

Fig. 3. ORTEP view (Johnson, 1976) of the other molecule constituting the asymmetric unit for compound (2).

atoms of two water molecules belonging to two other entities. Distances O(2)—first water oxygen and O(4)—second water oxygen are 2.79 and 2.84 Å, with angles around the corresponding hydrogens equal to 171 and

156.3°, respectively. Each perchlorate anion is then connected to three different Cu atoms through a first O(2)—O_{H2O} hydrogen bond, and through a second O(4)—O_{H2O} hydrogen bond involving a different water molecule, in addition to semicoordinated O(1).

Compound (2). The unit cell contains four [CuL₄(CF₃SO₃)₂] molecules corresponding to two asymmetric units (Fig. 2 and 3). For both coppers, the environment is octahedral. The basal plane includes four N atoms of four isoquinoline molecules arranged as propeller blades. Two trifluoromethanesulfonate anions are semicoordinated by oxygen in apical positions (Table 4). The dihedral angle between the two basal planes of Cu(1) and Cu(2) is 81°.

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Structure of Bis(pyrazine)-5,10,15,20-tetraphenylporphinatoiron(II), TPPFe(py₂)₂

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Abstract. [Fe(C₄₄H₂₈N₄)(C₄H₄N₂)₂], *M_r* = 828.77, monoclinic, *P*2₁/*c*, *a* = 13.157 (4), *b* = 16.000 (5), *c* = 19.350 (5) Å, β = 93.15 (5)°, *V* = 4067.3 Å³, *Z* = 4, *D_x* = 1.353 g cm⁻³, Cu *K*α, λ = 1.54184 Å, μ = 33.395 cm⁻¹, *F*(000) = 1720, *T* = 293 K. The final *R* value is 0.052 for 3612 significant [*I* > 3σ(*I*)] reflections. The octahedral FeN₆ coordination group exhibits equatorial Fe—N bond lengths from 1.975 (3) to 1.993 (2) Å; the different Fe—N bonds to the axial pyrazine ligands [1.970 (3), 2.010 (3) Å] are attributable to steric repulsions.

Introduction. The stereochemical parameters of the six-coordinate iron(II) porphyrins are of interest because of their physical properties and as models for conducting bridged macrocyclic metal complexes (Hanack, 1983, 1985). Only two structures of bis(amine) derivatives of tetraphenylporphinatoiron(II) (TPPFe) are known. These are the compounds with the bis-axial ligands piperidine (Radonovich, Bloom & Hoard, 1972) and 1-methylimidazole [the latter has been cited (Scheidt, 1977) but, to the best of our knowledge, not yet published (Steffen, Reed, Sayler &

Hoard, 1987)]. Here we report the structure of the monomeric compound $\text{TPPFe}(\text{pyz})_2$ (pyz = pyrazine) obtained by reaction of TPPFe or $\text{TPPFe}(\text{py})_2$ (py = pyridine) with pyrazine (Mezger, 1983). Owing to the bridging function of the bidentate ligand pyrazine, polymeric complexes $\text{TPPFe}(\text{pyz})_n$ can be synthesized; however, we prepared no single crystal suitable for X-ray analysis.

Experimental. A blue-black prismatic crystal of approximate dimensions $0.3 \times 0.3 \times 0.4$ mm was mounted on a glass fiber; Enraf–Nonius CAD-4 κ -axis diffractometer, Cu $K\alpha$ radiation, graphite monochromator. Cell constants were obtained from least-squares refinement, using the setting angles of 25 reflections in the range $11 < \theta < 26^\circ$. From the systematic absences of $0k0$: $k = 2n + 1$ and $h0l$: $l = 2n + 1$, the space group was determined to be $P2_1/c$. The data were collected to a max. θ of 54° , using the ω/θ scan technique with variable scan rate; $h + 13$, $k \pm 16$, $l \pm 20$; 8999 reflections measured; three standard reflections with no significant intensity variation; Lorentz and polarization corrections, empirical absorption correction (ψ scan) (North, Phillips & Mathews, 1968), relative transmission 0.931–0.998, 4919 unique reflections ($R_{\text{int}} = 0.029$). The structure was solved by direct methods (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). Hydrogen atoms were calculated in idealized positions [$d(\text{C}—\text{H}) = 0.95$ Å] and added only to the structure factor calculations. Full-matrix least-squares refinement (on F) of all Fe, N and C atomic positions with anisotropic thermal parameters. Secondary-extinction correction (Zachariasen, 1963) with a final coefficient 7.63×10^{-7} , refined in least squares. 3612 observed [$I > 3\sigma(I)$] reflections, 551 variables, $R = 0.052$, $wR = 0.062$, $\sum w|\Delta F|^2$ minimized, unit weights, $S = 2.880$, $(\Delta/\sigma)_{\text{max}} = 0.001$; final difference Fourier map with $|\Delta\rho| < 0.61$ e Å $^{-3}$. Scattering factors from *International Tables for X-ray Crystallography* (1974). Calculations were performed on PDP 11/60 (Institut für Anorganische Chemie) and VAX 11/750 (Zentrum für Datenverarbeitung der Universität Tübingen) computers using the *Structure Determination Package SDP-Plus*, Version 1.1 and *VAXSDP*, Version 2.2 (Frenz, 1978).

Discussion. Positional and thermal parameters are listed in Table 1, selected distances and angles in Table 2.* Fig. 1 and Fig. 2 show the molecular structure along with the atomic numbering scheme.

* Lists of structure factors, anisotropic thermal parameters, H-atom positions, least-squares-planes data and further bond lengths and angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43832 (29 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters U_{eq} (Å 2) with e.s.d.'s in parentheses*

	$U_{\text{eq}} = \frac{1}{3}(U_{11} + U_{22} + U_{33})$		
	x	y	z
Fe	0.75912 (6)	0.03648 (5)	0.74874 (4)
N1	0.8474 (3)	−0.0632 (3)	0.7576 (2)
N2	0.6683 (3)	−0.0129 (3)	0.8170 (2)
N3	0.6674 (3)	0.1349 (3)	0.7360 (2)
N4	0.8516 (3)	0.0874 (3)	0.6825 (2)
N5	0.6781 (3)	−0.0183 (3)	0.6730 (2)
N6	0.5439 (4)	−0.0849 (4)	0.5690 (3)
N7	0.8391 (3)	0.0931 (3)	0.8268 (2)
N8	0.9497 (4)	0.1706 (4)	0.9385 (3)
C1	0.9328 (4)	−0.0795 (3)	0.7208 (3)
C2	0.9719 (4)	−0.1621 (4)	0.7381 (3)
C3	0.9120 (4)	−0.1936 (4)	0.7868 (3)
C4	0.8365 (4)	−0.1319 (3)	0.7991 (3)
C5	0.7632 (4)	−0.1408 (4)	0.8481 (3)
C6	0.6835 (4)	−0.0850 (3)	0.8551 (3)
C7	0.6005 (4)	−0.0980 (4)	0.8994 (3)
C8	0.5342 (4)	−0.0357 (4)	0.8866 (3)
C9	0.5765 (4)	0.0179 (3)	0.8360 (3)
C10	0.5289 (4)	0.0908 (4)	0.8099 (3)
C11	0.5736 (4)	0.1452 (4)	0.7647 (3)
C12	0.5282 (4)	0.2224 (4)	0.7421 (3)
C13	0.5934 (5)	0.2585 (4)	0.6990 (3)
C14	0.6782 (4)	0.2038 (3)	0.6952 (3)
C15	0.7595 (4)	0.2180 (4)	0.6539 (3)
C16	0.8414 (4)	0.1644 (3)	0.6497 (3)
C17	0.9270 (4)	0.1786 (4)	0.6082 (3)
C18	0.9877 (4)	0.1114 (4)	0.6156 (3)
C19	0.9399 (4)	0.0543 (3)	0.6601 (3)
C20	0.9785 (4)	−0.0247 (3)	0.6767 (3)
C21	0.7709 (4)	−0.2159 (3)	0.8949 (3)
C22	0.8471 (4)	−0.2210 (4)	0.9460 (3)
C23	0.8536 (5)	−0.2894 (4)	0.9909 (3)
C24	0.7842 (5)	−0.3523 (4)	0.9844 (3)
C25	0.7075 (5)	−0.3488 (4)	0.9332 (4)
C26	0.7009 (5)	−0.2805 (4)	0.8887 (3)
C27	0.4251 (4)	0.1124 (4)	0.8305 (3)
C28	0.3445 (5)	0.1069 (5)	0.7837 (3)
C29	0.2483 (5)	0.1349 (6)	0.7997 (4)
C30	0.2344 (5)	0.1671 (5)	0.8646 (4)
C31	0.3137 (5)	0.1716 (5)	0.9121 (4)
C32	0.4091 (5)	0.1440 (5)	0.8956 (3)
C33	0.7548 (4)	0.2952 (4)	0.6083 (3)
C34	0.6950 (6)	0.2970 (5)	0.5495 (4)
C35	0.6862 (7)	0.3682 (6)	0.5080 (4)
C36	0.7366 (7)	0.4376 (5)	0.5268 (4)
C37	0.797 (1)	0.4369 (5)	0.5847 (5)
C38	0.8087 (8)	0.3648 (4)	0.6253 (4)
C39	1.0766 (4)	−0.0496 (3)	0.6469 (3)
C40	1.1639 (5)	−0.0569 (4)	0.6895 (3)
C41	1.2566 (5)	−0.0796 (5)	0.6616 (4)
C42	1.2609 (5)	−0.0915 (4)	0.5916 (4)
C43	1.1747 (5)	−0.0836 (4)	0.5495 (3)
C44	1.0832 (4)	−0.0640 (4)	0.5764 (3)
C45	0.6550 (4)	0.0217 (4)	0.6133 (3)
C46	0.5897 (5)	−0.0112 (4)	0.5632 (3)
C47	0.5697 (6)	−0.1256 (4)	0.6272 (3)
C48	0.6348 (5)	−0.0932 (4)	0.6784 (3)
C49	0.8279 (7)	0.1695 (5)	0.8454 (5)
C50	0.8833 (8)	0.2063 (5)	0.8985 (5)
C51	0.9606 (8)	0.0933 (6)	0.9210 (5)
C52	0.9069 (8)	0.0558 (6)	0.8677 (5)

The porphinato core is slightly distorted; the atom C2 exhibits the largest deviation, 0.239 (6) Å, from the mean plane (Table 3). The dihedral angles between that plane and the planes of the peripheral phenyl groups I, II, III and IV are 66.6 (1), 73.7 (1), 80.9 (1) and 67.7 (1)°. In TPPFe (Collman, Hoard, Kim, Lang & Reed, 1975) the molecular symmetry is described as S_4 (quasi- D_{2d}), in $\text{TPPFe}(\text{piperidine})_2$ the porphinato core has D_{4h} symmetry. However, in the title compound, the departures from planarity of the porphinato core are of

Table 2. *Selected distances (Å) and angles (°)*

Fe—N1	1.975 (3)	Fe—N4	1.990 (2)
Fe—N2	1.993 (2)	Fe—N5	1.970 (3)
Fe—N3	1.991 (3)	Fe—N7	2.010 (3)
N1—C1	1.388 (4)	N3—C11	1.390 (4)
N1—C4	1.374 (4)	N3—C14	1.368 (4)
N2—C6	1.378 (4)	N4—C16	1.388 (4)
N2—C9	1.373 (4)	N4—C19	1.370 (4)
C1—C2	1.451 (5)	C11—C12	1.430 (5)
C2—C3	1.358 (5)	C12—C13	1.358 (5)
C3—C4	1.430 (5)	C13—C14	1.423 (5)
C4—C5	1.396 (5)	C14—C15	1.388 (5)
C5—C6	1.390 (5)	C15—C16	1.382 (5)
C6—C7	1.439 (5)	C16—C17	1.437 (5)
C7—C8	1.338 (5)	C17—C18	1.342 (5)
C8—C9	1.435 (5)	C18—C19	1.424 (5)
C9—C10	1.405 (5)	C19—C20	1.394 (5)
C10—C11	1.387 (5)	C20—C1	1.383 (4)
C5—C21	1.505 (5)	C15—C33	1.518 (5)
C10—C27	1.484 (5)	C20—C39	1.497 (5)
N5—C45	1.342 (4)	N7—C49	1.283 (5)
N5—C48	1.332 (4)	N7—C52	1.304 (6)
N6—C46	1.331 (5)	N8—C50	1.270 (6)
N6—C47	1.330 (5)	N8—C51	1.292 (6)
C45—C46	1.364 (5)	C49—C50	1.361 (7)
C47—C48	1.375 (5)	C51—C52	1.357 (7)
N1...N3	3.965 (3)	C5...C15	6.859 (5)
N2...N4	3.982 (3)	C10...C20	6.835 (5)
N5...N7	3.979 (3)		

N1—Fe—N2	89.6 (1)	N2—Fe—N7	89.4 (1)
N1—Fe—N3	177.5 (1)	N3—Fe—N4	89.1 (1)
N1—Fe—N4	90.5 (1)	N3—Fe—N5	87.7 (1)
N1—Fe—N5	89.8 (1)	N3—Fe—N7	91.4 (1)
N1—Fe—N7	91.0 (1)	N4—Fe—N5	91.6 (1)
N2—Fe—N3	90.8 (1)	N4—Fe—N7	89.2 (1)
N2—Fe—N4	178.6 (1)	N5—Fe—N7	178.8 (1)
N2—Fe—N5	89.8 (1)		
Fe—N1—C1	126.6 (2)	Fe—N3—C11	126.1 (2)
Fe—N1—C4	128.1 (2)	Fe—N3—C14	128.8 (2)
C1—N1—C4	105.3 (3)	C11—N3—C14	105.0 (3)
Fe—N2—C6	127.8 (2)	Fe—N4—C16	127.6 (2)
Fe—N2—C9	127.1 (2)	Fe—N4—C19	127.2 (2)
C6—N2—C9	105.1 (3)	C16—N4—C19	105.1 (3)
N1—C1—C2	109.9 (3)	N3—C11—C12	110.2 (3)
N1—C1—C20	126.1 (3)	N3—C11—C10	126.5 (3)
C2—C1—C20	124.0 (3)	C12—C11—C10	123.3 (3)
C1—C2—C3	106.6 (3)	C11—C12—C13	106.8 (3)
C2—C3—C4	107.2 (3)	C12—C13—C14	107.0 (3)
N1—C4—C3	111.0 (3)	N3—C14—C13	111.0 (3)
N1—C4—C5	125.2 (3)	N3—C14—C15	124.8 (3)
C3—C4—C5	123.8 (3)	C13—C14—C15	124.1 (3)
C4—C5—C6	123.7 (3)	C14—C15—C16	124.1 (3)
C4—C5—C21	117.6 (3)	C14—C15—C33	117.3 (3)
C6—C5—C21	118.7 (3)	C16—C15—C33	118.5 (3)
N2—C6—C5	125.0 (3)	N4—C16—C15	125.4 (3)
N2—C6—C7	110.3 (3)	N4—C16—C17	109.6 (3)
C5—C6—C7	124.5 (3)	C15—C16—C17	125.0 (3)
C6—C7—C8	106.9 (3)	C16—C17—C18	107.1 (3)
C7—C8—C9	107.3 (3)	C17—C18—C19	107.4 (3)
N2—C9—C8	110.3 (3)	N4—C19—C18	110.7 (3)
N2—C9—C10	125.6 (3)	N4—C19—C20	125.6 (3)
C8—C9—C10	124.0 (3)	C18—C19—C20	123.7 (3)
C9—C10—C11	123.5 (3)	C19—C20—C1	123.5 (3)
C9—C10—C27	119.7 (3)	C19—C20—C39	117.6 (3)
C11—C10—C27	116.9 (3)	C1—C20—C39	118.9 (3)

remarkable magnitude and the high symmetry above is significantly disturbed. This distortion is accompanied by small differences in the bond lengths of chemically equivalent bonds. The N—C bonds in the core vary from 1.368 (4) to 1.390 (4) Å, the bond lengths between the β -carbon atoms of the pyrrole rings from 1.338 (5) to 1.358 (5) Å. Distances from the α -carbon atoms to the β -carbon atoms are in the range 1.423 (5)–1.451 (5) Å, to the methine carbon atoms 1.382 (5)–1.405 (5) Å. We wish to emphasize that, within the accuracy of the experimental structural

results, these are minor variations and agree with the fact that the porphinato core possesses some flexibility and variability in size. A large part of the deformation is probably required by the steric interactions. Compared with bis(imidazole)tetraphenylporphinatoiron(III) chloride (Collins, Countryman & Hoard, 1972), the steric requirements of pyrazine are substantially more demanding than those of imidazole, a consequence of the differing internal angles of six- and five-membered rings. For minimum steric interactions between axial

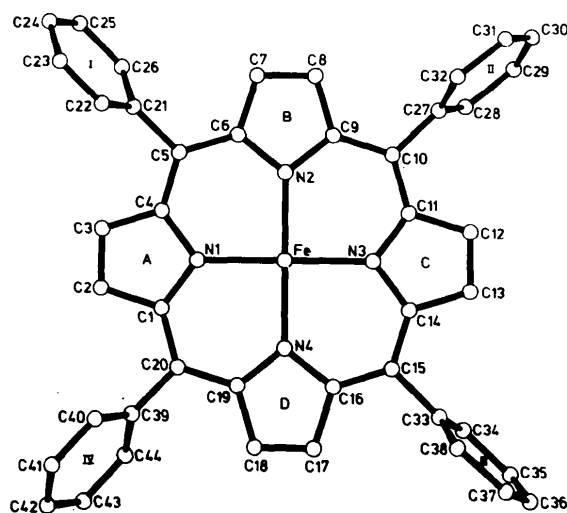


Fig. 1. The tetraphenylporphinato core. The axial pyrazine ligands are omitted for clarity.

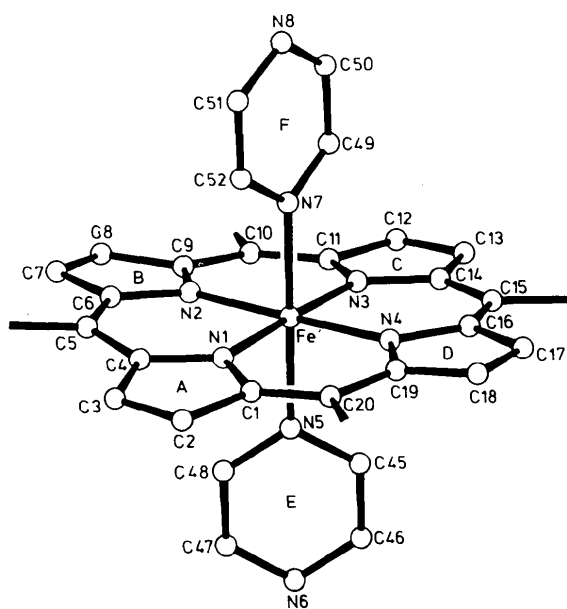


Table 3. *Perpendicular displacements of the atoms from the least-squares plane of the porphinato core*

The equation of the plane is of the form: $-0.4741u - 0.4557v - 0.7543w + 15.4902 = 0$, where u, v, w are orthogonalized coordinates. Atoms with negative displacements are toward the pyrazine ring *F* side of the plane.

Distance (Å)		Distance (Å)	
Atoms in plane			
Fe	−0.031 (1)	C9	0.016 (5)
N1	0.020 (4)	C10	0.148 (5)
N2	−0.064 (4)	C11	0.109 (5)
N3	0.002 (4)	C12	0.146 (6)
N4	−0.048 (4)	C13	0.082 (6)
C1	0.124 (5)	C14	0.005 (5)
C2	0.239 (6)	C15	−0.025 (6)
C3	0.158 (6)	C16	0.086 (5)
C4	0.007 (5)	C17	−0.141 (6)
C5	−0.160 (5)	C18	−0.133 (6)
C6	−0.168 (5)	C19	−0.043 (5)
C7	−0.179 (6)	C20	0.059 (5)
C8	−0.038 (6)		
Other atoms			
N5	1.937 (4)	N7	−2.041 (4)
N6	4.722 (5)	N8	−4.864 (6)

ligands and the porphinato core, the planes of the two pyrazine ligands should be in superposition on the lines C5...C15 and C10...C20, respectively. Such an orientation allows a maximum and equidistant separation from the N and α -C atoms of the pyrrole rings. In the title compound these interactions are represented by the angles between the reference plane {C5, C15, Fe, N5, N7} and the planes {Fe, N5, C45} and {Fe, N7, C49}, which are 3.9 (1) and 37.0 (1)°. The latter two describe the planes of the pyrazine rings *E* and *F*, which make an angle of 40.9 (1)°. The corresponding values in TPPFe⁺(imidazole)₂ are 6, 63 and

57°. These values reflect that the pyrazine ring *F* is not well orientated to minimize steric repulsions and, consequently, the pyrrole rings *A* and *C* are displaced away from the atoms of that ligand. This steric repulsion might be responsible too for the stretched Fe—N7 bond length of 2.010 (3) Å compared with the distance $d(\text{Fe—N5}) = 1.970$ (3) Å.

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Actinide Structural Studies. 12.* 4,4'-Bipyridinium Di- μ -hydroxo-bis[dinitratodioxouranate(VI)] Monohydrate

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Abstract. $[\text{C}_{10}\text{H}_{10}\text{N}_2][\text{U}_2\text{O}_4(\text{OH})_2(\text{NO}_3)_4] \cdot \text{H}_2\text{O}$, $M_r = 998.3$, monoclinic, Pn , $a = 13.336$ (3), $b = 5.555$ (2), $c = 15.433$ (3) Å, $\beta = 94.25$ (1)°, $V = 1140.1$ (5) Å³, $Z = 2$, $D_x = 2.91$, $D_m = 2.85$ (2) g cm⁻³, $\lambda(\text{Mo K}\alpha) = 0.71069$ Å, $\mu = 135.5$ cm⁻¹, $F(000) = 904$, $T =$

290 K, $R = 0.026$ for 1920 unique observed $[I/\sigma(I) \geq 3.0]$ reflections. The hydroxy-bridged anion contains uranyl groups [U—O 1.785 (14) Å] equatorially coordinated by two bidentate NO₃⁻ groups [U—O 2.52 (2) Å] and two hydroxide groups [U—O 2.36 (3) Å]. The bipyridinium anions are slightly twisted about the central C—C bond [dihedral angle

* Part 11: Alcock & Roberts (1987).