Synthesis and Crystal Structure of Bis-tetrahydrofuranate-{(5,10,15,20-(tetrakis-pentafluorophenyl)porphyrinato)magnesium(II)}

Takuya SAWADA and Haruo AKASHI[†]

Research Institute of Natural Sciences, Okayama University of Science, Ridai-cho, Kita, Okayama 700-0005, Japan

The title compound, bis-tetrahydrofuranate-{(5,10,15,20-(tetrakis-pentafluorophenyl)porphyrinato)magnesium(II)} ([Mg(THF)₂(TFPP)]), crystallized in the monoclinic space group *C2/c* with the following unit-cell parameters: *a* = 23.940(6) Å, *b* = 12.007(4) Å, *c* = 23.882(6) Å, β = 90.795(4)°, *V* = 6864(3) Å³ and *Z* = 4. The crystal structure was solved by direct methods, and refined by full-matrix least-squares procedures to a final *R*-value of 0.0604 for 4933 observed reflections. A porphyrin ligand coordinated to the magnesium atom, and four pentafluorophenyl groups bonded to the *meso* position of the porphyrin skeleton.

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It is well known that **H₂TFPP** (= 5,10,15,20-tetrakis(pentafluorophenyl)porphyrin) and its chlorin derivatives (for example, **H₂TFPC** (= 5,10,15,20-tetrakis(pentafluorophenyl)chlorin)) generate a singlet oxygen by light irradiation under atmospheric oxygen.¹

In the course of our study towards the preparation of metal complexes of **H₂TFPP** and **H₂TFPC**, we undertook the reaction of MgCl₂ with **H₂TFPP**. As expected, refluxing of the reaction mixture for 48 h gave **Mg(TFPP)** (= 5,10,15,20-tetrakis(pentafluorophenyl)porphyrinato)magnesium). Crystals of [Mg(THF)₂(TFPP)] (= bis-tetrahydrofuranate-{(5,10,15,20-(tetrakis-pentafluorophenyl)porphyrinato)magnesium(II)}) suitable for X-ray structure analysis were obtained by the recrystallization of **Mg(TFPP)** from the tetrahydrofuran/toluene mixture solvent. Since its structure was unambiguously determined by single-crystal X-ray crystallographic analysis, herein we describe the synthesis and properties (MALDI-TOF MS, ¹H NMR and X-ray crystal structure) of [Mg(THF)₂(TFPP)].

H₂TFPP was prepared according to a literature procedure.² [Mg(THF)₂(TFPP)] was prepared by the following method: to a dehydrated benzonitrile (50 mL) solution of **H₂TFPP** (1.0 g, 1.0 mmol) was added MgCl₂ anhydride (980 mg, 10 mmol) and the resulting solution was refluxed for 48 h. The color of the solution gradually changed from red-brown to red. The solution was filtered and the solvent was removed. The red residue was chromatographed on a silica-gel column with a dichloromethane/hexane (2/1) mixture to yield a red powder of crude **Mg(TFPP)**, after removal of the solvent (810 mg). The red powder was recrystallized from the tetrahydrofuran/toluene (1/4) mixture solvent to obtain a crystalline product of [Mg(THF)₂(TFPP)]·4C₆H₅CH₃ (Yield: as single crystals, 240 mg, 16%). *Anal.* Found (Calcd for C₄₄H₈N₄F₂₀Mg·4C₆H₅CH₃): C, 63.01 (63.34); H, 3.33 (2.95); N, 4.09 (4.10)%. MALDI-TOF MS (*m/z*, non-matrix) Calcd for C₄₄H₈N₄F₂₀Mg ([M]⁺) 996.03, Found 996.09. ¹H NMR (399.78 MHz, CDCl₃, CHCl₃ = 7.26 ppm): δ (ppm) = 8.96 (8H, s, β -pyrrole *H*). The structure of [Mg(THF)₂(TFPP)] deduced from these data was confirmed by

single-crystal X-ray structure analysis.

The structure was solved using the SHELXTL program package software.³ All of the non-hydrogen atoms were refined anisotropically. All hydrogen atoms were included in the refinement at calculated positions, riding on their carrier atoms (C-H 0.95 Å). The isotropic thermal parameters of hydrogen atoms were constrained to 1.2 *U*_{eq}, to which they were attached. The refinement details and structural parameters are summarized in Table 1. The chemical structure is shown in Fig. 1. An ORTEP drawing of the complex is given in Fig. 2. Magnesium

Table 1 Crystal and experimental data

Chemical formula: C ₈₀ H ₅₆ F ₂₀ Mg ₁ N ₄ O ₂	
Formula weight = 1509.60	
<i>T</i> = 93 K	
Crystal system: monoclinic	Space group: <i>C2/c</i> (#15)
<i>a</i> = 23.940(6) Å	
<i>b</i> = 12.007(4) Å	β = 90.795(4)°
<i>c</i> = 23.882(6) Å	
<i>V</i> = 6864(3) Å ³	<i>Z</i> = 4
<i>D</i> _{calc} = 1.461 g/cm ³	
Radiation: Mo <i>K</i> α (λ = 0.71075 Å)	
μ (Mo <i>K</i> α) = 1.335 mm ⁻¹	<i>F</i> (0 0 0) = 3088
Crystal size = 0.20 × 0.20 × 0.20 mm ³	
No. of reflections collected = 23286	
No. of independent reflections = 6288 (<i>R</i> _{int} = 0.0484)	
θ range for data collection: 3.25 to 26.05°	
Data/Restraints/Parameters = 6288/0/484	
Good-of-fit on <i>F</i> ² = 1.083	
<i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)] : <i>R</i> 1 = 0.0604	
<i>R</i> indices (all data): <i>R</i> 1 = 0.0793, <i>wR</i> 2 = 0.1653	
(Δ/σ) _{max} = 0.000	
(Δρ) _{max} = 0.41 eÅ ⁻³	(Δρ) _{min} = -0.40 eÅ ⁻³
Measurement: Rigaku Saturn724	
Program system: Crystalstructure 4.2	
Structure determination: SHELX-97	
Structure refinement: SHELXL-97	
CCDC deposition number: 1585859	

[†] To whom correspondence should be addressed.

Fig. 1 Chemical structure of $[Mg(THF)_2(TFPP)] \cdot 4C_6H_5CH_3$.

Fig. 2 ORTEP drawing of $[Mg(THF)_2(TFPP)]$ with the atom labeling scheme. Displacement ellipsoids are drawn at the 50% probability level. Hydrogen atoms have been omitted for clarity.

atom adopts the octahedral coordination geometry, and bonds to four nitrogen atoms of the porphyrin ring and two oxygen atoms of two tetrahydrofuran molecules. Mg1, O1 and O2 atoms lie on a crystallographic the two-fold axis. The magnesium atom lies on the porphyrin plane. The selected bond distances and bond angles are listed in Table 2. The average magnesium-nitrogen bond distance is 2.073(3)Å. The tetrahydrofuran

Table 2 Selected bond distance (Å), bond angles (°)

Bond distance			
Mg1-O1	2.153(3)	Mg1-O2	2.152(3)
Mg1-N1	2.074(2)	Mg1-N2	2.073(2)
N1-C1	1.372(3)	N1-C4	1.361(3)
N2-C6	1.366(3)	N2-C9	1.367(3)
C1-C2	1.448(4)	C2-C3	1.355(4)
C3-C4	1.444(4)	C4-C5	1.412(4)
C5-C6	1.412(4)	C6-C7	1.444(4)
C7-C8	1.350(4)	C8-C9	1.444(4)
C9-C10	1.410(4)		
Bond angle			
O1-Mg1-O2	180.000(3)	O1-Mg1-N1	89.74(7)
N1-Mg1-N2	89.89(8)	N1-Mg1-N2 ¹	90.11(8)

Symmetry codes: (1) $-x+1, y, -z+1/2$.

molecules occupy the two axial position. The average magnesium-oxygen bond distance is 2.153(7)Å. As related compounds, structures of magnesium tetraphenylporphyrin complexes involving water and methanol coordination have been reported by McKee and co-workers.⁴ There are no striking differences in the Mg-N and Mg-O distances between $[Mg(THF)_2(TFPP)]$ and the compounds, which are reported in the text.⁴

The two pentafluorophenyl groups are bonded to *meso* positions of the porphyrin skeleton. Two crystallographically independent phenyl rings are twisted with respect to the porphyrin plane. The dihedral angles between the porphyrin plane and phenyl rings a (C11-C12-C13-C14-C15-C16) and b (C17-C18-C19-C20-C21-C22) are 83.7(8)° and 97.9(9)°, respectively.

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