Table V. Selected Interatomic Distances (A) and Angles (Deg) for Ethynyl-Bridged Metal Derivatives

compd	bridging dist short M	bridging dist long M	C≡C (bridging)	M–C (terminal)	$\angle$C≡C–C	$\angle$M–C–M (bridge)	$\angle$M–C≡C	$\angle$M′–C≡C	$\angle$C–M–C (terminal)
$Al_2(\mu\text{-}C{\equiv}CMe)_2Me_4$[a] (gas phase)	2.050 (15)	2.15 (3)	1.229 (4)	1.956 (5)	167.8 (1.6)	92.0 (1)	158.3 (1.9)	109.7 (1.3)	120.8
$Al_2(\mu\text{-}C{\equiv}CPh)_2Ph_4$[b]	1.992	2.184	1.207	1.904		91.73	171.6		
$Ga_2(\mu\text{-}C{\equiv}CPh)_2Me_4$[c]	2.004 (7)	2.375 (7)	1.183 (6)	1.952 (8)	180 (2)	86.7 (3)	172.8 (7)	93.8 (5)	126.86
$In_2(\mu\text{-}C{\equiv}CMe)_2Me_4$[d]	2.193 (14)	2.933 (23)	1.212 (20)	2.185 (av)	178.6 (1.3)		177 (1)		129.8 (4)
$Be_2(\mu\text{-}C{\equiv}CPh)_2Me_2$[e]	1.85	1.89	1.17	1.75	178	77	147	1.36	
$[Cu_6(C_6H_4NMe_2\text{-}2)_4\text{-}(C{\equiv}CC_6H_4Me\text{-}4)_2]_2$[f]	2.028	2.054	1.17		177.9	75	148.1	137.2	
HC≡CH[g]			1.204 (2)						

[a] Reference 5. [b] Reference 4. [c] This work. [d] Reference 6. Note that the In–C_β distance is 2.989 (24) A, i.e., nearly equivalent to the In–C_α distances. [e] Reference 17. [f] Reference 16. [g] Reference 18.

V and a careful review of the behavior of the indium species in solution[6,10] suggests that the major differences are observed only in the solid state since the indium derivative forms a relatively stable dimer in solution with behavior similar to that observed for the aluminum and gallium derivative and presumably, therefore, with a similar structure.

Other studies have shown that both copper[16] and beryllium[17] form derivatives which contain ethynyl-bridge bonds. The bonding in these species has been discussed in detail, and it has been concluded that the ethynyl moiety contributes one electron to the bridge bond in the copper compound. This conclusion was based on the short (compared to 1.204 (2) Å in acetylene) C≡C distance of 1.17 Å observed and on the large separation between the bridged copper atoms of 2.47 Å.[16] A similar proposal was made for the beryllium system which again has a 1.17 Å C≡C distance and no available "low energy" metal orbitals for interaction with the π-electron system on the ethynyl groups.[16]

In both aluminum derivatives, for which structures are known, and for the gallium derivative studied in this work, it is quite clear that the molecular unit is held together by bridging ethynyl groups which enter into two distinctly different bonding interactions: one, as evidenced by the Ga-C bond distance of 2.004 (7) Å and the C≡C—Ga angle of 172.8 (7)^0, is essentially a gallium-carbon σ bond while the second is best described as a strong interaction between the second gallium atom and the π electrons of the carbon-carbon triple bond and is characterized by the location of the gallium atom which permits significant metal-π-electron interaction. This is shown in the indium derivatives where the metal atom is shifted toward the π electrons and is located almost at the midpoint of the carbon-carbon triple bond with the two metal-carbon distances nearly equivalent at 2.93 and 2.99 Å, respectively.

Variations in carbon-carbon triple bond lengths were suggested by ten Hoedt et al.[16] as a measure of the metal-π-electron interaction. These bond distances for several ethynyl-bridged derivatives, along with other parameters, have been collected in Table V. Examination of these data show that the carbon-carbon triple bond distances for the aluminum and indium derivatives are greater than that observed in acetylene, as expected from ten Hoedt's proposal, but that the carbon-carbon triple bond distance found in the gallium derivative is significantly less than that in acetylene and is within the values reported for species which presumably have no metal-π-electron interaction. Therefore, it appears that the carbon-carbon triple bond length does not serve as an effective measure of the metal-π-electron interaction, and other criteria must be sought.

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Registry No. $Ga_2(\mu\text{-}C{\equiv}CPh)_2Me_4$, 18744-50-8.

Supplementary Material Available: Listings of observed and calculated structure amplitudes (7 pages). Ordering information is given on any current masthead page.

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Preparation and Molecular Stereochemistry of Fluoro(*meso*-tetraphenylporphinato)iron(III)

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The molecular stereochemistry of a number of five-coordinate high-spin (porphinato)iron(III) complexes, Fe(P)(X), has been determined, including those for X = Cl,[3] Br,[4] and I.[5] We have completed the series of halide derivatives by preparing and determining the molecular stereochemistry of a fluoro complex, fluoro(*meso*-tetraphenylporphinato)iron(III), hereinafter written as Fe(TPP)(F).

Experimental Section

Fe(TPP)(F) was prepared by the reaction of a $CHCl_3$ solution of $[Fe(TPP)]_2O$[6,7] (500 mg/100 mL) with an aqueous 5% HF solution in a polyethylene separatory funnel. After the $CHCl_3$ layer was washed with water, the $CHCl_3$ solution was concentrated. Crystals (about 300 mg) were obtained by allowing pentane to diffuse into the solution. This material was recrystallized by dissolving it in $CHCl_3$ and diffusing pentane into the solution. The IR spectrum exhibits a Fe–F band[8] at 600 cm^{-1}. Anal. Calcd for $C_{44}H_{28}N_4FFe$: C, 76.86; H, 4.10; N,

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Table I. Structural Parameters of the Atoms in Crystalline FeTPPF[a]

	coordinates			anisotropic thermal parameters,[b] Å^2					
atom	10^4x	10^4y	10^4z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Fe	0	0	486 (1)	2.16 (3)	2.16 (3)	3.49 (2)	0	0	0
F	0	0	2321 (3)	4.04 (16)	4.04 (16)	3.74 (12)	0	0	0
N	364 (1)	1462 (1)	0	2.43 (5)	2.29 (5)	4.35 (6)	0.00 (4)	0	0
C_1	−284 (1)	2261 (1)	0	2.80 (6)	2.38 (6)	4.27 (7)	0.07 (4)	0	0
C_2	274 (1)	3182 (1)	0	3.34 (7)	2.21 (6)	5.92 (9)	−0.08 (5)	0	0
C_3	1249 (1)	2936 (1)	0	3.16 (7)	2.44 (6)	5.65 (9)	−0.37 (5)	0	0
C_4	1313 (1)	1864 (1)	0	2.69 (6)	2.42 (5)	4.06 (7)	−0.28 (4)	0	0
C_5	2205 (1)	1329 (1)	0	2.49 (6)	2.77 (6)	3.90 (7)	−0.31 (4)	0	0
C_6	3165 (1)	1906 (1)	0	2.50 (6)	2.74 (6)	4.37 (8)	−0.20 (4)	0	0
C_7	4920 (1)	3006 (2)	0	2.56 (7)	3.31 (8)	9.68 (16)	−0.46 (6)	0	0
C_8	3613 (1)	2178 (1)	1207 (2)	4.06 (6)	6.21 (8)	4.90 (7)	−1.54 (6)	−0.28 (5)	−0.40 (6)
C_9	4488 (1)	2733 (2)	1199 (2)	4.09 (7)	6.34 (9)	7.24 (10)	−1.46 (6)	−1.24 (6)	−1.43 (8)

	coordinates					coordinates			
atom	10^4x	10^4y	10^4z	B, Å^2	atom	10^4x	10^4y	10^4z	B, Å^2
H_2[c]	−17	3831	0	4.67	H_8	3318	1978	2054	5.91
H_3	1816	3371	0	4.63	H_9	4795	2929	2038	6.44
H_7	5520	3386	0	5.46					

[a] The numbers in parentheses are the estimated standard deviations. [b] B_{ij} is related to the dimensionless β_{ij} employed during refinement as $B_{ij} = 4\beta_{ij}/a^*_i a^*_j$. [c] Each hydrogen atom carries the same subscript as the carbon atom to which it is attached. Their isotropic thermal parameters were fixed at one unit higher than the bonded carbon atom (B(H) = B(C) + 1.0 Å^2).

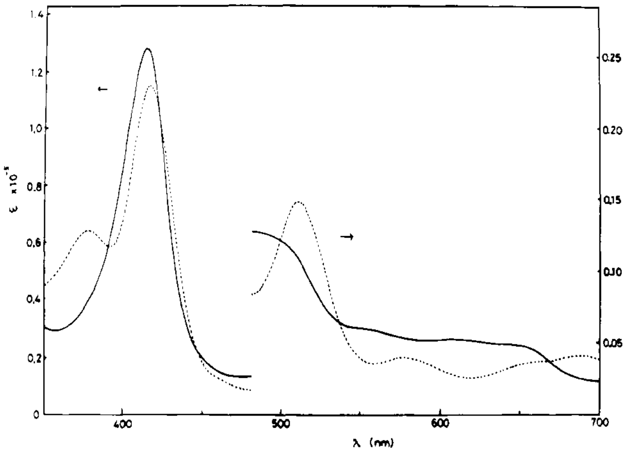

Figure 1. UV–visible spectra of Fe(TPP)(F) (solid line) and Fe(T-PP)(Cl) (dashed line) in $CHCl_3$ solution.

8.15. Found: C, 75.99; H, 4.01; N, 8.03. Figure 1 shows the visible spectrum of Fe(TPP)(F) in $CHCl_3$. A spectrum of Fe(TTP)(Cl) in $CHCl_3$ is also shown for comparison.

Preliminary examination of a crystal of Fe(TPP)(F) with dimensions of 0.4 × 0.5 × 0.7 mm established that the Laue symmetry and systematic absences were consistent with the tetragonal space groups $I4$, $I\bar{4}$, and $I4/m$. Lattice constants, a = 13.381 (2) and c = 9.767 (2) Å, came from a least-squares refinement that utilized the setting angles of 60 reflections, collected at $\pm 2\theta$. These constants led to a calculated density of 1.306 g/cm^3 for a cell content of two Fe(TPP)(F) molecules; the experimental density was 1.30 g/cm^3. All measurements were made at the ambient laboratory temperature of 20 ± 1 °C.

Diffracted intensities were measured by θ–2θ scanning with use of graphite-monochromated Mo Kα radiation ($\bar{\lambda}$ = 0.71073 Å). The scan range used was 0.75° below Kα_1 to 0.75° above Kα_2. Backgrounds were collected at the extremes of the scan for 0.5 times the time required for the scan itself. All independent data to $(\sin\theta)/\lambda$ < 0.789 Å^{-1} were measured. Four standard reflections, measured periodically, showed no trend with time. Variable 2θ scan rates were used as described previously;[9] the slowest was 1.0°/min and the fastest was 12.0°/min. Net intensities were reduced to relative squared amplitudes, $|F_o|^2$. Reflections having $F_o > 3\sigma(F_o)$ were taken to be observed. A total of 1465 unique data, 86% of the theoretical number possible, were used in the subsequent solution and refinement of the structure.

Table II. Coordination Group Parameters for (Porphinato)iron(III) Halide Complexes

complex[a]	Fe-N[b]	ΔN_4	Δ (core)	Fe-X	ref
Fe(TPP)(F)	2.072 (1)	0.47	0.47	1.792 (3)	this work
Fe(TPP)(Cl)	2.060 (3)	0.39	0.39	2.193 (3)	3
Fe(Proto IX)(Cl)	2.062 (10)	0.48	0.55	2.218 (6)	17
Fe(TPP)(Br)	2.069 (9)	0.49	0.56	2.348 (2)	4
Fe(TPP)(I)	2.066 (11)	0.46	0.53	2.554 (2)	5

[a] Abbreviations: Proto IX, protoporphyrin IX dianion; TPP, *meso*-tetraphenylporphyrin dianion. [b] All distances have units of Å.

The structure was solved by the heavy-atom method.[10] The necessity of choosing between the space groups $I4$, $I\bar{4}$, and $I4/m$ has been encountered a number of times,[3,11-14] and in all but one occasion,[14] the choice of $I4/m$ appeared proper. Accordingly, the choice of $I4/m$ was made for Fe(TPP)(F), and all subsequent developments of structure solution and refinement were consistent with this choice of space group. Isotropic full-matrix least-squares refinement smoothly converged.[15] A difference Fourier synthesis gave the approximate positions of all hydrogen atoms in the asymmetric unit of structure; these atoms were then assigned to their theoretically calculated positions (C–H = 0.95 Å, B(H) = B(C) + 1.0 Å^2), and their contributions to the calculated structure amplitudes were included in subsequent cycles of refinement. Anisotropic temperature factors were now included, and the structure refined to convergence. This led to a conventional residual (R_1) of 0.048, a weighted residual (R_2) of 0.068, and an error fit of 2.33. The final data/parameter ratio was 20.1/1. A final difference Fourier synthesis was featureless with the largest peak having a height of 0.13 e/Å^3. Final atomic coordinates and the

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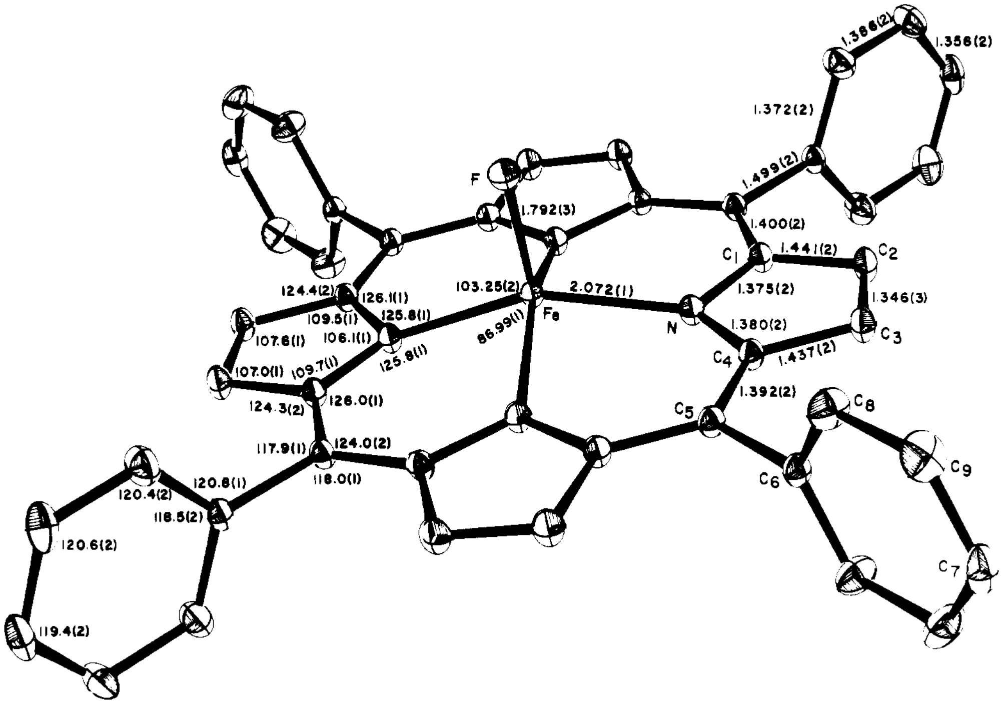

Figure 2. Computer-drawn view of the Fe(TPP)(F) molecule. The numbering scheme for the crystallographically unique atoms is shown as are the individual bond distances and angles with their respective estimated standard deviations.

associated thermal parameters are reported in Table I. A listing of the final observed and calculated structure amplitudes (×10) is available as supplementary material.

Results and Discussion

Figure 2 presents a perspective view of the Fe(TPP)(F) molecule. The figure also illustrates the numbering scheme employed for the unique atoms and the individual values for the bond distances and angles in the molecule. A table of values is also given in the supplementary material. In space group $I4/m$, the Fe(TPP)(F) molecule is disordered with statistical $4/m$—C_{4h} symmetry. The porphinato core in Fe(TPP)(F) thus has crystallographically required planarity. The anisotropic temperature factors (Table I) do not appear to be disguising any significant nonplanarity of the core.

The coordination group parameters for Fe(TPP)(F) are typical of those for a high-spin five-coordinate (porphinato)iron(III) complex.[16] Table II summarizes four coordination group parameters for the (porphinato)iron(III) halide complexes.[17] The parameters are the average Fe–N bond distance, the iron to axial ligand distance, the displacement of the iron(III) atom from the mean plane of the four nitrogen atoms and the mean plane of the core. In Fe(TPP)(F) and Fe(TPP)(Cl), these two displacements are equal because of the planarity of the respective cores. It can be seen that the displacements in Fe(TPP)(Cl) are smaller than any other derivative; it is possible that this smaller displacement is a consequence of molecular packing.[18]

The axial Fe–F distance of 1.792 (3) Å in Fe(TPP)(F) is significantly shorter than the value normally observed, about 1.92 Å, for terminal Fe–F distances in polymeric fluorides[19] or in monomeric octahedral complexes.[20] It was originally noted by Hoard[16] that the axial distances in high-spin five-coordinate (porphinato)iron(III) complexes are particularly short. This pattern persists for all the halide derivatives listed in Table II.

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Registry No. Fe(TPP)F, 55428-47-2; [Fe(TPP)]$_2$O, 12582-61-5.

Supplementary Material Available: Table III, bond distances and angles in Fe(TPP)(F), and a listing of structure factor amplitudes (×10) (6 pages). Ordering information is given on any current masthead page.

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Conformation of Tris(dimethylamino)phosphine: An MNDO Study

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The molecular conformations of aminophosphorus(III) compounds have attracted quite a bit of attention recently. The various conformational models (drawn with planar nitrogens) are shown in Figure 1. Model compounds have been prepared which contain nitrogen "lone-pair" orbitals whose

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