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Bis (pyridine) (2,3,12,13-tetrabromo-5, 10, 15, 20-tetraphenylporphyrin) iron (II) pyridine solvate

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Abstract

The title compound, (C₄₄H₂₄Br₄N₄)(C₅H₅N)₂Fe·C₅H₅N, is located on a two-fold axis that passes through Fe and the pyridine ligands. Only slight asymmetry, 0.010 Å elongation due to the Br substituents, is seen in the Fe–N_p distances. The pyridine ligands are twisted 19.2° from each other.

Comment

The title compound [Fe(TPPBr₄)(py)₂] is a low-spin bis(pyridine)iron(II) complex that was studied as part of a program of ways to achieve control of axial ligand orientation in iron porphyrin derivatives (Safo *et al.*, 1991). Two effects are possible with this porphyrin ligand: the effect from the four β-pyrrole electron-withdrawing substituents and the possible conformation effects of the peripherally crowded but asymmetrically substituted porphyrin.

The molecular structure of the title compound is shown in Fig. 1. The core asymmetry is very small with Fe–N_p bond distances of 1.971 (2) and 1.981 (2) Å, with only a very small elongation caused by the bromo substituents. This is very much less than some derivatives, for example two different crystalline forms of high-spin [Fe(TPPBr₄)]₂O (Kadish *et al.*, 1997; Li *et al.*, 2000) have Fe–N_p bond distances that differ by greater than 0.05 Å. A similar, even larger difference is seen in [Zn(TPPBr₄)] (Zou *et al.*, 1997). However, small differences (1.90 and 1.91 Å) are also seen in [Ni(TPPBr₄)] (Zou *et al.*, 1994) and in two crystalline forms of [Fe(TPPBr₄)(NO)] (Scheidt *et al.*, 2000) suggesting that the magnitude of the asymmetry in the porphyrin hole size is related to the natural bond lengths and strength of the bonds. The average 1.976 (7) Å bond length is at the very low end of distances observed for low-spin iron(II) (Scheidt, 2000). The small size of the central hole is the result, at least in part, of the core conformation in [Fe(TPPBr₄)(py)₂]. The core is substantially distorted from planarity by a combination of both ruffling and saddling. The deformation shows asymmetry because of the two types of pyrrole rings leading to overall core symmetry of C₂ and not S₄. Unlike the case of [Fe(TFPPBr₈)(py)₂] where the strongly saddled core led to a near perpendicular orientation of the two axial pyridine ligand planes (Grinstaff *et al.*, 1995), the core appears to have had little effect on the orientation of the two pyridine planes; the angle between the two pyridines is 19.18 (13)°. It has been previously noted that coplanar axial ligands are typically seen in iron(II) porphyrin systems (Safo *et al.*, 1997). The axial Fe–N_{py} bond distances of 2.000 (3) and 2.040 (3) Å are within the normal range observed.

Examination of crystal packing (Fig. 2) shows the pyridine to be in a channel perpendicular to (001). The porphyrins pack in pairs of chains also perpendicular to (001) and alternating concave up and concave down along a chain.

Experimental

The β -pyrrole substituted tetrabromotetraphenylporphyrin derivative (H_2TPPBr_4) was synthesized following the reported method (Callot, 1974). The perchlorato- and chloroiron(III) derivatives were prepared by modified literature methods (Alder *et al.*, 1970; Buchler, 1975; Dolphin *et al.*, 1977). The bispyridine ligated iron complex was prepared by stirring the perchlorate derivative with pyridine under argon for 1 h. Single crystals were obtained by liquid diffusion of hexane into a CH_2Cl_2 solution. The crystals grown exhibited iron in +2 oxidation state (UV-vis λ_{max} = 436, 540, 576 nm).

<i>Crystal data</i>	
$C_{54}H_{34}Br_4FeN_6 \cdot C_5H_5N$	Mo $K\alpha$ radiation
$M_r = 1221.46$	$\lambda = 0.71073 \text{ \AA}$
Monoclinic	Cell parameters from 8017 reflections
$C2/c$	$\theta = 2.55\text{--}28.5^\circ$
$a = 18.4633 (5) \text{ \AA}$	$\mu = 3.658 \text{ mm}^{-1}$
$b = 19.9786 (6) \text{ \AA}$	$T = 100 (2) \text{ K}$
$c = 14.4636 (4) \text{ \AA}$	Block
$\beta = 114.688 (1)^\circ$	Dark red
$V = 4847.5 (2) \text{ \AA}^3$	$0.15 \times 0.11 \times 0.11 \text{ mm}$
$Z = 4$	Crystal source: synthesized
$D_x = 1.674 \text{ Mg m}^{-3}$	
D_m not measured	
<i>Data collection</i>	
Bruker x8-ApexII CCD diffractometer	4952 reflections with $>2\sigma(I)$
ϕ and ω scans	
Absorption correction:	$R_{int} = 0.0391$
multi-scan <i>SADABS</i> , Sheldrick (2004)	$\theta_{max} = 28.55^\circ$
Please give reference	$h = -24 \rightarrow 24$
$T_{min} = 0.60, T_{max} = 0.67$	$k = -26 \rightarrow 26$
51139 measured reflections	$l = -19 \rightarrow 19$
6171 independent reflections	every 0. reflections
	frequency: 0. min
<i>Refinement</i>	
Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0578P)^2 + 9.6451P]$
$R[F^2 > 2\sigma(F^2)] = 0.0365$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.1082$	$(\Delta/\sigma)_{max} = 0.001$
$S = 1.095$	$\Delta\rho_{max} = 1.032 \text{ e \AA}^{-3}$
6171 reflections	$\Delta\rho_{min} = -1.020 \text{ e \AA}^{-3}$
323 parameters	Extinction correction: none
H-atom parameters constrained	Scattering factors from <i>International Tables for Crystallography</i> (Vol. C)

The molecule of pyridine cocrystallized with the porphyrin is about an inversion center at (0, 1/2, 1/2). The N position in this pyridine solvate could not be determined due to the crystallographically imposed disorder. Thus, all pyridine atoms were refined as C and the three associated H atoms were included at 0.8333 occupancy. All H atoms were refined using a riding model with C—H distances equal to 0.95 Å and U_{iso} equal to 1.2($U_{\text{iso}}\text{C}$).

Data collection: APEX2 (Bruker–Nonius AXS, 2004). Cell refinement: APEX2/*SAINT* (Bruker–Nonius AXS, 2004). Data reduction: *SAINT/XPRED* (Bruker–Nonius AXS, 2004; Sheldrick, 2003). Program(s) used to solve structure: *SHELXS-97* (Sheldrick, 2001). Program(s) used to refine structure: *SHELXL97* (Sheldrick, 2001). Molecular graphics: *XP* (Sheldrick, 1998). Software used to prepare material for publication: XCIF (Sheldrick, 2001)/*enCIFer* (CCDC, 2004).

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Fig. 1. Thermal ellipsoid plot of $\text{Fe}(\text{TPPBr}_4)(\text{py})_2$. Ellipsoids drawn at 50% probability. Unique part of molecule drawn with solid bonds. H atoms and solvent omitted for clarity. Symmetry code: (i) $-x, y, -z+1 \frac{1}{2}$.

Fig. 2.
View of crystal packing perpendicular to (001).