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Hydrothermal Synthesis and Crystal Structure of Non-Metallated Porphyrin

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A non-metallated porphyrin TCPP·4H_2O (**1**) [TCPP = *meso*-tetra(4-carboxyphenyl)porphyrin] has been obtained from a solvothermal reaction and structurally characterized by single-crystal X-ray diffraction. The porphyrin is characteristic of an isolated structure and a saddle-distorted non-planar porphyrin macrocycle. The TCPP molecules and lattice water molecules interconnect together through abundant hydrogen bonding interactions to form a three-dimensional supramolecular network.

Keywords: Solvothermal reaction, Crystal structure, Porphyrin, *meso*-Tetra(4-carboxyphenyl)porphyrin.

INTRODUCTION

Porphyrins are one kind of the most widely investigated compounds. They have abundant and interesting properties and they play vital roles in nature for many decades. They show potential applications in the areas like catalysis, medicine, solar energy conversion and so forth[1-3]. Porphyrins can self-assemble together to form an aggregation and porphyrin supramolecular assemblies can be used as sensors, molecular-level electronics, molecular recognition and photonic materials. Up to date, more and more porphyrin supramolecular assemblies have been synthesized *via* non-covalent interactions such as hydrogen bonding interactions and π-π stacking interactions[4,5]. We report herein the synthesis and X-ray crystal structure of a non-metallated porphyrin TCPP·4H_2O (**1**) [TCPP = *meso*-tetra(4-carboxyphenyl)porphyrin] which is obtained *via* a solvothermal reaction and features a three-dimensional supramolecular network.

EXPERIMENTAL

Synthesis of TCPP·4H_2O (1): All reactants of A.R. grade are commercially obtained and used without further purification. This compound is prepared by mixing $ZnBr_2$ (0.1 mmol, 23 mg), TCPP (0.05 mmol, 40 mg) and 10 mL ethanol in a 25 mL Teflon-lined stainless steel autoclave and heated at 433 K for 10 days. After being slowly cooled down to room temperature at 6 K/h, red crystals are obtained.

X-ray structure determination: The intensity data set is collected on Rigaku Mercury CCD X-ray diffractometer with graphite monochromated MoK_α radiation (λ = 0.71073 Å) by ω scan technique. Crystal Clear software is used for data reduction and empirical absorption correction[6]. The crystal structure is solved by direct method with the Siemens SHELXTL™ Version 5 package of crystallographic software[7]. The difference Fourier maps based on the atomic positions generate all non-hydrogen atoms. The structure is refined with a full-matrix least-squares refinement on F^2. All non-hydrogen atoms are refined anisotropically. CCDC 974906.

RESULTS AND DISCUSSION

The summary of the crystallographic data and structural analysis is listed in Table-1. The bond lengths and bond angles are given in Table-2. An ORTEP drawing of the molecular structure of **1** together with the atomic numbering scheme is depicted in Fig. 1. The results of X-ray diffraction analysis reveal that the crystal structure of **1** consists of isolated and neutral TCPP molecules and lattice water molecules. Compound **1** crystallizes in the space group *Cmca* of the orthorhombic system with eight formula units in one cell. All the crystallographically independent atoms locate on general positions except for O1W, O3W, N1 and N3 atoms which resides at the crystallographic inversion center. The macrocyclic 24-membered ring of the porphyrin is saddle-distorted non-planar and

TABLE-1
SUMMARY OF CRYSTALLOGRAPHIC DATA AND STRUCTURE ANALYSIS

m.f.	$C_{48}H_{40}N_4O_{12}$	Index ranges	$-33 \le h \le 38$, $-19 \le k \le 19$, $-20 \le l \le 19$
f.w.	864.84	Reflections collected	20763
Colour	Red	Independent, observed reflections (R_{int})	3039, 923 (0.4462)
Crystal size/mm^3	0.22 0.18 0.015	$d_{calcd.}$ (g/cm^3)	1.279
Crystal system	Orthorhombic	μ (mm^{-1})	0.093
Space group	*Cmca*	T (K)	293(2)
a (Å)	32.0911(11)	F(000)	3616
b (Å)	16.262 (2)	R1, wR2	0.0994, 0.1313
c (Å)	17.207 (2)	S	0.956
V (Å^3)	8980.0 (17)	Largest and Mean Δ/σ	0, 0
Z	8	$\Delta\sigma$(max, min) (e/Å^3)	0.171, -0.161
$2\theta_{max}$ (°)	50		

TABLE-2
SELECTED BOND LENGTHS (Å) AND BOND ANGLES (°)

O(1)-C(17)	1.254(12)	N(1)-C(2)-C(1)	104.1(8)
O(2)-C(17)	1.270(11)	C(4)-C(3)-C(2)	125.2(9)
O(3)-C(24)	1.176(8)	C(4)-C(3)-C(11)	119.6(8)
O(4)-C(24)	1.353(8)	C(2)-C(3)-C(11)	115.1(9)
N(1)-C(2)#1	1.386(9)	C(5)-C(4)-C(3)	124.9(9)
N(1)-C(2)	1.386(9)	C(5)-C(4)-N(2)	107.9(7)
N(2)-C(7)	1.389(10)	C(3)-C(4)-N(2)	126.4(8)
N(2)-C(4)	1.434(9)	C(4)-C(5)-C(6)	109.2(8)
N(3)-C(9)#1	1.317(7)	C(7)-C(6)-C(5)	108.2(8)
N(3)-C(9)	1.317(7)	C(6)-C(7)-N(2)	109.9(8)
C(1)-C(1)#1	1.458(14)	C(6)-C(7)-C(8)	131.3(9)
C(1)-C(2)	1.543(11)	N(2)-C(7)-C(8)	118.4(8)
C(2)-C(3)	1.347(9)	C(9)-C(8)-C(7)	125.3(7)
C(3)-C(4)	1.348(10)	C(9)-C(8)-C(18)	119.6(6)
C(3)-C(11)	1.472(11)	C(7)-C(8)-C(18)	114.7(7)
C(4)-C(5)	1.331(10)	N(3)-C(9)-C(8)	130.7(6)
C(5)-C(6)	1.375(10)	N(3)-C(9)-C(10)	107.0(6)
C(6)-C(7)	1.334(9)	C(8)-C(9)-C(10)	122.0(6)
C(7)-C(8)	1.452(10)	C(10)#1-C(10)-C(9)	107.0(3)
C(8)-C(9)	1.421(8)	C(12)-C(11)-C(16)	115.1(8)
C(8)-C(18)	1.477(9)	C(12)-C(11)-C(3)	122.7(8)
C(9)-C(10)	1.445(9)	C(16)-C(11)-C(3)	122.1(8)
C(10)-C(10)#1	1.340(11)	C(11)-C(12)-C(13)	124.6(9)
C(11)-C(12)	1.334(10)	C(12)-C(13)-C(14)	122.3(10)
C(11)-C(16)	1.439(11)	C(13)-C(14)-C(15)	115.5(9)
C(12)-C(13)	1.344(11)	C(13)-C(14)-C(17)	123.1(10)
C(13)-C(14)	1.355(12)	C(15)-C(14)-C(17)	121.5(9)
C(14)-C(15)	1.438(11)	C(16)-C(15)-C(14)	121.3(9)
C(14)-C(17)	1.543(14)	C(15)-C(16)-C(11)	121.2(10)
C(15)-C(16)	1.333(11)	O(1)-C(17)-O(2)	128.6(12)
C(18)-C(19)	1.377(10)	O(1)-C(17)-C(14)	116.4(11)
C(18)-C(23)	1.417(10)	O(2)-C(17)-C(14)	114.8(11)
C(19)-C(20)	1.398(10)	C(19)-C(18)-C(23)	120.3(8)
C(20)-C(21)	1.434(10)	C(19)-C(18)-C(8)	117.4(8)
C(21)-C(22)	1.391(10)	C(23)-C(18)-C(8)	122.0(8)
C(21)-C(24)	1.537(10)	C(18)-C(19)-C(20)	120.2(8)
C(22)-C(23)	1.385(9)	C(19)-C(20)-C(21)	118.7(7)
C(2)#1-N(1)-C(2)	117.2(12)	C(22)-C(21)-C(20)	121.2(7)
C(7)-N(2)-C(4)	104.5(7)	C(22)-C(21)-C(24)	116.3(7)
C(9)#1-N(3)-C(9)	112.1(9)	C(20)-C(21)-C(24)	122.5(7)
C(1)#1-C(1)-C(2)	107.1(4)	C(23)-C(22)-C(21)	118.6(7)
C(3)-C(2)-N(1)	130.8(10)	C(22)-C(23)-C(18)	121.0(8)
C(3)-C(2)-C(1)	125.1(8)	O(3)-C(24)-O(4)	125.0(8)
O(4)-C(24)-C(21)	112.3(7)	O(3)-C(24)-C(21)	122.7(8)

Symmetry transformations used to generate equivalent atoms: #1 -x, y, z

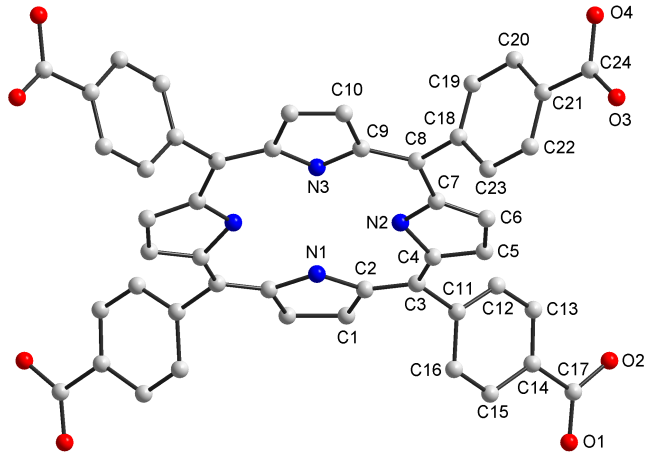

Fig. 1. ORTEP drawing of 1 showing 20 % thermal ellipsoids. The hydrogen atoms and lattice water molecules were omitted for clarity

the displacement of the atoms on the equatorial mean plane is within -0.333 Å to +0.373 Å. The porphyrin macrocycle in **1** shows a four-saddle conformation and the pyrrole rings slightly distort in an alternant mode either upward and downward with respect to the mean plane of the saddle-distorted porphyrin core. The displacement of the nitrogen atoms are within -0.048 Å to +0.049 Å from their mean N4 plane. The dihedral angles between the porphyrin macrocycle and the phenyl rings are 102.4º and 52.99º, respectively. In compound **1**, there are abundant hydrogen bonding interactions, namely, N···N and O···O hydrogen-bonding interactions. The TCPP molecules and lattice water molecules interconnect together through these hydrogen bonding interactions to yield a three-dimensional supramolecular network, as shown in Fig. 2.

Conclusion

We synthesized a non-metallated porphyrin TCPP·4H_2O (**1**) [TCPP = *meso*-tetra(4-carboxyphenyl)porphyrin] with a solvothermal reaction and structurally characterized it with single-crystal X-ray diffraction. The title compound is characterized by an isolated structure and a saddle-distorted non-planar porphyrin macrocycle. The molecules connect together *via* abundant hydrogen bonding interactions to complete a three-dimensional supramolecular network.

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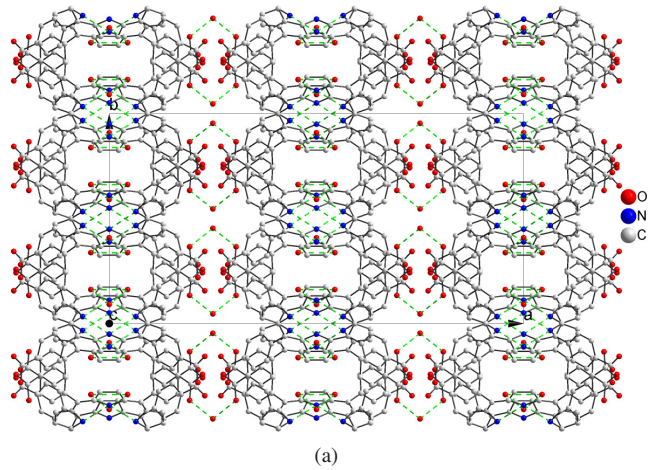
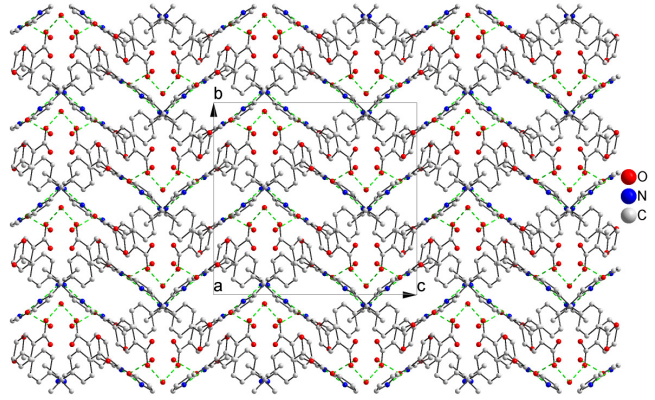


(a)



(b)

Fig. 2. Crystal packing diagram with the dashed lines representing hydrogen-bonding interactions (Å): N(1)···N(2) 2.966(11), N(1)···N(2)(-x, y, z) 2.966(11), N(2)···N(3) 2.902(9), O1W···O1(1/2-x, y, 5/2-z) 2.636, O1W···O1 2.636, O2W···O2W(-x, y, z) 2.846, O2W···O3W 2.669, O3W···O2W(-x, y, z) 2.669

REFERENCES

1. T. Ren, *Chem. Rev.*, **108**, 4185 (2008).
2. J.A. Faiz, V. Heitz and J.-P. Sauvage, *Chem. Soc. Rev.*, **38**, 422 (2009).
3. R. De Zorzi, N. Guidolin, L. Randaccio, R. Purrello and S. Geremia, *J. Am. Chem. Soc.*, **131**, 2487 (2009).
4. M. Yuasa, K. Oyaizu, A. Yamaguchi and M. Kuwakado, *J. Am. Chem. Soc.*, **126**, 11128 (2004).
5. M. Shirakawa, N. Fujita and S. Shinkai, *J. Am. Chem. Soc.*, **127**, 4164 (2005).
6. Rigaku CrystalClear Version 1.35, Rigaku Corporation (2002).
7. Siemens SHELXTL™ Version 5 Reference Manual, Siemens Energy & Automation Inc., Madison, Wisconsin, USA (1994).