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Structure and Spectroscopic Properties of Five-Coordinate (2-Methylimidazolato)- and Six-Coordinate (Imidazole)(imidazolato)iron(II) "Picket-Fence" Porphyrins

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The synthesis and characterization of the sodium 222 cryptated salts of the five-coordinate high-spin (2-methylimidazolato)iron(II) derivative **1** and the six-coordinate (imidazole)(imidazolato)iron(II) complex **2** of "picket-fence" porphyrin are reported. **1** crystallizes as the 2-methylimidazole bis(chlorobenzene) solvate, $C_{102}H_{121}N_{14}O_{10}NaCl_2Fe$, in the monoclinic space group $P2_1$ with two formula units in the unit cell. At -100 °C, the unit cell parameters are $a = 13.430$ (4) Å, $b = 26.163$ (6) Å, $c = 14.398$ (4) Å, and $\beta = 103.12$ (2)°. The structure was solved with 3393 observed reflections, and refinements led to conventional R and weighted R_w factors of 0.068 and 0.086, respectively. The mean Fe-N_p bond length is 2.106 (20) Å. The displacements of the iron atom relative to the 4N_p and 24-atom-core mean planes are respectively 0.524 (10) and 0.647 (10) Å. The 2-methylimidazole axial ligand is located inside the molecular cavity of the picket-fence porphyrin. The Fe-N(2-MeIm) (2-MeIm = 2-methylimidazolato) bond distance of 2.002 (15) Å is not very accurate but, nevertheless, significantly shorter than the Fe-N(2-MeHIm) (2-MeHIm = 2-methylimidazole) bond length of 2.095(6) Å in [FeTP_{piV}P(2-MeHIm)] (TP_{piV}P = picket-fence porphyrin). **2** crystallizes as the THF solvate (THF = tetrahydrofuran), $C_{92}H_{115}N_{14}O_{11}NaFe$, in the monoclinic space group $P2_1/n$ with four formula units in the unit cell. At -100 °C, the unit cell parameters are $a = 30.974$ (9) Å, $b = 22.753$ (5) Å, $c = 12.596$ (4) Å, and $\beta = 111.71$ (2)°. The structure of **2** was solved by using 3757 observed reflections and refined to R and R_w values, respectively, of 0.052 and 0.069. The average Fe-N_p bond distance of 1.995 (9) Å is consistent with those of other six-coordinate low-spin ferrous porphyrins. The Fe-N(ligand) bond lengths are 1.930 (5) and 1.953 (5) Å. The neutral HIm ligand (HIm = imidazole) cannot be distinguished from the anionic deprotonated Im group (Im = imidazolato) by comparison of the Fe-N bond distances, especially not when one takes into account the orientation of the ligand mean planes relative to the porphyrin ring. However, consideration of the structures of several iron picket-fence porphyrin derivatives with anionic ligands indicates that the group located inside the molecular cavity is, most probably, the deprotonated imidazole. For compound **1**, UV-visible and Mössbauer spectral results are consistent with the presence of a high-spin five-coordinate ferrous porphyrin in chlorobenzene solution and in the solid state. For compound **2**, the spectral properties are consistent with the presence of a low-spin six-coordinate ferrous derivative in THF solution and in the solid state. The high-spin five-coordinate species **1** with a nitrogen donor axial ligand shows also an unusually large quadrupole splitting of $\Delta E_q = 3.51$ mm/s at 77 K.

Introduction

A zero-field Mössbauer spectrum characterized by a quadrupole doublet with an unusually large splitting has been found in hydroxylamine oxidoreductase from *Nitrosomonas europaea*.³ This multiheme enzyme contains several *c*-type hemes along with an unusual prosthetic group termed P-460.^{3,4} Although the precise nature of this P-460 group is unknown, spectral evidence suggests that in its reduced state it is a five-coordinate high-spin ferrous heme-like moiety. Indeed, its UV-vis spectrum shows a strong band at 463 nm with an extinction coefficient compatible with a red-shifted Soret-type absorbance. It binds CO with high affinity to give a species with a strong Soret-type band located at 444 nm. The 4.2 K zero-field Mössbauer spectrum consists of a quadrupole doublet with an isomer shift δ of 0.96 mm/s. The quadrupole splitting ΔE_q of 4.21 mm/s is much larger than the splittings observed, so far, for all other ferrous heme proteins.^{3,4}

It has been shown recently that unusually large quadrupole splittings are also a distinctive feature of five-coordinate high-spin ferrous porphyrins with an anionic oxygen donor or halide ion as an axial ligand of iron.⁵⁻⁹ In order to find out whether such unusually large quadrupole splittings occur also with anionic nitrogen donor ligands, we have studied the structures and zero-field Mössbauer properties of the five-coordinate high-spin iron(II) "picket-fence" porphyrin complex [FeTP_{piV}P(2-MeIm)]⁻ and the six-coordinate low-spin derivative [FeTP_{piV}P(Im)(HIm)]⁻.

Table I. Crystallographic Data for **1** and **2**

	1	2
formula	$C_{102}H_{121}N_{14}O_{10}NaCl_2Fe$	$C_{92}H_{115}N_{14}O_{11}NaFe$
fw	1852.93	1671.87
<i>a</i> , Å	13.430 (4)	30.974 (9)
<i>b</i> , Å	26.163 (6)	22.753 (5)
<i>c</i> , Å	14.398 (4)	12.596 (4)
β , deg	103.12 (2)	111.71 (2)
<i>U</i> , Å ³	4923.9	8810.3
<i>Z</i>	2	4
<i>D</i> _{calc} , g cm ⁻³	1.250	1.260
space group	$P2_1$ (No. 4)	$P2_1/n$ (No. 14)
wavelength, Å	1.5418	1.5418
μ , cm ⁻¹	22.812	19.410
temp, °C	-100	-100
abs min/max	0.77/1.15	0.81/1.26
<i>R</i> (<i>F</i>)	0.068	0.052
<i>R</i> _w (<i>F</i>)	0.086	0.069

The structures and spectral properties of these two complexes are the subject of this paper.

Experimental Section

General Procedures. All manipulations were carried out under argon unless otherwise stated. THF and toluene were distilled twice over Na/benzophenone under nitrogen. Acetonitrile was distilled over phosphorus pentoxide. Chlorobenzene was treated with sulfuric acid, washed with water, and distilled over phosphorus pentoxide. Pentane and hexane were distilled over CaH₂. All solvents were degassed in vacuo prior to use. Silver triflate (Aldrich) and Kryptofix 222 (Merck) were used without further purification. Sodium imidazolato (NaIm) and 2-methylimidazolato (Na2-MeIm) were obtained by a slight modification of a published procedure.¹⁰ The *meso*-5,10,15,20-tetrakis(*o*-pivalamidophenyl)porphyrin H₂TP_{piV}P and its corresponding ferric chloro

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[FeTP_{piv}P(Cl)] and triflate [FeTP_{piv}P(Tf)] complexes were synthesized as previously described.^{11,12}

Mössbauer Spectroscopy. The Mössbauer spectra were accumulated with a standard apparatus in the constant-acceleration mode with a Co/Rh source (ca. 1.8 GBq). Isomer shifts are given relative to α -Fe at room temperature.

X-ray Crystallography. Systematic searches in reciprocal space using a Philips PW1100/16 automatic diffractometer showed that crystals of [FeTP_{piv}P(2-MeIm)][NaC222]·2-MeHIm·2C₆H₅Cl (**1**) (C222 = 222 cryptate) and [FeTP_{piv}P(Im)(HIm)][NaC222]·THF (**2**) belong to the monoclinic system. These crystals loose partly, at room temperature and under inert atmosphere, their molecules of solvation and had to be mounted on the sample holders at low temperature.

Quantitative data were obtained at -100 °C by using a gas-flow device fabricated in-house. Results are given in Table I. The resulting data sets were transferred to a VAX computer, and for all subsequent calculations the Enraf-Nonius SDP/VAX package¹³ was used with the exception of a local data reduction program.

Three standard reflections measured every 1 h during the entire data collection periods showed no significant trend. The raw step-scan data were converted to intensities by using the Lehmann-Larsen method¹⁴ and then corrected for Lorentz and polarization factors. The structures were solved by using the heavy-atom method. After refinement of the heavy atoms, difference-Fourier maps revealed maxima of residual electronic density close to the positions expected for hydrogen atoms; they were introduced in structure factor calculations by their computed coordinates (C-H = N-H = 0.95 Å) and isotropic temperature factors such as $B(H) = 1.3B_{\text{eq}}(C \text{ or } N) \text{ \AA}^2$ but were not refined (the hydrogen atoms of Im and the solvents of **1** were omitted). At this stage empirical absorption corrections were applied with the method of Walker and Stuart,¹⁵ since face indexation was not possible under the cold gas stream. Full least-squares refinements: $\sigma^2(F^2) = \sigma^2_{\text{ounis}} + (p/l)^2$. The absolute configuration of **1** was determined by comparing the refinements using x, y, z and $-x, -y, -z$ coordinates. Final difference maps revealed no significant maxima. The scattering factor coefficients and anomalous dispersion coefficients come respectively from refs 16a and 16b. The crystals of both derivatives contain 222-cryptated sodium cations. Furthermore, those of **1** are solvated by methylimidazole and chlorobenzene molecules, and those of **2**, by THF. The mean thermal motion of the sodium cryptates and the molecules of solvation is rather high; therefore, the diffusion power of the crystals is low and consequently the ratios of observed data versus the number of refined parameters are poor for both compounds. Thus, the reported standard deviations as calculated from the least-squares refinements could be slightly underestimated.

[FeTP_{piv}P(2-MeIm)][NaC222]·2-MeHIm·2C₆H₅Cl (**1**). [Fe^{III}TP_{piv}P(Cl)] (100 mg, 0.09 mmol) or [FeTP_{piv}P(OSO₂CF₃)] (100 mg, 0.08 mmol) was stirred in 40 mL of dry degassed toluene with zinc amalgam containing 1% zinc (5 g). After 3 h of stirring, the reddish highly air-sensitive solution was filtered ($\lambda_m = 419, 441, 538 \text{ nm}$) and transferred by needle into a toluene solution (40 mL) containing sodium 2-methylimidazololate (50 mg, 0.48 mmol) and Kryptofix 222 (100 mg, 0.26 mmol). The obtained green precipitate was washed with dry degassed toluene, dried under vacuum, and redissolved in chlorobenzene, and the resulting solution was filtered. Slow diffusion of hexane into the chlorobenzene solutions under inert atmosphere produced single crystals of **1** suitable for X-ray studies. UV-vis (C₆H₅Cl): λ_m (log ϵ) = 408 (3.43), 450 (4.09), 532 (2.09), 572 (3.20), 612 nm (2.83).

[FeTP_{piv}P(Im)(HIm)][NaC222]·THF (**2**). This compound was obtained by a procedure similar to that used for **1** by needle transfer of the filtered red, air-sensitive solution into a toluene solution (40 mL) containing sodium imidazololate (50 mg, 0.55 mmol) and Kryptofix 222 (100 mg, 0.26 mmol). The bright red precipitate thus obtained was washed with toluene, dried in vacuo, and redissolved in degassed THF, and the resulting solution was filtered. Slow diffusion of pentane into the THF solutions under inert atmosphere yielded single crystals of **2**. UV-vis

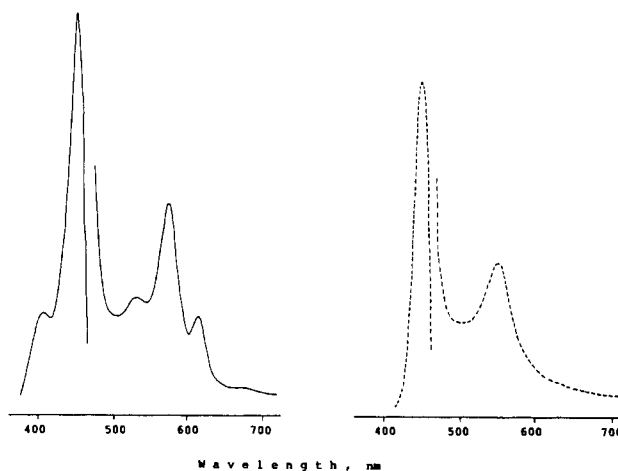


Figure 1. UV-vis spectra (PhCl solution, room temperature) of **1** (solid line) and **2** (dashed line).

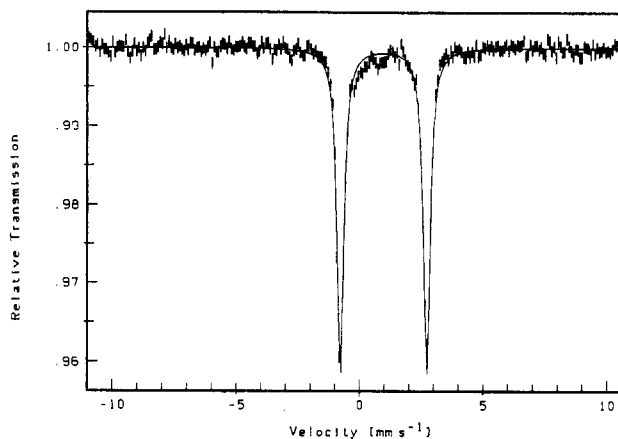


Figure 2. Mössbauer spectrum (77 K, $H = 0$) of the solid [FeTP_{piv}P(2-MeIm)][NaC222] compound **1**.

(THF, C₆H₅Cl, or CH₃CN): λ_m (log ϵ) = 442 (4.00), 544 nm (3.47).

Both **1** and **2** are very air-sensitive in solution and in the microcrystalline state.

Results and Discussion.

Spectroscopic Properties. Both derivatives **1** and **2** are almost insoluble in toluene (see Experimental Section), in contrast to the high-spin ferrous 2-methylimidazole derivative [FeTP_{piv}P(2-MeHIm)] and the low-spin ferrous 1-methylimidazole complex [FeTP_{piv}P(1-MeIm)₂] (1-MeIm = 1-methylimidazole), in which the axial ligands are neutral molecules. Moreover, the Soret bands of the solution UV-vis spectra of **1** and **2** (Figure 1) are clearly red-shifted ($\lambda_m = 408, 450 \text{ nm}$ for **1** and 442 nm for **2**) with respect to the positions of these bands in the spectra of [FeTP_{piv}P(2-MeHIm)] ($\lambda_m = 370, 436 \text{ nm}$) and of [FeTP_{piv}P(1-MeIm)₂] ($\lambda_m = 432 \text{ nm}$). The red-shifted Soret bands in the spectra of **1** and **2** and the insolubility of these compounds in toluene are consistent with the presence of an anionic axial ligand in both derivatives.¹⁷

The zero-field Mössbauer spectrum of **1**, obtained at 77 K (Figure 2), with an isomer shift of $\delta = 0.97$ (0.02) mm/s is typical for a high-spin ferrous species.^{18,19} The quadrupole splitting of $\Delta E_Q = 3.51$ (0.02) mm/s at 77 K is unusually large and lies close to that measured for [FeTP_{piv}P(OCH₃)]⁻⁸ ($\Delta E_Q = 3.64$ (0.03) mm/s at 77 K). Thus, unusually large quadrupole splittings are not only obtained when high-spin ferrous porphyrins are ligated to an anionic oxygen donor or a halide ion but also when the axial

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Table II. Positional Parameters and Their Estimated Standard Deviations for **1**^a

atom	x	y	z	B, Å ²	atom	x	y	z	B, Å ²
Fe	0.4794 (1)	0.128	0.6866 (1)	3.05 (4)	C65	0.1631 (9)	0.1869 (5)	0.8899 (9)	3.9 (3)
C1	0.3771 (8)	0.1907 (5)	0.8231 (8)	2.9 (3)	C66	0.083 (1)	0.2101 (6)	0.920 (1)	5.3 (4)
C2	0.4009 (9)	0.2268 (5)	0.9014 (9)	3.7 (3)	C67	0.0368 (9)	0.2514 (7)	0.8724 (9)	5.4 (4)
C3	0.5085 (9)	0.2285 (5)	0.9345 (8)	3.6 (3)	C68	0.064 (1)	0.2677 (6)	0.793 (1)	5.1 (4)
C4	0.5452 (9)	0.1966 (4)	0.8709 (9)	3.3 (3)	C69	0.1456 (9)	0.2446 (5)	0.759 (1)	4.7 (4)
C5	0.6524 (9)	0.1874 (5)	0.8749 (9)	3.5 (3)	N70	0.1724 (7)	0.2573 (4)	0.6723 (7)	4.5 (3)
C6	0.6928 (8)	0.1554 (5)	0.8171 (8)	3.1 (3)	C71	0.1384 (9)	0.2942 (5)	0.6093 (9)	4.0 (3)
C7	0.7985 (8)	0.1455 (5)	0.8269 (8)	3.4 (3)	O72	0.0764 (8)	0.3266 (4)	0.6236 (8)	7.7 (3)
C8	0.8081 (8)	0.1089 (5)	0.7632 (9)	3.7 (3)	C73	0.181 (1)	0.2963 (5)	0.5206 (9)	4.3 (3)
C9	0.7058 (9)	0.0945 (5)	0.7118 (9)	3.6 (3)	C74	0.235 (1)	0.2459 (7)	0.505 (1)	7.3 (5)
C10	0.6844 (9)	0.0545 (5)	0.650 (1)	4.4 (3)	C75	0.263 (1)	0.3407 (6)	0.533 (1)	7.1 (5)
C11	0.581 (1)	0.0349 (5)	0.6137 (9)	4.6 (4)	C76	0.092 (1)	0.3075 (7)	0.435 (1)	8.1 (5)
C12	0.559 (1)	-0.0085 (6)	0.546 (1)	6.3 (4)	N77	0.4804 (9)	0.1811 (7)	0.5872 (9)	8.4 (4)
C13	0.457 (1)	-0.0160 (6)	0.534 (1)	5.9 (4)	C78	0.502 (1)	0.2379 (6)	0.619 (1)	7.5 (5)
C14	0.4178 (8)	0.0232 (5)	0.5828 (8)	3.8 (3)	C79	0.503 (1)	0.2648 (9)	0.543 (1)	8.7 (6)
C15	0.3131 (9)	0.0292 (5)	0.5851 (9)	4.3 (3)	N80	0.4874 (8)	0.2274 (6)	0.4567 (8)	6.8 (4)
C16	0.2721 (8)	0.0684 (5)	0.6282 (9)	3.6 (3)	C81	0.476 (1)	0.1874 (8)	0.506 (1)	8.0 (5)
C17	0.1650 (9)	0.0743 (6)	0.6263 (9)	4.7 (4)	C82	0.457 (1)	0.1384 (7)	0.442 (1)	10.0 (5)
C18	0.1538 (8)	0.1159 (5)	0.6776 (8)	3.9 (3)	N83	0.454 (1)	0.7823 (6)	0.6918 (9)	7.3 (4)
C19	0.2561 (8)	0.1370 (5)	0.7143 (8)	3.3 (3)	C84	0.398 (2)	0.7665 (9)	0.764 (1)	9.9 (6)
C20	0.2781 (8)	0.1769 (5)	0.7760 (8)	2.9 (3)	C85	0.383 (1)	0.8068 (9)	0.808 (1)	10.3 (6)
N21	0.4657 (7)	0.1742 (4)	0.8015 (7)	3.6 (2)	N86	0.436 (1)	0.8519 (7)	0.779 (1)	11.4 (5)
N22	0.6353 (6)	0.1234 (4)	0.7486 (6)	3.1 (2)	C87	0.474 (2)	0.8320 (8)	0.712 (1)	8.9 (6)
N23	0.4931 (6)	0.0548 (4)	0.6265 (7)	3.4 (2)	C88	0.557 (2)	0.863 (1)	0.667 (2)	16.5 (8)
N24	0.3251 (6)	0.1068 (4)	0.6823 (6)	2.9 (2)	Na	0.4123 (4)	0.4886 (2)	0.9154 (3)	4.2 (1)
C25	0.7245 (9)	0.2101 (5)	0.9616 (9)	3.7 (3)	NC1	0.4384 (9)	0.0033 (6)	0.928 (1)	8.3 (4)
C26	0.751 (1)	0.1807 (6)	1.043 (1)	5.6 (4)	CC2	0.489 (2)	0.0092 (9)	0.853 (1)	10.5 (6)
C27	0.818 (1)	0.2026 (7)	1.124 (1)	6.2 (4)	CC3	0.584 (1)	-0.0235 (8)	0.860 (1)	9.1 (6)
C28	0.852 (1)	0.2502 (6)	1.119 (1)	6.2 (4)	OC4	0.6573 (9)	-0.0146 (5)	0.9398 (9)	8.7 (3)
C29	0.827 (1)	0.2781 (7)	1.039 (1)	5.8 (4)	CC5	0.727 (1)	0.0251 (7)	0.936 (1)	7.1 (4)
C30	0.7640 (9)	0.2603 (6)	0.9604 (8)	3.8 (3)	CC6	0.773 (2)	0.030 (1)	1.024 (1)	14.0 (7)
N31	0.7351 (8)	0.2880 (5)	0.8779 (8)	5.2 (3)	OC7	0.731 (1)	0.0490 (5)	1.089 (1)	11.0 (4)
C32	0.775 (1)	0.3330 (6)	0.855 (1)	5.4 (4)	CC8	0.777 (2)	0.061 (1)	1.194 (1)	17.1 (9)
O33	0.8408 (9)	0.3557 (5)	0.905 (1)	9.6 (4)	CC9	0.813 (2)	0.012 (1)	1.254 (2)	13.9 (9)
C34	0.728 (1)	0.3544 (7)	0.754 (1)	6.8 (5)	NC10	0.729 (1)	-0.0228 (7)	1.257 (1)	10.4 (6)
C35	0.757 (1)	0.3224 (8)	0.678 (1)	8.1 (5)	CC11	0.770 (2)	-0.071 (1)	1.263 (2)	15.2 (8)
C36	0.608 (1)	0.3578 (7)	0.734 (1)	6.6 (4)	CC12	0.776 (1)	-0.092 (1)	1.171 (1)	16.9 (9)
C37	0.766 (2)	0.4109 (7)	0.746 (1)	11.3 (6)	OC13	0.661 (1)	-0.0979 (5)	1.1033 (9)	10.2 (4)
C38	0.7689 (8)	0.0254 (5)	0.6279 (9)	4.6 (3)	CC14	0.598 (2)	-0.1356 (8)	1.106 (2)	13.4 (9)
C39	0.790 (1)	-0.0230 (6)	0.659 (1)	6.6 (4)	CC15	0.491 (2)	-0.1276 (6)	1.032 (2)	10.5 (7)
C40	0.870 (1)	-0.0542 (6)	0.642 (1)	5.8 (4)	OC16	0.4587 (7)	-0.0789 (5)	1.0619 (8)	7.4 (3)
C41	0.923 (1)	-0.0338 (7)	0.583 (1)	6.6 (5)	CC17	0.365 (2)	-0.0655 (8)	1.008 (1)	10.0 (6)
C42	0.905 (1)	0.0135 (6)	0.543 (1)	5.6 (4)	CC18	0.379 (2)	-0.045 (1)	0.910 (1)	11.1 (7)
C43	0.829 (1)	0.0454 (6)	0.5679 (9)	4.7 (3)	CC19	0.384 (1)	0.0451 (7)	0.939 (2)	12.4 (6)
N44	0.8073 (7)	0.0964 (5)	0.5347 (8)	4.4 (3)	CC20	0.447 (2)	0.0891 (8)	0.996 (2)	11.9 (7)
C45	0.859 (1)	0.1280 (7)	0.482 (1)	6.8 (4)	OC21	0.498 (1)	0.0740 (6)	1.088 (1)	13.7 (4)
O46	0.9233 (8)	0.1064 (6)	0.4426 (9)	12.1 (4)	CC22	0.433 (2)	0.073 (1)	1.151 (2)	15 (1)
C47	0.836 (1)	0.1821 (7)	0.480 (1)	6.8 (5)	CC23	0.512 (3)	0.065 (1)	1.241 (2)	34 (1)
C48	0.849 (1)	0.205 (1)	0.392 (1)	9.8 (6)	OC24	0.508 (1)	0.0067 (8)	1.2284 (9)	12.6 (5)
C49	0.915 (2)	0.2071 (8)	0.563 (2)	10.0 (7)	CC25	0.573 (2)	-0.019 (2)	1.311 (2)	21 (1)
C50	0.730 (1)	0.1960 (8)	0.501 (2)	9.4 (6)	CC26	0.670 (2)	-0.001 (1)	1.309 (2)	20.2 (9)
C51	0.2442 (9)	-0.0161 (6)	0.5461 (9)	4.6 (3)	CII	0.8876 (4)	0.4025 (2)	0.1924 (3)	8.5 (1)
C52	0.253 (1)	-0.0620 (6)	0.596 (1)	5.8 (4)	CS1	0.0891 (9)	-0.0438 (6)	0.867 (1)	5.2 (4)
C53	0.195 (1)	-0.1036 (7)	0.569 (1)	7.0 (5)	CS2	0.080 (1)	-0.0452 (7)	0.957 (1)	7.1 (4)
C54	0.120 (1)	-0.0995 (7)	0.484 (1)	7.8 (5)	CS3	0.065 (1)	0.0020 (9)	1.002 (1)	9.3 (6)
C55	0.107 (1)	-0.0557 (7)	0.426 (1)	7.8 (4)	CS4	0.061 (1)	0.0468 (7)	0.952 (1)	7.6 (5)
C56	0.1726 (9)	-0.0115 (6)	0.459 (1)	5.5 (4)	CS5	0.066 (1)	0.0470 (7)	0.863 (1)	7.4 (4)
N57	0.1665 (8)	0.0342 (5)	0.4075 (8)	6.0 (3)	CS6	0.084 (1)	0.0018 (7)	0.821 (1)	7.7 (5)
C58	0.112 (1)	0.0448 (8)	0.321 (1)	7.0 (5)	CI2	0.3154 (9)	0.2186 (4)	1.1519 (7)	20.4 (4)
O59	0.060 (1)	0.0143 (6)	0.266 (1)	12.9 (5)	CS7	0.253 (2)	0.2766 (7)	1.139 (1)	10.3 (6)
C60	0.129 (1)	0.0957 (8)	0.287 (1)	7.5 (5)	CS8	0.274 (2)	0.318 (1)	1.082 (3)	21 (1)
C61	0.156 (2)	0.134 (1)	0.360 (2)	11.9 (7)	CS9	0.220 (4)	0.363 (1)	1.065 (3)	30 (2)
C62	0.033 (2)	0.114 (1)	0.211 (2)	14 (1)	CS10	0.164 (2)	0.374 (2)	1.114 (2)	19 (1)
C63	0.217 (2)	0.091 (1)	0.240 (2)	15 (1)	CS11	0.112 (2)	0.331 (1)	1.131 (2)	15.9 (9)
C64	0.1952 (9)	0.2021 (5)	0.8110 (9)	3.5 (3)	CS12	0.156 (2)	0.285 (1)	1.156 (2)	14.1 (9)

^a Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $(4/3)[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos \gamma)\beta(1,2) + ac(\cos \beta)\beta(1,3) + bc(\cos \alpha)\beta(2,3)]$.

ligand of iron is an anionic nitrogen donor base. By contrast, the Mössbauer parameters of **2**, derived from a spectrum obtained at 77 K ($\delta = 0.38$ (0.02) mm/s and $\Delta E_q = 0.91$ (0.02) mm/s), indicate the presence of a six-coordinate low-spin ferrous porphyrin derivative.^{18,19}

Structure of [FeTP_{pv}P(2-Melm)][NaC222]·2MeHIm·2C₆H₅Cl (1**).** The geometry of the five-coordinate high-spin ferrous porphyrinate [FeTP_{pv}P(2-Melm)]⁻ is illustrated in Figure 3. This

figure also gives the numbering scheme used for the atoms. The perpendicular displacements of the iron and the porphyrin core atoms from the least-squares plane of the 24 core atoms of the porphyrin are given, in units of 0.01 Å, in Figure 4. The atomic coordinates are listed in Table II. Selected bond lengths and angles are reported in Table III.

The asymmetric units of the crystals of **1** contain one formula unit [FeTP_{pv}P(2-Melm)][NaC222]·2-MeHIm·2C₆H₅Cl. The

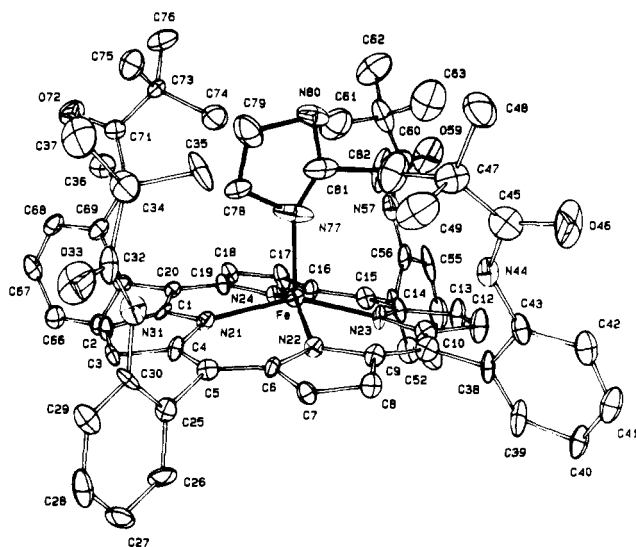


Figure 3. ORTEP plot of the porphyrinate anion $[\text{FeTP}_{\text{piv}}\text{P}(2\text{-MeIm})]^-$, showing the numbering scheme used. Ellipsoids are scaled to enclose 50% of the electronic density. Hydrogen atoms are omitted.

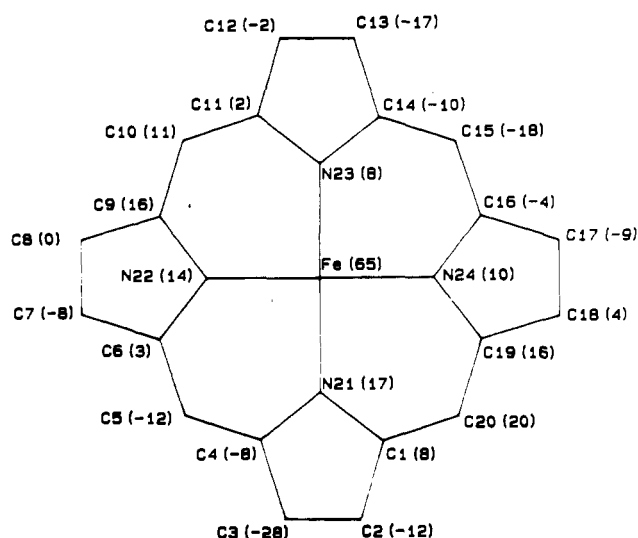


Figure 4. Formal diagram of the porphyrinato core of $[\text{FeTP}_{\text{piv}}\text{P}(2\text{-MeIm})]^-$. The numbers in parentheses indicate the perpendicular displacement for each atom in units of 0.01 Å from the mean plane of the 24-atom core.

$\text{Fe}-\text{N}_p$ bond lengths (Table III) range from 2.083 (8) to 2.130 (9) Å. The corresponding mean value is 2.106 (20) Å. The displacements of the metal relative to the 4 N_p and the 24-atom-core mean planes are, respectively, $\Delta(4 \text{N}_p) = 0.524$ (10) Å and $\Delta(\text{core}) = 0.647$ (10) Å. The C_t-N_p distance is 2.040 (12) Å (C_t = centroid of the 4 N_p atoms). Thus, the position of iron in $[\text{FeTP}_{\text{piv}}\text{P}(2\text{-MeIm})]^-$ relative to the porphyrin ring is very close to that in the five-coordinate high-spin iron(II) "picket-fence" porphyrin complexes $[\text{Fe}^{\text{II}}\text{TP}_{\text{piv}}\text{P}(\text{X})]^-$, where X is an anionic oxygen donor such as CH_3CO_2^- and $\text{C}_6\text{H}_5\text{O}^-$ or a halide ion.⁵ In contrast, the displacement of the metal relative to the 4 N_p mean plane ($\Delta(4 \text{N}_p) = 0.524$ (10) Å) is significantly larger than in the five-coordinate high-spin 2-methylimidazole complexes $[\text{FeTP}_{\text{piv}}\text{P}(2\text{-MeHIm})]$ (0.40 Å)²⁰ and $[\text{FeTPP}(2\text{-MeHIm})]$ (0.42 Å).²¹ The 2-methylimidazololate axial ligand is located inside the molecular cavity of the picket-fence porphyrin. This is the geometry that is usually present in five-coordinate picket-fence porphyrin complexes with anionic axial ligands.^{5,8,22} Although

Table III. Selected Bond Distances (Å), Angles (deg), and Averages for **1^a**

$\text{Fe}-\text{N}_{21}$	2.096 (10)	$\text{Fe}-\text{N}_{24}$	2.130 (9)
$\text{Fe}-\text{N}_{22}$	2.083 (8)	$\text{Fe}-\text{N}_p$	2.106 (20)
$\text{Fe}-\text{N}_{23}$	2.116 (10)	$\text{Fe}-\text{N}_{77}$	2.002 (15)
$\text{N}_{21}-\text{Fe}-\text{N}_{22}$	87.3 (4)	$\text{N}_{22}-\text{Fe}-\text{N}_{24}$	151.0 (4)
$\text{N}_{21}-\text{Fe}-\text{N}_{23}$	151.3 (4)	$\text{N}_{22}-\text{Fe}-\text{N}_{77}$	100.1 (4)
$\text{N}_{21}-\text{Fe}-\text{N}_{24}$	85.0 (4)	$\text{N}_{23}-\text{Fe}-\text{N}_{24}$	86.1 (3)
$\text{N}_{21}-\text{Fe}-\text{N}_{77}$	100.0 (5)	$\text{N}_{23}-\text{Fe}-\text{N}_{77}$	108.8 (4)
$\text{N}_{22}-\text{Fe}-\text{N}_{23}$	87.4 (3)		
Porphyrin Ring ^a			
$\text{N}-\text{C}_\alpha$	1.37 (2)	$\text{C}_\beta-\text{C}_\beta$	1.36 (3)
$\text{C}_\alpha-\text{C}_\beta$	1.44 (2)	$\text{C}_\alpha-\text{C}_m$	1.39 (3)
$\text{N}-\text{C}_\alpha-\text{C}_\beta$	109.7 (1.5)	$\text{C}_\alpha-\text{C}_\beta-\text{C}_\beta$	106.8 (1.8)
$\text{C}_\alpha-\text{N}-\text{C}_\alpha$	106.6 (1.7)	$\text{N}-\text{C}_\alpha-\text{C}_m$	125.6 (1.5)
$\text{C}_m-\text{C}_{\text{phe}}$	1.49 (3)	$\text{C}_{\text{am}}-\text{O}$	1.22 (4)
$\text{C}_{\text{phe}}-\text{C}_{\text{ph}}$	1.38 (3)	$\text{C}_{\text{am}}-\text{C}_{\text{ter}}$	1.49 (5)
$\text{C}_{\text{phe}}-\text{N}_{\text{am}}$	1.40 (2)	$\text{C}_{\text{ter}}-\text{C}_{\text{ter}}$	1.53 (5)
$\text{N}_{\text{am}}-\text{C}_{\text{am}}$	1.35 (3)		
$\text{C}_{\text{phe}}-\text{C}_{\text{phe}}$	120 (3)		
Crown Ether			
$\text{N}-\text{C}$	1.40 (6)	$\text{C}-\text{O}$	1.43 (9)
$\text{C}-\text{C}$	1.49 (8)		

^a C_α , C_β , C_m , C_{phe} , C_{am} , N_{am} , and C_{ter} stand respectively for the α and β pyrrole carbon atoms, methine carbon atoms, phenyl carbon atoms, amido carbon and nitrogen atoms, and *tert*-butyl carbon atoms.

not very accurate, the $\text{Fe}-\text{N}$ axial bond length of 2.002 (15) Å is nevertheless significantly shorter than in the iron(II) derivatives with the neutral ligand $[\text{FeTP}_{\text{piv}}\text{P}(2\text{-MeHIm})]$ (2.095 (6) Å)²⁰ and $[\text{FeTPP}(2\text{-MeHIm})]$ (2.161 (5) Å).²¹ A comparison of the $\text{Fe}-\text{N}$ axial bond lengths in these 2-methylimidazololate and 2-methylimidazole derivatives must take into account the orientation of the axial ligand mean plane relative to the porphyrin ring. As Hoard et al.²³ have pointed out, a convenient measure of this orientation is the dihedral angle ϕ formed by the coordinate plane containing two opposite nitrogens and the axial ligand mean plane. Due to steric interactions between the α -hydrogens of the axial ligand and the porphyrinato core, which are at maximum at $\phi = 0^\circ$, a value of ϕ smaller than 45° is associated with a longer $\text{Fe}-\text{N}$ axial bond.^{23,24} The value of $\phi = 14.7$ (9)° found in $[\text{FeTP}_{\text{piv}}\text{P}(2\text{-MeIm})]^-$ is smaller than that of 22.8° present in $[\text{FeTPP}(2\text{-MeHIm})]$. However, the $\text{Fe}-\text{N}$ axial bond length is shorter in the anionic complex (2.002 (15) Å) than in the neutral species (2.095 (6) Å). Thus, at least a part of the difference of 0.093 Å in these bond lengths may result from a stronger bond with the deprotonated 2-methylimidazole ligand. A shortening of 0.06 Å has also been observed in the axial bond distance of the ferric imidazololate derivative $[\text{FeTPP}(4\text{-MeIm})_2]^-$ relative to that in the ferric imidazole complex $[\text{FeTPP}(\text{HIm})_2]^+$.²⁵ The axial ligand of $[\text{FeTP}_{\text{piv}}\text{P}(2\text{-MeIm})]^-$ lies inside the molecular cavity, whereas in $[\text{FeTP}_{\text{piv}}\text{P}(2\text{-MeHIm})]$ it is bonded to iron on the nonprotected face of the porphyrin ring. The orientation (ϕ) of the 2-MeIm anion inside the molecular cavity is, however, not due to steric interactions of the ligand with the pivalamide pickets of the porphyrin. The shortest contacts observed are quite long: $\text{C}82 \cdots \text{C}50 = 3.87$ Å; $\text{C}82 \cdots \text{C}61 = 3.95$ Å. The $\text{Fe}-\text{N}$ axial bond is slightly tipped away by 6.4° from the normal to the 4 N_p mean plane and by 5.1° with respect to the normal of the 24-atom-core mean plane. As shown by Figure 4, the porphyrin ring has an irregular domed conformation. The doming present is also indicated by the separation of 0.123 (10) Å of the 4 N_p and 24-atom-core mean planes. Despite its irregularity, these two mean

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Table IV. Positional Parameters and Their Estimated Standard Deviations for 2^a

atom	x	y	z	B, Å ²	atom	x	y	z	B, Å ²
Fe	0.40383 (4)	0.22386 (5)	0.13412 (9)	3.10 (3)	C60	0.6019 (3)	0.3028 (4)	0.0548 (8)	6.5 (3)
C1	0.4068 (2)	0.1945 (3)	0.3706 (6)	3.5 (2)	C61	0.5594 (3)	0.3336 (4)	0.0149 (8)	7.6 (3)
C2	0.3852 (2)	0.2090 (3)	0.4632 (6)	4.1 (2)	C62	0.6039 (4)	0.2962 (5)	0.1746 (9)	9.7 (3)
C3	0.3543 (2)	0.2482 (3)	0.4321 (6)	3.7 (2)	C63	0.6395 (4)	0.3386 (5)	0.024 (1)	14.2 (5)
C4	0.3560 (2)	0.2577 (3)	0.3190 (5)	3.0 (2)	C64	0.4544 (2)	0.1187 (3)	0.4670 (5)	3.1 (2)
C5	0.3257 (2)	0.2929 (3)	0.2589 (5)	2.8 (2)	C65	0.4383 (3)	0.0627 (3)	0.4695 (6)	4.3 (2)
C6	0.3251 (2)	0.3002 (3)	0.1506 (6)	2.8 (2)	C66	0.4514 (3)	0.0259 (3)	0.5549 (7)	5.2 (2)
C7	0.2926 (2)	0.3346 (3)	0.0842 (6)	3.9 (2)	C67	0.4821 (3)	0.0456 (3)	0.6390 (6)	4.5 (2)
C8	0.3017 (2)	0.3311 (3)	-0.0176 (6)	4.2 (2)	C68	0.4983 (3)	0.1005 (3)	0.6381 (6)	4.4 (2)
C9	0.3396 (2)	0.2942 (3)	-0.0161 (5)	3.0 (2)	C69	0.4844 (3)	0.1382 (3)	0.5516 (6)	3.8 (2)
C10	0.3599 (2)	0.2800 (3)	-0.1060 (5)	2.9 (2)	N70	0.4989 (2)	0.1964 (3)	0.5506 (5)	4.7 (2)
C11	0.3977 (2)	0.2487 (3)	-0.1062 (5)	2.9 (2)	C71	0.5363 (3)	0.2191 (4)	0.5941 (7)	6.7 (3)
C12	0.4211 (3)	0.2359 (3)	-0.1968 (5)	3.8 (2)	O72	0.5633 (2)	0.1889 (3)	0.6437 (7)	13.8 (3)
C13	0.4561 (2)	0.2038 (3)	-0.1600 (6)	3.4 (2)	C73	0.5455 (3)	0.2840 (4)	0.5831 (7)	6.8 (3)
C14	0.4547 (2)	0.1959 (3)	-0.0475 (5)	2.5 (2)	C74	0.5717 (4)	0.2914 (5)	0.4887 (8)	8.8 (3)
C15	0.4855 (2)	0.1609 (3)	0.0146 (5)	3.0 (2)	C75	0.5028 (4)	0.3200 (4)	0.556 (1)	9.5 (4)
C16	0.4843 (2)	0.1511 (3)	0.1208 (5)	2.9 (2)	C76	0.5700 (5)	0.3067 (5)	0.6864 (9)	31.6 (5)
C17	0.5148 (2)	0.1135 (3)	0.1856 (6)	3.6 (2)	N77	0.4409 (2)	0.2912 (2)	0.1681 (4)	3.4 (2)
C18	0.5020 (2)	0.1117 (3)	0.2819 (6)	3.9 (2)	C78	0.4365 (3)	0.3449 (4)	0.1215 (6)	5.2 (2)
C19	0.4637 (2)	0.1464 (3)	0.2825 (5)	3.1 (2)	N79	0.4680 (2)	0.3825 (3)	0.1595 (5)	5.6 (2)
C20	0.4410 (2)	0.1563 (3)	0.3727 (5)	3.1 (2)	C80	0.4938 (3)	0.3513 (4)	0.2308 (7)	5.5 (2)
N21	0.3877 (2)	0.2255 (2)	0.2821 (4)	2.6 (1)	C81	0.4780 (3)	0.2959 (4)	0.2357 (7)	5.0 (2)
N22	0.3535 (2)	0.2767 (2)	0.0862 (4)	2.9 (1)	N82	0.3671 (2)	0.1548 (2)	0.1014 (4)	3.1 (1)
N23	0.4200 (2)	0.2239 (2)	-0.0153 (4)	2.5 (1)	C83	0.3784 (3)	0.0994 (4)	0.0959 (9)	7.1 (3)
N24	0.4539 (2)	0.1721 (2)	0.1832 (4)	3.0 (1)	N84	0.3474 (2)	0.0609 (3)	0.0682 (6)	6.6 (2)
C25	0.2898 (2)	0.3239 (3)	0.3058 (5)	3.1 (2)	C85	0.3128 (3)	0.0937 (4)	0.0570 (8)	6.3 (3)
C26	0.2499 (2)	0.2950 (3)	0.3094 (6)	4.2 (2)	C86	0.3232 (3)	0.1492 (4)	0.0759 (9)	8.3 (3)
C27	0.2144 (2)	0.3248 (4)	0.3426 (6)	4.6 (2)	Na	0.3069 (1)	-0.0044 (1)	0.5973 (2)	4.79 (8)
C28	0.2186 (2)	0.3831 (4)	0.3673 (6)	4.5 (2)	N87	0.3310 (2)	0.9238 (3)	0.7671 (6)	6.3 (2)
C29	0.2567 (3)	0.4134 (3)	0.3657 (6)	4.5 (2)	C88	0.3754 (3)	0.9344 (5)	0.7951 (9)	9.4 (3)
C30	0.2933 (2)	0.3838 (3)	0.3356 (6)	3.7 (2)	C89	0.3870 (3)	0.9951 (4)	0.8125 (8)	7.7 (3)
N31	0.3348 (2)	0.4092 (2)	0.3369 (5)	4.3 (2)	O90	0.3664 (2)	1.0310 (2)	0.7280 (5)	6.3 (2)
C32	0.3468 (3)	0.4642 (4)	0.3558 (7)	5.5 (2)	C91	0.3729 (3)	1.0911 (4)	0.7435 (8)	7.2 (3)
O33	0.3207 (2)	0.5032 (3)	0.3622 (7)	9.7 (2)	C92	0.3345 (3)	1.1230 (4)	0.7053 (9)	8.6 (3)
C34	0.3951 (3)	0.4796 (4)	0.3570 (7)	5.2 (2)	O93	0.3161 (2)	1.1073 (3)	0.6080 (5)	8.2 (2)
C35	0.4042 (3)	0.5306 (4)	0.4378 (9)	8.3 (3)	C94	0.2787 (4)	1.1367 (4)	0.557 (1)	10.4 (4)
C36	0.4021 (3)	0.4992 (5)	0.2452 (8)	7.9 (3)	C95	0.2717 (4)	1.1250 (5)	0.4421 (9)	8.8 (3)
C37	0.4240 (3)	0.4277 (4)	0.3948 (7)	6.3 (3)	N96	0.2658 (3)	1.0645 (3)	0.4198 (6)	7.6 (2)
C38	0.3365 (2)	0.2984 (3)	-0.2103 (6)	3.6 (2)	C97	0.2169 (3)	1.0504 (5)	0.4107 (9)	9.0 (3)
C39	0.2978 (2)	0.2722 (3)	-0.2479 (6)	3.9 (2)	C98	0.2106 (3)	0.9903 (4)	0.4361 (8)	7.6 (3)
C40	0.2730 (3)	0.2886 (4)	-0.3422 (6)	4.6 (2)	O99	0.2270 (2)	0.9754 (3)	0.5387 (5)	6.4 (2)
C41	0.2874 (3)	0.3326 (4)	-0.4016 (6)	4.5 (2)	C100	0.1978 (3)	0.9881 (4)	0.6146 (8)	7.3 (3)
C42	0.3258 (3)	0.3612 (3)	-0.3681 (6)	4.4 (2)	C101	0.2221 (3)	0.9697 (5)	0.7243 (9)	10.1 (3)
C43	0.3515 (2)	0.3457 (3)	-0.2712 (5)	3.6 (2)	O102	0.2592 (2)	1.0031 (3)	0.7465 (5)	6.9 (2)
N44	0.3892 (2)	0.3753 (3)	-0.2310 (5)	4.1 (2)	C103	0.2813 (4)	0.9862 (6)	0.8455 (9)	10.1 (4)
C45	0.4016 (3)	0.4301 (4)	-0.2519 (7)	5.8 (2)	C104	0.3040 (3)	0.9301 (5)	0.8507 (8)	7.8 (3)
O46	0.3792 (2)	0.4606 (3)	-0.3151 (6)	9.8 (2)	C105	0.3247 (5)	0.8618 (5)	0.726 (1)	12.0 (4)
C47	0.4425 (3)	0.4546 (4)	-0.1917 (7)	5.8 (3)	C106	0.3395 (4)	0.8501 (4)	0.626 (1)	12.4 (4)
C48	0.4748 (3)	0.4073 (5)	-0.1481 (9)	8.5 (3)	O107	0.3284 (2)	0.8918 (3)	0.5467 (6)	9.8 (2)
C49	0.4651 (4)	0.4941 (5)	-0.269 (1)	12.5 (4)	C108	0.3538 (5)	0.8893 (6)	0.454 (1)	14.5 (5)
C50	0.4309 (4)	0.4905 (6)	-0.098 (1)	14.1 (4)	C109	0.3375 (4)	0.9322 (6)	0.379 (1)	14.0 (4)
C51	0.5203 (2)	0.1286 (3)	-0.0369 (6)	2.9 (2)	O110	0.3423 (2)	0.9882 (3)	0.4239 (5)	8.7 (2)
C52	0.5127 (2)	0.0715 (3)	-0.0669 (6)	3.6 (2)	C111	0.3310 (3)	1.0378 (7)	0.3492 (8)	12.7 (4)
C53	0.5447 (2)	0.0372 (3)	-0.1064 (6)	4.0 (2)	C112	0.2848 (4)	1.0478 (6)	0.3265 (9)	11.5 (4)
C54	0.5840 (2)	0.0623 (3)	-0.1189 (6)	3.9 (2)	O113	0.2159 (4)	0.2031 (5)	-0.096 (1)	22.3 (5)
C55	0.5913 (3)	0.1216 (4)	-0.0944 (7)	5.0 (2)	C114	0.2129 (5)	0.1439 (7)	-0.147 (1)	16.9 (5)
C56	0.5596 (2)	0.1546 (3)	-0.0497 (6)	3.8 (2)	C115	0.1842 (5)	0.1109 (7)	-0.070 (1)	16.5 (6)
N57	0.5663 (2)	0.2128 (3)	-0.0175 (5)	4.8 (2)	C116	0.1949 (5)	0.1427 (6)	0.030 (1)	17.3 (6)
C58	0.6034 (3)	0.2404 (4)	0.0083 (7)	6.1 (3)	C117	0.2036 (6)	0.2033 (9)	0.009 (2)	24.7 (9)
O59	0.6395 (2)	0.2194 (3)	0.0011 (6)	10.1 (2)					

^aAnisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $(4/3)[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos \gamma)\beta(1,2) + ac(\cos \beta)\beta(1,3) + bc(\cos \alpha)\beta(2,3)]$.

planes are almost parallel. Their dihedral angle is only 1.4°. As usual, the pyrrole rings are almost planar. The dihedral angles between their adjacent mean planes range from 1.7 to 16.8°, the mean value being 9.0°. Agreements between chemically equivalent bond distances and angles within the porphyrin ring and the pivalamide pickets are satisfactory (Table III). The 2-MeIm anionic ligand is essentially planar with the five atoms displaced less than 0.2 Å from the mean ligand plane. The 2-methyl group lies also in this plane. The 2-MeHIm and chlorobenzene molecules of solvation display the expected geometries.

Structure of [FeTP_{piv}P(Im)(HIm)]NaC222·THF (2). The geometry of the six-coordinate, low spin ($S = 0$) iron(II) por-

phyrinate [FeTP_{piv}P(Im)(HIm)]⁻ is displayed in Figure 5. The numbering scheme used for the atoms is also indicated in this figure. The perpendicular displacements of the iron and the porphyrin core atoms relative to the 24-atom-core mean plane of the porphyrin ring are given in Figure 6. The atomic coordinates are listed in Table IV. Selected bond lengths and angles are reported in Table V.

The asymmetric units of the crystals contain one formula unit [FeTP_{piv}P(Im)(HIm)][NaC222]·THF (2). The Fe-N_p bond distances within the porphyrin unit range from 1.986 (5) to 2.006 (5) Å (Table V). The mean value of these bond distances of 1.995 (9) Å is not significantly different from those of other six-coor-

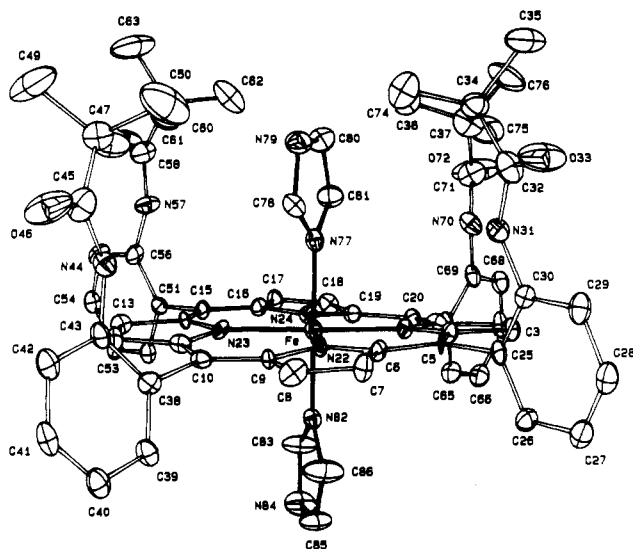


Figure 5. ORTEP plot of the porphyrinate anion $[\text{FeTP}_{\text{piv}}\text{P}(\text{Im})(\text{HIm})]^-$, showing the numbering scheme used. Ellipsoids are scaled to enclose 50% of the electronic density. Hydrogen atoms are omitted.

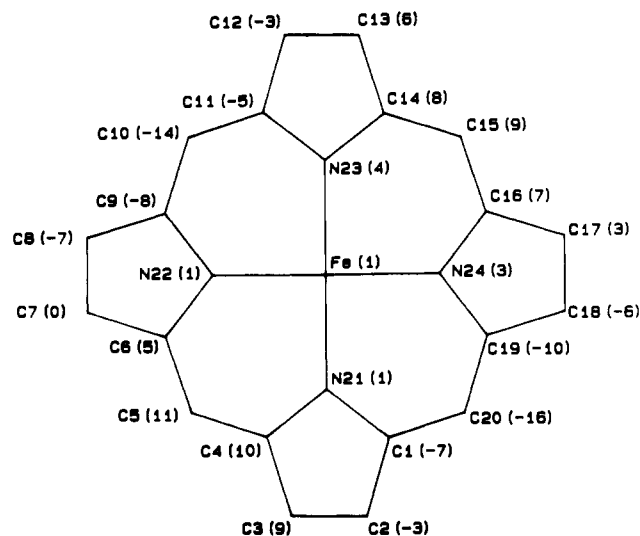


Figure 6. Formal diagram of the porphyrinato core of $[\text{FeTP}_{\text{piv}}\text{P}(\text{Im})(\text{HIm})]^-$. The numbers in parentheses indicate the perpendicular displacement for each atom in units of 0.01 Å from the mean plane of the 24-atom core.

dinate low-spin ferrous porphyrin derivatives such as $[\text{FeTPP}(\text{piperidine})_2]$ (2.004 (4) Å),²⁶ $[\text{FeTPP}(\text{CO})(\text{py})]$ (2.02 (3) Å),²⁷ $[\text{FeDeut}(\text{CO})(\text{THF})]$ (1.98 (3) Å),²⁸ $[\text{FeTPP}(\text{py})_2]$ (1.993 (6) Å),²⁹ and $[\text{FeTPP}(i\text{-C}_3\text{H}_7\text{NO})(i\text{-C}_3\text{H}_7\text{NH}_2)]$ (1.993 (10) Å).³⁰ The iron atom lies in the mean plane of the 24 core atoms of the porphyrin ($\Delta(\text{core}) = 0.01$ Å). One of the two axial ligands of iron in **2** is an imidazolite group (Im) whereas the other is a neutral imidazole molecule (HIm). With L_a to denote the axial ligand located inside the molecular cavity of the porphyrin and L_b to denote the ligand bonded to iron on the nonprotected face of the ring, $\text{Fe}-L_a = 1.930$ (5) Å and $\text{Fe}-L_b = 1.953$ (5) Å. The difference between these two values is not statistically significant. Moreover $\phi(L_a) = 25.1^\circ$ whereas $\phi(L_b) = 11.7^\circ$. Thus, the Fe-N axial bond distances do not allow the deprotonated imidazole group

Table V. Selected Bond Distances (Å), Angles (deg), and Averages for **2**^a

Fe-N21	1.988 (5)	Fe-Np	1.995 (9)
Fe-N22	2.001 (5)	Fe-N77	1.930 (5)
Fe-N23	2.006 (5)	Fe-N82	1.953 (5)
Fe-N24	1.986 (5)		
N21-Fe-N22	89.7 (2)	N22-Fe-N82	90.4 (2)
N21-Fe-N23	178.8 (2)	N23-Fe-N24	91.0 (2)
N21-Fe-N24	89.8 (2)	N23-Fe-N77	89.9 (2)
N21-Fe-N77	89.3 (2)	N23-Fe-N82	90.5 (2)
N21-Fe-N82	90.4 (2)	N24-Fe-N77	88.9 (2)
N22-Fe-N23	89.5 (2)	N24-Fe-N82	90.1 (2)
N22-Fe-N24	179.3 (2)	N77-Fe-N82	179.0 (2)
N22-Fe-N77	90.6 (2)		
Porphyrin Ring ^a			
N-C _α	1.37 (1)	C _{phe} -N _{am}	1.39 (1)
C _α -C _β	1.44 (1)	N _{am} -C _{am}	1.32 (1)
C _β -C _γ	1.33 (1)	C _{am} -O	1.21 (1)
C _α -C _m	1.38 (2)	C _{am} -C _{ter}	1.52 (1)
C _m -C _{phe}	1.49 (1)	C _{ter} -C _{ter}	1.52 (1)
C _{phe} -C _{phe}	1.38 (2)		
N-C _α -C _β	109.7 (1.2)	N-C _α -C _m	126.1 (1.4)
C _α -N-C _α	106.0 (9)	C _{phe} -C _{phe}	120.0 (9)
C _α -C _β -C _γ	107.2 (9)		
Crown Ether			
N-C	1.45 (5)	C-O	1.41 (4)
C-C	1.44 (4)		

^aC_α, C_β, C_m, C_{phe}, C_{am}, N_{am}, and C_{ter} stand respectively for the α and β pyrrole carbon atoms, methine carbon atoms, phenyl carbon atoms, amido carbon and nitrogen atoms, and *tert*-butyl carbon atoms.

(Im) to be distinguished from the neutral HIm ligand. However as indicated above, the anionic axial ligand in general lies inside the cavity formed by the pivalamide pickets in iron picket-fence porphyrin complexes with anionic axial ligands.^{5,8,23} Thus, most probably, ligand L_a is the deprotonated imidazole ring. The two Fe-N axial bonds are slightly tipped away by 0.8° (L_a) and 0.2° (L_b) from the normal of the 4 N_p mean plane and by 0.9° (L_a) and 0.5° (L_b) away from the normal to the 24-atom-core mean plane. The relative orientation of the two axial ligand mean planes (dihedral angle) is 36.8° .

As shown in Figure 6, the porphyrinato core has a ruffled conformation. The pyrrole rings are, as usual, almost planar. The dihedral angles between their adjacent mean planes range from 3.7 to 6.8° with the mean value of 5.8° . As for **1**, the agreement between chemically equivalent bond distances and angles within the porphyrin ring and the pivalamide pickets is satisfactory (Table V). The axial ligands Im and HIm are planar and like the THF molecule of solvation present the expected geometries.

In conclusion, a large quadrupole splitting of $\Delta E_q = 3.51$ mm/s at 77 K occurs in the five-coordinate ferrous porphyrinate $[\text{FeTP}_{\text{piv}}\text{P}(2\text{-MeIm})]^-$ where the axial ligand is an anionic nitrogen donor base. Thus, unusually large quadrupole splittings are not only a distinctive feature of five-coordinate high-spin ferrous porphyrins having an anionic oxygen donor or a halide ion as axial ligand of iron. Furthermore, five-coordinate ferrous imidazolite complexes appear to be excellent models, in terms of their Mössbauer spectra, of the heme site of hydroxylamine oxidoreductase from *N. europaea*.

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Supplementary Material Available: Tables SI-SIV, SVI-SIX, and SXI, listing anisotropic thermal parameters, hydrogen positional parameters, complete bond distances, complete bond angles, and experimental X-ray parameters for **1** and **2** (30 pages); Tables SV and SX, listing observed and calculated structure factor amplitudes ($\times 10$) for all observed reflections for **1** and **2** (28 pages). Ordering information is given on any current masthead page.

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