Table III

Compound	Temp, °K	δ, mm/sec[a]	Δ, mm/sec	Ref
$[(PPFe)_2O]$[b]	298	0.58	0.74	6
	298	0.58	0.54	3
	5	0.68	0.98	3
$[(PPDFe)_2O]$[c]	298	0.66	0.66	6
$[(DPDFe)_2O]$[d]	298	0.55	0.57	3
$[(TPPFe)_2O]$	298	0.55	0.62	12
	77	0.67	0.66	12
	4.2	0.68	0.67	12
$[(SalenFe)_2O]$[e]	300	0.61	0.73	12
	80	0.65	0.81	13

[a] Relative to sodium nitroprusside. [b] PP = protoporphyrin dianion. [c] PPD = protoporphyrin dimethyl ester dianion. [d] DPD = deuteroporphyrin dimethyl ester dianion. [e] Salen = *N*,*N*′-ethylenebis(salicylidenimine) dianion.

(uncertainty in measurement, ±0.03 mm/sec.). There is little dependence of the splitting on the porphine substituent, in contrast to the mononuclear pentacoordinate iron(III) complexes of these same porphines.[9] The relatively small values of the quadrupole splittings in these compounds indicate high spin iron(III) because for such an *S*-state ion only lattice effects contribute to the electric field gradient. Much greater splittings are expected for $S = {}^3/_2$ and $S = {}^1/_2$ ground states of iron(III); about 2.5 mm/sec for $S = {}^3/_2$[10] and about 1.5 mm/sec for $S = {}^1/_2$.[11] Also, low spin iron(III) compounds usually show smaller isomer shifts.

The Mössbauer data obtained for these complexes can be compared with the data in the literature on similar binuclear compounds of 5-coordinated iron(III), containing oxygen bridges (see Table III).[12,13]

The absence of magnetic broadening of the peaks is due to strong spin-spin coupling between the two $S = {}^5/_2$ iron(III) ions *via* the oxygen bridge, leading to very rapid relaxation. Magnetic measurements indicate the coupling to be antiferromagnetic.[3,14] Recently the exchange coupling constant J in the Hamiltonian $H = -JS_1 \times S_2$ has been measured[15] for $[(TPPFe)_2O]$ ($J = -309\ cm^{-1}$) and for the tetrakis(*p*-tolyl) derivative ($J = -335\ cm^{-1}$). These values are significantly greater than the value of $J = -200\ cm^{-1}$ found for the salen complex, $[(salen\text{-}Fe)_2O]$, from magnetic susceptibility data.[16]

Acknowledgment. This work was supported by the Division of Biology and Medicine, Atomic Energy Commission, through contract AT(30-1) 3859.

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(9) M. A. Torréns, D. K. Straub, and L. M. Epstein, *J. Amer. Chem. Soc.*, **94**, 4157 (1972).

(10) L. M. Epstein and D. K. Straub, *Inorg. Chem.*, **8**, 560 (1969).

(11) V. I. Goldanskii and R. H. Herber, Eds., "Chemical Applications of Mössbauer Spectroscopy," Academic Press, New York, N. Y., 1968.

(12) C. Maricondi, Ph.D. Thesis, Department of Chemistry, University of Pittsburgh, 1969.

(13) R. R. Berrett, B. W. Fitzsimmons, and A. A. Owasu, *J. Chem. Soc. A*, 1575 (1968).

(14) C. Maricondi, W. Swift, and D. K. Straub, *J. Amer. Chem. Soc.*, **91**, 5205 (1969).

(15) P. D. W. Boyd and T. D. Smith, *Inorg. Chem.*, **10**, 2041 (1971).

(16) J. Lewis, F. E. Mabbs, and A. Richards, *J. Chem. Soc. A*, 1014 (1967).

Mössbauer Studies on Hemin Derivatives of α,β,γ,δ-Tetraarylporphines

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Abstract: The Mössbauer spectra of α,β,γ,δ-tetrakis(*p*-chlorophenyl)porphinatoiron(III) chloride and iodide, α,β,γ,δ-tetrakis(*p*-methoxyphenyl)porphinatoiron(III) chloride, bromide, iodide, azide, thiocyanate, acetate, and trifluoroacetate, and α,β,γ,δ-tetrakis(pentafluorophenyl)porphinatoiron(III) chloride and bromide have been measured at 298, 78, and 4.2°K. At 298 and 78°K the spectra show a broad asymmetric peak with a shoulder on the high-energy side; at 4.2°K this asymmetric broadening reverses for several of the hemins, particularly the *p*-methoxyphenyl derivatives, to the low-energy side. A change in the direction of the magnetic axis with respect to V_{zz} is postulated to account for this reversal. The quadrupole splittings depend upon the phenyl substituent as well as the axial ligand.

Studies of the effect of the porphine substituents on the electronic environment of the iron in a hemin have been carried out by a variety of physical methods.[2] Mössbauer measurements have shown that the quadrupole splitting values found for hemins are sensitive to the nature of the fifth group and also to the substituents on the porphine ring.[3] Most of the measurements on iron porphyrins have employed porphyrins with varying substituents on the 1, 2, . . ., 8 positions, *i.e.*, directly attached to the conjugated system. It is of interest to determine just how minimal structural changes in the porphyrin can be and still give different Mössbauer parameters for the iron complexes. This paper reports a Mössbauer study of hemin complexes with α,β,γ,δ-tetrakis(substituted phenyl)porphines which supplements work on the unsubstituted series.

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(1) Taken in part from the Ph.D. dissertation of M. A. Torréns, University of Pittsburgh, 1970.

(2) J. E. Falk, "Porphyrins and Metalloporphyrins," Elsevier, New York, N. Y., 1964.

(3) For references see C. Maricondi, D. K. Straub, and L. M. Epstein, *J. Amer. Chem. Soc.*, **94**, 4157 (1972).

Table I. Analytical Data on Hemin Derivatives

Compound	C Calcd	C Found	H Calcd	H Found	N Calcd	N Found	Halogen Calcd	Halogen Found
[PMXPPFeCl]	69.95	70.26	4.37	4.20	6.80	6.84	4.31	4.55
[PClPPFeCl]	62.72	63.11	2.85	3.25	6.65	6.45	21.06	20.94
[PFPP^{57}FeCl]							3.34	2.98
[PMXPP^{57}FeBr]					6.45	6.49	9.22	8.86
[PFPP^{57}FeBr]							7.22	6.55
[PMXPPFeI]					6.11	5.98	13.83	13.06
[PClPPFeI]	56.59	56.11	2.58	2.59	6.00	6.10	13.61 (I)	14.14
[PMXPPFeCH$_3$CO$_2$]	70.84	70.80	4.60	4.57	6.61	6.76		
[PMXPPFeCF$_3$CO$_2$]	66.59	66.43	4.00	3.94	6.22	6.23	6.33	5.88
[PMXPPFeNCS]	69.50	65.28	4.26	3.87	8.27	7.71	3.78 (S)	3.62
[PMXPPFeN$_3$]	69.31	66.12	4.34	3.83	11.82	9.10		

In these complexes, the aryl groups are not conjugated to the porphine ring.

Experimental Section

All chemicals were reagent grade and used without further purification. The μ-oxo-bis[$\alpha,\beta,\gamma,\delta$-tetrasubstituted porphinatoiron(III)] compounds were prepared as described in the previous paper[4] and were analytically and spectroscopically pure.

Conversion of μ-Oxo Compounds into Halide Derivatives. The chlorides and bromides were prepared by stirring vigorously for 6 hr or longer benzene solutions of the μ-oxo derivatives (about 60 mg in 50 ml of benzene) with 10 ml of a saturated aqueous solution of sodium chloride or bromide made strongly acidic with hydrochloric or hydrobromic acid. The iodides, which were the hardest to obtain pure, were prepared by stirring the benzene solutions with concentrated aqueous hydriodic acid. When hydriodic acid is used, a bright green benzene-insoluble precipitate, probably a chlorin, forms, which is removed by filtering the mixture through glass wool.

The μ-oxo derivatives give greenish brown benzene solutions; upon addition of the acidic halide the color changes to brown or reddish brown. This color change is quite characteristic and serves as a quick qualitative indication that the halide derivative has formed.

The benzene layer was then carefully removed, poured into water without shaking (to avoid reversion to the μ-oxo derivative), again separated from the aqueous layer, and dried overnight over anhydrous sodium sulfate. After the dried benzene solution was filtered through glass wool, it was evaporated to dryness under vacuum with gentle heating. The crystalline residue was dissolved in methylene chloride and the solution filtered and allowed to stand in a desiccator over pentane until crystallization was complete. The bright violet crystals were collected, washed with pentane, and dried in vacuum at 100° for several hours.

Acetato-$\alpha,\beta,\gamma,\delta$-tetrakis($p$-methoxyphenyl)porphinatoiron(III) ([PMXPPFeCH$_3$CO$_2$]). About 70 mg of the corresponding μ-oxo derivative was dissolved in 50 ml of benzene and stirred for over 10 hr with 10 ml of a saturated aqueous solution of sodium acetate containing acetic acid. This procedure was repeated three times. The benzene layer was then treated in the same way as for the preparation of the halides.

Trifluoroacetato-$\alpha,\beta,\gamma,\delta$-tetrakis($p$-methoxyphenyl)porphinatoiron(III) ([PMXPPFeCF$_3$CO$_2$]). About 70 mg of the μ-oxo derivative was dissolved in 50 ml of benzene, 10 ml of trifluoroacetic anhydride was added, and the mixture refluxed for 1–2 hr. The solvent mixture was evaporated to dryness under vacuum and the crystalline residue washed well with pentane and dried in vacuum at 100° for 20 hr.

Thiocyanato-$\alpha,\beta,\gamma,\delta$-tetrakis($p$-methoxyphenyl)porphinatoiron(III) ([PMXPPFeNCS]). A solution of 60 mg of the μ-oxo derivative in 50 ml of benzene was stirred with a saturated aqueous solution of sodium thiocyanate made strongly acidic with sulfuric acid. The complex was isolated and recrystallized twice in the usual way.

Azido-$\alpha,\beta,\gamma,\delta$-tetrakis($p$-methoxyphenyl)porphinatoiron(III) ([PMXPPFeN$_3$]). This was prepared exactly analogously to the thiocyanate, except dilute aqueous sodium azide acidified with sulfuric acid was used.

The yields of the hemin derivatives, based on the μ-oxo complexes as starting materials, were about 80%, except for the iodide derivatives which averaged about 50%, due to the chlorin by-product.

Elemental analyses were performed by Galbraith Laboratories or Alfred Bernhardt. The results are given in Table I. The azide gave a low nitrogen analysis but appeared to be spectroscopically pure.

Mössbauer spectra were obtained as described previously.[4] A sodium nitroprusside absorber (splitting 1.705 mm/sec) was used to calibrate the velocity scale and provide the zero reference for the isomer shifts. Frequent checks were also made with ^{57}Fe foil. The data were fit with a least-squares approximation assuming Lorentzian line shapes of equal width and plotted with a Calcomp plotter. The estimated uncertainty in both the isomer shifts and quadrupole splittings is ±0.04 mm/sec.

Results

Mössbauer spectra were measured at 298, 78, and 4.2°K on all the compounds listed in Table I. The spectra showed the general characteristics associated with the hemins: an unsymmetrical, broad, unresolved doublet at 298 and 78°K and a much more symmetrical and resolved doublet at 4.2°K (see Figures 1 through 7). Mössbauer parameters at 4.2°K are given in Table II.

Table II. Mössbauer Data for Pentacoordinated Derivatives at 4.2°K

Compound	δ, mm/sec[a]	Δ, mm/sec	Γ, mm/sec[b]	R[c]
1. [PClPPFeCl]	0.71	0.73	0.33	0.93
2. [PClPPFeI]	0.77	1.04	0.35	1.16
3. [PFPPFeCl]	0.65	0.85	1.20	0.81
4. [PFPPFeBr]	0.70	1.04	0.72	1.31
5. [PMXPPFeNCS]	0.69	0.63	0.62	0.70
6. [PMXPPFeN$_3$]	0.71	0.67	0.57	0.80
7. [PMXPPFeCH$_3$CO$_2$]	0.73	0.92	0.49	0.96
8. [PMXPPFeCl]	0.64	1.03	0.81	0.48
9. [PMXPPFeBr]	0.65	1.07	1.02	0.65
10. [PMXPPFeCF$_3$CO$_2$]	0.65	1.10	0.91	0.58
11. [PMXPPFeI]	0.76	1.33	0.72	0.60

[a] Relative to sodium nitroprusside. [b] Full width at half-maximum. [c] Lower velocity peak over higher velocity peak.

The nonhalide derivatives showed the same behavior as the halide derivatives: *e.g.*, for the acetate derivative [PMXPPFeCH$_3$CO$_2$], a strong absorption appears near zero velocity broadened on the positive velocity (higher energy) side. At 78°K, the broadening becomes very distinct, resembling the bromide derivative and at 4.2°K (see Figure 4) a well-resolved symmetric pair of lines is found. The acetate derivative is the only one from the (PMXPPH$_2$) series for which a symmetric doublet is

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[4] M. A. Torréns, D. K. Straub, and L. M. Epstein, *J. Amer. Chem. Soc.*, **94**, 4160 (1972).

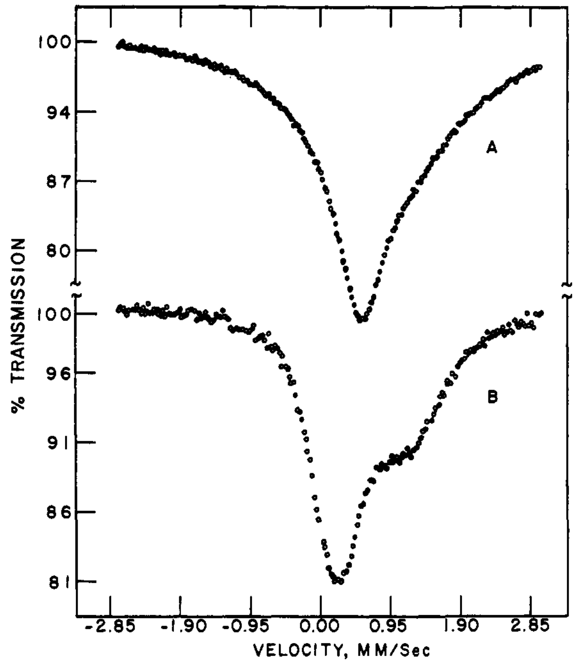

Figure 1. Mössbauer spectra at 78°K of A [PFPP^{57}FeCl] and B [PFPP^{57}FeBr].

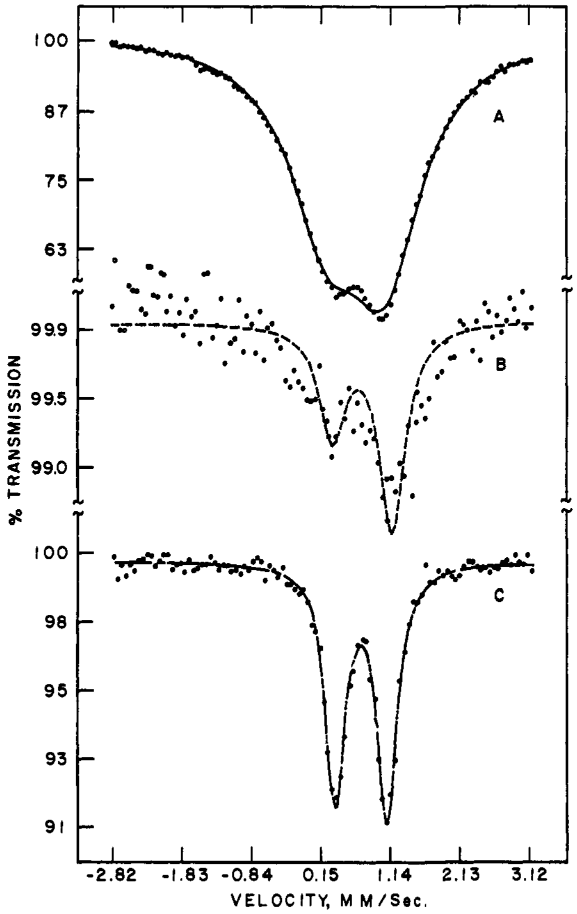

Figure 2. Mössbauer spectra at 4.2°K of A [PFPP^{57}FeCl], B [PMXPPFeCl], and C [PClPPFeCl].

obtained at liquid helium temperature. Although the line widths are still 2.5 times the natural line width, they are the narrowest of all the derivatives in this series.

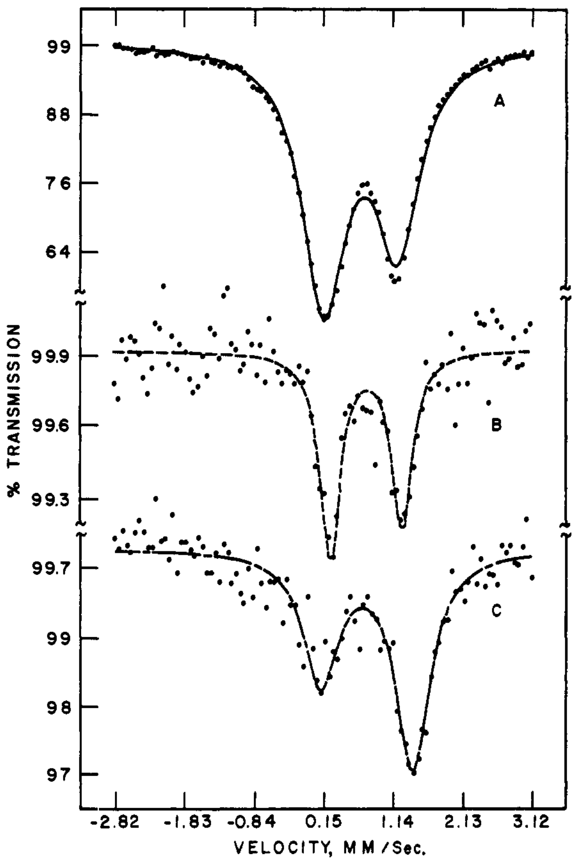

Figure 3. Mössbauer spectra at 4.2°K of A [PFPP^{57}FeBr], B [PClPPFeI], and C [PMXPPFeI].

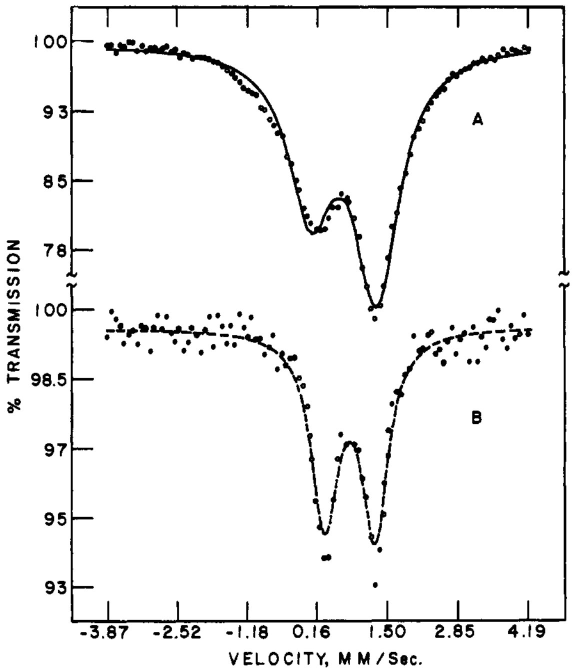

Figure 4. Mössbauer spectra at 4.2°K of A [PMXPPFeBr] and B [PMXPPFeCH$_3$CO$_2$].

A similar derivative with trifluoroacetate showed a more diffuse spectrum at 298°K than the acetate. Figure 7 shows the spectrum at 20°K; two broad lines can be seen which are of equal intensity, with approximate values of $\delta = 0.7$ mm/sec, $\Delta = 1.0$ mm/sec, and

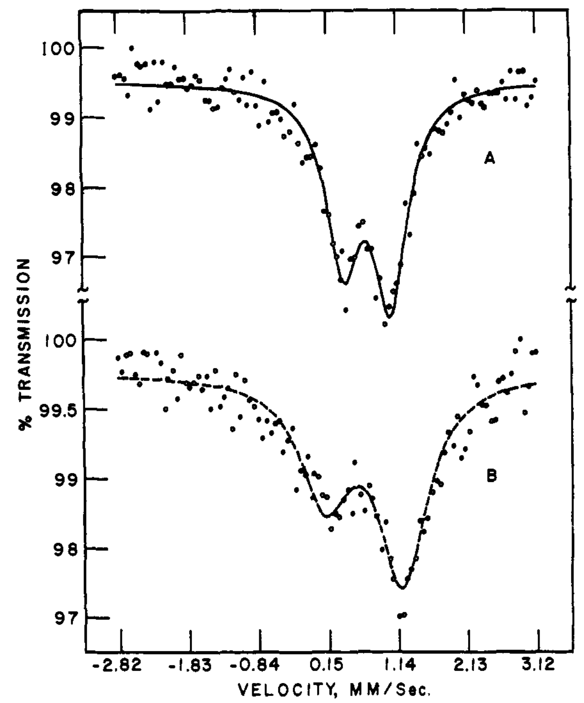

Figure 5. Mössbauer spectra at 4.2°K of A [$PMXPPFeN_3$] and B [$PMXPPCF_3CO_2$].

Γ = 1.1 mm/sec. Figure 5 shows the spectrum at 4.2°K.

It appears that between 78 and 4.2°K there is a transition temperature where the initially asymmetric pair becomes symmetric in all of these hemins. Upon further decrease in temperature the peaks again become asymmetric, but now it is the lower energy peak which is broadened.

The peaks in the azide complex [$PMXPPFeN_3$] are not as resolved at 298°K as those of the acetate derivative. At 4.2°K the lower energy peak is broadened and less intense (see Figure 5).

Discussion

Isomer Shifts. The isomer shifts (δ) at 4.2–6°K of the hemins reported in this study (Table II) and those reported in the literature[3,5] (Table III) cover the range 0.58–0.77 mm/sec, with an average value of 0.67 mm/sec. A value of about 0.7 mm/sec is expected for high spin, 5-coordinated iron(III) with little π bonding (the average δ values at 78°K for several iron(III) complexes of fluoride, chloride, water,[6] and various silicates[7] are 0.6 ± 0.1 mm/sec for 4-coordinated iron(III) and 0.8 ± 0.1 mm/sec for 6-coordinated iron(III)).

Table III. Mössbauer Parameters at 4.2–6°K for Hemins Reported in the Literature

Hemin[a]	δ, mm/sec	Δ, mm/sec	Ref
[TPPFeNCS]	0.66	0.49	3
[TPPFeCl]	0.68	0.46	3
[TPPFeBr]	0.72	0.72	3
[TPPFeI]	0.72	0.75	3
[DPFeF]	0.61	0.78	5
[$DPFeCH_3CO_2$]	0.67	0.81	5
[$DPFeN_3$]	0.65	0.83	5
[PPFeCl]	0.61	0.83	5
[MPFeCl]	0.58	0.93	5
[DPDFeCl]	0.58	0.89	5
[DPDFeBr]	0.64	1.02	5

[a] Abbreviations: TPP, $\alpha,\beta,\gamma,\delta$-tetraphenylporphine dianion; DP, deuteroporphyrin IX dimethyl ester dianion; PP, protoporphyrin IX dianion; MP, mesoporphyrin IX dianion; and DPD, 2,4-diacetyldeuteroporphyrin IX dimethyl ester dianion.

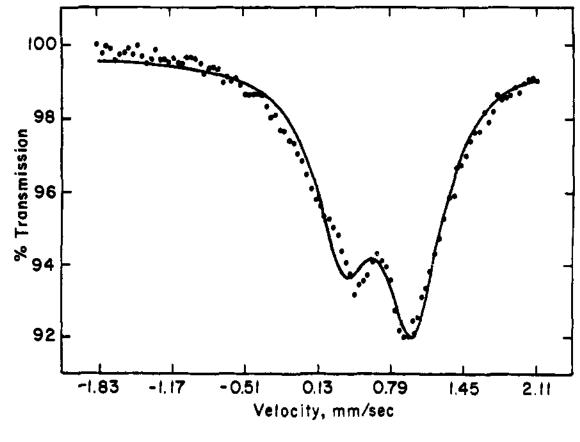

Figure 6. Mössbauer spectrum of [PMXPPFeNCS] at 4.2°K.

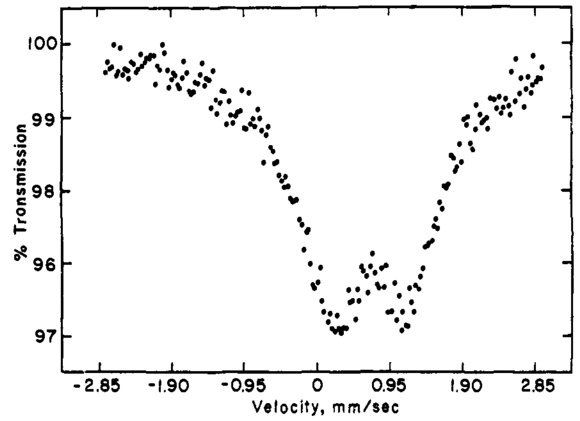

Figure 7. Mössbauer spectrum of [$PMXPPFeCF_3CO_2$] at 20°K.

The dependence of δ on the fifth group in a given porphine series results in the following order of decreasing δ values: $F^- < Cl^- \sim CF_3CO_2^- < Br^- \sim NCS^- \sim N_3^- < CH_3CO_2^- < I^-$. The order is due to increasing π bonding to the iron.[8]

The dependence of δ on the phenyl substituents in a given halide series is not so marked: for the four chlorides, the range of δ values is 0.64–0.71 mm/sec; for the three bromides, 0.65–0.70 mm/sec; and for the three iodides, 0.72–0.77 mm/sec. Except perhaps for the chlorides, the ranges are within experimental error. A dependence is clearly shown, however, when comparing methine-substituted to pyrrole-substituted porphines.

Quadrupole Splittings. For the chloride derivatives, the order of increasing Δ values is [TPPFeCl] < [PClPPFeCl] < [PFPPFeCl] < [PMXPPFeCl]. The same porphine order holds for the bromide and iodide de-

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(5) T. H. Moss, A. J. Bearden, and W. S. Caughey, *J. Chem. Phys.*, **51**, 2624 (1969).

(6) V. I. Goldanskii and R. H. Herber, Ed., "Chemical Applications of Mössbauer Spectroscopy," Academic Press, New York, N. Y., 1968.

(7) G. M. Bancroft, A. G. Maddock, and R. G. Burns, *Geochim. Cosmochim. Acta*, **31**, 2219 (1967).

(8) G. Harris, *J. Chem. Phys.*, **48**, 2191 (1968).

rivatives. This dependence of Δ on the phenyl substituents is unexpected, since the phenyl rings are not conjugated to the porphyrin ring (they are probably nearly perpendicular to this ring) and any electronic effects of these substituents must be transmitted to the porphine π system by the σ bond between the phenyl group and the methine carbon. Substituent effects on the quadurpole splittings (and on the zero field splitting, for that matter) have been observed previously, but with substituents directly on the porphine ring (the 1, 2,..., 8 positions).[3]

It has been established from X-ray data[9,10] that the four nitrogen atoms in the porphine ring are not strictly planar, and the magnitude of the porphine skeleton ruffling depends upon the substituents as well as the coordinated metal ion. No $\alpha,\beta,\gamma,\delta$-tetrakis(substituted phenyl)porphine complexes have been studied by X-ray spectroscopy, so there is no incontrovertible evidence that the seemingly very minimal change resulting from *p*-chloro or *p*-methoxy substitution, for example, affects the conformation of the porphine ring. Since the porphines are all symmetrically tetrasubstituted, the nitrogens should be electronically equivalent. Since there is no evidence to the contrary, we could ascribe the differences in Δ to postulated differences in the dispositions of the nitrogen atoms in the ring. If the phenyl substituents do affect the conformations of the four nitrogens, it is still not known whether this effect is electronic or morphological in origin. Comprehensive measurements of a few of these compounds in homogeneous frozen solution are required to settle the point definitely; these have not yet been made.

Another source of differences in the splitting could be differences in the distance of the iron from the mean porphyrin plane. In chlorohemin ([PPFeCl]) and in [TPPFeCl] these distances are 0.475[11] and 0.383 Å,[12] respectively, so the distance is sensitive to the nature of the porphyrin.

The quadrupole splitting is very sensitive to the nature of the fifth ligand in the hemins. For the seven derivatives of [PMXPPFeX], Δ varies by more than a factor of two, and increases in the order $NCS^- \sim N_3^- < CH_3CO_2^- < Cl^- < Br^- < CF_3CO_2^- < I^-$. This ordering is consistent with data on the other hemins investigated so far (see Table III). The thiocyanate appears to be bonded to the iron through the nitrogen atom: the value of Δ is very close to that of the azide derivative and the smallest of any of the [PMXPPFeX] complexes, indicating the most symmetrical electronic environment for the iron. Sulfur bonded thiocyanate should be more analogous to bromide or iodide with regard to size and polarizability and thus give a much larger splitting than the one observed.

The relationship between Δ and *D*, the zero field splitting parameter, has been discussed in a preceding paper.[3] Moss, *et al.*,[5] made a Mössbauer study of a series of porphyrin derivatives and observed the temperature range in which the asymmetry of the peaks disappeared. They noticed that this temperature range rises in the same order as the quadrupole splitting for different axial ligand substitutions. In the series they studied they found the following order for increasing value of Δ: $F^- < CH_3CO_2^- < N_3^- < Cl^- < Br^-$. This is the same order followed by *D*.[13]

Although a direct correlation might be made between the temperature range of the disappearance of peak asymmetry and *D* for a given series of the same porphyrin, it may not hold for the same axial ligand with different porphyrins. For example, [PClPPFeCl] (also (PClPPFeI]) gave at 4.2°K the smallest line widths obtained for any of the halides listed in Table II, indicating *D* to be larger for [PClPPFeCl] than for [PFPPFeCl] or [PMXPPFeCl] or even [PMXPPFeI]. However, the ($PClPPH_2$) complexes have smaller Δ values than the other two porphine derivatives, leading to the opposite conclusion regarding *D* values, if *D* is assumed to vary directly with Δ. Presumably the Δ values are a more reliable guide in predicting the relative magnitudes (but not absolute magnitudes when different types of axial ligands are considered) of *D*.

Another example is seen in two derivatives of the same porphine: [$PMXPPFeCH_3CO_2$] and [$PMXPPFeCF_3CO_2$]. The Mössbauer spectra for these two derivatives at 4.2°K (Figures 4 and 5) show a symmetric doublet for the acetate but an asymmetric doublet for the trifluoroacetate, from which one might infer that *D* is larger for the acetate. The trifluoroacetate has the significantly larger Δ value. The difference in Δ values between the acetate and trifluoroacetate can be explained by invoking the greater electron-withdrawing ability of the CF_3 group. This effect will remove the axial negative charge further from the iron, thus providing a less negative contribution to the electric field gradient along the axis.

The unusual reversal of the asymmetric broadening from the high-energy to the low-energy side of the Mössbauer absorption upon decrease in temperature of the sample (discussed in ref 3 with regard to [TPPFeNCS]) is shown to the greatest extent by the [PMXPPFeX] derivatives. (The effect is best seen in Figures 4 and 6 for the bromide and thiocyanate complexes.) That there are some temperatures between 78 and 4.2°K at which the spectra are symmetrical is indicated by the spectrum of [$PMXPPFeCF_3CO_2$] at about 20°K. (This was the only sample studied at a temperature between 78 and 4.2°K.)

The reversal of intensities can be explained by a change of the magnetic axis direction within the molecule, from collinearity with V_{zz} at higher temperatures to perpendicularity at the lower temperatures. The component of the field gradient with respect to such an axis is $V_{zz}/2$ so that the lower energy line becomes the $\pm 3/2 \rightarrow \pm 1/2$ transition and is magnetically broadened. The same characteristic spectra at 4.2°K are shown by all [PMXPPFeX] derivatives, even the bromide and iodide, for which *D* must be larger than 10 cm^{-1}, based on the measured values of similar hemins. At 4.2°K for $D = 10\ cm^{-1}$, the $\pm ^3/_2$ electronic level is 0.2% populated, so this level cannot be the source of the magnetic broadening and asymmetry. A possible explanation of this spin flip leading to the reversed magnetic broadening has been suggested by Ooster-

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[9] J. L. Hoard, M. J. Hamor, and T. A. Hamor, *J. Amer. Chem. Soc.*, **85**, 2334 (1963).

[10] M. J. Hamor, T. A. Hamor, and J. L. Hoard, *ibid.*, **86**, 1938 (1964).

[11] D. F. Koenig, *Acta Crystallogr.*, **18**, 663 (1965).

[12] J. L. Hoard, G. H. Cohen, and M. D. Glick, *J. Amer. Chem. Soc.*, **89**, 1992 (1967).

[13] P. L. Richards, W. S. Caughey, H. Eberspaecher, G. Feher, and M. Malley, *J. Chem. Phys.*, 47, 1187 (1967).

huis.[14] When $M_s = \pm^1/_2$, the major component of the spin vector is in the xy plane and the nucleus will sense this component provided that the precession time of the spin vector about the z axis is long compared to the Larmor precession time of the nuclear spin. Oosterhuis estimates that the precession time will be 10^{-8} sec or greater if the magnetic field along the z axis (due to neighboring magnetic dipoles in the lattice) is about 10 G; this is sufficiently long to observe magnetic broadening. If this explanation is correct, the phenomenon should be general for these high spin ferric compounds with large positive D, and its extent will depend on the magnitude of the adventitious magnetic field along the z axis. One might suppose this broadening could be quenched by application of a modest external field (<1000 G), although attempts by Oosterhuis to observe such a quenching have so far been unsuccessful.[14]

Acknowledgments. We wish to thank Professor W. Oosterhuis, Department of Physics, Carnegie-Mellon University, for many helpful discussions. This work was supported by the Division of Biology and Medicine, Atomic Energy Commission, through contract AT(30-1) 3859.

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(14) W. Oosterhuis, Carnegie-Mellon University, private communication.

Pyridinium Iodide Salts. Correlation of Experimental Parameters with Self-Consistent Extended Hückel (SCEH) Calculations

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Abstract: Pyridinium iodide salts possess an iodide to ring charge-transfer (CT) band; two such bands are generally observed in nonpolar solvents. Both the absolute and relative energies of these bands are sensitive to the nature and position of the substituent on the pyridinium ring, as well as to the nature of the solvent. Self-consistent extended Hückel (SCEH) calculations have been performed for the unsubstituted and the 2-, 3-, and 4-cyano (and acetyl) pyridinium ions. The calculated difference between the energy of the first (lowest) and second (next highest) vacant molecular orbital of the pyridinium ion is in good agreement with the observed separation of the two CT bands in methylene chloride. This supports other experimental results which indicate that the second CT band does not arise from the excited state ($^2P_{1/2}$) of the iodine atom. These and other results of the calculation are discussed in terms of various experimental parameters.

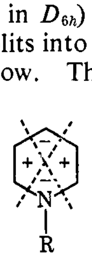
The first (long wavelength) electronic absorption band of pyridinium iodide salts has been studied extensively. It arises from charge transfer from iodide to the pyridinium ion.[1,2] In nonpolar solvents a second CT band, at shorter wavelength than the first, is observed and has been ascribed to the first excited state of the iodine atom ($^2P_{1/2}$).[3] Recent experimental results indicate that the second band may in fact result from charge transfer to the second vacant molecular orbital of the pyridinium ion.[2,4] We have therefore performed self-consistent extended Hückel (SCEH) calculations on various pyridinium ions and compared the results with experimental parameters including CT band energies.

Calculations and Experimental

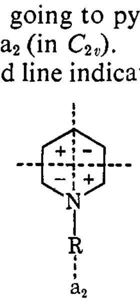
The calculations were performed by the method suggested by Harris[5] using a modified procedure of Kalman and Clarke.[6] All valence orbitals and electrons were included. The electron affinities of the pyridinium ions were taken as the negative of the ionization potential of the corresponding pyridinyl radicals. The band energies and the rate constants were determined in methylene chloride.[2]

Results and Discussion

Band Energies. The lowest unoccupied molecular orbital (LUMO) in benzene is a doubly degenerate π orbital (E_{2u} in D_{6h}) and on going to pyridine or pyridinium ion splits into b_1 and a_2 (in C_{2v}). These orbitals are shown below. The dotted line indicates the nodes.



b_1



a_2

The lowest energy orbital has been assigned as b_1 by Kosower and Poziomek on the basis of infrared

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(1) E. M. Kosower and J. A. Skorcz, *J. Amer. Chem. Soc.*, **82**, 2195 (1960).

(2) R. A. Mackay, J. R. Landolph, and E. J. Poziomek, *ibid.*, **93**, 5026 (1971), and references therein.

(3) E. M. Kosower, J. A. Skorcz, W. M. Schwarz, Jr., and J. W. Patton, *ibid.*, **82**, 2188 (1960).

(4) J. W. Verhoeven, I. P. Dirkx, and Th. J. de Boer, *Tetrahedron*, **25**, 3395 (1969).

(5) F. E. Harris, *J. Chem. Phys.*, **48**, 4027 (1968).

(6) B. Kalman and G. Clarke, *ibid.*, submitted for publication.