Synthesis, Stereochemistry, and Structure-Related Properties of $\alpha,\beta,\gamma,\delta$-Tetraphenylporphinatoiron(II)

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Abstract: Reduction of chloro-$\alpha,\beta,\gamma,\delta$-tetraphenylporphinatoiron(III) by bis(acetylacetonato)chromium(II) under anaerobic conditions yields $\alpha,\beta,\gamma,\delta$-tetraphenylporphinatoiron(II), Fe(TPP), which crystallizes from the benzene–ethanol solution in the tetragonal system. Pertinent crystal data are: space group, $I\bar{4}2d$; a = 15.080 (9) and c = 14.043 (9) Å; $\rho_{\rm exptl}$ = 1.38 and $\rho_{\rm calcd}$ = 1.39 g/cm^3 for Z = 4; required molecular symmetry, S_4. Intensities of 1164 reflections having $(\sin\theta)/\lambda < 0.71$ Å^{-1}, recorded with Zr-filtered Mo Kα radiation on a Picker FACS-I diffractometer, were used in anisotropic full-matrix least-squares refinement of the 112 structural parameters. The length of the Fe$^{\rm II}$–N bonds in the *intermediate*-spin (S = 1) Fe(TPP) molecule is 1.972 (4) Å, as compared with 2.086 (4) Å in *high*-spin (S = 2) 2-methylimidazole-$\alpha,\beta,\gamma,\delta$-tetraphenylporphinatoiron(II), with 2.004 (3) Å in *low*-spin (S = 0) bis(piperidine)-$\alpha,\beta,\gamma,\delta$-tetraphenylporphinatoiron(II), and with Cu–N = 1.981 (7) Å in Cu(TPP). The foregoing assignment of spin states to the three iron(II) porphyrins is fully confirmed by the Mossbauer spectra recorded for them in zero and in large applied magnetic fields at temperatures ranging from 4.2 to 300°K. Recrystallized Fe(TPP) conforming to the theoretical composition has an effective magnetic moment of ~4.4 BM at room temperature. Determination of the anisotropic magnetic susceptibilities as a function of temperature for the tetragonal crystal, when considered in conjunction with the Mossbauer data, should lead to a more detailed specification of the electronic configuration of the intermediate-spin iron(II) atom in Fe(TPP) than that given in this paper.

The preparation[3] of $\alpha,\beta,\gamma,\delta$-tetraphenylporphinatoiron(II), Fe(TPP), through the reduction of chloro-$\alpha,\beta,\gamma,\delta$-tetraphenylporphinatoiron(III), (Cl)Fe(TPP), by bis(acetylacetonato)chromium(II) exemplifies an essential step in a versatile synthetic route to a variety of iron(II) porphyrins (eq 1). This reaction, which must be carried out

$$\mathrm{(Cl)Fe^{III}(TPP)} + \tfrac{1}{2}[\mathrm{Cr(acac)_2}]_2 \xrightarrow{\text{benzene}} \mathrm{Fe^{II}(TPP)} + \mathrm{ClCr(acac)_2} \qquad (1)$$

under strictly anaerobic conditions, clearly affords Fe(TPP), a 14-electron complex devoid of axial ligands. The same general method has been essential to the synthesis of "picket-fence" iron(II) porphyrins[4-6] which serve as structural models for the active sites in hemoglobin and myoglobin. The utility of Fe(TPP) as a synthetic intermediate is most simply exemplified in the preparation[3]—long awaited[7,8]—of single crystals containing a high-spin (S = 2) iron(II) porphyrin; the X-ray analysis of structure reported in a forthcoming paper[9] provides the experimentally determined stereochemistry of the 2-methylimidazole-$\alpha,\beta,\gamma,\delta$-tetraphenylporphinatoiron(II) molecule, (2-MeIm)Fe(TPP), for detailed comparison with that anticipated from 1965 onward[7,8] for the typical high-spin iron(II) porphyrin.

Our immediate concern, however, is to report the synthesis, molecular stereochemistry, and structure-related properties of Fe(TPP) as an example of a rare type of complex in which the d^6 iron(II) atom is constrained by the macrocyclic ligand to effectively square-planar coordination and, it will appear, to the unusual spectroscopic state of intermediate spin (S = 1). The most significant feature of the theoretical orbital pattern of D_4 symmetry described by Griffith[10] and considered by him to apply generally to iron porphyrins and phthalocyanines is the requirement that the 3d$_{x^2-y^2}$ orbital (with its four lobes directed toward the complexed nitrogen atoms) be always of higher energy than the other 3d orbitals. It is the presence or absence of an odd electron in the 3d$_{x^2-y^2}$ orbital of the metal atom in a four-coordinate iron porphyrin (or iron phthalocyanine, Fe(Phc)) that determines[10] whether the spectroscopic state is respectively high spin (S = 2) or intermediate spin (S = 1).

Stereochemical data that were available in 1965 for four-coordinate metalloporphyrins[11,12] and for two five-coordinate high-spin ferric porphyrins (with methoxo[7] and chloro[13] as axial ligands) provided a substantial part of the evidence which led Hoard et al.[7] to conclude that the stereochemistry of the coordination group in any iron porphyrin is strongly correlated with the spin state of the iron atom. The predicted dependence of stereochemistry on spin state in four-coordinate iron(II) porphyrins[7] may be summarized as follows. An intermediate-spin iron(II) atom should be precisely centered among the four complexed nitrogen atoms with an Fe–N bond distance <2.01 Å. A high-spin iron(II) atom should lie substantially out of plane from the nitrogen atoms (probably by ≥0.45 Å) with an Fe–N bond distance >2.07 Å.

Our X-ray analysis of structure for an excellent crystal of Fe(TPP) leads to a molecular configuration of S_4 (quasi-D_{2d}) symmetry in which the length of the four equivalent complexing bonds is 1.972 (4) Å. The conclusion that this bond distance corresponds to excision of the odd electron from the 3d$_{x^2-y^2}$ of the iron atom is fully supported by our analysis of the trend in M(II)–N bond lengths within the sequence of four-coordinate metalloporphyrins that includes M = Fe, Co, Ni, and Cu. Detailed comparisons of the Mossbauer spectra given by crystalline Fe(TPP) with those recorded from crystals of (2-MeIm)Fe(TPP)·C$_2$H$_5$OH[3,9] (the ethanol solvate of the high-spin (2-MeIm)Fe(TPP) species) and of the low-spin (S = 0) bis(piperidine)-$\alpha,\beta,\gamma,\delta$-tetraphenylporphinatoiron(II), (Pip)$_2$Fe(TPP),[14] are also in full agreement with the assignment of intermediate spin to the iron(II) atom in Fe(TPP). At every temperature in the range from 4.2 to 300°K, both the isomer shift and the quadrupole splitting given by (2-MeIm)Fe(TPP)·C$_2$H$_5$OH are much larger than those recorded from crystalline Fe(TPP). Subsequently recorded

Mossbauer spectra from crystals of the four-coordinate iron(II) derivative of the "picket-fence" porphyrin[4-6,15] are, by contrast, fully compatible with the presence of ***high***-spin iron; these spectra, as reported elsewhere,[15] differ only in minor details from those afforded by (2-MeIm)Fe(TPP)·C_2H_5OH. This difference in the spin state of the iron atom in crystals of the two four-coordinate species is expected, of course, to be reflected in an equally distinctive difference in the geometry of the coordination groups. The most interesting possibility is that the iron atom in the "picket-fence" species may be drawn out-of-plane (and into the high-spin state) through intramolecular interactions with the oxygen atoms of appropriately oriented "pickets".

The correlation of magnetic susceptibility with electronic structure in Fe(TPP) is an interesting problem for further theoretical and experimental investigation. Repeated measurements of the susceptibility of crystalline Fe(TPP) at 25° lead to a magnetic moment of ~4.4 BM, as compared with the spin-only values of 2.8 and 4.9 BM expected for two and four unpaired electrons, respectively. Magnetic moments approaching the spin-only value for $S = 2$ also have been reported[16,17] for two other recent preparations of Fe(TPP) that, however, were not otherwise characterized by physical methods. The possibility that these magnetic data are associated with a temperature-dependent equilibrium mixture of spin states in Fe(TPP) is incompatible with the structural parameters derived from our X-ray analysis and, indeed, is surely excluded by the character of the Mossbauer spectra as recorded in the temperature range from 4.2 to 300°K.

Phthalocyaninatoiron(II), which also exhibits an "anomalously" large paramagnetism relative to the spin-only value for $S = 1$, has received intensive study by numerous investigators.[18] Dale[18h] has recently shown that the magnetic properties of the Fe(Phc) molecule, as it exists in the monoclinic crystal structure,[19,20] depart significantly from the tetragonal symmetry expected for the externally unconstrained species and, moreover, that a special feature of the molecular packing precludes the accurate calculation of the principal molecular susceptibilities from those determined for the crystal. In the tetragonal crystal of Fe(TPP), by contrast, the required molecular symmetry of S_4 is conducive to simplicity of interpretation. Determinations of the principal susceptibilities as functions of the temperature, when considered in conjunction with the Mossbauer data, should provide cogent evidence for or against each of the several detailed electronic configurations that may appear to be theoretically admissible for the electronic configuration of the iron(II) atom in Fe(TPP). Some progress toward this end is feasible on the basis of the information now at hand; see Discussion of Results.

Experimental Section

Preparation of Fe(TPP). All manipulations involving solutions of ferrous porphyrins were carried out in an inert atmosphere ($O_2 < 2$ ppm) within a glove box (a Vacuum Atmospheres "Drilab"). Schlenk tube techniques were used to facilitate the isolating, washing, and drying of the crystalline products and to minimize solvent evaporation into the regenerating system (a Vacuum Atmospheres "Dri-Train" HE-35). Benzene was deaerated by distillation from Na–K alloy under nitrogen. Ethanol was degassed by way of three freeze-pump-thaw cycles. Heptane was deaerated by bubbling nitrogen through it for 25 min, using a fine porosity, fritted glass, dispersion tube. $[Cr(acac)_2]_2$, *meso*-tetraphenylporphyrin, and (Cl)Fe(TPP) were prepared following published methods.[21-23]

A mixture of (Cl)Fe(TPP) (1.0 g), $[Cr(acac)_2]_2$ (0.5 g), benzene (100 ml), and ethanol (10 ml) was quickly brought to boiling and allowed to simmer until dissolution of the reactants was completed (1-5 min). Following the addition of 60 ml of ethanol, the solution was set aside to await possible crystallization during cooling. Subsequent additions (2 hr later) of 80 ml of ethanol and (4 hr later) of 50 ml of heptane led to crystallization of Fe(TPP) when the solution was allowed to stand overnight. The purple crystals were filtered onto a coarse frit, washed with ethanol, and dried under vacuum; the yield, 0.88 g, was 85% of theoretical. This product, as judged by elemental analysis (Cl <0.2%) and the absence of maxima attributable to (Cl)Fe(TPP), $[Cr(acac)_2]_2$, or $O[Fe(TPP)]_2$ in the visible spectrum recorded for a benzene solution, approached chemical purity. Further purification of the Fe(TPP) used in all subsequent physical studies was achieved by recrystallization from scrupulously oxygen-free benzene–ethanol solution. Elemental analyses of the recrystallized Fe(TPP) were performed in the Stanford University Microanalytical Laboratory. Anal. Calcd for $C_{44}H_{28}N_4Fe$: C, 79.05; H, 4.2; N, 8.4; Fe, 8.4. Found: C, 79.0; H, 4.45; N, 8.65; Fe, 8.4.

X-Ray Analysis of Structure. Photographically recorded X-ray patterns afforded by single crystals of Fe(TPP) displayed the Laue symmetry and the systematic absences of spectra that are required by the pair of tetragonal space groups,[24] $I4_1md$ and $I\bar{4}2d$. The crystal used for the precise measurement of lattice constants and diffracted intensities with Zr-filtered Mo Kα radiation on a Picker FACS-1 automated diffractometer was of truncated tetragonal-bipyramidal habit with a basal edge of 0.5 mm and a length along the unique axis of 0.3 mm. It was sealed within a thin-walled quartz capillary as a precaution against oxidation during the extended period of intensity measurement. The angular settings of 50 reflections paired at 25 values of $\pm 2\theta$ in the range, $19 < |2\theta| < 22°$, were determined using the automatic centering program supplied with the diffractometer. Least-squares refinement of the diffraction geometry of these reflections led to the lattice constants (λ 0.71069 Å), $a = 15.080$ (9) and $c = 14.043$ (9) Å. For a cell containing four molecules of Fe(TPP), the density was calculated to be 1.39 g/cm^3 as compared with the experimental value obtained by flotation of 1.38 g/cm^3. All measurements were made at the ambient laboratory temperature of 19 ± 1°.

The measurement of diffracted intensities utilized θ–2θ scanning at a takeoff angle of 3° on the automated diffractometer. The range of each scan, taken at 1°/min., included a base width of 1.8° and an increment of $\Delta(2\theta) = (0.692 \tan \theta)°$ to allow for spectral dispersion; background counts of 40-sec duration were taken at both limits of the scan. All of the 1329 independent reflections having $(\sin \theta)/\lambda < 0.71$ Å^{-1} were thus scanned. The intensities of three reflections, periodically monitored as standards, displayed no trend with time. Net intensities were reduced to relative squared amplitudes, $|F_o|^2$, without correction for the absorption of X-radiation in the encapsulated crystal. The maximum error in any structure amplitude arising from the neglect of absorption in the crystal was estimated to be ~3%. Reflections retained as objectively observed satisfied the criterion, $|F_o| > 0.50\sigma_F$, wherein σ_F is the estimated standard deviation as specified elsewhere.[14] Some 1164 of the 1329 reflections scanned were thus retained for the structure analysis.

The assignment of crystalline Fe(TPP) to the structural type based upon $I\bar{4}2d$ that was earlier shown[11] to be taken by isomorphous crystals of Cu(TPP) and Pd(TPP) was strongly supported by the marked similarities in the lattice constants and other data describing the unit cells. Confirmation of this assignment was then provided by a smoothly converging refinement of structure in which the atomic coordinates reported[11] for Cu(TPP) served as the initial approximation to the coordinates in Fe(TPP). Full-matrix least-squares refinement,[25] anisotropic except for the isotropic treatment accorded the hydrogen atoms, and standard values for the atomic form factors[26] were employed. The function minimized was $\Sigma w(|F_o| - s|F_c|^2)$ wherein w is the weight and s is the scaling factor. A Fourier difference synthesis (using Zalkin's program (FORDAP)) afforded the approximate positions of all hydrogen atoms in the asymmetric unit of structure; these atoms were then assigned to theoretically calculated positions (C–H = 1.0 Å), with isotropic thermal parameters fixed at somewhat larger values than those of the associated carbon atoms, and their contributions to the calculated structure amplitudes were included in subsequent cycles of refinement. Inclusion of the imaginary component, $\Delta f''$ of the form factor of the iron atom[27] in the refinement enabled us to conclude that the experimentally measured intensities were those of the set $\{\bar{h}\bar{k}\bar{l}\}$ rather than those of the originally assigned set $\{hkl\}$.

Final least-squares refinement that utilized empirical weights, w

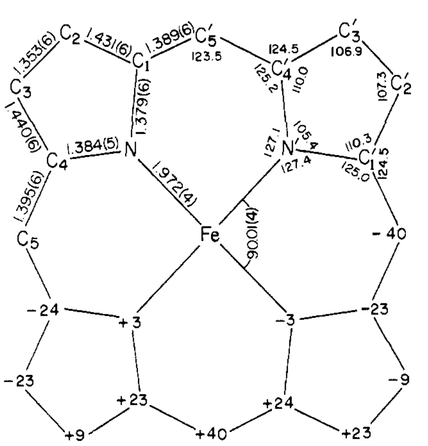

Figure 1. Diagram of the porphinato core displaying, on the upper half, the numbering scheme used for the atoms in Table I and the values of all structurally independent bond parameters. The number in parentheses following each bond distance (and the NFeN angle) is the estimated standard deviation (esd) in the last significant figure; other angles carry an esd of 0.3–0.4°. On the lower half of the diagram, the numbered symbol for the atom is replaced by its perpendicular displacement, in units of 0.01 Å, from the mean plane of the porphinato core; the S_4 symmetry of the pattern is thus exhibited.

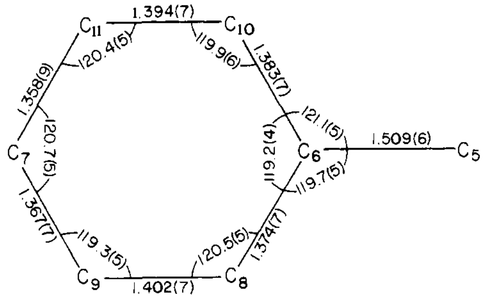

Figure 2. Diagram of a peripheral phenyl group displaying the numbering scheme used for the atoms in Table I and the values, with estimated standard deviations, of all bond parameters.

$= 1/\sigma^2$, of the type specified earlier[14] led to a conventional residual (R_1) of 0.074 and a weighted residual (R_2) of 0.047. A final difference synthesis displayed a peak density of 1.1 e/Å^3 at the origin, the site of the iron atom, and a pair of smaller peaks, 0.7 e/Å, lying on the c axis at ±0.90 Å from the metal atom. The data/parameter ratio of 1164/112 = 10.4, large as compared with the analogous ratios of 4.15 and 4.25 in the respective structure analyses of Cu(TPP) and Pd(TPP), led to estimated standard deviations for C-N and C-C bond lengths[28] in Fe(TPP) that range downward from one-half to one-third of those reported from the earlier studies. The atomic coordinates and the associated thermal parameters in the asymmetric unit of structure are listed in Table I.[29]

Magnetic susceptibilities were measured at room temperature by the Faraday method on 20–40-mg samples using a Cahn 7600 system calibrated with $CoHg(NCS)_4$. The effective magnetic moment of 5.2 BM obtained for (2-MeIm)Fe(TPP)·C_2H_5OH was in accord with the expectation,[3,7] subsequently confirmed,[9] that the (2-MeIm)Fe(TPP) molecule would exhibit high-spin five-coordinate geometry. Rather surprisingly, however, a preparation of $(Pip)_2Fe(TPP)$ having very nearly the theoretical composition displayed a small paramagnetism (~1 BM) of roughly the same magnitude as that reported earlier for crystals of this complexed species that had been separated mechanically from a second phase of undetermined composition.[14] The effective moment of 4.4 BM for Fe(TPP), uncorrected for diamagnetism, was the mean of 13 measurements falling between 4.0 and 4.6 BM.

Mossbauer Studies. Mossbauer spectra from crystalline powders of Fe(TPP), (2-MeIm)Fe(TPP)·C_2H_5OH, and $(Pip)_2Fe(TPP)$ were recorded using 150-mg samples as vacuum grease mulls in a constant acceleration spectrometer[30] which was calibrated using the known line positions of a metallic iron foil absorber. All isomer shifts were determined relative to the center of symmetry of the iron foil spectrum recorded at room temperature. Mossbauer spectra were recorded in zero applied magnetic field at four temperatures in the range 4.2–300°K for each of the three compounds; the observed isomer shifts displayed the expected changes with temperature caused by the second-order Doppler effect.[31] The additional spectra that were recorded in large applied magnetic field, 3.2 teslas, at one or more temperatures for each compound were of critical importance to the unambiguous assignment of $(Pip)_2$-Fe(TPP) and Fe(TPP) to the spin states, $S = 0$ and $S = 1$, respectively. The special characteristics and the interpretation of these spectra are best presented in connection with the experimental data listed in Table III.

Discussion of Results

We consider first the results of the structure analysis. Bond parameters in the porphinato core of the Fe(TPP) molecule are displayed on the diagram of the core, Figure 1, and those in the peripheral phenyl substituents are similarly reported in Figure 2.

Although the bond parameters in the porphinato core, as classified chemically, are repeated in groups of four and eight, the molecular symmetry of S_4-$\bar{4}$ (which is fully delineated for the core in Figure 1) is compatible with structural equivalence only within a group of four. We emphasize, however, that the structural data for the core approximate rather closely to the geometry of D_{2d} in which equality of the bond parameters of any given chemical type is preserved. The largest deviation from D_{2d} geometry in a pairing of bond parameters that are nonequivalent in S_4 symmetry occurs in the C_1-C_2 and C_3-C_4 bonds; even so, the apparent difference in the bond lengths, 0.009 Å, is only 50% larger than the estimated standard deviation in each bond length. The large mismatching in the magnitudes (but not the signs) of the out-of-plane displacements of the C_2 and C_3 carbon atoms (Figure 1) does represent an objectively significant departure from D_{2d} geometry. The S_4 (quasi-D_{2d}) ruffling of the porphinato core may be described[32] as a circular standing wave with crests at one pair of oppositely situated methine-carbon atoms and troughs of equal magnitude at the other pair.

Four of the six C-C bond distances entered in Figure 2 for a peripheral phenyl group display the usual foreshortening that is associated with thermal motion of the group as a quasi-rigid body; the pattern of the foreshortening is that discussed earlier[33] in connection with the still more precise determination of structure for crystalline dichloro-*meso*-tetraphenylporphinatotin(IV). The planes of the phenyl groups in crystalline Fe(TPP) are rotated each nearly 10° from the perpendicularity with the mean plane of the porphinato core that corresponds to D_{2d} geometry.

Consideration of the anisotropic thermal parameters listed in Table I for the iron atom and for the atoms in the 16-membered inner ring of the porphinato core (Figure 1) shows that the largest values for the root-mean-square amplitudes of vibration, u_i, correspond very nearly (exactly for the iron atom) to vibration parallel to the unique $\bar{4}$ axis of the molecule. Calculated values for these amplitudes are confined to the narrow range from 0.201 Å for the iron atom to about 0.215 Å for the four C_1 carbon atoms. For vibration nearly (exactly for the iron atom) perpendicular to the $\bar{4}$ axis, the calculated amplitudes range upward from 0.161 Å for the iron atom to ~0.19 Å for the C_1 carbon atoms. These data are compatible only with a fully ordered structure that has the iron atom precisely centered in the molecule and a sharply defined Fe-N bond length (1.972 (4) Å) which, it appears, must arise from just one spin state. The conclusion that this bond distance corresponds to intermediate-spin iron(II) is supported by the observed dependence of metal-nitrogen bond length on atomic number

Table I. Structural Parameters of the Atoms in Crystalline Fe(TPP)[a]

Atom type	Fractional coordinates			Anisotropic thermal parameters (Å²)					
	10^4x	10^4y	10^4z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Fe	0	0	0	2.03 (3)	2.03 (3)	3.17 (5)	Zero by symmetry		
N	1131 (2)	655 (2)	−21 (4)	2.3 (1)	2.4 (1)	3.3 (2)	0.0 (1)	0.0 (2)	−0.2 (2)
C_1	1966 (3)	326 (3)	168 (4)	2.1 (2)	2.9 (2)	3.6 (3)	−0.3 (1)	−0.5 (2)	0.0 (2)
C_2	2605 (3)	1028 (3)	161 (4)	2.9 (3)	3.2 (3)	5.3 (3)	−0.6 (2)	−0.8 (2)	0.0 (2)
C_3	2169 (3)	1784 (3)	−61 (5)	2.8 (2)	3.1 (2)	5.9 (3)	−0.5 (2)	−0.3 (3)	0.8 (3)
C_4	1247 (3)	1556 (3)	−163 (4)	2.6 (2)	2.7 (2)	3.4 (3)	−0.3 (2)	−0.1 (2)	0.3 (2)
C_5	565 (3)	2171 (3)	−286 (4)	2.5 (2)	2.0 (2)	3.4 (2)	0.0 (1)	0.1 (2)	0.3 (2)
C_6	818 (3)	3109 (3)	−543 (4)	2.2 (2)	2.5 (2)	3.9 (2)	0.0 (2)	−0.2 (2)	0.4 (2)
C_7	1315 (4)	4818 (3)	−1030 (4)	4.3 (3)	3.2 (3)	5.9 (3)	−0.8 (2)	−0.2 (2)	0.9 (2)
C_8	1021 (4)	3316 (3)	−1470 (4)	4.6 (3)	2.7 (2)	4.5 (3)	−0.3 (2)	0.1 (2)	0.1 (2)
C_9	1259 (4)	4183 (4)	−1723 (4)	5.8 (3)	4.0 (3)	4.5 (3)	−1.1 (2)	0.6 (2)	1.2 (2)
C_{10}	869 (4)	3764 (3)	145 (4)	6.9 (3)	2.7 (2)	4.1 (3)	−1.1 (2)	−0.1 (3)	0.1 (2)
C_{11}	1110 (4)	4624 (3)	−112 (5)	6.3 (3)	2.6 (2)	5.1 (3)	−0.7 (2)	−0.4 (3)	−0.5 (2)

[a] The figure in parentheses following each datum is the estimated standard deviation in the last significant figure.

of the metal atom as summarized in Table II for a sequence of four relevant S_4-ruffled metalloporphyrins.

As pointed out in an earlier analysis[32] and fully confirmed by subsequent observations,[34-36] an S_4 ruffling of the porphinato core in a four- or six-coordinate metalloporphyrin is conducive to significant shortening of the M–N bonds relative to those in a planar conformation whenever the preferred value of the M–N bond distance to nitrogen atoms of monodentate ligands is appreciably less than 2.01 Å. The shortening of the M–N distance that is attributable to ruffling is ~0.020 Å in Cu(TPP) and is 0.030 Å in the somewhat more strongly S_4-ruffled conformation reported[37] for the 1,2,. . .,8-octaethylporphinatonickel(II) molecule, Ni(OEP), in one crystalline polymorph. Since we do not have experimental determinations of the bond parameters in Ni(TPP) and Co(TPP), we enter in Table II the Ni–N distance[37] from Ni(OEP) and an estimated value for the Co–N distance in Co(TPP) that is fully consistent with the extensive data now available for low-spin cobalt(II) and cobalt(III) porphyrins.[35] We then conclude that the pattern of bond distances in Table II is correlated with the required presence of an odd electron in the $3d_{x^2-y^2}$ orbital of the d^9 copper(II) atom and the absence of such an electron in the $3d_{x^2-y^2}$ orbital of the intermediate-spin iron(II), low-spin cobalt(II), and diamagnetic nickel(II) atoms. The observation that Fe–N ≤ Cu–N is especially to be emphasized; given *high*-spin iron(II), the difference in the nuclear charges carried by the metal atoms surely must require Fe–N ≫ Cu–N. We note, indeed, that the length (2.086 Å) of the complexing bonds to porphinato nitrogen atoms in the five-coordinate (2-MeIm)Fe(TPP) molecule is slightly larger than that (2.073 Å) of the corresponding bonds involving the d^{10} zinc(II) atom in a five-coordinate zinc porphyrin.[38] For a planar conformation of the core in Fe(TPP), the Fe–N distance is expected to be no longer—probably a little shorter—than the 2.004 Å observed for the equatorial bonds in the low-spin $(Pip)_2Fe(TPP)$ molecule.[14]

Table II. Complexing Bond Lengths in a Sequence of S_4-Ruffled Four-Coordinate Metalloporphyrins[a]

Metalloporphyrin	Fe(TPP)	Co(TPP)	Ni(OEP)	Cu(TPP)
Metal atom	d^6 Fe	d^7 Co	d^8 Ni	d^9 Cu
Spin state, S	1	½	0	½
M–N distance, Å	1.972 (4)	1.955[b]	1.929 (3)	1.981 (7)

[a] The figure in parentheses following a bond distance is the estimated standard deviation in the last significant figure. [b] Interpolated from relevant data obtained for other cobalt porphyrins; see text.

Table III. Mossbauer Data for Three Iron(II) Porphyrins

Compound	Temp, °K	Isomer shift[a] (mm/sec)	Quadrupole split (mm/sec)	Spin state S	Magnetic moment (BM)
Fe(TPP)	4.2	0.52	1.51	1	4.4
	77	0.50	1.51		
	195	0.47	1.52		
	300	0.42	1.52		
$(Pip)_2Fe(TPP)$	4.2	0.51	1.44	0	~1.0
	77	0.50	1.44		
	195	0.47	1.49		
	300	0.42	1.52		
(2-MeIm)Fe(TPP)[b]	4.2	0.93	2.28	2	5.2
	77	0.92	2.26		
	195	0.87	1.97		
	300	0.82	1.74		

[a] Relative to metallic iron; measurements are accurate to ±0.01 mm/sec. [b] Crystalline (2-MeIm)Fe(TPP)·C_2H_5OH.

In view of the small paramagnetism which has been observed in the crystalline preparations of $(Pip)_2Fe(TPP)$ used for structure determination[14] and for the recording of the Mossbauer spectra (see Experimental Section), it is useful to cite recently published structural evidence which supports the earlier conclusion that $(Pip)_2Fe(TPP)$ is a low-spin species wherein the six 3d electrons of the Fe(II) atom are paired in the d_{xy}, d_{xz}, and d_{yz} orbitals. We note first that the axial Fe–N bonds to piperidine nitrogen atoms are stretched to a length of 2.127 (3) Å as the consequence of severe steric interactions between piperidine hydrogen and, for the most part, porphinato nitrogen atoms.[14] Substitution of the low-spin isoelectronic cobalt(III) atom for iron(II) to give the cation, $[(Pip)_2Co(TPP)]^+$, leads to a tightening of the equatorial and axial Co–N bond distances to 1.978 (3) and 2.060 (3) Å, respectively.[39] Reduction of the cobalt(III) to low-spin cobalt(II) by the insertion of an electron in the d_{z^2} orbital yields the neutral $(Pip)_2Co(TPP)$ species in which the equatorial Co–N distance is almost unchanged, 1.987 (2) Å, whereas the axial Co–N distance becomes 2.436 (2) Å.[40] This striking result makes it the easier to understand why the retention of an odd electron in the $3d_{x^2-y^2}$ orbital of a high-spin iron atom is incompatible with the centering of this atom in the porphinato core.

Isomer shifts and quadrupole splittings from the Mossbauer studies are listed in Table III. Since the parameters listed for (2-MeIm)Fe(TPP)·C_2H_5OH are clearly alien to both Fe(TPP) and $(Pip)_2Fe(TPP)$, the details of the Mossbauer spectra afforded by this high-spin species are more appropriately discussed elsewhere.[9]

Both the $(Pip)_2Fe(TPP)$ and the Fe(TPP) spectra in zero or small magnetic field are of the simple quadrupole type. The observed constancy of the quadrupole splitting in Fe(TPP) between 4.2 and 300°K indicates that even at room temperature there is no significant orbital excitation of the iron valence electrons. It would seem that the nearly identical isomer shifts and the not very different quadrupole splittings that are observed for Fe(TPP) and $(\mathrm{Pip})_2\mathrm{Fe(TPP)}$ must be ascribed to a fundamental similarity in the bonding interactions of the metal atom with the macrocyclic porphinato ligand—specifically, to the excision of the unpaired electron from the $3d_{x^2-y^2}$ orbital of the iron(II) atom and utilization of this orbital as an acceptor of electron density from the porphinato nitrogen atoms. That this similarity does not extend to the spin states of the iron atoms in the two compounds is shown by the Mossbauer spectra recorded in an applied magnetic field of 3.2 teslas at 4.2°K for $(\mathrm{Pip})_2\mathrm{Fe(TPP)}$ and over a range of temperature for Fe(TPP).

These data were fitted by least squares using a model in which each principal component of the internal magnetic field, H_i^{I}, is assumed to be proportional to the corresponding component of the applied field, H_i^{A}, and the component of the effective field, H_i^{E}, is given by

$$H_i^{\mathrm{E}} = H_i^{\mathrm{A}} + H_i^{\mathrm{I}} = H_i^{\mathrm{A}}(1 + \omega_i), \quad i = x, y, z \qquad (2)$$

The refined models for Fe(TPP) and $(\mathrm{Pip})_2\mathrm{Fe(TPP)}$ share two general features: the gradient of the electric field is positive, i.e., $V_{zz} > 0$, and the asymmetry parameter, $\eta = (V_{xx} - V_{yy})/V_{zz}$, is nearly or exactly zero. We note that the S_4 symmetry required of the Fe(TPP) molecule in the crystal requires $\eta = 0$ and the close approximation of the coordination group in the $(\mathrm{Pip})_2\mathrm{Fe(TPP)}$ molecule to D_{4h} geometry[14] is compatible with η very small.

The least-squares fitting of the $(\mathrm{Pip})_2\mathrm{Fe(TPP)}$ data gives no indication of a significant internal magnetic field; i.e., all ω_i in eq 2 are zero. This result together with the observed isomer shift and the magnitude of the quadrupole splitting are fully compatible with the spin state, $S = 0$, for the iron atom. The small paramagnetism detected by susceptibility measurement has no observable analog in the Mossbauer spectra, nor, we remark, did the similarly detected small paramagnetism in the crystalline $(\mathrm{Pip})_2\mathrm{Fe(TPP)}$ used for structure analysis give rise to detectable EPR signals at temperatures ranging from 14.2 to 296°K.[14] Clarification of the general problem thus posed might be facilitated by the study of analogous low-spin bis(1-alkylimidazole)iron(II) derivatives of $\mathrm{H_2(TPP)}$ in which the stronger complexing of the axial ligands should contribute both to ease of purification and to a lesser probability for inclusion of statistically distributed five-coordinate species in the crystal.[14]

Referring again to eq 2, the least-squares fitting of the Fe(TPP) data gives $\omega_z = 0$ and $\omega_x = \omega_y = \omega_\perp$ in evident agreement with S_4 symmetry. The observed dependence of $\omega_\perp$ on temperature is illuminating; $\omega_\perp$ is nearly constant at ~1.5 in the range from 4.2 to 33°K, but it is reduced to little more than half this value at 100°K. Such behavior requires a low-lying spin singlet with a doublet, or a near doublet, roughly 70 cm^{-1} above it.

In attempting to select the particular electronic configuration of the iron atom that can lead to a very small, temperature independent, quadrupole splitting and a magnetic susceptibility of ~4.4 BM at room temperature, it turns out that any rational configuration seems to demand a substantial contribution to the electric field gradient from the electrons in the filled, deep lying, bonding orbital which involves the $d_{x^2-y^2}$ iron orbital as the acceptor of electron density from the porphinato nitrogen atoms. Considered as electron density in the $d_{x^2-y^2}$ orbital, the needed contribution would correspond formally to at least 50% iron character in the bonding orbital, an orbital which would seem necessarily to be of predominantly ligand character. Dr. B. W. Dale points out, however, that the effect of the bonding electrons on the electric field gradient might well be enhanced by having a large effective value of the Sternheimer antishielding factor; this factor is less than unity for an electron in a d orbital but is ~10 for remote charges. Otherwise put, bonding electron density residing on the nitrogen atoms might contribute more effectively to the electric field gradient than would an equal charge in the $d_{x^2-y^2}$ orbital.

The theoretical treatment by Zerner et al.[41] for a four-coordinate, in-plane, iron porphyrin yields an orbital scheme which derives from the configuration, $(d_{xy})^2 (d_{xz},d_{yz})^3 (d_{z^2})^1$, for the iron(II) atom. Given a contribution to the electric field gradient from the filled bonding orbital discussed above that corresponds effectively to one electron in the $d_{x^2-y^2}$ iron orbital, this model would provide the observed quadrupole interaction, including sign. It does not, unfortunately, exhibit the required magnetic properties. In similar circumstances, the $(d_{xz},d_{yz})^4 (d_{xy})^1 (d_{z^2})^1$ configuration would give a *negative* quadrupole interaction.

Although the configuration, $(d_{xy})^2 (d_{z^2})^2 (d_{xz},d_{yz})^2$, would require a still larger contribution to the electric field gradient from the filled bonding orbital in order to fit the observed quadrupole splitting, the orbital separations needed to match the Mossbauer data give rise to a predicted Bohr magneton number of about four at room temperature. This configuration affords the currently most promising basis for the more detailed treatment of the problem that is in prospect.

Supplementary Material Available. A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 204 × reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for \$4.00 for photocopy or \$2.50 for microfiche, referring to code number JACS-75-2676.

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Carbon–Phosphorus Bond Cleavage in Triphenylphosphine Complexes. Reactions of η^5-(Cyclopentadienyl)carbonyltriphenylphosphinerhodium and -iridium with Pentacarbonylmethylmanganese and -rhenium. Isolation of Bridged Diphenylphosphido–Heterodinuclear Metal Complexes[1]

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Abstract: The reactions of $(\eta^5\text{-}C_5H_5)M(CO)[P(C_6H_5)_3]$, M = Rh or Ir, with $CH_3M'(CO)_5$, M' = Mn or Re, have resulted in isolation of two types of heterodinuclear metal complexes, $(\eta^5\text{-}C_5H_5)M\text{-}\mu\text{-}[C(C_6H_5)O]\text{-}\mu\text{-}[C(CH_3)O]\text{-}\mu\text{-}[P(C_6H_5)_2]\text{-}Mn(CO)_3$ (**1**) (M = Ir, **1a**; Rh, **1b**) and $(\eta^5\text{-}C_5H_5)\overline{M\text{-}\mu\text{-}[P(C_6H_5)_2]\text{-}M'}(CO)_4$ (**2**) (M–M' = Ir–Mn, **2a**; Rh–Mn, **2b**; Rh–Re, **2c**), both containing bridging diphenylphosphido ligands. The new complexes are characterized through infrared, ^{1}H NMR, and mass spectral data. The analogous reaction of $(\eta^5\text{-}C_5H_5)Co(CO)[P(C_6H_5)_3]$ with $CH_3Mn(CO)_5$ leads only to ligand interchange giving $(\eta^5\text{-}C_5H_5)Co(CO)_2$ and $CH_3Mn(CO)_4[P(C_6H_5)_3]$.

In view of the demonstrated donor properties of $(\eta^5\text{-}C_5H_5)Ir(CO)[P(C_6H_5)_3]$ in forming adducts with $HgCl_2$, $ZnBr_2$, and $TlCl_3$[2] and our earlier interest in donor–acceptor complexes of transition metals,[3] we combined the aforementioned iridium complex and the corresponding cyclopentadienylcobalt and -rhodium derivatives as potential donors with $CH_3Mn(CO)_5$ and $CH_3Re(CO)_5$ as potential acceptors.[4] We found no evidence of simple adducts of these molecules when combined at ambient temperatures or slightly above. Instead, a number of other transformations were observed at elevated temperatures which experiments and results are set forth below.

Results and Discussion

The Systems Ir–Mn and Rh–Mn. Combination of $(\eta^5\text{-}C_5H_5)Ir(CO)[P(C_6H_5)_3]$ and $CH_3Mn(CO)_5$ in refluxing toluene resulted in gas evolution and preponderant production (80% yield) of a yellow, crystalline, air-stable substance, **1a.** In cyclohexane solution the compound exhibits three stretching absorptions of terminal carbonyl groups as listed in Table I.

Investigation of the analogous system $(\eta^5\text{-}C_5H_5)Rh(CO)[P(C_6H_5)_3]$ with $CH_3Mn(CO)_5$ in refluxing benzene yielded a slightly different product mix from which only a small yield of an analog of **1a,** namely about 5.8% of a yellow compound, **1b,** was isolated. This compound showed corresponding absorptions in the infrared analogous to **1a** (see Table I). Only one other product was isolated from the mixture and is discussed below.

Further characterization of products **1a** and **1b** provided the following data. The proton magnetic resonance (^{1}H NMR) spectra of these compounds are complicated by the presence of 0.5 mol of benzene of crystallization for each mole of molecular complex; the phenyl region indicates overlap of the resonances of these two. Accordingly, a sample of **1a** was recrystallized from a mixture of benzene-d_6 and pentane, and its ^{1}H NMR spectrum obtained in benzene-d_6 solution gave satisfactory integrals. The chemical shifts and relative areas, tabulated in Table I, are given as follows. For **1a,** four principal features are observed: a broad multiplet centered at τ 2.51 followed by three sharp singlets, one at τ 2.96, another at τ 5.26, and the third at τ 7.55. The total relative intensity under the first two peaks, which are in the phenyl region, is 15 while that of the third in the η^5-cyclopentadienyl region is 5 and that of the highest resonance, 3. There was no evidence of any other signals from τ 1.80 to 35.0. The ^{1}H NMR spectrum for **1b** was almost identical with that of **1a** with corresponding resonances at τ 2.52 and 3.02, 5.30, and 7.55 in the same relative intensities as described for **1a.** The chemical shifts and relative areas of the resonances suggested complexes containing three phenyl groups, an η^5-cyclopentadienyl group,