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단 신

5, 10, 15, 20-철(II)사페닐포르피린의 결정구조

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Crystal Structure of 5, 10, 15, 20-Tetraphenylporphine iron(II)

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INTRODUCTION

The porphyrin ring system is known to stabilize metal ions in unusual spin and oxid ation states. This is the case for iron (II) porphyrins, which in the absense of axial ligands exist in the square-planar intermediate-spin S=1 configuration.[1] Nuclear magnetic resonance (NMR) studies confirm that the S=1 spin state is retained in non-coordinating solvents. However, the electronic structural definition is complicated by mixing of an ^3E_g excited state into the $^3A_{2g}$ ground state.[2] The energy of the d_{z2} orbital, and hence the degree of excited state mixing, is readily perturbed by molecular interactions in the vacant axial iron ligation sites.

The previous structural work on iron (II) tetraphenylporphyrin, TPPFe, utilized a benzene-ethanol crystallization solvent that yielded a tetragonal crystal of I-42d space group with no solvent of crystallyzation.[1] The present report describes the structure of TPPFe in an alternative space group that contains toluene of crystallization. *Fig.* 1. exhibits ORTEP[4] drawing and atomic labeling scheme of the title compound. The compound was produced in an attempt to crystallize an unstable tributyltin-iron (III) porphyrin complex. Given the toluene of solvation, it was of interest to compare structures and search for perturbations that might result from axial site interaction by the solvate molecule.

EXPERIMENTAL

Sample preparation. The crystal was obtained from the homolyzed product of the TPPFe (III) $SnBu_3$ complex, generated by the reaction of butyl-iron (III) porphyrin with excess Bu_3SnH in toluene solution under anaerobic conditions in a septum-

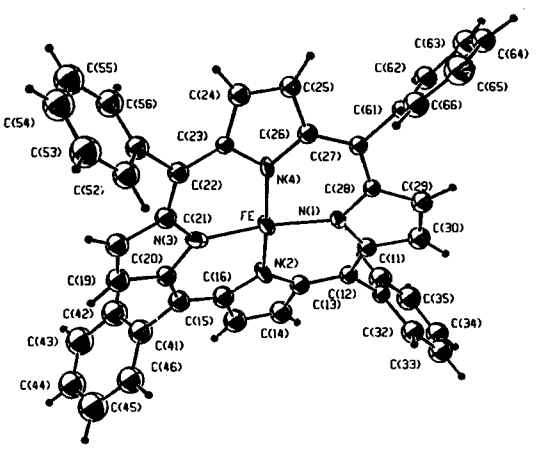


Fig. 1. An ORTEP drawing of the crystal structure of 5, 10, 15, 20-tetraphenylporphine iron(II).

sealed 5 mm NMR tube.[2] The toluene (0.5 mL)/ Bu_3SnH(0.2 mL) solution of 4 mM TPPFe (III) $SnBu_3$ was placed in a freezer(-24°C) for two weeks for crystal growth.

$$\text{TPPFe (III)R} + \text{ex } Bu_3SnH \xrightarrow{\text{tol}} \text{TPPFe (III)}SnBu_3 + RH \xrightarrow[-24^\circ C]{\text{tol}} \text{TPPFe (II)} + 1/2\,Bu_3SnSnBu_3$$

Volatile hydrocarbon (RH) product was detected by GC-MS, and hexabutylditin was quantitatively measured by nuclear magnetic resonance spectroscopy.

Structure determination. Plate-like purple crystal, $0.23\times0.17\times0.09$ mm^3, was mounted in a thin-walled glass capilary on an Enraf-Nonius CAD-4 diffractormeter. Preliminary examination and data collection were performed with MoKα1 radiation (λ=0.71073 Å). The structure was determined by the direct methods.[2] Fe and N atoms were refined with anisotropic thermal motion parameters. All C atoms refine isotropically. All hydrogen atoms were located from electron density difference maps, but were placed at 0.95 Å from carbon atoms and given isotropic temperature factors 1.1 times that of the atoms to which they were attached. One disordered solvent molecules were modeled by placing C atoms with partial occupancy (0.5 or 0.25) at positions obtained from difference density maps. Those that refined to reasonable isotropic thermal parameters were retained. No attempt was made to sort out proper connectivity. Crystallographic data and details of the data collection are given in *Table* 1. Final atomic positions for non-hydrogen and hydrogen atoms are listed in *Table* 2. *Table* 3 shows bond lengths and angles.

Table 1. Crystal data and structure refinement for TPPFe (II)

Chemical Formular	$C_{44}H_{28}Fe\ N_4.\ C_7H_8$
Formular weight	760.7
Temperature	295 K
Radiation type	MoK α
Radiation wavelength	0.71073
Crystal system	Triclinic
Space group	Pi
Unit cell dimensions	a=9.334(2) Å
	b=14.881(4) Å
	c=13.629(3) Å
Cell volume	1735(2) Å^3
Z	2
Density	1.46 Mg/m^3
Absorption coefficient	4.77 mm^{-1}
Crystal size	$0.23\times0.17\times0.09$ mm^3
R	0.068
wR	0.076
Goodness-of-Fit on F^2	1.38
θ range for data collection	16° to 21°
Reflections collected	5418
Independent reflections	4487
Scan range	1.0+0.35 tanθ°
Index range	$-1\le h\le17$, $-15\le k\le9$
	$-31\le l\le0$

[a] α and γ were constrained to be 99.42 (2)° and 91.32 (2)° and 91.32 (2)° in the refinement of cells parameters.

Table 2. Atomic coordinates and equivalent isotropic displacement parameters (Å) for 5, 10, 15, 20-tetraphenylporphin iron (II)

atom	x	y	z	U (eq) or U*
Fe	0.2620(3)	0.4143(2)	0.0377(2)	0.0374(6)
N (1)	0.303(1)	0.4612(7)	−0.0769(7)	0.0266(4)
N (2)	0.292(1)	0.2912(7)	−0.9218(7)	0.0393(4)
N (3)	0.260(1)	0.3730(7)	0.1656(8)	0.0380(4)
N (4)	0.198(1)	0.5322(7)	0.0837(7)	0.0342(4)
C (11)	0.352(1)	0.4144(9)	−0.1542(9)	0.0355(4)
C (12)	0.343(1)	0.3198(9)	−0.1807(9)	0.0329(4)
C (13)	0.308(2)	0.2614(9)	−0.120(1)	0.0380(4)
C (14)	0.300(2)	0.164(1)	−0.142(1)	0.0545(5)
C (15)	0.291(2)	0.133(1)	−0.056(1)	0.0557(5)
C (16)	0.286(2)	0.212(1)	0.019(1)	0.0469(5)
C (17)	0.293(2)	0.2110(9)	0.122(1)	0.0443(4)
C (18)	0.285(1)	0.2867(9)	0.192(1)	0.0380(4)
C (19)	0.296(2)	0.289(1)	0.300(1)	0.0507(5)
C (20)	0.271(2)	0.373(1)	0.339(1)	0.0494(5)
C (21)	0.242(2)	0.4256(9)	0.256(1)	0.0418(1)
C (22)	0.187(2)	0.5102(9)	0.256(1)	0.0393(4)
C (23)	01.50(1)	0.5571(8)	0.1709(9)	0.0279(4)
C (24)	0.082(2)	0.6339(9)	0.162(1)	0.0431(4)

U* is for hydrogen atoms.

RESULTS AND DISCUSSION

Cystallization of TPPFe (II) from toluene yielded on disordered solvate molecule per unit cell with partial occupation of open channels. The iron (II) to toluene distance of 8Å is such that no axial site perturbation is expected by the solvate molecule. The disordered toluene has closest contact with the phenyl group represented by the carbon a-

Table 3. Bond lengths (Å) andangles (deg) for 5, 10, 15, 20-tetraphenylporphine iron (II)

Fe-N(1)	1.96(1)	Fe-N(2)	1.95(1)
Fe-N(3)	1.95(1)	Fe-N(4)	1.95(1)
N(1)-C(11)	1.39(2)	N(1)-C(28)	1.40(2)
N(2)-C(13)	1.40(2)	N(2)-C(16)	1.39(2)
N93)-C(18)	1.39(2)	N(3)-C(21)	1.41(2)
N(4)-C(23)	1.41(2)	N(4)-C(26)	1.38(2)
N(1)-Fe-N(2)	90.1(2)	N(1)-Fe-N(3)	170.0(6)
N(1)-Fe-N(4)	90.5(5)	N(2)-Fe-N(3)	90.5(5)
N(2)-Fe-N(4)	170.9(7)	N(3)-Fe-N(4)	90.5(5)
Fe-N(1)-C(11)	128.0(1)	Fe-N(1)-C(28)	126.0(1)
C(11)-N(1)-C(28)	105.0(1)	Fe-N(2)-C(13)	128.0(1)
Fe-N(2)-C(16)	127.0(1)	C(13)-N(2)-C(16)	105.0(1)
Fe-N(3)-C(18)	128.0(1)	Fe-N(3)-C(21)	128.0(1)
C(18)-N(3)-C(21)	104.0(1)	Fe-N(4)-C(23)	127.0(1)
Fe-N(4)-C(26)	127.0(1)	C(23)-N(4)-C(26)	105.0(1)
N(1)-C(11)-C(12)	124.0(1)	N(1)-C(11)-C(30)	110.0(1)
N(2)-C(13)-C(12)	124.0(1)	C(24)-C(25)-C(26)	106.0(1)
N(4)-C(26)-C(25)	110.0(1)	N(4)-C(26)-C(27)	124.0(1)
N(1)-C(28)-C(27)	125.0(1)	N(1)-C(28)-C(29)	109.0(1)
N(2)-C(13)-C(14)	110.0(1)	N(2)-C(16)-C(15)	110.0(1)
N(2)-C(16)-C(17)	124.0(2)	N(3)-C(18)-C(17)	124.0(1)
N(3)-C(18)-C(19)	110.0(1)	N(3)-C(21)-C(20)	110.0(1)
N(3)-C(21)-C(22)	124.0(1)	N(4)-C(23)-C(22)	123.0(1)
N(4)-C(23)-C(24)	109.0(1)		

toms C (41)-C (46).

The average Fe-N distances of 1.95 (1) Å in the present structure are only slightly shorter than the 1.972 (4) Å for the previously reported structure.[1] Some distortion from porphyrin ring planarity is necessary to accomodate these relatively short iron-nitrogen distances. In the earlier solvate-free structure the porphyrin ring is distorted by an S_4 "ruffling" in which alternating methine carbon atoms lie above and below the mean porphyrin plane. A different type of distortion is seen in the present structure. This porphyrin assumes a "saddle" shape in which alternating pyrrole groups are rotated above and below the porphyrin plane. Associated with this distortion are reasonably close contacts of approximately 3.3 Å each between pyrrole carbon atoms C (24) and C (25), and the iron atom of an adjacent molecule. These carbon atoms and the entire pyrrole groups are rotated out of the mean porphyrin plane towards the iron atom. Carbon atoms C (29) and C (30) make correspondingly close contacts with the iron atoms of another iron porphyrin that lies below the porphyrin plane. The phenyl ring that lies between these two pyrrole residue (C (61)-C (66)) assumes a dihedral angle of 122° with the porphyrin plane to sterically accomodate the close iron-pyrrole contacts.

In summary, considerable variation is seen in porphyrin ring distortions for the solvated and solvate-free crystalline compounds. Given the sensitivity to contributions from excited state mixing in the four-coordinate S=1 iron (II) porphyrins, the solid state electronic properties of the two crystalline material may well differ.

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Supplementary Material Available. *Table* of observed and calculated factors (98 pages) are available from B-.H. S

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