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Synthesis and Crystal Structure of Novel Zinc Porphyrin $ZnTCPP(H_2O)\cdot MeOH$ [TCPP = *meso-tetra*(4-carboxyphenyl)porphyrin]

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In order to study new porphyrin complexes, a novel zinc porphyrin $ZnTCPP(H_2O)\cdot MeOH$ [TCPP = *meso-tetra*(4-carboxyphenyl)porphyrin; MeOH = methanol] has been designed, prepared and characterized by a single-crystal X-ray diffraction method. The title complex crystallizes in the orthorhombic system with a *Cmca* space group with eight molecules per unit cell. Zinc porphyrin has an isolated structure in which the zinc ion coordinates to four $N_{porphyrin}$ atoms and one O_{water} atoms.

Key Words: Crystal, Porphyrin, Solvothermal, Zinc, X-ray.

INTRODUCTION

To deeply reveal the photosynthetic process in nature, a number of scientists have devoted their attention to study the syntheses, crystal structures and photophysical properties of diverse photosynthetic model porphyrin complexes[1-3]. Up to date, these porphyrin complexes have obtained more and more research interest not only due to their biological relativity, but also because of their broad potential applications in the fields such as solar energy transfer[4,5], molecular-based photonics and optoelectronics[6,7], *etc*. TCPP [*meso-tetra*(4-carboxyphenyl)-porphyrin] is a very useful porphyrin because it can be adopted as a photosensitizer in many artificial photosynthesis systems. As a result, the optical properties and photophysical behaviours of the TCPP have gained increasing attention. Moreover, to our best of knowledge, zinc plays a vital role in many areas of chemical and biological systems like biotabs and bioluminescence, *etc*. Based on the above reasons, we recently focus on the investigation of new zinc-TCPP complexes. In this work, the synthesis and crystal structure of a novel zinc porphyrin, $ZnTCPP(H_2O)\cdot MeOH$ [TCPP = *meso-tetra*(4-carboxyphenyl) porphyrin; MeOH = methanol] with an isolated crystal structure are reported, which was prepared from a solvothermal reaction.

EXPERIMENTAL

Synthetic process: All chemicals and solvents used in the synthesis are reagent grade. A mixture of $ZnBr_2$ (0.5 mmol, 113 mg), TCPP (0.2 mmol, 158 mg) and methanol (10 mL) was added to a stainless steel reactor with a Teflon liner at 160 ºC for 5 days. After 15 h cooling down to room temperature, red block crystals of the title complex were obtained, isolated by filtration and washed with water (yield *ca.* 22 %).

Single-crystal X-ray diffraction data measurements were conducted on a Rigaku Mercury CCD diffractometer with graphite-monochromated MoK_α radiation (λ = 0.71073 Å). For solution and refinement, I used the programs SHELXS97 (Sheldrick, G.M. Acta Crystallogr., Sect. A 1990, 46, 467) and SHELXL97 (Sheldrick, G. M. SHELXL-97. Program for the Solution and Refinement of Crystal Structures, University of Göttingen, Germany, 1997). The structure was solved by the direct method and refined by full-matrix least-squares on F^2. Anisotropic thermal parameters were used for the non-hydrogen atoms and isotropic parameters for the hydrogen atoms. Hydrogen atoms were added geometrically and refined using a riding model. Weighted R factors (wR) and all of the goodness-of-fit (S) values are based on F^2; conventional R factors (R) are based on F, with F set to zero for negative F^2. The weighting scheme is $w = 1/[s^2Fo^2 + (0.04)^2 + P]$, where $P = (Fo^2 + 2Fc^2)/3$. The important crystal data are summarized in Table-1, while the selected bond lengths and bond angles are listed in Table-2.

RESULTS AND DISCUSSION

The crystal structure of the zinc porphyrin was determined by a single-crystal X-ray diffraction method. Crystallographic data and structural analysis of the complex are listed in Table-1. Some important bond distances and bond angles of the zinc

TABLE-1
CRYSTALLOGRAPHIC DATA AND STRUCTURAL ANALYSIS OF THE TITLE COMPLEX

Empirical formula	$C_{49}H_{30}N_4O_{10}Zn$
Formula weight	900.14
Crystal system	Orthorhombic
Space group	*Cmca*
Unit cell dimensions	a = 31.660(6) Å b = 15.860(6) Å c = 17.861(3) Å
Z	8
V	8968(6) $Å^3$
D_c	1.333 Mg/m^3
Absorption coefficient	0.611 mm^{-1}
Crystal size	0.30 mm × 0.22 mm × 0.20 mm
No. of reflections collected/unique	25712/3857 [$R_{(int)}$ = 0.0618]
Goodness-of-fit	1.001
Parameter/restraints/data (obs.)	296 / 7 / 1902
Final *R* indices	R^1 = 0.0681, wR^2 = 0.1468
R indices (all data)	R^1 = 0.1162, wR^2 = 0.1668
Index ranges	$-37 \le h \le 37$, $-18 \le k \le 18$, $-21 \le l \le 16$
Largest and Mean Delta/Sigma	0, 0
Largest difference peak (e·$Å^{-3}$)	0.974, -0.386

TABLE-2
SELECTED BOND LENGTHS AND BOND ANGLES OF THE TITLE COMPLEX

Bond lengths (Å)		Bond angles (°)	
Zn(1)-N(1)	2.041(4)	N(1)-Zn(1)-N(3)	167.83(16)
Zn(1)-N(2)	2.071(3)	N(1)-Zn(1)-O(1W)	96.65(18)
Zn(1)-N(2)#1	2.071(3)	N(2)-Zn(1)-N(2)#1	172.64(15)
Zn(1)-N(3)	2.067(4)	N(2)-Zn(1)-N(3)	89.42(7)
Zn(1)-O(1W)	2.230(5)	N(2)-Zn(1)-N(3)#1	89.42(7)
Bond angles (°)		N(2)-Zn(1)-O(1W)	93.67(7)
N(1)-Zn(1)-N(2)	89.80(7)	N(2)#1-Zn(1)-O(1W)	93.67(7)
N(1)-Zn(1)-N(2)#1	89.80(7)	N(3)-Zn(1)-O(1W)	95.52(16)

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

porphyrin are shown in Table-2. A crystal structure of the present complex is given in Fig. 1, from the figure the tetrapyrrole nature and the molecular dimension can be clearly observed. The X-ray single-crystal diffraction analyses reveal that the title complex features an isolated structure with neutral ZnTCPP(H_2O) and methanol molecules. The central 24-membered porphyrin macrocycle is approximate coplane with the displacement of the atoms in the equatorial average plane between +0.339 Å and -0.421 Å. The zinc ion locates at the center of the nearly coplanar porphyrin macrocycle. The coordination environment of the zinc ion can be described as a slightly distorted square pyramid, *i.e.* the zinc ion is pentacoordinated by one oxygen atom of the coordinating water molecule and four pyrrole nitrogen atoms of the TCPP ligand (Fig. 1). The bond lengths of the Zn-$N_{porphyrin}$ range from 2.041(4) Å to 2.071(3) Å with a mean value of 2.063(4) Å, which can be comparable with those found in the references[8,9]. The bond distance of the Zn-O_{water} is 2.230(5) Å which is comparable with the reported[10,11]. Between the macrocyclic ring and the phenyl rings, the dihedral angles are 56.8(3)° and 78.4(2)°. The crystal packing structure of the title complex is shown in Fig. 2, from which a three-dimensional supramolecular motif can be found. The three-dimensional supramolecular motif is constructed from the intermolecular hydrogen bonds between the carboxylic groups of the neighboring TCPP molecules. The methanol molecules are resided in the voids of the three-dimensional supramolecular framework (Fig. 2b).

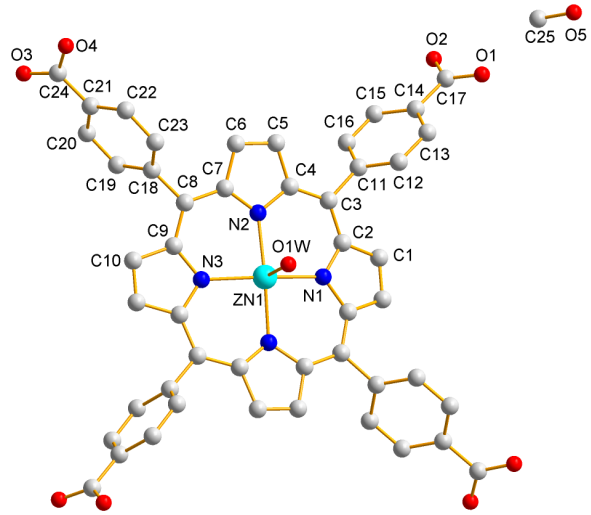

Fig. 1. Molecular structure of the title complex with the hydrogen atoms being omitted for clarity

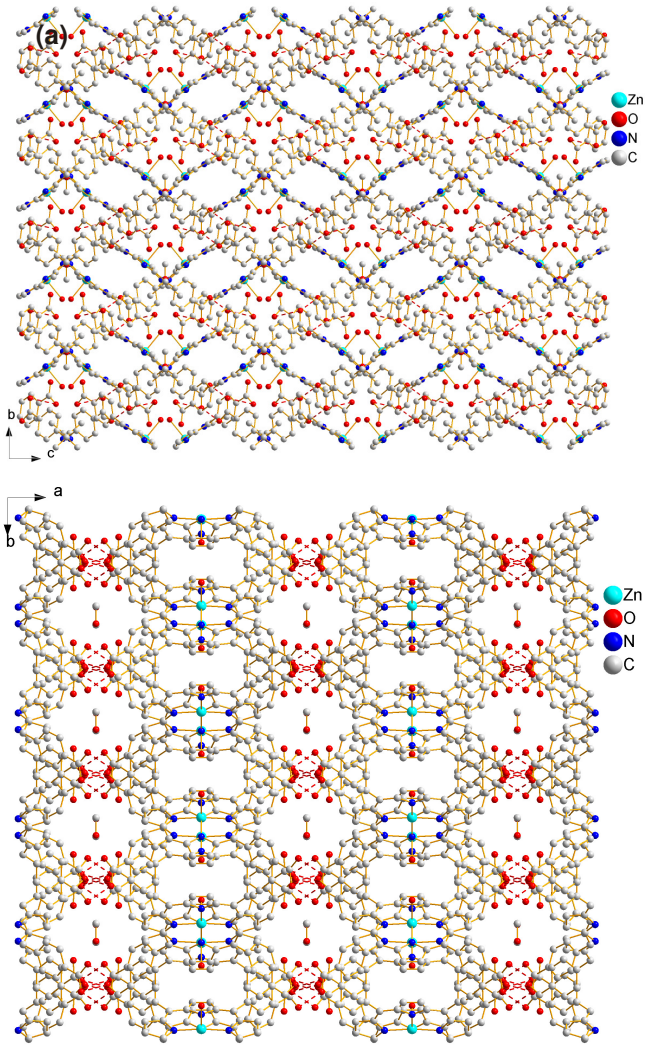

Fig. 2. A packing diagram of the title complex viewed from different axes with the red dashed lines representing hydrogen bonds: O(2)-H(2A)···O(3) 3.103(4) Å, 148°; O(4)-H(4A)···O(3) 2.643(4) Å, 173°

In summary, by virtue of a solvothermal reaction, we have synthesized a novel zinc-porphyrin complex ZnTCPP(H_2O)·MeOH which exhibits an isolated crystal structure, determined by a single-crystal X-ray diffraction method. With the view to gain deeper insights into the porphyrin complexes, further study in laboratory will aim at the investigation on other metalloporphyrins.

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