Inorganica Chimica Acta, *158* (1989) 167–180

The Synthesis and Spectral Properties of Hemins Derived from Tetra(*p*-tolyl)-porphyrin

CARL D. SHAFFER and DAREL K. STRAUB*

Department of Chemistry, University of Pittsburgh, Pittsburgh, PA 15260, U.S.A.

(Received August 9, 1988)

Abstract

Some 32 novel hemin alkoxides, aryloxides, hydroxamates, sulfonates, oximates and other derivatives have been prepared and their infrared, visible and Mössbauer spectra measured. Room temperature Mössbauer spectra can be classified into four general types: A, unsymmetrical doublet with lower energy peak broadened; B, singlet (or perhaps symmetrical unresolved doublet); C, unsymmetrical doublet with higher energy peak broadened; and D, well-resolved symmetrical doublet. The type of spectrum, in general, depends upon the σ-basicity of the axial ligand, although this may not be true for every case. A similar dependence upon basicity is shown in the visible spectra of the hemin alkoxides and aryloxides. The infrared data indicate monodenticity even in those ligands which are commonly bidentate, e.g., the hydroxamates, cupferrate and the anion of 2-mercaptopyridine-*N*-oxide.

Introduction

Hemins (five coordinated iron(III)porphyrins) have been extensively investigated by a variety of physical methods [1, 2]. The fifth (or axial) ligand is usually a halide, pseudohalide, methoxide or carboxylate, but more recently hemins with perchlorate [3, 4], sulfonates [5, 6], various phenoxides [2], thiolates [2], SH^- [7], alkyls [8], aryls [8–10], $C(CN)_3^-$ [2, 6], PF_6^- [11], SbF_6^- [12], $B_{11}CH_{12}^-$ [13] etc. have been reported. These generally contain high spin ($S = 5/2$) iron(III), but with very weak axial ligands (e.g. ClO_4^-, SbF_6^-) the spin state is a quantum-mechanical admixture of $S = 5/2$ and $S = 3/2$, and with the very strong field alkyls and aryls, the iron(III) is low spin ($S = 1/2$). The iron(III) lies a few tenths of an Ångstrom above the mean plane of the four nitrogen atoms of the porphyrin dianion. The uniquely large zero field splitting parameter D for the $^6A_1$ ground state hemins varies from ~ +5 to ~ +16 cm^{-1} [14, 15]. Mössbauer spectra show strong dependence on the nature of the axial ligand and a weak dependence on the porphyrin ring substituents.

As a class, the hemins present unusual and interesting bonding situations for iron(III) in very strongly tetragonal crystal fields. We have been especially interested in delineating the types of Mössbauer spectra shown by the hemins [16, 17], and in this paper we give the results of our work on *meso*-tetra(*p*-tolyl)porphinatoiron(III) hemins with a wide variety of axial ligands.

Experimental

All solvents and starting materials were commercially available (usually reagent grade) and were used as received. The $\alpha,\beta,\gamma,\delta$-tetra(*p*-tolyl)porphyrin ($TTPH_2$) and its hemin chloride (TTPFeCl) were prepared by Adler's methods [18, 19]. The hemin chloride was purified by treating it in methylene chloride solution with gaseous hydrogen chloride until all the characteristic μ-oxo visible absorption bands disappeared, concentrating the solution, and precipitating by the slow addition of hexane. It was again recrystallized from methylene chloride–hexane.

A Nuclear Science scanning velocity spectrometer coupled with a Northern MS-900 1024 channel analyzer was used to measure Mössbauer spectra. The source was 100 mCi Co^{57} in rhodium at room temperature. Each spectrum consisted of 256 data points. The velocity scale was frequently calibrated with sodium nitroprusside (quadrupole splitting 1.712 mm/s) and periodically with iron foil. The analyzer output was computer fitted with a least-squares approximation assuming Lorentzian line shapes and plotted by a Calcomp plotter. Each peak was separately fitted.

Visible and near-infrared spectra were recorded on a Cary 14 recording spectrophotometer and infrared spectra were recorded on a Beckman IR-12 spectrophotometer using KBr disks.

All of the complexes described below were dried for at least 24 h under vacuum at room temperature.

---

*Author to whom correspondence should be addressed.

0020-1693/89/$3.50

All gave satisfactory analyses (Galbraith Laboratories) for C, H, N, and whenever applicable, Cl, F, S, P.

Preparation of TTPFe Methoxide, n-Propoxide, i-Propoxide and t-Butoxide

A solution of the sodium alkoxide, prepared by reaction of sodium metal with the neat alcohol, was added gradually to an almost saturated methylene chloride solution of TTPFeCl. The reddish-brown solution quickly turned green. A 10% molar excess of the alkoxide was used. The mixture was filtered and the filtrate evaporated on the hot plate until crystals formed. The crystalline solid was collected on a glass frit and washed with the corresponding hot alcohol.

Preparation of TTPFe 2,2,2-Trifluoroethoxide, Propargyloxide, Hexafluoroisopropoxide, Acetoneoximate and Cyclododecanoneoximate

Approximately a ten-fold molar excess of the alcohol or oxime was added to 50 ml of benzene containing 0.5 g (0.7 mmol) of $TTPFeOCH_3$. The solution was reduced in volume by heating until crystals formed. After cooling to room temperature, the crystals were recovered and washed well with hexane.

Preparation of TTPFe Phenoxide, p-Cresoxide and 2,4,6-Trimethylphenoxide

One-half gram of $TTPFeOCH_3$ was added to 50 ml of benzene containing a two molar excess of the alcohol. The solution was taken to near dryness and hexane was slowly added until crystals precipitated. The solution was filtered and the crystals were washed with hexane.

Preparation of TTPFe p-Nitrophenoxide, 2,4-Dinitrophenoxide, Picrate, Pentachlorophenoxide, Methanesulfonate, p-Toluenesulfonate, Diethyldithiophosphate and 8-Hydroxyquinolinate

One-half gram of TTPFe was added to 50 ml of CH_2Cl_2 containing a 1.5 molar excess of the acid. (Benzene and a 1.1 molar excess of acid were used in the case of picric acid.) The solution was reduced by heating to approximately 2 ml and ether was slowly added until the volume reached 40 ml. The volume was again reduced until a precipitate formed. The crystals were collected and washed with ether.

Preparation of TTPFe Salicylhydroxamate and N-Phenylbenzohydroxamate

One-half gram of $TTPFeOCH_3$ was added to a stirred mixture of a three molar excess of the hydroxamic acid in 75 ml of methylene chloride and the resulting mixture stirred for 30 min. After filtering, the solution was reduced in volume by heating while ether was gradually added until crystals precipitated from solution. The product was washed with ether.

Preparation of TTPFe Benzohydroxamate, Pyridine-N-oxide 2-Thiolate and Cupferrate

A solution of the acid was prepared by dissolving a slight molar excess of the corresponding sodium or ammonium salt in a dilute aqueous solution of sulfuric acid. The solution was then stirred for 10 min with a benzene solution containing 0.5 g of $TTPFeOCH_3$. The benzene layer was separated and dried over anhydrous sodium sulfate. The product was obtained by reducing the volume and slowly adding hexane. The crystals were washed with ether.

Preparation of TTPFe Complexes with N-Hydroxysuccinimide and N-Hydroxyphthalimide Anions

An excess of a saturated acetone solution of the *N*-hydroxyimide was added to a methylene chloride solution of $TTPFeOCH_3$. The mixture was taken to dryness under vacuum at low heat. The residue was stirred with benzene and the insoluble, excess *N*-hydroxyimide was removed by filtration. Crystals were obtained by decreasing the volume and slowly adding hexane.

Preparation of $TTPFeH_2PO_4$, $TTPFeH_2PO_3$ and $TTPFeH_2PO_2$

Approximately 1 ml of a 50% aqueous solution of the acid was stirred vigorously for 15 min with 50 ml of methylene chloride containing 0.5 g of $TTPFeOCH_3$. Both $TTPFeH_2PO_4$ and $TTPFeH_2PO_3$ precipitated out of solution immediately and were washed with distilled water and dried. The hypophosphite solution was decanted to remove the aqueous acid and was reduced in volume, followed by the addition of hexane. The crystals were collected and washed with ether.

Preparation of TTPFe Trifluoromethanesulfonate

Several drops of the concentrated aqueous acid were added to 50 ml of benzene containing 0.5 g $TTPFeOCH_3$ and the mixture stirred vigorously for 15 min. The benzene solution was decanted from the aqueous acid, reduced in volume to about 20 ml and filtered while hot. The product crystallized from solution upon cooling to room temperature. The crystals were washed with ether.

Results and Discussion

Syntheses

A hemin methoxide is a useful starting material for the preparation of hemin complexes with unusual axial ligands. We have investigated specifically the formation of TTPFeX derivatives from $TTPFeOCH_3$, and have found that $TTPFeOCH_3$ offers the following advantages: (i) it is easy to prepare pure from TTPFeCl and sodium methoxide in a methanol–methylene chloride solution; (ii) it has

TABLE 1. [TTPFeX] Mössbauer Data[a]

X	δ[b]	ΔE_Q[c]	Γ_1[d]	Γ_2[e]	C[f]	Type	pK_a of HX[i]
t-Butoxide	0.74	0.22	2.00	0.44	4.0	A	19
i-Propoxide	0.45	0.74	0.70	0.54	12.3	A	17.1
n-Propoxide	0.62	0.49	1.64	0.92	4.0	A	16.1
Methoxide	0.70	0.36	1.68	0.64	3.9	A	15.5
Propargyloxide	0.54	0.55	0.72	0.84	3.7	A	13.6
2,2,2-Trifluoroethoxide	0.57		1.20		17.4	B	12.4[j]
2,2,2-Trifluoroethoxide[g]	0.52	0.30	1.48	8.27			
2,2,2-Trifluoroethoxide(LN)	0.64		1.61		1.1	B	
2,4,6-Trimethylphenoxide	0.64		1.56		3.6	B	10.9
2,4,6-Trimethylphenoxide(LN)	0.62		1.76			B	
p-Cresoxide	0.56		0.76		5.4	B	10.3
Acetoneoximate	0.60		0.98		5.9	B	12.4[j]
Acetoneoximate(LN)	0.67		2.04		1.9	B	
Cyclododecanoneoximate	0.61		1.46		11.4	B	
Cyclododecanoneoximate[g]	0.60	0.07	1.02	2.54			
Phenoxide	0.51	0.27	0.60	1.56	2.3	C	10.0
p-Nitrophenoxide	0.61	0.78	0.80	1.12	7.1	C	7.2
p-Nitrophenoxide(LN)	0.62	0.63	0.92	1.56	0.66	C	
2,4-Dinitrophenoxide	0.58	0.91	0.64	0.80	7.8	C	4.0
2,4-Dinitrophenoxide(LN)	0.64	0.91	0.56	0.88	1.5	C	
Picrate	0.60	1.16	0.64	0.80	10.5	C	0.3
Picrate(LN)	0.68	1.11	0.56	0.92	1.1	C	
Pentachlorophenoxide	0.46	0.37	0.68	5.20	7.4	C	4.8[k]
8-Hydroxyquinoline anion	0.52	0.27	0.86	2.06	4.2	C	9.9[l]
Hexafluoro-i-propoxide	0.65	0.32	1.08	2.40	9.2	C	9.3
Hexafluoro-i-propoxide[h]	0.57		1.50				
Benzohydroxamate	0.67	0.88	1.04	1.00	10.1	C	8.4[m]
N-Phenylbenzohydroxamate	0.54	0.51	0.74	1.58	5.2	C	8.1[n]
N-Phenylbenzohydroxamate(LN)	0.84	0.87	1.08	1.22	2.7	C	
Salicylhydroxamate	0.94	1.27	1.36	3.32	5.3	C	7.5[m]
N-Hydroxysuccinimide anion	0.51	0.52	0.74	2.06	5.6	C	5.1[n]
N-Hydroxysuccinimide anion(LN)	0.54	0.50	0.83	2.78	1.3	C	
N-Hydroxyphthalimide anion	0.53	0.20	1.02	1.87	2.6	C	
N-Hydroxyphthalimide anion(LN)[h]	0.51		1.97				
2-Mercaptopyridine-*N*-oxide anion	0.69		1.28		12.4	B	4.7[o]
2-Mercaptopyridine-*N*-oxide anion(LN)	0.78		1.42		1.7	B	
Cupferrate[t]	0.43	0.96	1.10	1.70	11.2	A	4.1[p]
Cupferrate[t](LN)	0.58	1.17	0.90	0.96	1.9	A	
O,O'-Diethyldithiophosphate	0.59	0.80	0.58	1.06	5.1	C	−0.1[q]
Methanesulfonate	0.44	0.56	0.84	3.10	9.6	C	strong
Methanesulfonate(LN)	0.52	0.52	0.88	3.20	1.8	C	
p-Toluenesulfonate	0.61	1.08	0.72	1.70	4.3	C	strong
p-Toluenesulfonate(LN)	0.64	1.09	0.72	2.18	0.71	C	
Trifluoromethanesulfonate	0.61	2.10	0.52	0.54	4.2	D	strong
H_2PO_2	0.60	1.15	0.40	0.40	2.1	D	1.1[r]
H_2PO_3	0.50	0.53	0.60	1.94	6.0	C	2.0[r]
H_2PO_4	0.47	0.52	0.60	1.50	7.4	C	1.1[r]
ClO_4	0.58	3.34	0.42	0.40	9.5	D	
ClO_4(LN)	0.66	3.60	0.42	0.40	4.1	D	
Cl	0.50	0.51	0.56	2.00	4.3	C	
1/2 O	0.58	0.58	0.36	0.32	13.5	D	

[a] At 298 K; those marked LN at 78 K. [b] Isomer shift (in mm/s) with respect to sodium nitroprusside. All are positive. [c] Quadrupole splitting in mm/s. All are positive. [d] Full width at half-maximum (in mm/s) for lower energy peak. [e] Full width at half-maximum (in mm/s) for higher energy peak. [f] Average baseline counts in millions. [g] Calculated as doublet. In these two cases the singlet description is better, by visual observation of the fit. [h] Calculated as singlet. In these two cases the doublet description is better, by visual observation of the fit. [i] Unless otherwise indicated, these values are taken from ref. 20. [j] Ref. 21. [k] Ref. 22. [l] Ref. 23. [m] Ref. 24. [n] Ref. 25. [o] Ref. 26. [p] Ref. 27. [q] Ref. 28. [r] Ref. 29. [s] Ref. 30. [t] Cupferrate is the anion of *N*-nitroso-β-phenylhydroxylamine.

good solubility in many organic solvents; (iii) it is very reactive toward even weakly acidic ligands, yet is stable enough in solution to be used without special precautions, such as an inert atmosphere; (iv) it gives the non (or very weakly) coordinating methanol as a sole side product, so that recrystallization, which many times results in μ-oxo contamination, is generally unnecessary, and (v) it gives a very noticeable color change upon reaction, from a distinctly greenish color to a reddish to reddish-brown color, providing an easy and rapid qualitative determination of the extent of the reaction. Except for the n-propoxide, i-propoxide and t-butoxide, all the hemins in Table 1 were prepared from $TTPFeOCH_3$.

Strong acids, especially *O,O'*-diethyldithiophosphoric acid ($(C_2H_5O)_2PS_2H$) and trifluoromethanesulfonic acid, readily remove the iron from $TTPFeOCH_3$, and protonate the porphyrin, as indicated by the rapid formation of the characteristic deep, bright green color of the diprotonated porphyrin. This side reaction was effectively eliminated by minimizing contact of the acid with $TTPFeOCH_3$.

Several acids (hydrocyanic, hydrofluoric, sulfuric, sulfurous, selenous, nitric, nitrous, metaperiodic, dipicrylamine, etc.) reacted with $TTPFeOCH_3$, but these were not further investigated, except for the hydrocyanic and hydrofluoric acid cases. Despite several attempts, pure TTPFeCN and TTPFeF have not yet been successfully isolated from the reaction mixtures. Chlorosulfonic acid gave only TTPFeCl.

Mössbauer Spectra

Mössbauer spectra of all hemin complexes were measured at room temperature; several were measured also at liquid nitrogen temperature. Spectra are shown in Figs. 1–10 and the relevant data are collected in Table 1. (For comparison purposes, data measured under the same conditions are included for the known chloride, perchlorate and μ-oxo complexes.) Several types of Mössbauer behavior were found at room temperature. For purposes

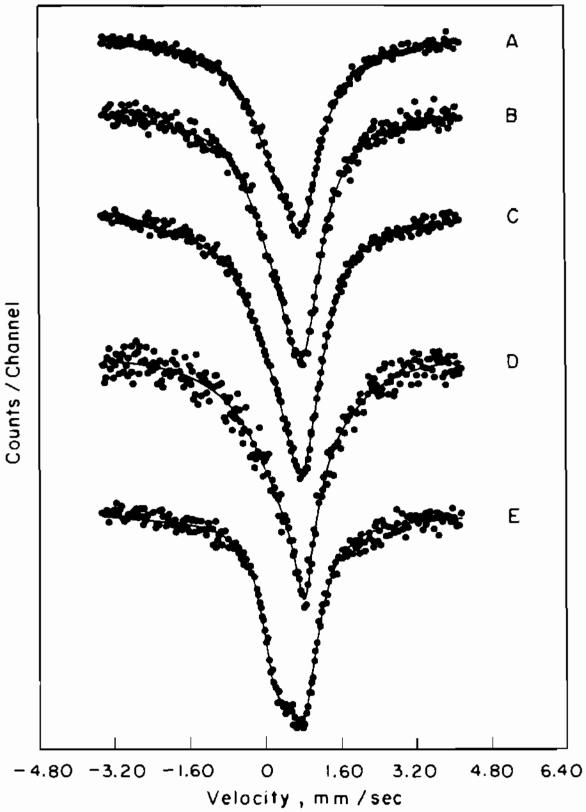


Fig. 1. Mössbauer spectra at 298 K of TTPFeX: A, X = methoxide; B, X = n-propoxide; C, X = i-propoxide; D, X = t-butoxide; E, X = propargyloxide.

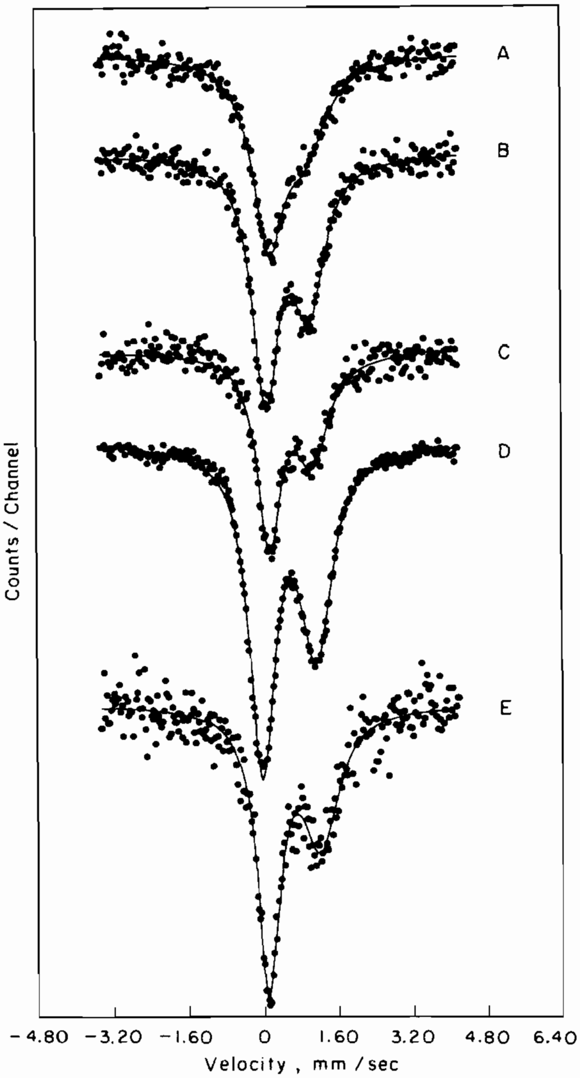


Fig. 2. Mössbauer spectra of TTPFeX: A, X = *p*-nitrophenoxide at 298 K; B, X = 2,4-dinitrophenoxide at 298 K; C, X = 2,4-dinitrophenoxide at 78 K; D, X = picrate at 298 K; E, X = picrate at 78 K.

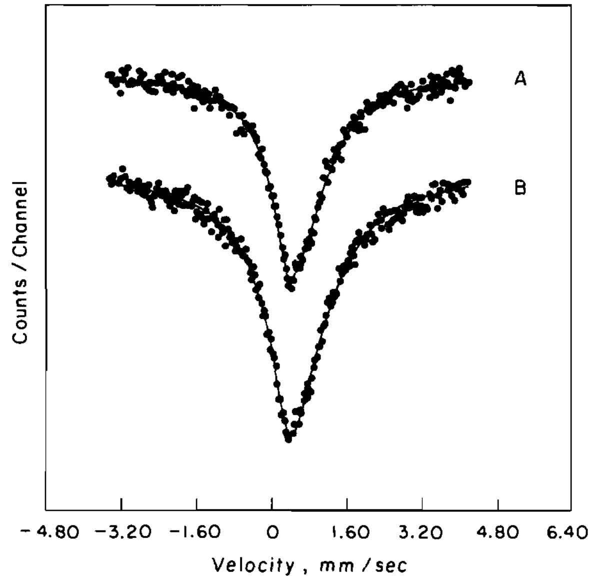


Fig. 3. Mössbauer spectra at 298 K of TTPFeX: A, X = phenoxide; B, X = 8-hydroxyquinoline anion.

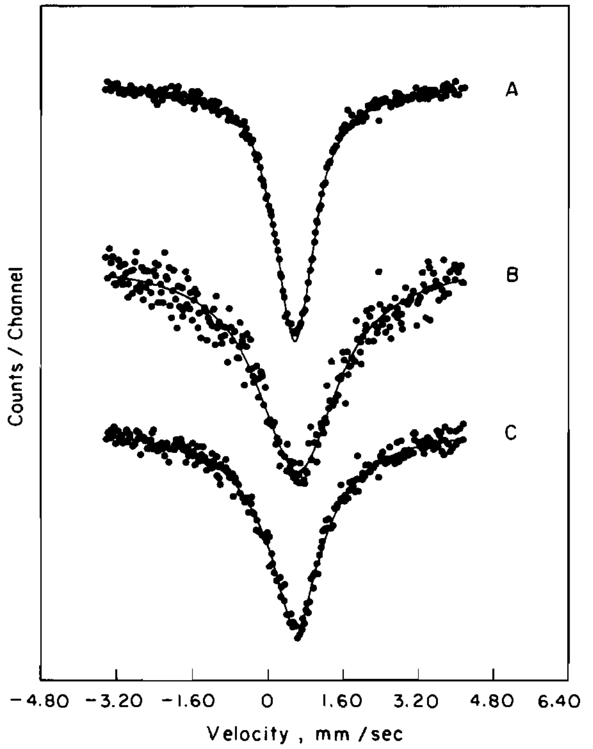


Fig. 4. Mössbauer spectra of TTPFeX: A, X = acetoneoximate at 298 K; B, X = acetoneoximate at 78 K; C, X = cyclododecanoneoximate at 298 K.

of discussion, spectral types are classified as A (unsymmetrical doublet, with the magnetically broadened peak appearing as a shoulder on the low energy side (left side) of a comparatively narrow peak), exemplified by the methoxide; B (singlet, or perhaps a reasonably symmetrical unresolved doublet) exemplified by the acetoneoximate; C (unsymmetrical doublet with the magnetically broadened peak toward the high energy side), exemplified by the p-nitrophenoxide (and TTPFeCl); and D (two well resolved peaks of equal or nearly equal intensities and widths) exemplified by $TTPFeH_2PO_2$.

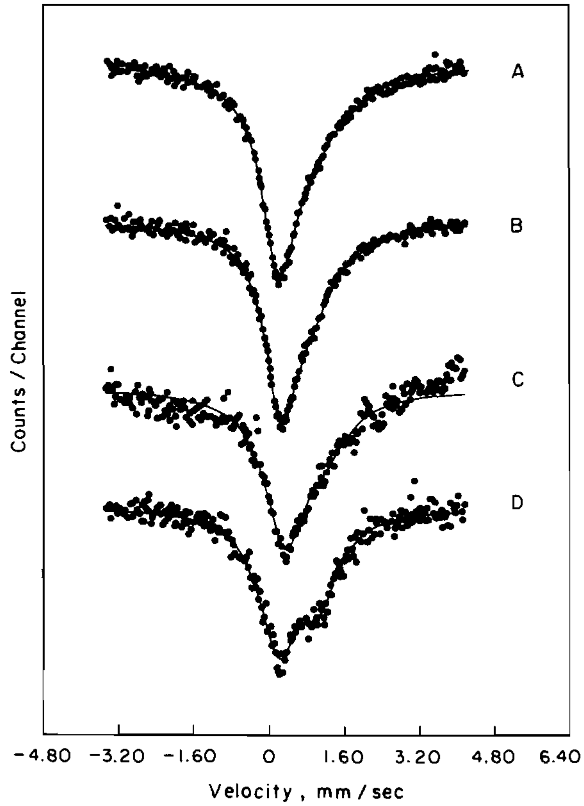


Fig. 5. Mössbauer spectra of TTPFeX: A, X = N-hydroxysuccinimide anion at 298 K; B, X = N-phenylbenzohydroxamate at 298 K; C, X = N-phenylbenzohydroxamate at 78 K; D, X = benzohydroxamate at 298 K.

The principal component of the electric field gradient, V_{zz}, (coincident with the C_4 axis) is known to be positive for octaethylporphyrin and tetraphenylporphyrin hemin chlorides and methoxides [15]. For the chlorides, the major axis of hyperfine magnetic field at the iron nucleus, H_z, is parallel to V_{zz}, and gives rise to a type C spectrum. For the methoxides, H_z is perpendicular to V_{zz}, and gives a type A spectrum. At low temperatures, the asymmetry in the hemin halide spectra reverses to the lower energy side [16, 17]. A detailed theoretical justification for this reversal has been given by Dattagupta [31]. It is not clear just how H_z depends on the bonding of the axial ligand. Perhaps L → Fe(III) π-bonding is involved; evidence for such π-interaction in $TTPFeOCH_3$ has been deduced from electron density distribution measurements [32].

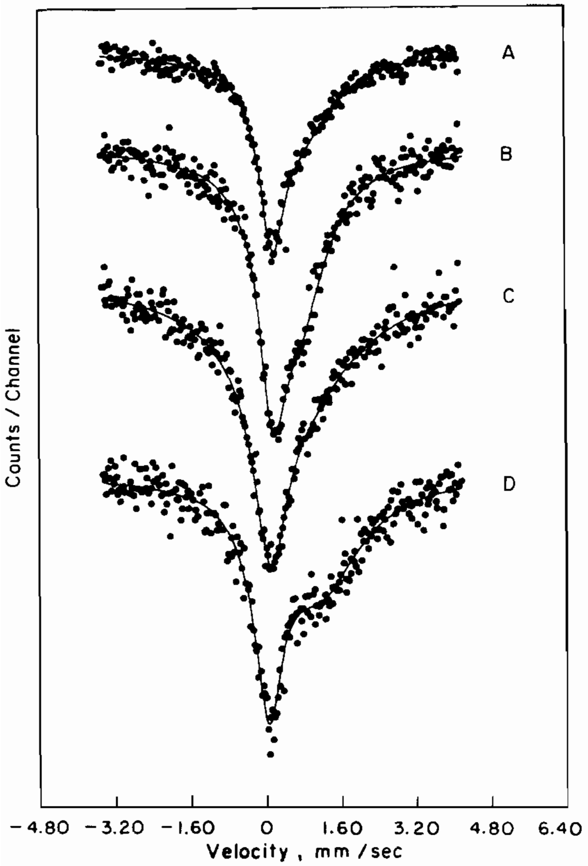


Fig. 6. Mössbauer spectra at 298 K of TTPFeX: A, X = H_2PO_3; B, X = H_2PO_4; C, X = methanesulfonate; D, X = *p*-toluenesulfonate.

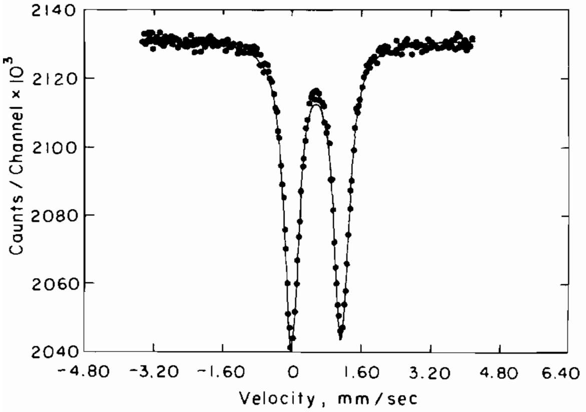


Fig. 7. Mössbauer spectrum of $TTPFeH_2PO_2$ at 298 K.

It is likely that V_{zz} is positive for all high spin hemins. We then conclude that the hemins showing type A spectra have H_z perpendicular to V_{zz}, and hemins showing type C spectra have H_z parallel to V_{zz}. The symmetrical type B spectrum (at room temperature, or at low temperatures [16, 17]) is apparently intermediate.

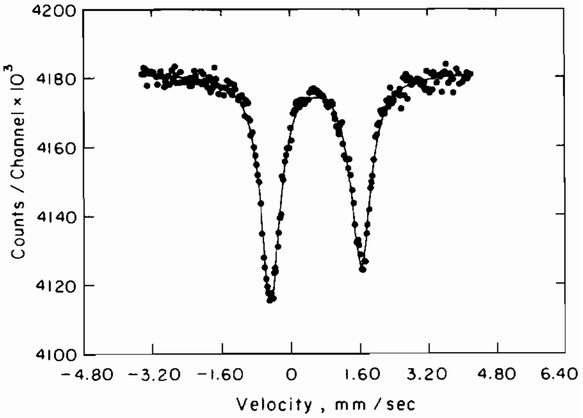


Fig. 8. Mössbauer spectrum of $TTPFeCF_3SO_3$ at 298 K.

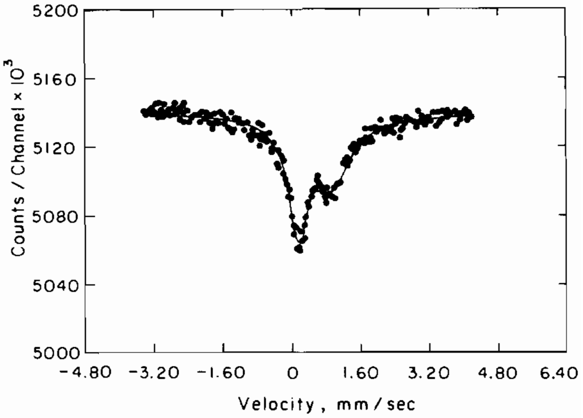


Fig. 9. Mössbauer spectrum of $TTPFeS_2P(OC_2H_5)_2$ at 298 K.

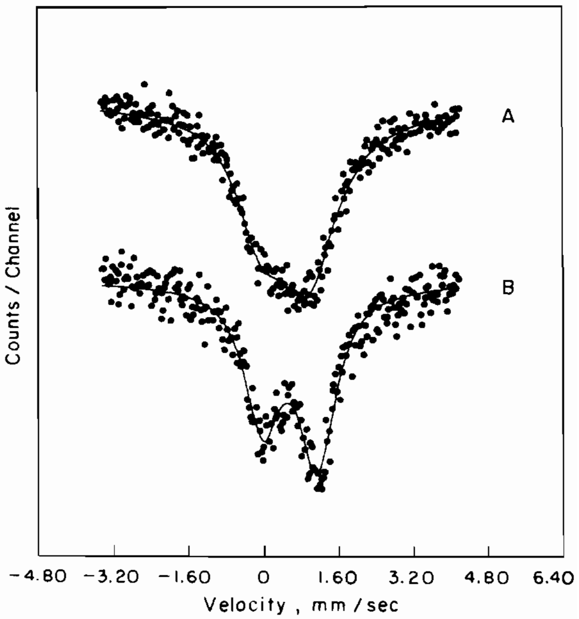


Fig. 10. Mössbauer spectra of TTPFe cupferrate: A, at 298 K; B, at 78 K.

The hemin perchlorates reported in the literature show type D behavior, with large quadrupole splittings [1, 3]; the closer the approach to a pure $S = 3/2$ case, the larger the splitting. Low spin ($S = 1/2$) hemins with alkyl [8] and aryl [8, 9] or SH [7] axial ligands also give Mössbauer spectra with widely split symmetrical doublets at room temperature. Thus, a type D spectrum is associated with hemins which are not purely high spin.

A more detailed discussion of the Mössbauer spectra and parameters is given below for groups of similar complexes. Little emphasis will be placed on the isomer shifts generally since these values are not meaningful when obtained from magnetically broadened, complex room temperature hemin spectra, where they can vary greatly in an apparently unsystematic fashion. However, shifts are meaningful for spectral types B and D. Also, little discussion will be devoted to the 78 K spectra, because no important additional information was obtained (except, perhaps, for the *N*-nitroso-β-phenylhydroxylamine, 'cupferron', case), although several spectra were measured at liquid nitrogen temperature.

Alkoxides

Seven alkoxides were investigated. All show a type A spectrum, except for trifluoroethoxide, type B, and hexafluoroisopropoxide, type C. There appears to be a general dependence of the quadrupole splitting upon the basicity of the axial ligand. (A listing of pK_a values is given in Table 1.) As explained above, differences in line broadenings preclude a linear dependence of Δ (at room temperrature) on pK_a, so that, for example, the t-butoxide with its greatest basicity, does not give the most resolved spectrum (however, it may be significant that its low energy peak is by far the most broadened). The trifluoroethoxide singlet is comparatively narrow, indicating a closer approach to a cubic crystal field. Thus the dividing line between type A and type B spectra for these alkoxides lies about pK_a = 13. The much less basic hexafluoroisopropoxide is type C.

Phenoxides

Eight of these were investigated, ranging from the comparatively basic 2,4,6-trimethylphenoxide to the rather acidic picrate. There seems to be a regular increase in splitting with decrease in pK_a. The trimethylphenoxide and *p*-cresoxide, each a singlet spectrum, have similar pK_as, so that it appears the flanking *ortho* methyl groups in the trimethylphenoxide do not provide any measurable amount of steric hindrance to the iron in forming a normal Fe–O bond, since if they did, a spectrum, for example like that of the phenoxide, should result. The dividing line between type B and type C spectra appears to be at about pK_a = 10. The picrate has the largest splitting, in accord with its small pK_a, but the value does not appear unduly great: the flanking nitro groups are probably not sterically important.

Oximates

Two oximates (the anions of acetone oxime and cyclododecanome oxime) were prepared. These oximes have pK_a values about 12, which, if they follow the same order as the alkoxides and phenoxides, should yield a singlet spectrum. Both actually do give singlet spectra. The tacit assumption is made that coordination occurs through the oxygen, not the nitrogen, of the oximate, which appears the more sterically reasonable.

Hydroxamates

Five hydroxamates were studied. These included two representatives of a special class of hydroxamic acid, *N*-hydroxysuccinimide and *N*-hydroxyphthalimide. Hydroxamates are commonly bidentate in ordinary complexes, and the possibility of bidenticity in these hemin hydroxamates must be considered. All five spectra are of type C. There are no striking differences, in either the general appearance of the spectra nor in the Mössbauer parameters, which might be evidence for any bidentate nature of the hydroxamate. In general, bidenticity might be expected to result in larger splittings and larger V_{zz} values than in comparable monodentate cases, since the negative charge is less concentrated along the z axis (although this would depend strongly upon the 'bite' of the bidentate ligand and its σ basicity).

The benzohydroxamate seems somewhat unusual. The two peaks have rather similar (small) widths, making the splitting and resolution much more apparent than in the salicylhydroxamate case. The salicylhydroxamate has a very broad high energy peak, making the fitted value of the quadrupole splitting very large. Salicylhydroxamic acid is a stronger acid than benzohydroxamic acid and the data in Table 2 show a general trend of larger width of the high energy peak with stronger acid. However, morphological origins of differences in hydroxamate spectra cannot be discounted without frozen solution data.

Phosphorus Oxyanions

Dihydrogen phosphate, hydrogen phosphite and hypophosphite hemins were studied. The dihydrogen phosphate and hydrogen phosphite spectra are of the common type C case, whereas the hypophosphite shows the uncommon type D spectrum. The difference is striking and unexpected, and certainly cannot be due to any great difference in basicity of the anion. The similarity of the hypophosphite spectrum to that of the perchlorate (except for

TABLE 2. Electronic Spectral Data for some TTPFeX Complexes[a]

X	Peak position[b], λ_{max} (nm)								
t-Butoxide	344s		418	510s	573	610	694s	775	
Methoxide	334		419	500s	581	632s		765	
Propargyloxide	342		418	508s	580	630s		860	
2,2,2-Trifluoroethoxide	337		418	500s	562s	631			
Hexafluoro-i-propoxide	342		417	494	563s	656		825	
2,4,6-Trimethylphenoxide	330s		418	487s	582s	632s			
p-Cresoxide	332		418	500s	567s	638	663	840	
Phenoxide	335		418	495s	558s	635		840	
8-Hydroxyquinoline anion			417	483	563s	635	665	850s	
p-Nitrophenoxide		362s	418	503	565s	640s	670	840	
2,4-Dinitrophenoxide		356	417	508	575s	654s	683	860	
Picrate			417	515	581	655s	690		
Acetoneoximate	320	350	419	513s		620	668s	860	
Cyclododecanoneoximate		340	419	506s	573s	616	666	775	
N-Hydroxysuccinimide anion		380	418	511	575	660	695	860	
N-Hydroxyphthalimide anion		365s	416	506	573s	650s	682	860	
Benzohydroxamate			403, 405s	500	544	578s	645, 668	870	
Salicylhydroxamate			416	508	572s	640s	680	860	
N-Phenylbenzohydroxamate		380	418, 425	508	578s	645	680	870s	
2-Mercaptopyridine-*N*-oxide anion	333		419	500	538	567s	645, 678	870s	
Cupferrate	350		408	478	535	568, 612	700	810	
O,O'-Diethyldithiophosphate	330	380s	417	518	580s		682	860	
Methanesulfonate	328s	380s	412	515	587s	650	687	880	
p-Toluenesulfonate		381	417	512	588, 609	660s	691	765	1008
Trifluoromethanesulfonate	333s	385s	410	515	588s		679	765	937
H_2PO_4	345s		414	505	575s	640s	678	860	
H_2PO_3	337s	368s	415	508	575	644s	681	850	
H_2PO_2	313s	365s	415	508	575s	642s	682	860	
ClO_4	330	402	420	520	590s		676	840	1060
1/2 O	319		409		572	614		770	
$(Im)_2^+Cl^-$[c]		356	419	465s	552	590s	650s		1145

[a]Measured in methylene chloride solution from 1100–300 nm. [b]s = shoulder. [c]Im is imidazole.

the much greater splitting of the latter) arouses the suspicion of a change in spin state of the iron in going from the dihydrogen phosphate to hypophosphite. The magnetic moment of solid protohemin hypophosphite has been reported: it is 5.62 BM at room temperature [33], *i.e.* an admixed spin state.

All three of these oxyanions have the possibility of being bidentate; no evidence for or against bidentate bonding can be deduced from the Mössbauer spectra.

Sulfonates

Complexes of three sulfonates – methanesulfonate, trifluoromethanesulfonate and *p*-toluenesulfonate – were studied. Both methanesulfonate and *p*-toluenesulfonate show the common type C spectrum but the much more apparent quadrupole splitting in the hemin *p*-toluenesulfonate is about twice that of the methanesulfonate, which is somewhat surprising since their pK_as are similar.

The very acidic trifluoromethanesulfonic acid gives a spectrum (type D) with relatively narrow peaks and large quadrupole splitting. The spectrum is comparable to those of hemin salts of other very strong acids, e.g. perchloric, and to the unusual hypophosphite spectrum.

Miscellaneous

This group includes the anions of 8-hydroxyquinoline (oxinate), 2-mercaptopyridine-*N*-oxide (or better, 1-hydroxy-2-thionohydropyridine) (abbreviated MPO), *N*-nitroso-*β*-phenylhydroxylamine ('cupferron') and diethyldithiophosphate. All of these ligands are commonly bidentate, but whether they are in the hemin complexes is uncertain from the Mössbauer data.

The spectra vary from the type B singlet (the MPO complex) through type C (oxinate with a barely noticeable splitting) to the unusual cupferrate case, ~type A, with unusually large splitting. What distinguishes the spectrum of the cupferrate from the usual type A spectrum is that the width of the high energy peak is greater than that of the low energy peak. Also, the greatest temperature dependence is found for this complex. At 78 K the splitting has increased somewhat (perhaps not significantly) but the peaks, especially the broader one, have become narrower and the resolution is consequently much greater.

It does not seem so reasonable to try to relate very closely the types of Mössbauer spectra shown by this group to the σ-basicity of the axial ligand, as was attempted empirically for the alkoxide and the phenoxide groups, since the coordinated atom or atoms (O (and N?) and S (and O?)) differ in their π acidities and basicities. If oxinate were to coordinate as a monodentate ligand through oxygen, a type C spectrum would be expected from its pK_a of 9.9. This is what is found. On the other hand, the MPO anion (proton loss occurs from the oxygen atom), if similarly coordinated, should also give a type C spectrum. The spectrum is a singlet. The *O,O′*-diethyldithiophosphoric acid is a quite strong acid, and a relatively large splitting might be expected for the diethyldithiophosphate complex although the anion must coordinate through (possibly) π-bonding sulfur atom(s).

Electronic Spectra

Spectral data are given in Table 2. In some cases it was necessary to add excess ligand to the methylene chloride solution to suppress the formation of the μ-oxo complex.

The conclusions regarding the structure of the hemins which can be drawn from electronic spectra in the 300–1100 nm range appear rather limited despite the number of peaks in this region and their variable positions and intensities. Probably all the TTPFeX hemins have at least one, and many times two, peaks on the high energy side of the Soret band, that is, between ~300 and ~400 nm. In a few cases (e.g., picrate, oximate) there is much stronger UV absorption into the visible by the excess ligand added to the solution to prevent formation of the μ-oxo complex that these peaks are obscured. Frequently these peaks are rather ill-defined shoulders and occur approximately in the 315–345 and 350–400 nm ranges.

The Soret peak, which is the strongest and sharpest of the peaks, occurs within the rather narrow range of ~410–420 nm. It has been long known that the position of the Soret peak in hemins depends mainly upon the porphyrin substituents and very little on the axial group; for example, in a series of ten hemins of deuteroporphyrin IX dimethyl ester the Soret peak varied from 383 to 401 nm [34].

Generally four peaks occur between the Soret peak and ~700 nm, in the approximate ranges 485–520, 560–590, 610–660 and 670–695 nm. The 560–590 nm peak is usually a poorly defined shoulder, as is the 610–660 nm peak. The positions and relative intensities of the peaks in the 450–700 nm region are the most sensitive to the nature of the axial ligand of all the peaks.

Finally, in the near infrared region there is usually a very broad and weak peak at approximately 860 nm, and in the cases involving derivatives of very strong acids, a very broad and weak band about 1000 nm. The ~860 nm peak is sometimes difficult to locate, especially when it appears as a shoulder on the ~680 nm peak. It is probably present in all the hemin spectra; for those few cases where it is not indicated in Table 2 it may have been an exceedingly ill-defined, very broad, weak shoulder. This peak appears characteristic of high-spin iron(III) porphyrins and sometimes has a high energy shoulder in solution and a low energy shoulder in crystal spectra. These are probably charge transfer transitions [35,36].

Alkoxides and phenoxides

The combined series of alkoxides and phenoxides provide the clearest evidence for the way in which the electronic spectra depend upon the nature of the axial ligands. This dependence is especially marked in the ~500–700 nm region. Figure 11 compares the spectrum of the μ-oxo complex (which could be considered as a member of the hemin alkoxide series) with the strongly basic alkoxide

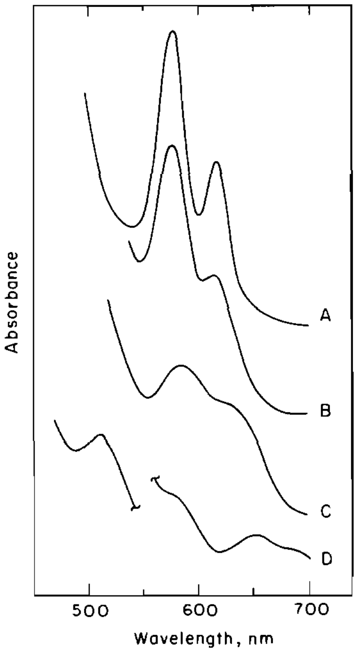


Fig. 11. Electronic spectra of methylene chloride solutions of: A, $(TTPFe)_2O$; B, TTPFe t-butoxide; C, TTPFe methoxide; D, TTPFe propargyloxide.

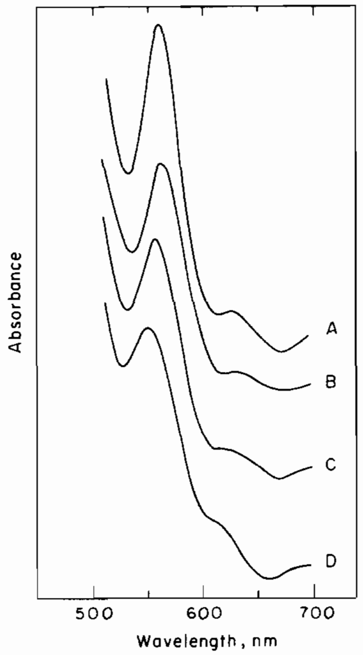


Fig. 12. Electronic spectra of methylene chloride solutions of: A, TTPFeCl; B, TTPFe picrate; C, TTPFe 2,4-dinitrophenoxide; D, TTPFe *p*-nitrophenoxide.

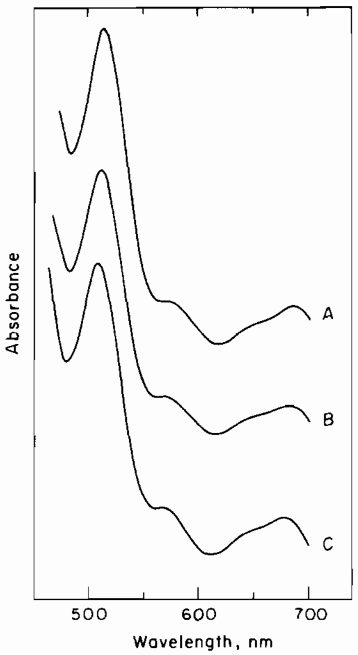


Fig. 13. Electronic spectra of methylene chloride solutions of: A, $TTPFeH_2PO_2$; B, $TTPFeH_2PO_3$; C, $TTPFeH_2PO_4$.

spectra. A regular change can be seen in the two major peaks in going from oxide through t-butoxide and propargyloxide. Spectra of the n-propoxide and i-propoxide are essentially identical to the methoxide spectrum. As the alkoxide or phenoxide becomes less and less basic, regular changes in the spectra continue to occur until the spectrum approaches that of the chloride, for the very weakly basic picrate. These changes are shown in Fig. 12. Interestingly, the spectrum of the acetoneoximate ($pK_a = 12.4$) is very similar to trifluoroethoxide ($pK_a = 12.5$), evidence that coordination probably takes place through the oxygen atom, rather than the nitrogen, in the oximates.

Phosphorus oxyanions

A comparison of the three spectra (500–700 nm) is shown in Fig. 13. The spectra are almost identical and show no evidence for any unusual structure of the hypophosphite, at least in methylene chloride solution.

Strong acid derivatives

Spectra of the methanesulfonate and *p*-toluenesulfonate are very similar, as might be expected. The two peaks between 300 nm and the Soret peak are somewhat better resolved in the *p*-toluenesulfonate. For the trifluoromethanesulfonate the ~590 nm shoulder is weaker and less resolved.

Hydroxamates

The spectrum of the salicylhydroxamate is shown in Fig. 14. Although benzohydroxamate and salicylhydroxamate are very similar structurally, distinct differences can be noted in their spectra, especially in the relative intensities of the two 640–700 nm region peaks, and the ~500 nm peak. The Soret peak of benzohydroxamate occurs at the exceptionally low energy of 430 nm and is somewhat asymmetric.

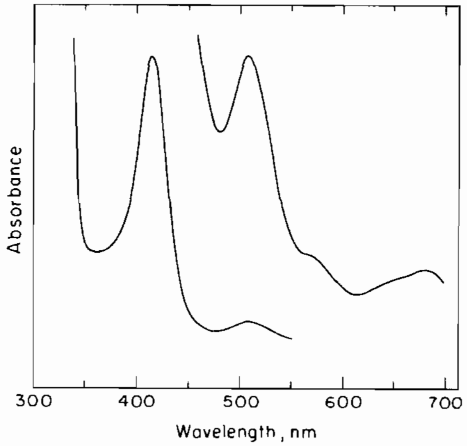


Fig. 14. Electronic spectrum of TTPFe salicylhydroxamate in methylene chloride.

Spectra of both hydroxyimide derivatives (not shown) have the same profile and are very similar to the salicylhydroxamate spectrum.

Miscellaneous

The cupferron derivative has a very high energy Soret peak. In this respect it resembles the low spin imidazole hemichrome [TTPFe•2Im]Cl, with a Soret peak at 406 nm [37]. In all other respects the two spectra are very different.

The spectrum of the oxine derivative strongly resembles that of *p*-methylphenoxide. Because the basicity of the two ligands is similar, the oxine anion is most probably monodentate.

The spectra of hemin diethyldithiophosphate (Fig. 15) in which coordination must take place through sulfur, and the MPO derivative (Fig. 16) are very dissimilar. This might be ascribed to non-sulfur coordination in the MPO derivative, but is more likely due to the large difference in basicity between the two ligands. The spectrum of the diethyldithiophosphate has a profile very similar to those of picrate and the sulfonates.

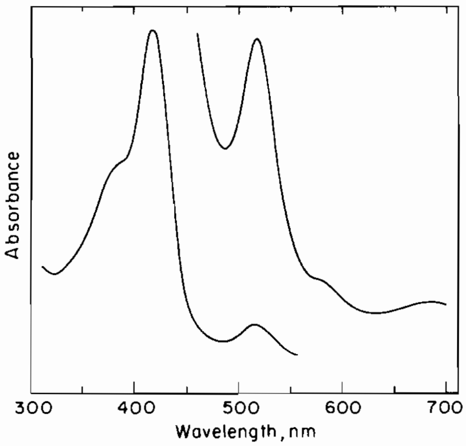


Fig. 15. Electronic spectrum of $TTPFeS_2P(OC_2H_5)_2$ in methylene chloride.

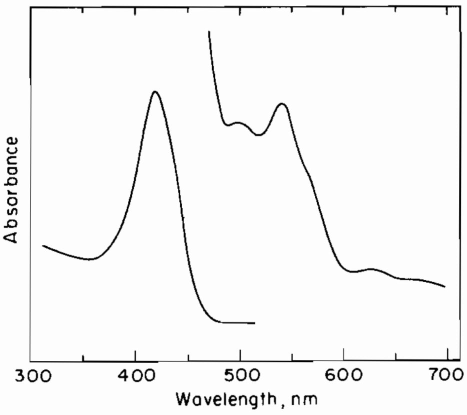


Fig. 16. Electronic spectrum of TTPFeMPO in methylene chloride.

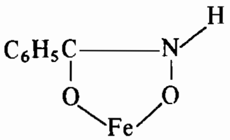
Infrared Spectra

Infrared spectra of most of the hemin complexes were measured in the 300–1700 cm^{-1} range (data given in Table 3), primarily to learn more about the possible structures of some of these complexes (especially the ones which contained potentially bidentate axial ligands, since both Mössbauer and electronic spectra were of little help in these cases) and to determine whether the Fe–O stretch varied with the basicity of the axial ligand in the alkoxide and phenoxide series. This latter objective was not realized since no Fe–O peaks could be positively identified in the complex spectrum of the iron-porphyrin group. Thus, none of the three alkoxides, methoxide, n-propoxide or t-butoxide, shows any peaks in addition to those of TTPFeCl.

Hydroxamates

Infrared data were especially helpful in elucidating the possible structures of the hemin hydroxamates. A striking characteristic of the spectra is a very strong, broad peak in the 1635–1650 cm^{-1} region for the benzohydroxamate and salicylhydroxamate and about 1710 cm^{-1} for the *N*-hydroxysuccinimide and *N*-hydroxyphthalimide derivatives. In order to determine how the position of this peak depended upon the state of the hydroxamate, several additional compounds, containing the free ligand, or coordinated as a bidentate group were investigated. Positions of characteristic peaks in cm^{-1} are: potassium benzohydroxamate, 1624; tris(benzohydroxamato)-iron(III), 1443, 1485, 1520, 1560, 1590; *N*-phenylbenzohydroxamic acid, 1373, 1625; tris(*N*-phenylbenzohydroxamato)iron(III), 1515; *N*-hydroxyphthalimide, 1710, 1745, 1790.

The 1624 cm^{-1} peak of the benzohydroxamate becomes markedly lower in energy upon bidentate coordination to iron(III). (The X-ray structure of tris(benzohydroxamato)iron(III) shows bidentate hydroxamate [38].) This peak is certainly a CO stretch [39, 40]. There is more double bond character to the CO bond, e.g. in $K^-C_6H_5CONO^-$, than in



The much higher energy of the CO stretch in *N*-hydroxyphthalimide, due to two electronically coupled CO groups, is expected.

The increase in CO stretching energy in the hemin hydroxamates over the ionic form, rather than the decrease expected for bidentate coordination, is definite evidence for monodentate coordination through the NO moiety of the hydroxamate, which strengthens the CO bond.

TABLE 3. Infrared Peaks Present in TTPFeX but Absent in TTPFe[a]

TTPFeX, X =	Peaks[b] (cm^{-1})
Methoxide, n-propoxide, t-butoxide, acetoneoximate, cyclododecanone-oximate, H_2PO_3	none
H_2PO_4	1030vb, s
H_2PO_2	1135s
Trifluoromethanesulfonate	1135s
Methanesulfonate	562s, 925s, 1155m, 1300m
p-Toluenesulfonate	565s, 680sd, 950sb, 1165s, 1308md
ClO_4	615w, 628m, 1087m, 1165m
p-Nitrophenoxide	470w, 670m, 756m, 870m, 1160w, 1285sb, 1578s
2,4-Dinitrophenoxide	488m, 688m, 750m, 925m, 1135m, 1280w, 1320s, 1587sd
Picrate	400w, 1287w, 1540m, 1587m, 1606m
Hexafluoro-i-propoxide	682s, 748s, 888m, 1100m, 1155m, 1260m, 1287s, 1365m
Benzohydroxamate	695m, 875w, 890w, 1152w, 1650sb
Salicylhydroxamate	458m, 662w, 755s, 912w, 1150w, 1240mb, 1635sb
N-Hydroxysuccinimide anion	482w, 660m, 1708vsb
N-Hydroxyphthalimide anion	695s, 882s, 1375m, 1712vsb
Cupferrate	680w, 690w, 753m, 937m, 1285m, 1385m, 1675s
2-Mercaptopyridine-*N*-oxide anion	752m, 1138m, 1265w, 1456s, 1538mb
O,O'-Diethyldithiophosphate	645s, 945s, b

[a]Range: 300–1700 cm^{-1}. Peaks due to the TTPFe group (specific values from the TTPFeCl spectrum, in cm^{-1}): 430s, 522m, 722s, 800s, 845w, 1000s, 1070m, 1112m, 1183m, 1206m, 1334m, 1406w, 1450wb, 1490w, 1512vw. The Fe–Cl stretch in TTPFeCl occurs as a strong peak at 363 cm^{-1}. [b]Abbreviations: w = weak, m = medium, s = strong, v = very, b = broad, d = doublet.

Cupferrate

The infrared spectrum of this hemin is puzzling; it shows a strong peak at 1675 cm^{-1} which, however, cannot be due to a C=O stretch. In the ammonium salt there is a strong, very broad peak, or perhaps a multiplet, centered at about 1440 cm^{-1}; in tris(cupferrato)iron(III) (where the cupferron anion is bidentate [41]) there is a strong, sharp peak at 1464 cm^{-1} (which might also exist in the ammonium salt, but hidden under the broad 1440 cm^{-1} band) and strong peaks at 1295 and 1205 cm^{-1}. These latter two appear to correspond to the 1260 and 1220 cm^{-1} peaks of the ammonium salt. There are no additional characteristic peaks in the 1500–1800 cm^{-1} region of either spectrum. The 1260 and 1295 cm^{-1} peaks are due to the N=O stretch [42]. In organic nitroso compounds, $R_2C–N=O$, the N=O stretch occurs generally at about 1560 cm^{-1} (the range, however, is wide, from about 1500 to about 1600 cm^{-1}), and in nitrosamines, $R_2N–N=O$, at about 1500 cm^{-1} [40]. Based on these data, the hemin 1675 cm^{-1} peak seems very high for N=O; its assignment remains uncertain.

The 1285 cm^{-1} peak in the cupferrate most probably represents a NO stretch in –N–O–Fe; the 1385 cm^{-1} peak, a N=O stretch. If this is so, then cupferrate is also monodentate like the hydroxamates.

2-Mercaptopyridine-N-oxide anion

The additional peaks in TTPFeMPO at 752, 1138, 1456 and 1538 cm^{-1} correspond quite closely to the strong peaks at 875, 1152, 1463 and 1545 cm^{-1} in NaMPO and at 753, 1147, 1460 and 1544 cm^{-1} in $Fe(MPO)_3$. The Fe–S stretch in $Fe(MPO)_3$ occurs at 350 cm^{-1}. The only infrared data reported in the literature [43] concern HMPO which exists almost completely as the monomeric internally H-bonded thione form; main peak assignments in cm^{-1} are: 1572, 1458, both ring stretches, and 1142, C=S stretch. The thione form greatly predominates over the tautomeric thiolate form in the free acid, its sodium salt, and apparently also in $Fe(MPO)_3$. The only real difference then, between monodentate and bidentate MPO (at least in its complexes with first row transition metal ions), should be the presence of an M–S absorption in the latter case. The fact that the infrared spectrum of TTPFeMPO shows no evidence of an Fe–S stretch is strong confirmation that the MPO ligand is monodentate, bonding through oxygen.

Phosphorus oxyanions

The hypophosphite anion (C_{2v}) has strong peaks at 1180–1230 cm^{-1} (PO_2 asymmetric stretch), 1040–1050 cm^{-1} (PO_2 symmetric stretch) and 808–810 cm^{-1} (PH_2 rock) [44]. The PO_2 symmetric stretch is especially split in complexes; thus, in $Sm(H_2PO_2)_3$, there are strong peaks at 1170, 1060 and 800 cm^{-1} [45]. Several other complexes show many additional strong peaks in the 1100–1200 cm^{-1} region [45, 46]. A careful examination of the spectrum of $TTPFeH_2PO_2$ shows only the strong 1135 cm^{-1} peak, a weak peak at 1265 cm^{-1}, and perhaps a peak at ~1072 cm^{-1}, although this overlaps a porphyrin peak. There are no additional peaks in the 1150–1250 cm^{-1} region, so the complex does not contain ionic hypophosphite. The PH_2 rock peak is hidden by a strong porphyrin peak at 800 cm^{-1}.

The spectra of hemin hydrogen phosphite and dihydrogen phosphate are uninformative, again because of interference by TTPFe absorption in characteristic regions. There is perhaps a shoulder at ~1012 cm^{-1} on the TTPFe 1000 cm^{-1} peak in the hydrogen phosphite spectrum, and perhaps a corresponding broad shoulder, 960–970 cm^{-1}, in the dihydrogen phosphate spectrum. The dihydrogen phosphate spectrum also has a very broad peak at 1030 cm^{-1}, and perhaps peaks at ~1150, 1230 cm^{-1}. Some of these are due to PO_3 deformations.

Conclusions

The syntheses of hemins with a wide variety of axial groups are easily effected from the reaction of a hemin methoxide with inorganic acids (e.g. perchloric, phosphoric acids) or organic acids (e.g. phenols, oximes, hydroxamic acids). From infrared data it appears that the axial group is monodentate in these hemins, even with those ligands, such as the hydroxamates, which are commonly bidentate.

Although satisfactory isomer shifts and quadrupole splittings generally cannot be extracted from hemin Mössbauer spectra measured much above liquid helium temperature, the several types of spectra and the striking dependence of line broadening and relative line intensities on the axial ligand in the room temperature Mössbauer spectra may prove to be more useful in characterizing the bonding in these compounds than isomer shift and quadrupole splitting values when only the ground state Kramers doublet ($Ms = \pm 1/2$) level is populated.

Acknowledgement

This work was supported by a grant from the National Institutes of Health (AM16995).

References

1 D. Dolphin (ed.), *The Porphyrins,* Academic Press, New York, 1978.
2 W. R. Scheidt and C. A. Reed, *Chem. Rev., 81* (1981) 543.
3 G. E. Toney, L. W. terHaar, J. E. Savrin, A. Gold, W. E. Hatfield and R. Sangaiah, *Inorg. Chem., 23* (1984) 2561.
4 G. E. Toney, A. Gold, J. Savrin, L. W. terHaar, R. Sangaiah and W. E. Hatfield, *Inorg. Chem., 23* (1984) 4350.
5 M. A. Phillippi, N. Baenziger and H. M. Goff, *Inorg. Chem., 20* (1981) 3904.
6 A. D. Boersma and H. M. Goff, *Inorg. Chem., 21* (1981) 581.
7 D. R. English, D. N. Hendrickson, K. S. Suslick, C. W. Eigenbrot, Jr. and W. R. Scheidt, *J. Am. Chem. Soc., 106* (1984) 7258.
8 A. Tabard, P. Cocolios, G. Lagrange, R. Gerardin, J. Hubsch, C. Lecomte, J. Zarembowitch and R. Guilard, *Inorg. Chem., 27* (1988) 110.
9 H. Ogoshi, H. Sugimoto, Z-I. Yoshida, H. Kobayashi, H. Sakai and Y. Maeda, *J. Organomet. Chem., 234* (1982) 185.
10 P. Dopplet, *Inorg. Chem., 23* (1984) 4009.
11 H. Goff and E. Shimomura, *J. Am. Chem. Soc., 102* (1980) 31.
12 K. Shelly, T. Bartczak, W. R. Scheidt and C. A. Reed, *Inorg. Chem., 24* (1985) 4325.
13 K. Shelly, C. A. Reed, Y. J. Lee and W. R. Scheidt, *J. Am. Chem. Soc., 108* (1986) 3117.
14 G. C. Brackett, P. L. Richards and W. S. Caughey, *J. Chem. Phys., 54* (1971) 4383.
15 D. H. Dolphin, J. R. Sams, T. B. Tsin and K. L. Wong, *J. Am. Chem. Soc., 100* (1978) 1711.
16 C. Maricondi, D. K. Straub and L. M. Epstein, *J. Am. Chem. Soc., 94* (1972) 4157.
17 M. A. Torréns, D. K. Straub and L. M. Epstein, *J. Am. Chem. Soc., 94* (1972) 4162.
18 A. D. Adler, F. R. Longo, J. D. Finarelli, J. Goldmacher, J. Assour and L. Korsakoff, *J. Org. Chem., 32* (1967) 476.
19 A. D. Adler, F. R. Longo, F. Kampas and J. Kim, *J. Inorg. Nucl. Chem., 32* (1970) 2443.
20 S. Patai (ed.), *The Chemistry of the Hydroxyl Group,* Interscience, New York, 1971, Ch. 7 and 20.
21 C. V. King and A. P. Marion, *J. Am. Chem. Soc., 66* (1944) 977.
22 R. A. Robinson and R. G. Bates, *J. Res. Bur. Stand., 70A* (1966) 553.
23 A. Alpert and J. N. Phillips, *J. Chem. Soc.,* (1956) 1294.
24 N. K. Dutt and T. Seshadri, *Bull. Chem. Soc. Jpn., 40* (1967) 2281.
25 W. Konig and R. Geiger, *Chem. Ber., 103* (1970) 2024.
26 N. A. Puttnam, *J. Chem. Soc.,* (1960) 2937.
27 P. J. Elving and E. C. Olson, *J. Am. Chem. Soc., 78* (1956) 4206.
28 R. H. Zucal and J. A. Dean, *Anal. Chem., 35* (1963) 988.
29 R. P. Bell, *Acids and Bases,* Methuen, London, 1969, p. 37.
30 J. Bessiere, *Anal. Chim. Acta, 52* (1970) 55.
31 S. Dattagupta, *Phys. Rev., 12B* (1975) 3584.
32 C. Lecomte, D. L. Chadwick, P. Coppens and E. D. Stevens, *Inorg. Chem., 22* (1983) 2982.
33 H. Havermann, W. Haberditzl and K.-H. Mader, *Z. Phys. Chem., 218* (1961) 71.
34 W. S. Caughey, in G. L. Eichhorn (ed.), *Inorganic Biochemistry,* Vol. 2, Elsevier, New York, 1973, Ch. 24.
35 D. W. Smith and R. P. J. Williams, *Struct. Bonding (Berlin), 7* (1970) 1.
36 T. Nozawa, S. Ookubo and M. Hatano, *J. Inorg. Biochem., 12* (1980) 253.

37 Unpublished observation from our laboratory.
38 von H. J. Lindner and G. Gottlicher, *Acta Crystallogr., Sect. B, 25* (1969) 832.
39 A. T. Pilipenko, E. A. Shpak and L. L. Shevchenko, *Russ. J. Inorg. Chem., 12* (1967) 237.
40 L. J. Bellamy, *The Infrared Spectra of Complex Molecules,* Wiley, New York, 3rd edn., 1975.
41 D. van der Helm, L. L. Merritt and R. Degeilh, *Acta Crystallogr., 18* (1965) 355.
42 R. S. Bottei and R. G. Scheggenburger, *J. Inorg. Nucl. Chem., 32* (1970) 1525.
43 A. R. Katrizky and R. A. Jones, *J. Chem. Soc.,* (1960) 2947.
44 M. Tsuboi, *J. Am. Chem. Soc., 79* (1957) 1351.
45 J. R. Ferraro and J. S. Ziomek, *J. Inorg. Nucl. Chem., 26* (1964) 1397.
46 D. E. C. Corbridge and E. J. Lowe, *J. Chem. Soc.,* (1954) 493.