for analysis of structure and dynamics of carbohydrates and their protein complexes. For example, Lemiuex and coworkers[8] have recently executed a brilliant tour de force in the synthesis of the blood group antigenic determinants. However, certain of the resonances in their ^{13}C NMR spectra have been assigned by comparison with the incorrect fucose and galactose assignments,[13,29] and it is not entirely clear what the correct assignments should be, given the demonstrated current uncertainty about the effects of derivatization upon ^{13}C chemical shifts. Carbon-13 labeling would be a decided advantage here and by extension in ^{13}C NMR studies of antigen-antibody reactions.

We have discussed the carbohydrate assignment problem at some length in order to prevent further propagation of errors and to introduce a cautionary note about the general reliability of the assignment methods which have been used. Although, in retrospect, the assignment difficulties have been evident since the initial reassignment of α-D-glucose in 1970,[14] there has been little recognition of this fact. Thus, relaxation studies of the interaction of methyl glycosides with conconavalin A[10] have been based on incorrect assignments, although it is unlikely that the particular incorrect assignment has led to significant error. Correct assignments of the ^{13}C resonances are the foundation upon which all further ^{13}C NMR work is based; uncertainties which exist in these assignments must be emphasized to avoid propagation of errors.

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References and Notes

(1) (a) University of California; (b) Michigan State University.
(2) (a) A. Allerhand and D. Doddrell, *J. Am. Chem.Soc.*, **93**, 2777 (1971); (b) D. E. Dorman and J. D. Roberts, *ibid.*, **93**, 4463 (1971).
(3) B. E. Lasker and M. L. Chiu, *Ann. N.Y. Acad. Sci.*, **222**, 971 (1973).
(4) P. Colson, H. J. Jennings, and I. C. P. Smith, *J. Am. Chem. Soc.*, **96**, 8081 (1974).
(5) P. A. J. Gorin, *Carbohydr. Res.*, **39**, 3 (1975).
(6) T. Usui, A. Sugiyama, S. Seto, L. Araya, T. Nislzawa, S. Imai, and K. Kosaka, *J. Biochem. (Tokyo)*, **78**, 225 (1975).
(7) C. F. Brewer and H. Keiser, *Proc. Natl. Acad. Sci. U.S.A.*, **72**, 3421 (1975).
(8) R. U. Lemieux and H. Driguey, *J. Am. Chem. Soc.*, **97**, 4009, 4063 (1975).
(9) D. R. Bundle, I. C. P. Smith, and H. J. Jennings, *J. Biol. Chem.*, **249**, 2275 (1974).
(10) J. R. Villafranca, *Arch. Biochim. Biophys.*, **160**, 465 (1974).
(11) C. F. Brewer, D. M. Marcus, A. P. Grollman, and H. Sternlicht, *Proc. Int. Conf. Stable Isot. Chem., Biol., Med., 1st,* 56–63 (1973); C. F. Brewer, D. Marcus, and A. P. Grollman, *Ann. N.Y. Acad. Sci.*, **222**, 978 (1973).
(12) R. T. Eakin, L. O. Morgan, C. T. Gregg, and N. A. Matwiyoff, *FEBS Lett.*, **28**, 259 (1972).
(13) D. E. Dorman and J. D. Roberts, *J. Am. Chem. Soc.*, **92**, 1355 (1970).
(14) H. J. Koch and A. S. Perlin, *Carbohydr. Res.*, **15**, 403 (1970).
(15) D. R. Bundle, H. J. Jennings, and I. C. P. Smith, *Can. J. Chem.*, **51**, 3812 (1973).
(16) P. A. J. Gorin, *Can. J. Chem.*, **51**, 2105 (1973).
(17) P. A. J. Gorin, *Can. J. Chem.*, **52**, 548 (1974).
(18) P. A. J. Gorin and M. Mazurek, *Can. J. Chem.*, **53**, 1212 (1975).
(19) A. S. Perlin and B. Casu, *Tetrahedron Lett.*, **34**, 2921 (1969).
(20) J. A. Schwarcz and A. S. Perlin, *Can. J. Chem.*, **50**, 3667 (1972).
(21) K. Bock and C. Pedersen, *J. Chem. Soc., Perkins Trans. 2*, 293 (1974).
(22) D. E. Dorman, *Ann. N.Y. Acad. Sci.*, **222**, 943 (1973).
(23) R. U. Lemieux, *Ann. N.Y. Acad. Sci.*, **222**, 915 (1973).
(24) R. E. London, V. H. Kollman, and N. A. Matwiyoff, *J. Am. Chem. Soc.*, **97**, 3565 (1975).
(25) A. Murray III and D. L. Williams, "Organic Syntheses with Isotopes", Interscience, New York, N.Y., 1958, p 990.
(26) J. K. N. Jones and R. A. Wall, *Can. J. Chem.*, **38**, 2290 (1960).
(27) D. F. Mowery, "Methods in Carbohydrate Chemistry", Vol. II, R. L. Whistler and M. L. Wolgrow, Ed., Academic Press, New York, N.Y., 1963, p 328.
(28) P. W. Austin, F. E. Hardy, J. G. Buchanan, and J. Baddiley, *J. Chem. Soc.*, 5350 (1963).
(29) A. S. Perlin, B. Casu, and H. J. Koch, *Can. J. Chem.*, **48**, 2596 (1970).
(30) A. S. Perlin, N. Cyr, R. G. S. Ritchie, and A. Parfondry, *Carbohydr. Res.*, **37**, C1 (1974).
(31) J. A. Schwarcz, N. Cyr, and A. S. Perlin, *Can. J. Chem.*, **53**, 1872 (1975).
(32) L. M. Jackman and S. Sternhell, "Applications of NMR Spectroscopy in Organic Chemistry", Pergamon Press, New York, N.Y., 1969.
(33) J. L. Marshall and D. E. Miiller, *J. Am. Chem. Soc.*, **95**, 8305 (1973).
(34) M. Barfield, I. Burfitt, and D. Doddrell, *J. Am. Chem. Soc.*, **97**, 2631 (1975).
(35) D. E. Dorman, S. J. Angyal, and J. D. Roberts, *J. Am. Chem. Soc.*, **92**, 1351 (1970).
(36) N. A. Matwiyoff and D. G. Ott, *Science*, **181**, 1125 (1973).

Metal–Metal Interactions Involving Metalloporphyrins. 4. A New Antiferromagnetic Phase of Tetraphenylporphinatoiron(III) Fluoride

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Abstract: Tetraphenylporphinatoiron(III) fluoride (TPPFeF) has been found to exist in two different solid phases. The α-phase is a normal $S = 5/2$ paramagnet and is the solid which has been studied earlier. The isomorphic β-phase is an antiferromagnet which shows a sharp room temperature Mössbauer spectrum. The two solids dissolve to produce solutions containing monomeric, paramagnetic TPPFeF but the original α- or β-phase re-form upon precipitation. The presence of trace amounts of excess HF in solution is required for formation of the β-phase. Solid $(TPPFe)_2FBF_4$ has been prepared and is also antiferromagnetic. Molecular weight and conductivity studies indicate that a stable fluoride bridged dimer does not exist in solution.

Hemin halides (porphyrin $Fe^{III}X$) have been the subject of extensive study. Structural work[1] has shown them to be monomeric five-coordinate Fe(III) complexes and magnetic[2] studies have found them to be normal $S = 5/2$ systems. Their Mössbauer spectra are characteristically broad above liquid He temperatures due to spin relaxation effects at the isolated high spin Fe(III) centers.[3,4] On the other hand, the presence of potentially bridging axial ligands has allowed the formation of dimers stable even in solution, such as (porphyrin Fe)$_2$O[5-8] and (porphyrin Fe)$_2$N.[9] They are antiferromagnetic solids and show sharp room temperature Mössbauer spectra.

Hemin fluoride (usually deutroporphyrin IX dimethyl ester iron(III) fluoride) has always been previously observed as a normal $S = 5/2$ system. Caughey and co-workers[10-13] prepared the material from hemin acetate and NaF and characterized it by magnetic studies, NMR, and Mössbauer spectroscopy. Later EPR studies have used the same method of preparation.[14,15] Momenteau, Mispelter, and Lexa have also used EPR to study the formation of six-coordinate difluoro hemins and found them to be high spin in frozen solution.[16]

While attempting the preparation of a hemin fluoroborate we noted the formation of products with unusually sharp room temperature Mössbauer spectra. Some of these materials contained only hemin fluoride but in a new antiferromagnetic phase. Because of our interest an intermetallic effects among hemins we have characterized this compound.

Experimental Section

All solvents and chemicals were reagent grade and except where noted were used without further purification.

Mössbauer spectra and magnetic susceptibilities were measured as previously reported.[9] Isomer shifts are given relative to metallic iron.

Molecular weights were measured by vapor pressure osmometry on a Mechrolab unit in CHCl$_3$ at 37 °C. The solvent was passed through an alumina column immediately prior to use. The instrument was calibrated with benzil and checked with μ-oxobis-[tetraphenylporphinatoiron(III)] and tetraphenylporphinatoiron(III) chloride.

Solution conductivities were measured with a Wayne-Kerr conductance bridge using nitrobenzene distilled from alumina immediately prior to use. The cell was calibrated with an aqueous KCl solution and the system was checked with a nitrobenzene solution of (n-C$_4$H$_9$)$_4$NNO$_3$.

Magnetic susceptibilities in CHCl$_3$ solution were determined by the Evans method on a Varian T-60 spectrometer at the probe temperature. The solvent was passed through an alumina column prior to the addition of Me$_4$Si and solute. The method was checked using tetraphenylporphinatoiron(III) chloride.

***meso*-Tetraphenylporphine**, C$_{44}$H$_{30}$N$_4$ (TPPH$_2$), was purchased from the Strem Chemical Co.

μ-Oxo-bis[tetraphenylporphinatoiron(III)], [(TPPFe)$_2$O], was prepared as previously reported.[9]

α-Tetraphenylporphinatoiron(III) Fluoride (α-TPPFeF). In a typical preparation, 400 mg of (TPPFe)$_2$O was dissolved in 200 ml of C$_6$H$_6$ or CH$_2$Cl$_2$. A solution containing 15 ml of 50% HF in H$_2$O and 45 ml of H$_2$O was added to the above and the mixture was shaken for several minutes during a minimum period of 15 min. The aqueous layer was discarded and the organic solution was washed twice with 50-ml aliquots of H$_2$O. The phases were carefully separated, and the water layer was discarded. The organic solvent was removed in vacuo at 50 °C and the solid product was dried in vacuo at 100 °C for 12 h.

Anal. Calcd for C$_{44}$H$_{28}$N$_4$FeF: C, 76.86; H, 4.10; N, 8.15; Fe, 8.12; F, 2.76. Found: C, 77.42; H, 4.29; N, 7.72; Fe, 8.31; F, 2.67.

β-Tetraphenylporphinatoiron(III) Fluoride, (β-TPPFeF). In a typical preparation 400 mg of (TPPFe)$_2$O was dissolved in 200 ml of C$_6$H$_6$ or CH$_2$Cl$_2$. A solution of 15 ml of 50% HF in H$_2$O and 45 ml of H$_2$O was added to the above and the mixture was shaken for several minutes during a minimum period of 15 min. The phases were carefully separated, and the aqueous HF layer was discarded. The organic solvent was removed in vacuo at 50 °C and the solid product was dried in vacuo at 100 °C for 12 h.

Anal. Calcd for C$_{44}$H$_{28}$N$_4$FeF: C, 76.86; H, 4.10; N, 8.15; Fe, 8.12; F, 2.76. Found: C, 77.31; H, 4.45; N, 8.01; Fe, 7.39; F, 2.59.

Reaction of β-Tetraphenylporphinatoiron(III) Fluoride and Boron Trifluoride. β-TPPFeF (100 mg) was dissolved in C$_6$H$_6$ or CH$_2$Cl$_2$ (75 ml). The solution was purged with N$_2$ and BF$_3$ gas was bubbled through the solution for 10–15 s. The solvent was removed in vacuo at 50 °C and the solid product was dried on a vacuum line for 12 h and submitted for analysis in an evacuated ampule.

Anal. Calcd for ((TPPFe)$_2$FBF$_4$) C$_{88}$H$_{56}$N$_8$Fe$_2$BF$_5$: C, 73.25; H, 3.91; N, 7.77; Fe, 7.74; F, 6.58; B, 0.75. Found: C, 73.24; H, 4.20; N, 7.91; Fe, 7.90; F, 5.44; B, 0.72.

Table I. Observed Magnetic Moments[a] μ_{eff}, μ_B/Fe

T, K	α-TPPFeF	β-TPPFeF	(TPPFe)$_2$FBF$_4$
300	5.65	4.94	4.21
282	*b*	4.78	4.11
254	*b*	4.71	3.99
230	5.81	4.64	3.87
204	5.80	4.56	3.70
179	5.81	4.49	3.61
153	5.82	4.38	3.34
127	5.87	4.31	3.24
101	*b*	4.24	3.06
87	5.93	4.20	2.98

[a] ±0.05 μ_B. [b] Not measured.

Analyses were performed by the Bernhardt Laboratories, Elbach über Engelskirchen, West Germany.

Results

Solid State Properties of α- and β-TPPFeF. Although analytical data for α- and β-TPPFeF are indicative of the same stoichiometric formulation, it is apparent that the two solids are not isomorphic. The α-form is a blue crystalline appearing solid while the β-form is a brown powder. Powder diffraction patterns confirm the difference and allow for the identification of the dimorphs and the mixtures. The observed d spacings are (Å, relative intensity): α-TPPFeF, 9.75, 16; 8.10, 30; 5.20, 9; 4.95, 100; 4.29, 27; 3.51, 18; 3.20, 18. β-TPPFeF, 4.21, 27; 4.04, 13.

Magnetic susceptibility measurements on powdered samples also present very different results for the α- and β-forms of TPPFeF. As shown in Table I the magnetic moment of α-TPPFeF is essentially temperature independent whereas that of β-TPPFeF is strongly temperature dependent. Neither solid shows any dependence of magnetic moment on the field up to 6 kG at either room temperature or 87 K.

The Mössbauer spectra are very different for the two solids. α-TPPFeF shows a single broad unsymmetrical absorption at room temperature and 77 K. At 77 K the absorption peak is centered at 0.269 mm/s with a peak width (full width at half maximum) of 1.02 mm/s. β-TPPFeF shows a symmetrical quadrupoler spectrum at room temperature and 77 K. The observed parameters (± 0.005 mm/s) are: 300 K, $\delta = 0.322$ mm/s, $\Delta = 1.35$ mm/s; and 77 K, $\delta = 0.438$ mm/s, $\Delta = 1.26$ mm/s. The observed peak widths are ca. 0.5 mm/s.

Solution Properties of α- and β-TPPFeF. The visible spectra of α- and β-TPPFeF in CH$_2$Cl$_2$ are each a series of poorly defined shoulders. The absence of clearly discernible peaks makes it extremely difficult to distinguish between the two spectra. The similarity in the extinction coefficients, presented in Table II, supports the statement that the solution spectra are virtually identical for the α- and β-forms of TPPFeF. The only difference is the depth of the trough between 610 and 550 nm which is slightly greater for α-TPPFeF than for β-TPPFeF, as shown by the relative extinctions included in Table II.

Conductivity measurements indicated that α- and β-TPPFeF are both nonconductors in nitrobenzene at concentrations between 2.3 and 0.29 mM.

Molecular weight measurements at solute concentrations of 10 m*m* indicated that both α-TPPFeF (obsd, 673; calcd 686) and β-TPPFeF (obsd 676; calcd 686) are monomeric in CHCl$_3$.

Magnetic moments in CHCl$_3$ solution were determined at solute concentrations of 5 mg/ml by the Evans method. Both α- and β-TPPFeF were observed to have moments of 6.1 ± 0.2 μ_B at 35 °C.

Interconversion of α- and β-TPPFeF. No obvious method was found for the conversion of the α- to the β-form of TPPFeF

Table II. Optical Absorption Shoulders Observed in CH_2Cl_2

α-TPPFeF			β-TPPFeF			$(TPPFe)_2FBF_4$		
λ, nm	$10^{-3}\epsilon$	$\epsilon_\lambda/\epsilon_{610}$	λ, nm	$10^{-3}\epsilon$	$\epsilon_\lambda/\epsilon_{608}$	λ, nm	$10^{-3}\epsilon$	$\epsilon_\lambda/\epsilon_{608}$
645	4.50	0.87	645	3.83	0.95	642	4.12	0.88
610	5.17	1	608	4.02	1	608	4.70	1
585[a]	4.78	0.92	585[a]	3.92	0.98	590[a]	4.60	0.98
550	6.03	1.17	550	4.98	1.24	548	5.85	1.24
475	13.7	2.65	490	11.0	2.75	475	12.2	2.60

[a] Spectral absorption minimum.

in the solid state. The procedures used included exposure to heat, vacuum, air, and grinding. The two phases appear to be indefinitely stable as solids.

Dissolution of the pure solids (α or β) in pure solvents, including benzene, CH_2Cl_2, and $CHCl_3$, at concentrations between 5 and 20 mg/ml produces solutions which upon evaporation to dryness return solid residues in the same phase (α or β) as was dissolved!

Conversion between the phases can be accomplished by either mixing solutions of the α- and β-forms or by the addition of H_2O or H_2O–HF to the solutions followed by evaporation to dryness. The addition of a few drops of H_2O to a few milliliters of a CH_2Cl_2 solution of β-TPPFeF produces, upon drying, pure α-TPPFeF. The addition of only 20 mol % of HF (relative to TPPFeF) in H_2O to a CH_2Cl_2 solution of α-TPPFeF produces, upon drying, pure β-TPPFeF. A CH_2Cl_2 solution containing 90% (w/w) α-TPPFeF and 10% β-TPPFeF produces pure α-TPPFeF upon drying but a solution containing 50% (w/w) α-TPPFeF and 50% β-TPPFeF produces pure β-TPPFeF upon drying. The assays of α- and β-TPPFeF were carried out by both observation of powder patterns and Mössbauer spectra which can detect 5% of either phase.

Properties of $(TPPFe)_2FBF_4$. The addition of BF_3 gas to a solution of β-TPPFeF, immediately followed by evaporation of the solvent, produces a solid analytically consistent with the formulation, $(TPPFe)_2FBF_4$. The iron:porphine:boron ratio of 2:2:1 clearly eliminates $TPPFeBF_4$ as the product. The presence of the BF_4^- anion is indicated by the infrared spectrum[17] (KBr), in that $(TPPFe)_2FBF_4$ shows a strong peak at 1070 cm^{-1} which is absent in the spectrum of β-TPPFeF. The visible spectrum of $(TPPFe)_2FBF_4$ in CH_2Cl_2 is almost indistinguishable from those of α- and β-TPPFeF.

The magnetic moments of solid $(TPPFe)_2FBF_4$ given in Table I show a strong temperature dependence and lower values than found for β-TPPFeF.

The Mössbauer spectrum of $(TPPFe)_2FBF_4$ is sharp at room temperature and similar to that of β-TPPFeF. The observed parameters are: 300 K, $\delta = 0.308$ mm/s, $\Delta = 1.23$ mm/s; and 77 K, $\delta = 0.429$ mm/s, $\Delta = 1.59$ mm/s. The observed peak widths are ca. 0.7 mm/s. The spectrum at 77 K sometimes reveals the presence of an impurity with two additional symmetrical peaks at $\delta = 0.379$, and $\Delta = 3.04$ mm/s. Those peaks disappear after reprecipitation from CH_2Cl_2 and are never observed at room temperature.

Solution conductivity measurements in nitrobenzene, presented in Table III, provided values of Λ_0 (equivalent conductance at infinite dilution) from plots of $1/\Lambda$ vs. $c\Lambda$. A value of $\Lambda_0 = 32$ is normally found for 1:1 electrolytes in nitrobenzene and both $(n\text{-}Bu)_4NNO_3$ and $(TPPFe)_2FBF_4$ behave in that fashion.

The molecular weight of $(TPPFe)_2FBF_4$ was measured in $CHCl_3$ at 37 °C and was found to be concentration dependent. At a concentration of 10 mg of $(TPPFe)_2BF_4$/ml of $CHCl_3$ the observed mol wt = 556 and decreased with concentration to a value of mol wt = 457 at 2.5 mg/ml (the lowest concentration for which reproducible data could be obtained by the method used). The value of 457 g/mol is close to one-third of the formula wt = 1444.4 (calcd 480.5).

Table III. Observed Equivalent Conductances[a]

$10^3[(TPPFe)_2FBF_4]^b$	Λ
8.44	21.2
6.75	22.8
5.40	23.8
4.03	26.3
2.15	26.7
1.07	29.2
	$\lambda_0 = 31.7$
$10^3[(n\text{-}C_4H_9)_4NNO_3)]$	Λ
6.40	25.4
3.20	27.1
1.60	28.8
0.80	29.6
	$\Lambda_0 = 30.3$

[a] In nitrobenzene at room temperature. [b] Based on formula wt = 1441.4 g/mol.

Discussion

Previous studies[10-16] of the magnetic and Mössbauer properties of hemin fluorides have always involved preparations using NaF and not HF, as a source of F^- ion. They have found that the hemin fluorides are simple paramagnets and, of all the halides, show the most poorly resolved Mössbauer spectra at 77 K because of the low value of D, the zero field splitting parameter. Because of the normal magnetic moment and Mössbauer spectrum which we have observed for α-TPPFeF we conclude that the α-phase is the form which has been examined previously. This is consistent with the preparation used here because the α-phase results only when excess HF has been washed out of the solvent prior to precipitation of the hemin fluoride.

The Mössbauer spectrum of β-TPPFeF is anomolous among the hemin halides, in that the two peaks are sharp and clearly resolved even at 300 K. The only Fe(III) porphyrins which show sharp room temperature Mössbauer spectra are the antiferromagnetic (S $5/2$) dimers,[3,4] such as $(TPPFe)_2O$, and the paramagnetic ($S = 1/2$) six-coordinate hemichromes,[18] such as $[TPPFe(imidazole)_2]Cl$. The qualitative assignment of β-TPPFeF as antiferromagnetic is consistent with the temperature dependence of the magnetic moment as presented in Table I. The absence of low temperature data does not allow the quantitative evaluation of the spin coupling parameter, J, but it is clearly a smaller value than that found for the μ-oxo dimers.

In solution, α- and β-TPPFeF have identical properties. They are both nonconducting monomeric high spin complexes with essentially the same visible spectra. However, separate solutions of the two phases, upon drying maintain their identity and produce only the phase that was dissolved. The differences in the properties of the solids must then be only a solid state effect and determined by the conditions of precipitation. The one factor which we have been able to identify is the absence or presence of trace amounts of HF in the organic solvent. Removal of all HF from the solution by washing with H_2O always results in the formation of the α-phase. Addition of only 0.2 mol of HF/mol of TPPFeF always produces the pure β-phase. The small excess of HF required for formation of the β-phase is not analytically obvious, since the fluoride analysis of β-TPPFeF is not high. This is consistent with the fact that solutions containing 50% α- and β-TPPFeF produce pure α-TPPFeF upon drying. In order for the HF in the solid β-TPPFeF to cause the conversion of α- to β-TPPFeF, the solution must contain a large fraction of the β-phase (e.g., 90% β-/10% α-TPPFeF).

The solution properties of β-TPPFeF force us to eliminate fluoride bridged dimers, similar to the μ-oxo dimers, as an explanation of the solid state behavior. Although discrete dimers may exist in the β-solid state and be totally dissociated in solution, a more likely possibility simply involves a difference in crystal packing for the α- and β-phases. This requires that in the solid β-form the monomeric five-coordinate TPPFeF molecules are stacked so as to force the alignment of ~FeF-FeF~ chains. Evidently the stacking is a crystal effect and breaks down in solution to form the observed monomers.

The effect of HF on the precipitation process is quite specific. Treatment of CH_2Cl_2 solutions of α-TPPFeF with excess aqueous NaF or by the addition of 0.2 mol of $(C_2H_5)_4NF$ per mol of hemin did not produce any β-TPPFeF, nor was it possible to produce any new phase of TPPFeCl similar to β-TPPFeF. Addition of HCl to solutions of TPPFeCl results only in the isolation of the normally observed paramagnetic solid.

Momenteau et al.[16] have observed that the addition of $(C_2H_5)_4NF$ to DMF solutions of deutroporphyrin IX dimethyl ester iron(III) fluoride resulted in the formation of six-coordinate porphyrin FeF_2^-. The corresponding $TPPFeF_2^-$ ion thus appears as a likely candidate for a role in the precipitation process of β-TPPFeF. However, the inability of $(C_2H_4)_4NF$ to effect the conversion of α- to β-TPPFeF eliminates the difluoride from that role. It is possible to speculate that the specificity of HF in the formation of the β-phase may be due to its small size or ability to hydrogen bond to coordinated fluoride. Either NaF or $(C_2H_5)_4NF$ might thus be excluded from the solid lattice. Because of the complexity of the process of precipitation it is not easy to rationalize the alteration of the solid structure of TPPFeF by the presence of trace amounts of HF. Of course only small changes in crystal packing might be required to allow the stacking of TPPFeF molecules and the resultant magnetic effects.

The preparation of $(TPPFe)_2FBF_4$ was carried out to determine if such a dimer might be stable in solution. In the solid, $(TPPFe)_2FBF_4$ is similar to β-TPPFEF in its Mössbauer parameters. The magnetic moment of $(TPPFe)_2FBF_4$ is also temperature dependent and lower than that of β-TPPFeF, indicating a somewhat greater antiferromagnetic interaction. The solution properties of $(TPPFe)_2FBF_4$ are unusual and illuminate the fragile nature of the TPPFe-F-FeTPP moiety. The conductivity of $(TPPFe)_2FBF_4$ indicates it is a 1:1 electrolyte consistent with $[(TPPF)_2F]^+BF_4^-$. However, molecular weight measurements produce a value only one-third of the formula weight. Consistent with both these observations is the proposed dissociation:

$$[(TPPFe)_2F]BF_4 \rightarrow TPPFeF + [TPPFe]^+ + BF_4^-$$

It is interesting to note that pure solid $TPPFeBF_4$, which was sought in the initial stage of this investigation, has still eluded our preparation. Because of the tendency of the BF_4^- to liberate F^-, preparations of hemin fluoroborate are always contaminated with hemin fluoride.

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References and Notes

(1) For reviews see E. B. Fleischer, *Acc. Chem. Res.*, **3**, 105 (1970), and J. L. Hoard, *Science*, **174**, 1295 (1971).
(2) C. Maricondi, W. Swift, and D. K. Straub, *J. Am. Chem. Soc.*, **91**, 5205 (1969).
(3) C. Maricondi, D. K. Straub, and L. M. Epstein, *J. Am. Chem. Soc.*, **94**, 4157 (1972).
(4) M. Blume, *Phys. Rev. Lett.*, **18**, 305 (1967).
(5) I. A. Cohen, *J. Am. Chem. Soc.*, **91**, 1980 (1969).
(6) A. B. Hoffman, D. M. Collins, V. W. Day, E. B. Fleischer, T. S. Srivastava, and J. L. Hoard, *J. Am. Chem. Soc.*, **94**, 3620 (1972).
(7) G. N. La Mar, G. R. Eaton, R. H. Holm, and F. A. Walker, *J. Am. Chem. Soc.*, **95**, 63 (1973).
(8) M. A. Torrens, D. K. Straub, and L. M. Epstein, *J. Am. Chem. Soc.*, **94**, 4160 (1972).
(9) D. A. Summerville and I. A. Cohen, *J. Am. Chem. Soc.*, **98**, 1747 (1976).
(10) N. Sadasivan, H. I. Eberspaecher, W. H. Fuchsman, and W. S. Caughey, *Biochemistry*, **8**, 534 (1969).
(11) W. S. Caughey and L. F. Johnson, *Chem. Commun.*, 1362 (1969).
(12) T. H. Moss, A. J. Bearden, and W. S. Caughey, *J. Chem. Phys.*, **51**, 2624 (1969).
(13) W. S. Caughey in "Inorganic Biochemistry", G. L. Eichhorn, Ed., Elsevier, New York, N.Y., 1973.
(14) H. Uenoyama and K. Sakai, *Spectrochim. Acta, Part A*, **31**, 1517 (1975).
(15) M. Sato and H. Kon, *Inorg. Chem.*, **14**, 2016 (1975).
(16) M. Momenteau, J. Mispelter, and D. Lexa, *Biochim. Biophys. Acta*, **320**, 652 (1973).
(17) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds", 2d ed, Wiley, New York, N.Y., 1970.
(18) L. M. Epstein, D. K. Straub, and C. Maricondi, *Inorg. Chem.* **6**, 1720 (1967).