beta = 90^\circ$ $c = 9.351(3)$ Å $\gamma = 120^\circ$
Volume	$8925(3)$ Å ³
Z	9
Density (calculated)	1.139 Mg m ⁻³
Absorption coefficient	0.653 mm ⁻¹
$F(0\ 0\ 0)$	3150
Crystal size	0.018 mm \times 0.016 mm \times 0.008 mm
Reflections collected	30,540
Independent reflections	3482 [$R(\text{int}) = 0.2106$]
Completeness to $\theta = 25.00^\circ$	99.5%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7457 and 0.5979
Refinement method	Full-matrix least-squares on F^2
Final R indices [$I > 2$ sigma(I)]	$R1 = 0.0692$, $wR2 = 0.1553$

Table 2. Selected bond lengths [\AA] and angles [$^\circ$].

Zn(1)–N(1)	2.071(5)
Zn(1)–N(2)	2.047(5)
Zn(1)–N(3)	2.393(5)
N(1)–Zn(1)–N(2)	89.03(18)
N(1)#1–Zn(1)–N(1)	179.998(2)
N(2)#1–Zn(1)–N(1)	90.97(18)
N(2)#1–Zn(1)–N(2)	179.998(1)
N(1)–Zn(1)–N(3)#2	83.35(18)
N(2)–Zn(1)–N(3)#2	93.23(19)
N(2)–Zn(1)–N(3)#3	86.77(19)
N(1)–Zn(1)–N(3)#3	96.65(18)
N(3)#2–Zn(1)–N(3)#3	180.000(1)

Symmetry transformations used to generate equivalent atoms: #1 $-x + 1, -y + 2, -z + 1$; #2 $y - 1/3, -x + y + 1/3, -z + 4/3$; #3 $-y + 4/3, x - y + 5/3, z - 1/3$.

at 298 K in the ω - 2θ scan mode. The single crystal structure of the metal-porphyrin framework was solved using direct methods (SHELXS-97) and refined by full-matrix least-squares based on F^2 using SHELXL-97. Hydrogens were generated geometrically. Crystallographic data and selected bond lengths and angles are given in tables 1 and 2, respectively. Powder XRD (Cu $K\alpha$ radiation, $\lambda = 1.54 \text{ \AA}$) was used to determine the phase purity of (trans-DPyP)Zn. Powder XRD data were recorded on a Bruker DiscoverD8 model diffractometer by depositing crushed crystals of (trans-DPyP)Zn on a plastic substrate, from $2\theta = 1^\circ$ up to 30° with 0.05° increment. The most intense diffraction peak at $2\theta = 5.2^\circ$ and the other 2θ values are 9.4, 10.7, and 14.9.

Results and discussion

The synthesis of (trans-DPyP)Zn was carried out at 100°C with DMF as solvent and the product is the same as the one reported by Hosseini *et al.* using $\text{CHCl}_3/\text{MeOH}$ as solvent. This demonstrates the robustness of the system, and the solvothermal method offers a faster synthetic method compared to the diffusion method which required many days compared with the 10hr solvothermal procedure. This opens the door to prepare similar compounds with a range of different solvate molecules. For comparison with the structures reported by Hosseini *et al.* here we include the crystal data of the structure isolated (table 1). Thermogravimetric analysis of (trans-DPyP)Zn showed $\sim 15\%$ weight loss around 160°C which is the boiling point of DMF. Based on the Thermogravimetric analysis (TGA) mass loss, we converted the $\sim 15\%$ mass of DMF into moles per unit formula (1.6). Since Hosseini *et al.* reported the robustness of the framework by exchanging the solvent molecules, we exchanged the DMF in the channels of the structure with dichloromethane by following the previously published procedure for MOFs [7]. We could not observe any significant amount of dichloromethane desorption from the TGA traces after exchanging the solvent from DMF to dichloromethane. As evidenced by PXRD, crystallinity was retained after exchanging the solvent (figure 2, black curve). Topologically, this porphyrin is related to a square planar tecton, and therefore related to an NbO structure type. However, it must be noted that in these types of structures there is a strong deformation from the cubic arrangement in the NbO, although the connectivity remains the same.

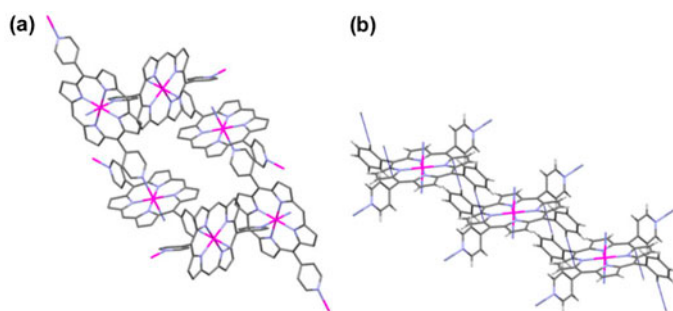


Figure 3. The coordination cycle of (trans-DPyP)Zn formed (a) and H- π interactions (b). The hydrogens on the phenyl rings have been omitted for clarity.

The Zn in the crystal structure is a distorted octahedral coordination geometry by coordinating with two pyridyl rings above and below the porphyrin plane. The axial coordination axis is tilted (83°) toward N1. The porphyrin structure itself presents a slight puckering and the aryls are not perpendicular to the mean plane of the porphyrin but tilted, and the dihedral angle of the phenyl ring is 68° while for the pyridyl ring it is 76° toward the porphyrin mean plane.

The coordination network is formed by a 6-membered macrocycle (figure 3). On this motif, each porphyrin has two free sites to extend the network. In addition to the coordination network, there is a reciprocal H $\cdots\pi$ interaction between a phenyl hydrogen (H12) and a pyridyl ring (N1, $1-x$, $2-y$, $-z$) with a distance of 2.80 Å, which generates a chain along the c axis.

In the crystal structure, the phenyl rings form channels along the c direction (figure 4) that run along the chain motif and are filled with disordered solvent molecules (the solvent

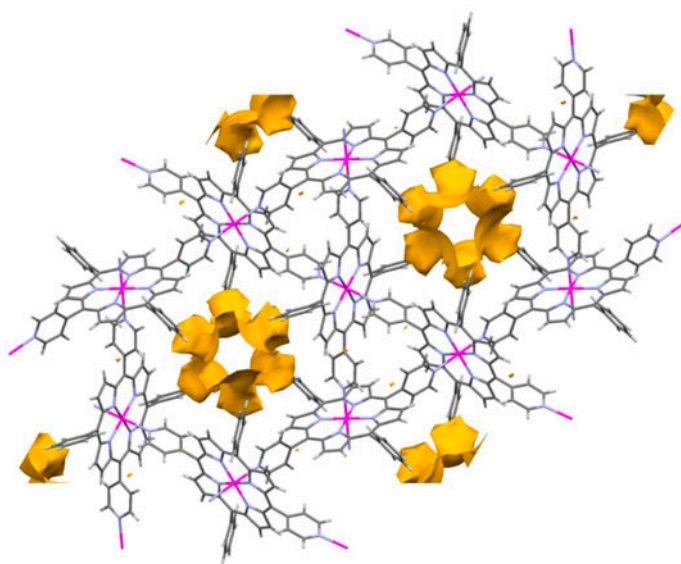


Figure 4. Crystal packing through the c axis showing the resulting solvent accessible channels (DMF: yellow-gold and voids in the middle) (see <http://dx.doi.org/10.1080/00958972.2013.830715> for color version).

could not be solved, so these were removed from the crystal structure using PLATON [8]). The volume of the channels represents around 20% of the unit cell volume and the solvent accessible volume is about 7% (620 Å).

Conclusion

A structurally rigid, robust, self-connecting metalated porphyrin was made using a solvothermal synthetic approach. We quantified the synthesis of (trans-DPyP)Zn using solvothermal approach. This 3-D metal-porphyrin framework was characterized by single-crystal XRD. We also obtained powder XRD data and TGA of (trans-DPyP)Zn which was not known before.

Acknowledgments

This work was generously supported by the NSF grant CHE-1110967 and the Robert A. Welch Foundation, grant # AH-0033.

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