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NOTE

Synthesis and Characterization of *meso*-Tetra(4-carboxyphenyl)porphyrin Complex of Palladium

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A porphyrinic compound Pd[TCPP-$(CH_3)_4$]·H_2O (**1**) [TCPP = *meso*-tetra(4-carboxyphenyl)porphyrin] has been prepared *via* solvothermal reactions and characterized by X-ray diffraction method. It features an isolated structure with a coplanar porphyrin macrocycle. The Pd[TCPP-$(CH_3)_4$] moieties and lattice water molecules link together by hydrogen bonding interactions to give a three-dimensional (3-D) supramolecular framework.

Keywords: Crystal, Porphyrin, Supermolecule, *meso*-Tetra(4-carboxyphenyl)porphyrin.

Porphyrin is a useful building block for constructing supramolecular assembly, therefore, it has recently gained much attention and lots of porphyrinic compounds have thus far been reported[1-3]. Porphyrinic compounds have important applications in many fields such as medicine, sensors, electronic materials, molecular recognition, gas adsorption, catalyst[4-6]. Porphyrinic supermolecules are self-assembled by porphyrins and they are able to be applied to photonic materials and molecular electronics. Nowadays, more and more porphyrinic supermolecules have been prepared through non-covalent interactions like π-π stacking effect, van der Waals force or hydrogen bonding interaction[7,8]. We describe in this work the solvothermal preparation and characterization of Pd[TCPP-$(CH_3)_4$]·H_2O (**1**).

Synthesis of Pd[TCPP-$(CH_3)_4$]·H_2O (1): All A.R. grade reagents are purchased and applied without further purification. Compound **1** is synthesized from the mixture of $PdCl_2$ (0.1 mmol, 17.7 mg), TCPP (0.1 mmol, 79 mg), 5 mL methanol and 5 mL H_2O in a 23 mL Teflon-lined stainless steel autoclave then kept at 453 K for one week. After being cooled to room temperature, red crystals were prepared.

X-ray structure determination: A red crystal with dimensions of 0.24 mm × 0.18 mm × 0.16 mm was used for X-ray diffraction data collection which was performed on a Rigaku Mercury CCD X-ray diffractometer with graphite monochro-mated MoK_α radiation (λ = 0.71073 Å). Data reduction and empirical absorption correction were carried out by CrystalClear software[9]. The structure was solved by direct methods using Siemens SHELXTL™ Version 5 software package[10]. Non-hydrogen atoms were found by direct methods and differential Fourier maps, while hydrogen atoms were obtained by theoretical calculations. The structure was refined by a full-matrix least-squares technique on F^2. CCDC 978605.

Table-1 shows the summary of the crystallographic parameters and structural analyses, while Table-2 lists the bond parameters. An ORTEP diagram with the atom labels is given in Fig. 1, showing the molecular structure of **1**. Single crystal X-ray diffraction method discovers that the molecular structure is comprised of one neutral and discrete Pd[TCPP-$(CH_3)_4$] moiety and one lattice water molecule. It is crystallized in the space group P2/c of monoclinic system with two molecules in a unit cell. Except for Pd1 and O1W atoms, other crystallographic independent atoms are resided at general positions. The bond length of Pd-N is 2.011(2) Å, which is normal and comparable with those reported[11,12]. The 24-membered macrocyclic porphyrin ring is almost coplanar. The deviation of the ring atoms apart from the average plane is very small and in the range of -0.054 ~ + 0.054 Å. All the carboxylic groups are methylated. The Pd[TCPP-$(CH_3)_4$] moiety and lattice water molecules connect together *via* hydrogen bonding interactions to form a 3-D supramolecular network (Fig. 2).

TABLE-1
SUMMARY OF CRYSTALLOGRAPHIC PARAMETERS AND STRUCTURAL ANALYSES

Formula	$C_{52}H_{38}N_4O_9Pd$	$2\theta_{max}$ (°)	50
Formula weight	969.26	Index ranges	-17 ≤ h ≤ 17, -8 ≤ k ≤ 8, -26 ≤ l ≤ 25
Colour	red	Reflections collected	13377
Crystal size/mm^3	0.24 0.18 0.16	Independent, observed reflections (R_{int})	4210, 2524 (0.0437)
Crystal system	monoclinic	$d_{calcd.}$ (g/cm^3)	1.311
Space group	P2/c	μ (mm^{-1})	0.436
a (Å)	15.0919(5)	T (K)	296(2)
b (Å)	7.2740(2)	F(000)	992
c (Å)	22.6189(4)	R1, wR2 (obs.)	0.0653, 0.1833
β (°)	98.510(5)	S	1.004
V (Å^3)	2455.73(11)	Largest and Mean Δ/σ	0, 0
Z	2	Δρ(max, min) (e/Å^3)	1.727, -0.506

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

Pd(1)-N(1)	2.011(2)	N(1)-Pd(1)-N(2)	89.5(1)
Pd(1)-N(1)#1	2.011(2)	N(1)#1-Pd(1)-N(2)	90.5(1)
Pd(1)-N(2)	2.011(2)	N(1)-Pd(1)-N(2)#1	90.5(1)
Pd(1)-N(2)#1	2.011(2)	N(1)#1-Pd(1)-N(2)#1	89.5(1)
N(1)-Pd(1)-N(1)#1	180.0(1)	N(2)-Pd(1)-N(2)#1	180.0(1)

Symmetry codes: # 1-x + 1, -y + 1, -z + 1

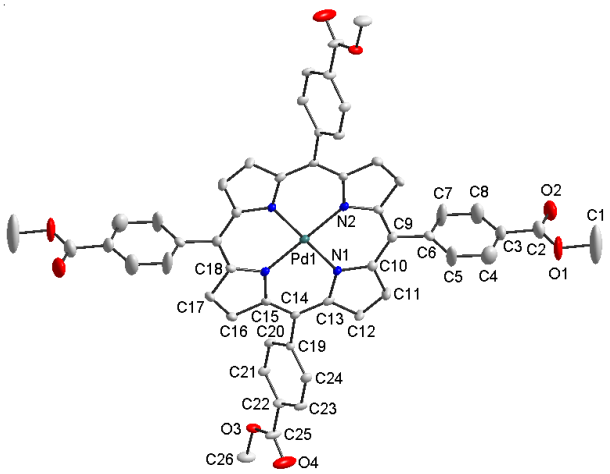

Fig. 1. An ORTEP diagram of **1** with 30 % thermal ellipsoids. The lattice water molecule and hydrogen atoms are omitted for clarity

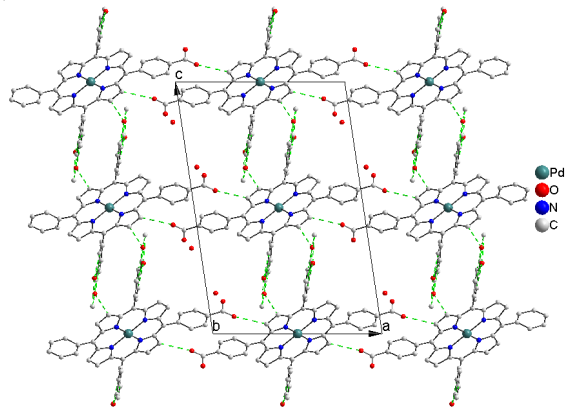

Fig. 2. A packing diagram of **1** with the dashed lines representing the hydrogen-bonding interactions (Å): C(11)-H(11A)···O(2)(2-x, -y, 1-z) 3.350(4), C(12)-H(12A)···O(3)(1-x, y, 1/2-z) 3.301(4), C(20)-H(20A)···O(4)(x, 1 + y, z) 3.287(4).

Conclusion

We obtained a porphyrinic compound Pd[TCPP-$(CH_3)_4$]·H_2O *via* solvothermal reactions and characterized it with X-ray diffraction analysis. It features an isolated structure and a 3-D supramolecular network.

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