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(5,10,15,20-Tetraphenylporphyrinato-κ^4N)bis(L-valine-κN methyl ester)iron(III) trifluoromethylsulfonate dichloromethane solvate

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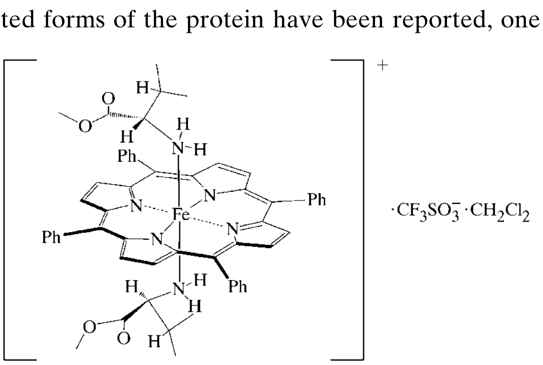
The title compound, $[Fe(C_{44}H_{28}N_4)(C_6H_{13}NO_2)_2](CF_3O_3S)\cdot CH_2Cl_2$, is the first amino ester complex of iron porphyrins to be investigated using X-ray diffraction and it can be considered as a model complex of cytochrome f. The Fe atom is six-coordinate to four N atoms of the porphyrin ring and to two N atoms of the axial amino ester ligands.

Comment

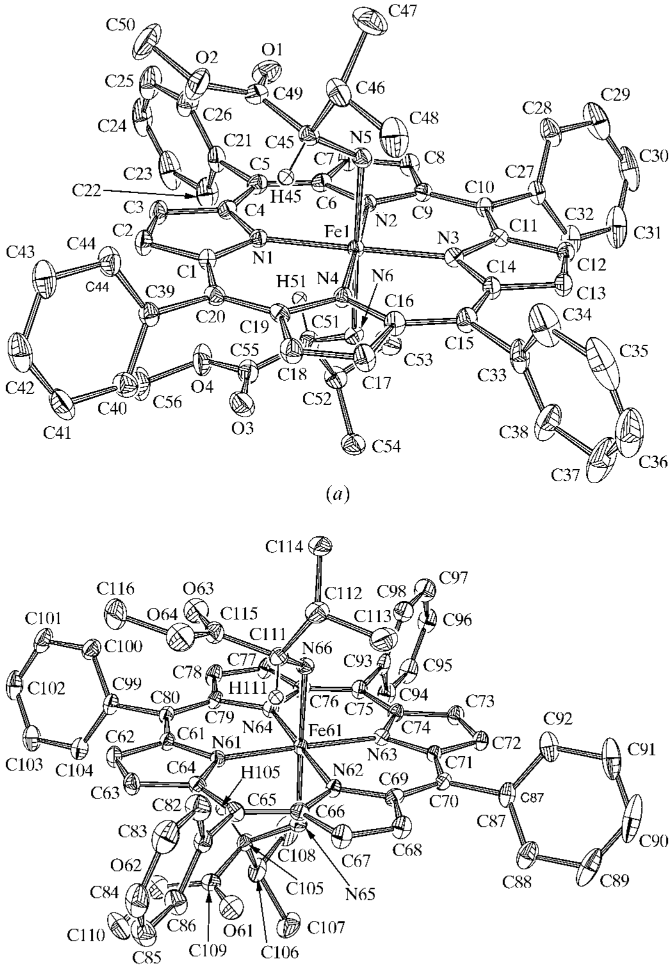
Cytochrome f is one of the four redox centres in the cytochrome b6f complex of the thylakoid membrane in oxygenic photosynthetic organisms. Cytochrome f is also the electron donor to the Cu-containing protein plastocyanin in some eukariotic algae and cyanobacteria, when growing in a Cu-deficient environment. The protein consists predominantly of β-sheets and has a unique ligation of the haem by the α-amino N atom of the N-terminal residue. The structures of two truncated forms of the protein have been reported, one from turnip (Martinez *et al.*, 1994, 1996) and the other from chlamydonas reinhardtii (Chi *et al.*, 2000). The present study of the title compound, (I), seems to be the only reported structure of an amino ester complex of iron porphyrins. The crystal structures of primary amine complexes of iron(II) porphyrins are the only other examples involving NH_2 groups and iron porphyrins that have been reported to date (Munro *et al.*, 1999).



(I)

The asymmetric unit of (I) is comprised of two independent ion pairs. In each molecule, the iron porphyrin differs slightly in the orientation of the C—Hα bonds of the axial ligands with respect to the porphyrin plane. Thus, the orientation of the ligands with respect to the N1—Fe—N3 axis is not equivalent for the two independent molecules. The angle between the N—Fe—N axis and the projection of the ligand C—Hα bond normal on to the porphyrin plane is 139.5 (2)° for molecule (I*a*) and 138 (1)° for molecule (I*b*) (Fig. 1).

The equatorial Fe—N distances average 1.998 (2) Å for (I*a*) and 1.997 (2) Å for (I*b*), which is as expected for low-spin iron(III) porphyrinate derivatives (Scheidt & Reed, 1981). The axial Fe—N bonds average 2.026 (2) Å for (I*a*) and 2.023 (2) Å for (I*b*). In $[(TPP)Fe(1\text{-}BuNH_2)_2]$, $[(TPP)Fe(Bz\text{-}NH_2)_2]$ and $[(TPP)Fe(PhCH_2CH_2NH_2)_2]$ (TPP is tetraphenylporphyrin; Munro *et al.*, 1999), the axial Fe—N distances are 2.039 (3), 2.043 (3) and 2.028 (2) Å, respectively.



(*a*)

(*b*)

Figure 1
The two crystallographically independent molecules of (I), *i.e.* (*a*) (I*a*) and (*b*) (I*b*). Displacement ellipsoids are drawn at the 50% probability level. Most H atoms have been omitted for clarity, but the H atoms on the chiral C atoms of the L-valine ligands are shown as ellipsoids.

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These three values are longer than those observed for (I) and reflect the increase in the oxidation state, from the ferrous state for the alkyl amine complexes to the ferric state for (I). Accordingly, a better σ donation from the ligated N atoms is expected in the ferric state.

All these distances are significantly longer than the Fe—NH_2 distance reported for the X-ray structure of turnip cytochrome f (1.94 Å; Martinez *et al.*, 1996). This is unexpected and the result was previously discussed by Munro and co-workers (Munro *et al.*, 1999).

Recently, a truncated form of cytochrome f from chlamydomonas reinhardtii has been crystallized and its structure determined to 2.0 Å resolution (Chi *et al.*, 2000). The distance between the Fe atom and the N atom of the amino group of the N-terminus residue (tyrosine) is 2.7 Å. Although the two protein structures display the same folding, the latter Fe—N distance is much longer. This situation will probably be solved with the structure determination of other cytochromes f.

Table 1
Selected geometric parameters (Å, °).

Fe1—N3	1.990 (2)	Fe61—N61	1.987 (2)
Fe1—N1	1.995 (2)	Fe61—N63	1.995 (2)
Fe1—N4	2.002 (2)	Fe61—N64	2.003 (2)
Fe1—N2	2.005 (2)	Fe61—N62	2.004 (2)
Fe1—N6	2.023 (2)	Fe61—N66	2.016 (2)
Fe1—N5	2.029 (2)	Fe61—N65	2.031 (2)
N3—Fe1—N1	179.20 (10)	N61—Fe61—N63	178.66 (10)
N3—Fe1—N4	90.61 (8)	N61—Fe61—N64	89.84 (8)
N1—Fe1—N4	89.58 (8)	N63—Fe61—N64	90.40 (8)
N3—Fe1—N2	89.34 (8)	N61—Fe61—N62	90.56 (8)
N1—Fe1—N2	90.47 (8)	N63—Fe61—N62	89.19 (8)
N4—Fe1—N2	179.78 (11)	N64—Fe61—N62	179.42 (9)
N3—Fe1—N6	88.74 (8)	N61—Fe61—N66	91.13 (8)
N1—Fe1—N6	92.05 (8)	N63—Fe61—N66	90.20 (8)
N4—Fe1—N6	89.08 (8)	N64—Fe61—N66	88.98 (9)
N2—Fe1—N6	91.13 (8)	N62—Fe61—N66	91.43 (8)
N3—Fe1—N5	89.02 (8)	N61—Fe61—N65	90.39 (8)
N1—Fe1—N5	90.20 (8)	N63—Fe61—N65	88.29 (8)
N4—Fe1—N5	90.83 (8)	N64—Fe61—N65	90.37 (8)
N2—Fe1—N5	88.95 (9)	N62—Fe61—N65	89.20 (8)
N6—Fe1—N5	177.75 (9)	N66—Fe61—N65	178.35 (9)

Experimental

The title compound was prepared from the trifluoromethanesulfonate complex of iron(III) porphyrin and three equivalents of L-valine methyl ester, as previously reported for the L-leucine methyl ester ligands (Morice *et al.*, 1998). Crystals of (I) suitable for X-ray analysis were obtained by slow evaporation of a CH_2Cl_2–hexane solution in the presence of a small excess of the amino ester.

Crystal data

$[Fe(C_{44}H_{28}N_4)(C_6H_{13}NO_2)_2]$-$(CF_3O_3S)\cdot CH_2Cl_2$
$M_r = 1164.90$
Triclinic, $P1$
$a = 11.3660$ (2) Å
$b = 14.4438$ (2) Å
$c = 17.6675$ (2) Å
$\alpha = 78.148$ (1)°
$\beta = 87.016$ (1)°
$\gamma = 75.485$ (1)°
$V = 2748.01$ (7) Å^3

$Z = 2$
$D_x = 1.408$ Mg m$^{-3$}
Mo $K\alpha$ radiation
Cell parameters from 16 340 reflections
$\theta = 1.0$–32.0°
$\mu = 0.48$ mm^{-1}
$T = 120$ (2) K
Prism, black
0.24 × 0.18 × 0.11 mm

Data collection

Nonius KappaCCD area-detector diffractometer
φ and ω scans
33 368 measured reflections
33 368 independent reflections

23 226 reflections with $I > 2\sigma(I)$
$\theta_{max} = 32°$
$h = -16 \rightarrow 16$
$k = -21 \rightarrow 21$
$l = -26 \rightarrow 26$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.049$
$wR(F^2) = 0.133$
$S = 0.99$
33 368 reflections
1406 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0690P)^2 + 0.0588P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.76$ e Å^{-3}
$\Delta\rho_{min} = -0.59$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0012 (4)
Absolute structure: Flack (1983), 14 286 Friedel pairs
Flack parameter = −0.008 (8)

The title compound crystallized in the triclinic space group $P1$ with two molecules in the asymmetric unit. The structure showed a pseudo-I centring. Previous studies at room temperature showed a rather large thermal motion, disordered trifluoromethanesulfonate anions and a large thermal motion for the two dichloromethane molecules, the consequence of which was a ratio of reflections to parameters which was too low. The use of the CCD technique at low temperature reduced this thermal motion and produced a significant increase in the reflections-to-parameter ratio. Furthermore, the trifluoromethanesulfonate anions were no longer disordered. After anisotropic refinement (cations, anions and solvent molecules), most of the H atoms were found in a difference Fourier map and treated as riding, with C—H = 0.93–0.98 Å and N—H = 0.90 Å. It was also possible to confirm the absolute configuration unambiguously using the Friedel pairs.

Data collection: *KappaCCD Server Software* (Nonius, 1999); cell refinement: *HKL SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *HKL DENZO* (Otwinowski & Minor, 1997) and *SCALEPACK*; program(s) used to solve structure: *SIR*97 (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 1998).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1557). Services for accessing these data are described at the back of the journal.

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