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A cytochrome b model, $[Fe(TPP)(4\text{-}MeHIm)_2]$-$[K(222\text{-}cryptand)]_2Cl_2$

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Key indicators

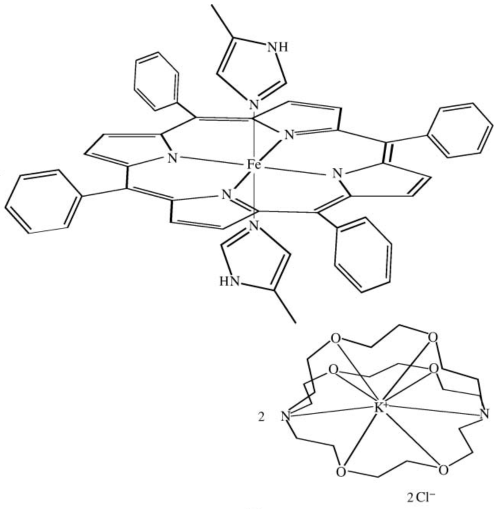
Single-crystal X-ray study
T = 100 K
Mean σ(C–C) = 0.002 Å
R factor = 0.043
wR factor = 0.128
Data-to-parameter ratio = 38.7

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The molecular structure of the title cytochrome b model, (5-methyl-4*H*-imidazole)(5,10,15,20-tetraphenylporphyrinato)-iron(II) bis[(222-cryptand)potassium(I)] dichloride, $[Fe(C_{44}H_{28}N_8)(C_4H_6N_2)_2][K(C_{18}H_{36}N_2O_6)]_2Cl_2$ or $[Fe(TPP)(4\text{-}MeHIm)_2][K(222\text{-}cryptand)]_2Cl_2$, is reported. This low-spin Fe^{II} tetraphenylporphyrinate is cocrystallized with the salt [K(222-cryptand)]Cl. The crystal structure has iron(II) on an inversion center. The average $Fe—N_p$ bond is 1.9952 (8) Å and the $Fe—N_{Im}$ distance is 2.0154 (8) Å. The porphyrin core is saddled; the two imidazole rings have a relative parallel orientation (N_p = porphyrinate N atom and Im = imidazole).

Comment

Safo *et al.* (1990) were among the first to structurally characterize six-coordinate iron(II) porphyrinates with imidazole derivatives as axial ligands $[Fe(Por)(ImX)_2]$. This study, and an additional study by Safo *et al.* (1997), investigated the electronic properties of these complexes as a result of their axial ligand orientations. We report here the molecular structure of another six-coordinate bis-imidazole ligated iron(II) porphyrinate, $[Fe(TPP)(4\text{-}MeHIm)_2]$. The molecular structure of $[Fe(TPP)(4\text{-}MeHIm)_2]$ mimics the parallel bis-histidine ligation of cytochrome b (Mathews *et al.*, 1979).



(I)

The molecular structure of the title compound, (I), with the atom-numbering scheme, is shown in Fig. 1. The Fe atom is located at a crystallographic inversion center. The unit cell, displayed in Fig. 2, contains one $[Fe(TPP)(4\text{-}MeHIm)_2]$ molecule, two $[K(222\text{-}cryptand)]^+$ cations and two Cl^- anions, half of these cell contents constituting the asymmetric unit. The average $Fe—N_p$ bond distance is 1.9952 (8) Å and the

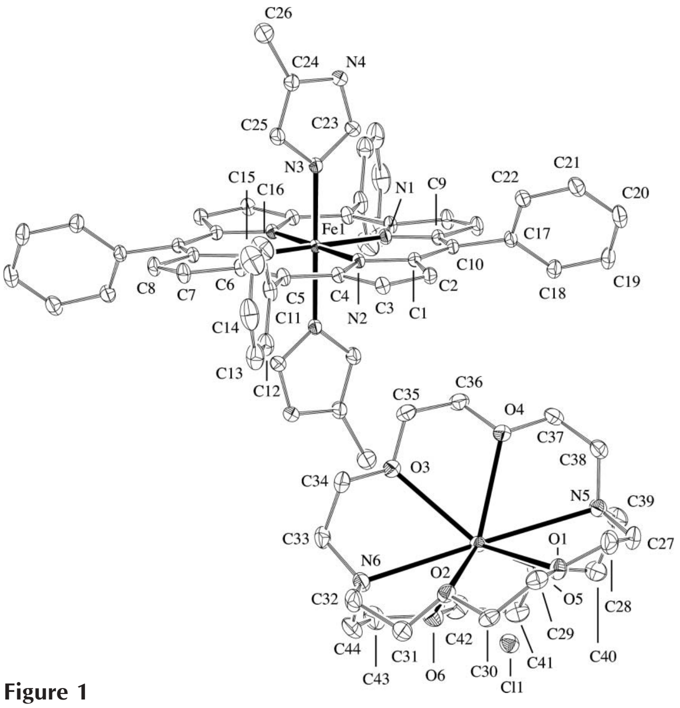


Figure 1
View of the title structure, showing 50% probability displacement ellipsoids. Unlabeled atoms are related to the labeled atoms by the symmetry operation ($-x$, $1 - y$, $1 - z$). H atoms and the symmetry-related K-centered cation and chloride anion have been omitted for clarity.

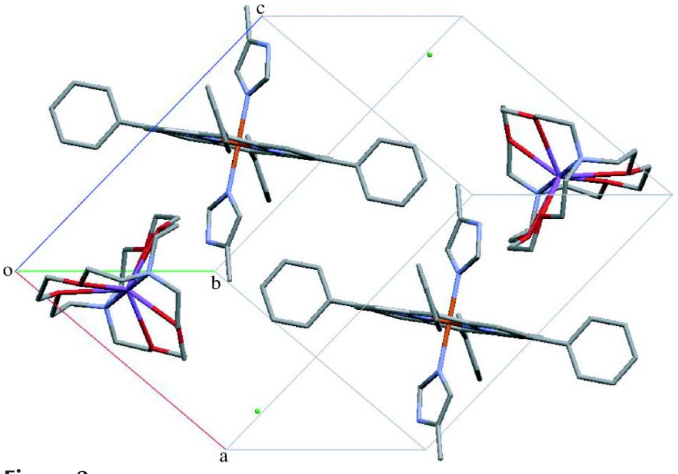


Figure 2
Packing diagram of the unit-cell contents of (I). For clarity, complete Fe complex molecules are shown. Fe atoms are located at the inversion centers ($0, \frac{1}{2}, \frac{1}{2}$) and ($1, \frac{1}{2}, \frac{1}{2}$). H atoms have been omitted.

axial Fe—N_{Im} distance is 2.0154 (8) Å. The axial ligands are parallel, as commonly found in previously reported iron(II) tetraphenylporphyrinates (Safo *et al.*, 1990). The absolute orientation of the axial ligand, the dihedral angle between the projection of the imidazole and the closest Fe—N_p bond, is 0.7 (2)°. The Fe—N_{Im} distance falls in the range of reported values for imidazole ligated iron(II) tetraphenylporphyrinates. These values are 2.004 (2), 2.017 (4) and 2.014 (5) Å for [Fe(TPP)(1-VinIm)$_2$], [Fe(TPP)(1-BzlIm)$_2$], [Fe(TPP)(1-MeIm)$_2$], respectively (Safo *et al.*, 1990). All distances are consistent with a low-spin iron(II) state (Scheidt, 2000).

Experimental

Experimental manipulations were performed under an atmosphere of argon. Toluene and hexane were distilled over sodium benzophenone ketyl. These solvents were further degassed by three freeze/pump/thaw cycles. [Fe(TPP)(NO)] (Scheidt & Frisse, 1975) (54 mg), 222-cryptand (122 mg) and potassium 4-methylimidazolate (15 mg) were added to toluene (40 ml). The solution was then transferred by cannula to glass tubes, where it was layered with hexane, and the tubes were sealed. After 30 d, X-ray quality crystals of (I) were isolated.

Crystal data

$[Fe(C_{44}H_{28}N_8)(C_4H_6N_2)_2]$-
$[K(C_{18}H_{36}N_2O_6)]_2Cl_2$
$M_r = 1734.85$
Triclinic, $P\overline{1}$
$a = 12.4441$ (2) Å
$b = 12.7433$ (2) Å
$c = 14.5723$ (2) Å
$\alpha = 73.504$ (1)°
$\beta = 81.836$ (1)°
$\gamma = 85.061$ (1)°
$V = 2190.74$ (6) Å^3

$Z = 1$
$D_x = 1.315$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 9508 reflections
$\theta = 2.4$–36.1°
$\mu = 0.40$ mm^{-1}
$T = 100$ (2) K
Thick plate, red
0.90 × 0.57 × 0.27 mm

Data collection

Bruker SMART APEX CCD diffractometer
ω and φ scans
Absorption correction: multi-scan (*SADABS*; Blessing, 1995)
$T_{min} = 0.718$, $T_{max} = 0.901$
79801 measured reflections

20486 independent reflections
16529 reflections with $I > 2\sigma(I)$
$R_{int} = 0.042$
$\theta_{max} = 36.0°$
$h = -19 \rightarrow 20$
$k = -21 \rightarrow 21$
$l = -24 \rightarrow 24$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.044$
$wR(F^2) = 0.128$
$S = 1.06$
20486 reflections
529 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.071P)^2 + 0.5056P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.92$ e Å^{-3}
$\Delta\rho_{min} = -0.96$ e Å^{-3}

H atoms were placed in calculated positions (C—H = 0.95–0.99 Å) and allowed to ride on the parent atom. U_{iso}(H) was set to $1.2U_{eq}$(C) or $1.5U_{eq}(C_{methyl})$. The crystal was not cut as others were found to crumble on contact.

Data collection: *APEX2* (Bruker, 2004); cell refinement: *APEX2* and *SAINT* (Bruker, 2004); data reduction: *SAINT* and *SHELXTL* (Sheldrick, 2001); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2004); software used to prepare material for publication: *SHELXTL*.

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