Crystal Structure of 5,10,15,20-Tetrakis{[4-(allyloxy)phenyl]-porphyrinato}zinc(II)

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The structure of the title compound, [Zn(C₅₆H₄₄N₄O₄)], was confirmed by low-temperature single-crystal analysis. The crystal system belongs to monoclinic with space group of *P*2₁/*n*. The crystal structure reveals that the Zn^{II} center adopts a square-planar coordination geometry and the molecules are stacked with a separation of 11.056(3) Å between the neighboring Zn centers along the crystallographic *b*-axis.

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The porphyrin derivatives containing reactive terminal-alkene groups are important for practical applications of porphyrin-based optoelectronic materials and devices, because the hybrid porphyrin/semiconductor architectures require the ability to attach the porphyrins to an electroactive surface in a reliable and robust manner.¹ The porphyrins with terminal-alkene groups are also useful building blocks to construct nano-structured oligoporphyrins through olefin-metathesis using Grubbs catalysts.² We here report on the crystal structure of *meso*-tetrakis{[4-(allyloxy)phenyl]porphyrinato}zinc(II), (**I**).

The title compound **I** was prepared by the reaction of 5,10,15,20-tetrakis[4-(4-hydroxyphenyl)porphyrinato]zinc(II) with allyl iodide in the presence of anhydrous Cs₂CO₃. The spectroscopic data are identical to those in the literature.³ Single crystals suitable for X-ray crystallography were grown by the slow diffusion of hexane into a solution of **I** in CH₂Cl₂ at room temperature. The crystal and experimental data are given in Table 1. The structures were solved by direct methods and refined with anisotropic temperature factors for non-hydrogen

atoms. All of the hydrogen atoms were placed in idealized positions and refined using a riding model. The atomic coordinates for non-hydrogen atoms are listed in Table 2. The selected bond lengths and bond angles are summarized in Table 3. The molecular structure of **I** with the atom-numbering scheme is given in Fig. 2.

In the crystal structure of **I**, the Zn atom lies on an inversion

Fig. 1 Chemical structure for **I**.

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Table 1 Crystal and experimental data

Formula: C ₅₆ H ₄₄ N ₄ O ₄ Zn
Formula weight = 902.32
Temperature: 173(2)K
Crystal size: 0.40 × 0.30 × 0.20 mm
Crystal color: red
Crystal description: block
Crystal system: monoclinic
Space group: <i>P</i> 2 ₁ / <i>n</i> <i>Z</i> = 2
<i>a</i> = 9.898(2) Å
<i>b</i> = 11.056(3) Å
<i>c</i> = 20.187(5) Å
β = 96.863(5)°
<i>V</i> = 2193.2(9) Å ³
<i>D</i> _x = 1.366 g/cm ³
Radiation: 0.71073 Å (Mo <i>K</i> _α)
2θ _{max} = 56.76°
<i>R</i> = 0.0644
<i>wR</i> = 0.1337
Goodness-of-fit = 0.934
(Δ/ <i>σ</i>) _{max} final cycle: 0.001
(Δρ) _{max} = 0.675 e Å ⁻³
(Δρ) _{min} = -0.523 e Å ⁻³
No. of reflections used = 4492 [<i>>2σ</i> (<i>I</i>)]
No. of parameters = 295
Diffractometer: Bruker SMART CCD system
Monochromator: graphite
Structure determination: SHELXTL ⁵
Refinement: full-matrix least-squares

CCDC 275933 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table 2 Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$)

Atom	x	y	z	U(eq)
Zn	10000	0	-5000	31(1)
O(1)	7350(4)	-1331(3)	-896(2)	49(1)
O(2)	13445(4)	7287(3)	-3512(2)	47(1)
N(1)	9018(4)	-1392(3)	-4603(2)	32(1)
N(2)	10115(4)	900(3)	-4117(2)	30(1)
C(1)	8555(5)	-2443(4)	-4919(2)	33(1)
C(2)	7841(5)	-3150(4)	-4475(2)	38(1)
C(3)	7871(5)	-2538(4)	-3898(2)	38(1)
C(4)	8626(5)	-1443(4)	-3970(2)	34(1)
C(5)	8926(5)	-567(4)	-3464(2)	35(1)
C(6)	9620(5)	516(4)	-3540(2)	35(1)
C(7)	9937(5)	1413(4)	-3024(2)	38(1)
C(8)	10579(5)	2331(4)	-3289(2)	38(1)
C(9)	10675(5)	2025(4)	-3979(2)	33(1)
C(10)	11299(5)	2751(4)	-4421(2)	32(1)
C(11)	8484(5)	-829(4)	-2797(2)	36(1)
C(12)	9034(5)	-1789(4)	-2411(2)	37(1)
C(13)	8669(5)	-2010(4)	-1778(2)	39(1)
C(14)	7728(5)	-1246(4)	-1523(2)	39(1)
C(15)	7151(6)	-318(4)	-1913(3)	45(1)
C(16)	7522(5)	-107(4)	-2538(2)	44(1)
C(17)	7663(6)	-2412(5)	-516(3)	49(1)
C(18)	9077(7)	-2491(5)	-186(3)	54(2)
C(19)	9830(7)	-3459(6)	-193(3)	71(2)
C(20)	11826(5)	3969(4)	-4174(2)	30(1)
C(21)	13189(6)	4134(4)	-3983(3)	43(1)
C(22)	13703(6)	5246(4)	-3756(3)	44(1)
C(23)	12834(6)	6219(4)	-3734(2)	36(1)
C(24)	11463(6)	6071(4)	-3917(2)	37(1)
C(25)	10967(5)	4938(4)	-4138(2)	37(1)
C(26)	12637(7)	8332(4)	-3523(3)	61(2)
C(27)	13606(8)	9388(5)	-3345(3)	79(2)
C(28)	13442(9)	10173(6)	-2923(4)	101(3)

Fig. 2 Molecular structure of **I** with the atom-numbering scheme. Displacement ellipsoids are shown at the 30% probability level.

center at a special position and adopts a square-planar coordination geometry with essentially identical distances of Zn-N1 [2.035(4)Å] and Zn-N2 [2.033(3)Å]. The porphyrin core, consisting of 24 atoms, is nearly planar; the deviation of the individual atoms from the mean plane does not exceed 0.01 Å. The *meso* phenyl rings attached to the C atoms C5 and C10 make dihedral angles of 64.4 (1) and 79.1(1)° with the core, respectively. The torsion angles of the allyloxy chains in **I**

Table 3 Selected bond lengths (Å) and angles (°)

Zn-N1	2.035 (4)	Zn-N2	2.033 (3)
C14-O1	1.365 (5)	C23-O2	1.377 (5)
O1-C17	1.433 (6)	O2-C26	1.404 (6)
C17-C18	1.479 (8)	C26-C27	1.526 (8)
C18-C19	1.305 (8)	C27-C28	1.241 (9)
N1-Zn-N2 ¹	89.78 (13)	N1-Zn-N2	90.22 (13)
C14-O1-C17	119.2 (4)	C23-O2-C26	118.2 (4)
O1-C17-C18	115.1 (4)	O2-C26-C27	106.5 (5)
C17-C18-C19	123.7 (6)	C26-C27-C28	124.5 (8)

Symmetry code: (i) $-x+2, -y, -z-1$.

Fig. 3 Perspective packing view of **I** down the crystallographic *b*-axis. H atoms have been omitted for clarity.

[O1-C17-C18-C19 = 134.7(6) and O2-C26-C27-C28 = 131.6(8)°] indicate that there is no intramolecular C-H...O interaction, as implied in the planar arrangement of an allyloxy chain.⁴

The unit-cell packing along the *b*-axis is shown in Fig. 3. The porphyrin rings are arranged in tilted stacks along the *b*-axis with no significant π - π interactions among the porphyrin rings. The separation between neighboring Zn centers along the *b*-axis amounts to 11.056(3)Å. The phenyl groups with allyloxy chains around the porphyrin rings may be obstructive for stacking through efficient π - π interactions between the porphyrin rings.

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