Mössbauer Studies on Oxo-Bridged Iron(III) Porphines

Manuel A. Torréns,[1] Darel K. Straub,* and L. M. Epstein

Contribution from the Department of Chemistry, University of Pittsburgh, Pittsburgh, Pennsylvania 15213. *Received May 21, 1971*

Abstract: The Mössbauer spectra of eight μ-oxo-bis[$\alpha,\beta,\gamma,\delta$-tetrakis(aryl, pyridyl or thienyl)porphinatoiron(III)] complexes have been measured at 298, 78, and 4.2°K. All of these show a well-resolved, reasonably symmetric doublet at the three temperatures. There is little dependence of the quadrupole splitting on the meso substituents, in contrast to the hemin cases. The two iron atoms, antiferromagnetically coupled through the oxygen, are most likely in a $S = {}^5/_2$ spin state.

Recent investigations have shown that compounds originally thought to be hemin hydroxides actually are dimers involving an oxygen atom bridging two 5-coordinated iron(III) ions.[2-4] These dimers are easily formed whenever hemin derivatives (*e.g.*, hemin itself) are treated with aqueous base. Monomeric, 6-coordinated iron(III) hydroxo complexes are unknown except perhaps for protein derivatives such as methemoglobin and metmyoglobin, where the large protein moiety sterically prevents dimerization.

The Mössbauer spectra of four of these μ-oxo complexes, [$(TPPFe)_2O$],[3] [$(DPDFe)_2O$],[5] [$(DPFe)_2O$],[6] and [$(PPDFe)_2O$][6] (TPP indicates $\alpha,\beta,\gamma,\delta$-tetraphenylporphine dianion; DP, deuteroporphyrin dimethyl ester dianion; PP, protoporphyrin dianion; and PPD, protoporphyrin dimethyl ester dianion), have been reported. In this paper we report the Mössbauer spectra of eight new μ-oxo-bis[tetraarylporphinatoiron(III)] complexes.

Experimental Section

All solvents were reagent grade and were used without further purification. Aldehydes and pyrrole were obtained from Baker, Fisher, or Aldrich and were used as received. Chromatographic grade alumina and silica gel were obtained from Fisher.

Preparation of Porphines. The $\alpha,\beta,\gamma,\delta$-tetrasubstituted porphines were prepared from pyrrole and the aldehyde in refluxing propionic acid according to the method of Adler, *et al.*[7] Some of the porphines crystallized directly from the reaction mixture, *viz.*, the *p*-methoxyphenyl, 2-thienyl, *p*-chlorophenyl, and 1-naphthyl derivative. Other porphines required some modification in the general procedure. In these cases the black precipitate formed upon neutralization of the reaction mixture with 10 *N* ammonium hydroxide was washed well with methanol, dissolved in methylene chloride or chloroform, and chromatographed on an alumina column prepared with acetone or cyclohexane.

All the porphines were purified by chromatography on an alumina column with subsequent recrystallization from chloroform or methylene chloride–methanol or cyclohexane mixtures.

Preparation of μ-Oxo-bis[$\alpha,\beta,\gamma,\delta$-tetrasubstituted porphinatoiron(III)] Complexes. A refluxing solution of the porphine in glacial acetic acid was treated with ferrous acetate solution (prepared by dissolving iron powder in acetic acid) and the mixture refluxed until reaction was complete. Completeness of reaction was determined spectrophotometrically. The solution, presumably containing the hemin acetate, was diluted with water and the complex extracted into benzene. The benzene solution was then stirred with dilute aqueous potassium hydroxide for several hours, washed with water, and finally dried over anhydrous sodium sulfate.

To remove unreacted porphine, the benzene solution was stirred with silica gel. The iron complex is absorbed much more strongly on the silica gel than the free porphine. The pink benzene solution was discarded and the silica gel containing the complex was extracted with benzene–chloroform mixtures until the wash liquid was colorless, indicating the complete removal of free porphine.

The complex was removed from the brown silica gel by stirring with a benzene–methanol mixture (20 ml of benzene and 2 ml of methanol). The filtrate was evaporated to dryness and the residue recrystallized twice from methylene chloride–ether. The crystals were dried in vacuum at 100° for 20 hr.

The above procedure was modified somewhat for complexes of the tetrapyridyl series. The reaction mixture was first neutralized with 2 *N* aqueous potassium hydroxide before benzene extraction. The benzene layer was stirred with aqueous potassium hydroxide, washed with water, dried over sodium sulfate, and evaporated to dryness. The residue was recrystallized several times from methylene chloride–ether mixtures. Silica gel was not used because the complexes are so strongly absorbed they are difficult to remove.

Elemental analyses were performed by Galbraith Laboratories or Alfred Bernhardt; the results are given in Table I. Despite several different preparations, the 4-pyridyl derivative always gave low carbon and nitrogen analyses.

Mössbauer spectra were obtained with a scanned velocity spectrometer operating in the time mode. A 20-mCi source consisting of ^{57}Co diffused into chromium kept at room temperature was used. Calibration with sodium nitroprusside (quadrupole splitting, 1.705 mm/sec) was carried out before and after each run. A diffuser type cryostat obtained from Janis Corp., Boston, Mass., was used for measurements at liquid nitrogen and liquid helium temperatures.

A computer program, written originally by P. A. Flinn of Carnegie-Mellon University and modified by G. Von Nieda of this laboratory, was used to fit the data with a least-squares approximation assuming Lorentzian line shapes. A Calcomp plotter was used to plot data.

Results

The Mössbauer spectra of eight different μ-oxo-bis-[porphinatoiron(III)] complexes were measured at room, liquid nitrogen, and liquid helium temperatures. All of the spectra consisted of two well-resolved peaks, the usual quadrupolar pair. A representative spectrum is shown in Figure 1. Values of the isomer shift and quadrupole splitting are given in Table II.

The doublets consisted of narrow lines whose widths varied very slightly, if at all, with the porphine substituents or with temperature. Slight variations were observed in the relative peak intensities with change in temperature. At 298°K the higher energy peak usually had the slightly greater intensity. The reverse was true at the lower temperatures, although the effects were much smaller. The room temperature differences are probably due to a Goldanskii effect.

---

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

[2] E. B. Fleischer and T. S. Srivastava, *J. Amer. Chem. Soc.*, **91**, 2403 (1969).

[3] I. A. Cohen, *ibid.*, **91**, 1980 (1969).

[4] J. L. Hoard and B. Hoffman, private communication.

[5] N. Sadasivan, H. I. Eberspaecher, W. H. Fuchsman, and W. S. Caughey, *Biochemistry*, **8**, 534 (1969).

[6] W. Karger, *Ber. Bunsenges. Phys. Chem.*, **68**, 793 (1964).

[7] A. D. Adler, F. R. Longo, and J. D. Finarelli, *J. Org. Chem.*, **32**, 476 (1967).

Table I. Analytical Results for Porphines and μ-Oxo-bis[porphinatoiron(III)] Derivatives

Compound[a]	C		H		N	
	Calcd	Found	Calcd	Found	Calcd	Found
2PYRPH$_2$	77.64	77.54	4.24	4.34	18.11	17.95
[(2PYRPFe)$_2$O]	69.67	69.38	3.66	3.36	16.25	16.12
3PYRPH$_2$	77.64	77.24	4.24	4.41	18.11	17.97
[(3PYRPFe)$_2$O]	69.67	69.68	3.66	3.58	16.25	16.17
4PYRPH$_2$	77.64	74.15	4.24	4.50	18.11	16.90
[(4PYRPFe)$_2$O]	69.67	67.71	3.66	3.56	16.25	15.26
OMXPPH$_2$	78.44	78.14	5.22	5.47	7.63	7.81
[(OMXPPFe)$_2$O]	71.55	71.53	4.64	3.33	6.96	6.77
PMXPPH$_2$	78.44	77.98	5.22	5.26	7.63	8.15
[(PMXPPFe)$_2$O]	71.55	72.41	4.64	4.87	6.96	6.98
NAPPH$_2$	88.12	87.69	4.71	5.40	6.88	6.73
[(NAPPFe)$_2$O]	81.34	79.04	4.22	4.28	6.33	6.15
PClPPH$_2$	70.20	70.33	3.45	3.30	7.44	7.58
[(PClPPFe)$_2$O][b]	64.25	64.08	3.04	3.33	6.82	6.82
2THPH$_2$	67.76	67.37	3.48	3.66	8.77	8.79
[(2THPFe)$_2$O]	60.88	60.46	2.82	3.10	7.89	7.88

[a] Porphines are abbreviated RPH$_2$, with R indicating the meso substituent: 2PYR, 2-pyridyl; 3PYR, 3-pyridyl; 4 PYR, 4-pyridyl, OMXP, *o*-methoxyphenyl; PMXP, *p*-methoxyphenyl; NAP, 1-naphthyl; PClP, *p*-chlorophenyl; 2THP, 2-thienyl. [b] *Anal.* Calcd for [(PClPPFe)$_2$O]: Cl, 18.87. Found: Cl, 18.86.

Table II. Mössbauer Parameters for the μ-Oxo Derivatives

Compound	Temp, °K	δ,[a] mm/sec	Δ, mm/sec	Γ,[b] mm/sec	R[c]
[(2PYRPFe)$_2$O]	298	0.60	0.61	0.31	0.97
	78	0.70	0.64	0.35	0.99
	4.2	0.72	0.70	0.37	1.03
[(3PYRPFe)$_2$O]	298	0.61	0.60	0.33	0.88
	78	0.69	0.63	0.33	1.02
	4.2	0.71	0.64	0.30	0.99
[(4PYRPFe)$_2$O]	298	0.59	0.60	0.31	0.82
	78	0.69	0.67	0.43	1.10
[(PMXPPFe)$_2$O]	298	0.60	0.59	0.39	0.74
	78	0.68	0.63	0.36	0.82
	4.2	0.69	0.63	0.34	0.96
[(OMXPPFe)$_2$O]	298	0.50	0.65	0.36	0.96
	78	0.59	0.65	0.38	1.10
[(NAPPFe)$_2$O]	298	0.60	0.70	0.36	0.95
	78	0.72	0.73	0.45	1.10
[(2THPFe)$_2$O]	298	0.60	0.57	0.36	0.92
	4.2	0.70	0.61	0.30	1.13
[(PClPPFe)$_2$O]	298	0.55	0.54	0.37	0.76
	4.2	0.68	0.66	0.38	1.01

[a] All δ values are relative to sodium nitroprusside. [b] Full width at half-maximum. [c] Intensity of left peak over intensity of right peak.

There is possibility for geometrical isomerism in the 2-thienyl, 2- and 3-pyridyl, *o*-methoxyphenyl, and 1-naphthyl derivatives. Interconversion of the possible isomers is probably relatively easy for the thienyl and pyridyl cases (Gottwald and Ullman[8] found such interconversion for tetrakis(*o*-hydroxyphenyl)porphine and its copper salt), much more difficult for the *o*-methoxyphenyl derivative, and probably impossible for the 1-naphthyl case. In the present study no attempt was made to separate any of the several theoretically possible geometrical isomers of [(NAPPFe)$_2$O].

Discussion

Values of the isomer shifts lie within very narrow ranges (omitting the *o*-methoxyphenyl complex which showed abnormally small values): 0.58 ± 0.03 mm/sec at 298°K, 0.70 ± 0.02 mm/sec at 78 and 4.2°K. These differences are within the uncertainty in the measurement (estimated at about ±0.03 mm/sec from replicate measurements). There is no dependence of the isomer shift on the porphine substituent. The temperature dependence is of the magnitude and direction expected for the second-order Doppler shift.

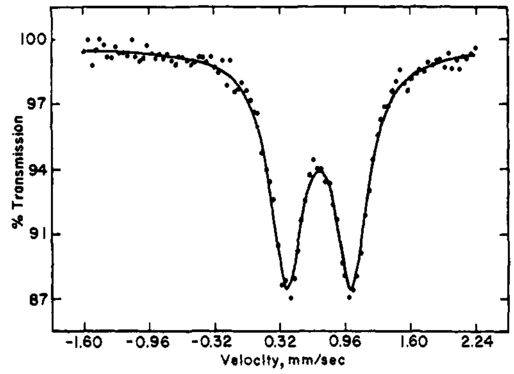

Figure 1. Mössbauer spectrum of [(2PYRPFe)$_2$O] at 78°K.

The quadrupole splittings also cover very restricted ranges: 0.62 ± 0.08 mm/sec at 298°K, 0.68 ± 0.05 mm/sec at 78°K, and 0.66 ± 0.04 mm/sec at 4.2°K

---

(8) L. K. Gottwald and E. F. Ullman, *Tetrahedron Lett.*, 3071 (1969).

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.

---

(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

Manuel A. Torréns,[1] Darel K. Straub,* and L. M. Epstein

Contribution from the Department of Chemistry, University of Pittsburgh, Pittsburgh, Pennsylvania 15213. Received May 21, 1971

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.

---

(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).