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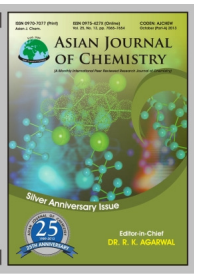

Crystal Structure of Dimethylformamide-tetraphenylporphyrinato-zinc(II)

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The title compound dimethylformamide-tetraphenylporphyrinato-zinc(II) was prepared by slow evaporation from its DMF solution. Its structure was determined by single crystal X-ray diffraction analysis. The crystals are monoclinic, space group $P2_1/c$ with a = 13.913(3), b = 9.3426, c = 29.539(6) Å, α = 90.00, β = 101.99(3), γ = 90.00°, V = 3756.0(13) Å^3, Z = 4, $F_{(000)}$ = 1560, D_c = 1.328 g/cm^3, μ = 0.698 cm^{-1}, the final R = 0.0803 and wR = 0.1853. A total of 26606 reflections were collected, of which 6498 were independent (R_{int} = 0.0991).

Key Words: Porphyrin, Synthesis, Crystal structure, Axial coordination.

INTRODUCTION

Heterocyclic compounds had received considerable attentions in industrial field[1]. Nitro-linked heterocyclic compounds exhibit diversity function, especially porphyrins. In recent years, metallo-tetraphenylporphyrins have been received more and more attention due to their potential application in photo-induced electron transfer and light-driven hydrogen evolution[2]. Metallo-tetraphenylporphyrin compounds with axial ligands coordinating to the metal center have already been reported[3].

In order to develop the coordination chemistry of metallo-tetraphenylporphyrin compounds, we initiate a study on tetraphenylporphyrinato-zinc(II) with N,N'-dimethylformamide as an axial ligand bound to zinc(II) center. In this paper, we report the crystal structure of dimethylformamide-tetraphenylporphyrinato-zinc(II).

EXPERIMENTAL

Crystal structure determination: The crystal of title compound with dimensions of 0.08 mm × 0.08 mm × 0.06 mm was mounted on a Rigaku Saturn CCD area-detector diffractometer with a graphite-monochromated MoK_α radiation (λ = 0.71073 Å) by using a phi and scan modes at 293(2) K in the range of 1.41° ≤ θ ≤ 25.02°. The crystal belongs to Monoclinic system with space group $P2_1/c$ and crystal parameters of a = 13.913(3), b = 9.3426, c = 29.539(6) Å, α = 90.00, β = 101.99(3), γ = 90.00°, V = 3756.0(13) Å^3, D_c = 1.328 g/cm^3, the absorption coefficient μ = 0.698 mm^{-1} and Z = 4. The structure was solved by direct methods with SHELXS-97[4] and refined by the full-matrix least squares method on F^2 data using SHELXL-97[5]. The empirical absorption corrections were applied to all intensity data. H atom of N-H was initially located in a difference Fourier map and were refined with the restraint Uiso(H) = 1.2Ueq(N). Other H atoms were positioned geometrically and refined using a riding model, with d(C-H) = 0.93-0.97 Å and Uiso(H) = 1.2Ueq(C) or 1.5Ueq(C-methyl). The final full-matrix least squares refinement gave R = 0.0803 and wR = 0.1853.

RESULTS AND DISCUSSION

Slow evaporation of the title compound in DMF afforded purple crystals suitable for X-ray analysis.

Structure of the title compound: The title compound has been confirmed by single crystal X-ray diffraction analysis. Crystallographic and refinement parameters are given in Table-1. The selected bond lengths and bond angles are listed in Tables 2-4, respectively. The structure was solved by direct methods. Anisotropic displacement parameters were applied to all nonhydrogen atoms in full-matrix least-square refinements based on F^2. The hydrogen atoms were set in calculated positions with a common fixed isotropic thermal parameter.

The molecular structure and the packing view of the title complex are shown in Figs. 1 and 2, respectively.

The title compound crystallizes in the monoclinic space group $P2_1/c$. The unit cell contains one molecule of tetraphenylporphyrinato-zinc(II) and one molecule of Me_2NCHO. As can be seen in Fig. 1, the molecular structure consists of a square-pyramidal five coordinate tetraphenylporphyrinato-zinc(II) with N,N'-dimethylformamide as an axial ligand. Generally, the average bond lengths and bond angles of ring systems

TABLE-1
CRYSTAL DATA AND STRUCTURE REFINEMENT FOR THE TITLE COMPLEX

Items	Values
Empirical formula	$C_{47}H_{35}N_5OZn$
Formula weight	751.17
Crystal system	Monoclinic
Unit cell dimensions	
a (Å)	13.913(3)
b (Å)	9.3426(19)
c (Å)	29.539(6)
Unit cell angles (°)	
α	90
β	101.99(3)
γ	90
Volume (Å^3)	3756.0(13)
Z	4
Temperature (K)	293(2)
Space group	$P2_1/c$
Wavelength (Å)	0.71073
Calculated density (g/cm^3)	1.328
Absorption coefficient (mm^{-1})	0.698
$F_{(000)}$	1560
Crystal size (mm)	0.08 × 0.08 × 0.06
Theta range for data collection (°)	1.41 –25.02
Reflections collected	26606
Independent reflections	6498 [$R_{(int)}$ = 0.0991]
Final R indices [I > 2σ(I)]	R_1 = 0.0803, wR_2 = 0.1853

TABLE-2
SELECTED BOND LENGTHS [Å] FOR THE TITLE COMPOUND

Bond lengths	X-Ray crystal	Bond lengths	X-Ray crystal
Zn(1)-N(1)	2.063(4)	N(1)-C(4)	1.366(6)
Zn(1)-N(3)	2.067(4)	N(1)-C(1)	1.384(6)
Zn(1)-N(2)	2.068(4)	N(2)-C(15)	1.363(6)
Zn(1)-N(4)	2.089(4)	N(3)-C(26)	1.363(7)
Zn(1)-O(1)	2.138(4)	N(4)-C(37)	1.368(7)

TABLE-3
SELECTED BOND ANGLES [°] FOR THE TITLE COMPOUND

Bond angles	X-Ray crystal	Bond angles	X-Ray crystal
N(1)-Zn(1)-N(3)	162.57(15)	N(1)-Zn(1)-O(1)	97.83(16)
N(1)-Zn(1)-N(2)	88.47(16)	N(3)-Zn(1)-O(1)	99.59(15)
N(1)-Zn(1)-N(4)	88.17(17)	N(2)-Zn(1)-O(1)	97.75(17)
N(2)-Zn(1)-N(4)	160.66(16)	N(4)-Zn(1)-O(1)	101.58(17)

TABLE-4
SELECTED TORSIONAL ANGELS (°) FOR THE TITLE COMPOUND

Bond angles	X-Ray crystal
N(3)-Zn(1)-N(1)-C(4)	99.0(7)
N(2)-Zn(1)-N(1)-C(4)	18.3(4)
N(4)-Zn(1)-N(1)-C(4)	179.2(4)
O(1)-Zn(1)-N(1)-C(4)	-79.3(4)
N(3)-Zn(1)-N(1)-C(1)	-92.9(6)
N(2)-Zn(1)-N(1)-C(1)	-173.7(4)
N(4)-Zn(1)-N(1)-C(1)	-12.7(4)
O(1)-Zn(1)-N(1)-C(1)	88.7(4)

(phenyl and pyrrole), carbonyl group and Me_2N group are normal ranges[6]. The twist angles between the porphyrin plane and four benzenes are 64.4, 103.4, 70.1 and 125.9°. The porphyrin ring is slightly ruffled with 0.0180 Å out-of-plane displacement of the central zinc because of axial coordination. The phenyl rings (C6, C7, C8, C9, C10, C11), (C17, C18, C19, C20, C21, C22), (C28, C29, C30, C31, C32, C33)

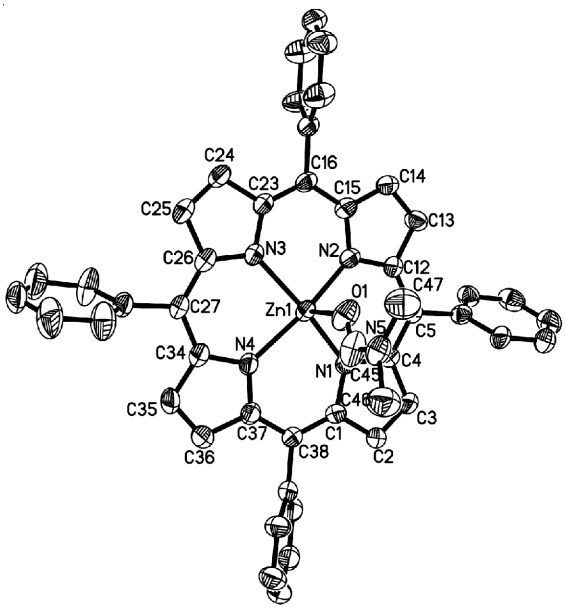

Fig. 1. Molecular structure of the title compound

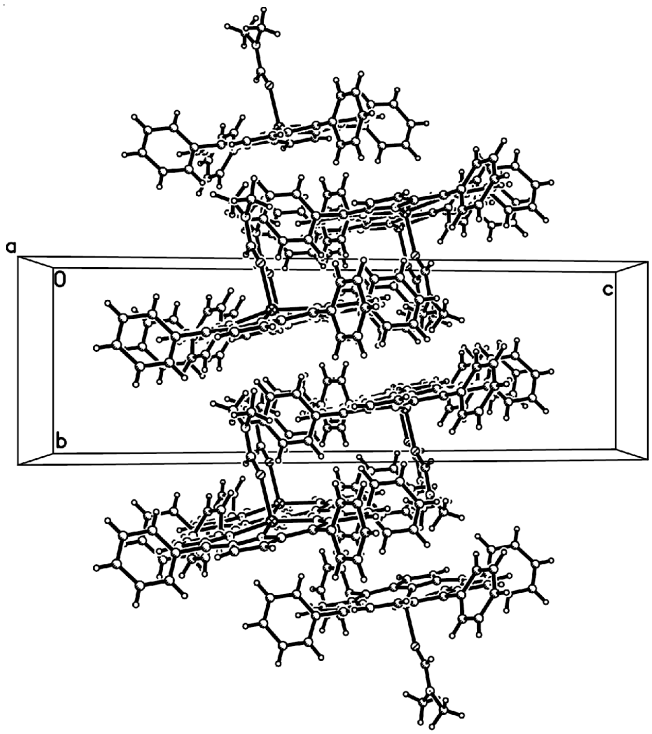

Fig. 2. Crystal packing for the title compound

and (C39, C40, C41, C42, C43, C44) are fairly planar with plane equation 11.192x + 4.321y + 5.840z = 12.0321, -7.104x + (-0.160y) + 27.973z = -2.4653, 11.438x + 3.534y + 7.253z = 11.9495 and -5.866x + (-3.709y) + 26.143z = -4.4032, respectively. The largest deviation from the least squares plane is 0.0160 Å.

As shown in Fig. 2, Van der Waals' interactions stabilize the solid state of the crystal structure in the crystal packing.

Supplementary material

CCDC 923237 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/ retrieving.html or from

the Cambridge CrystallographicData Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; email: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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