Furthermore, the values of Δ_1 increase from lanthanum to neodymium and then decrease gradually, indicating that the first three rare earth ions are too large to allow the most effective enhancement of chelation.

Acknowledgment.—This research was supported by a grant from the Graduate School of the University of Minnesota and by PHS Research Grant No. RG-8394 from the Division of General Medical Sciences, Public Health Service. The author also wishes to express his appreciation to Miss Judith Ann Loraas for help with the experimental measurements.

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α,β,γ,δ-Tetra-(4-pyridyl)-porphine and Some of its Metal Complexes

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Received December 20, 1961

A new porphyrin, α,β,γ,δ-tetra-(4-pyridyl)-porphine, has been synthesized and purified. The zinc, copper, and nickel complexes of this porphyrin have been prepared. The visible absorption spectra of these complexes were studied employing both chloroform and 1.0 *N* hydrochloric acid as solvents.

One of the limiting factors in the study of porphyrins and metalloporphyrins is their insolubility in aqueous solutions. Thus the study of the oxidation–reduction reactions of metalloporphyrins is hampered by their water insolubility.[1–3]

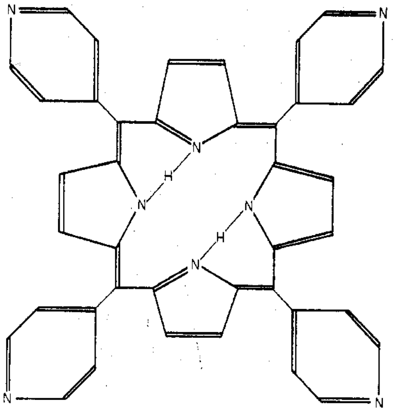

Fig. 1.—α,β,γ,δ-Tetra-(4-pyridyl)-porphine.

We have synthesized a new porphyrin, α,β,γ,δ-tetra-(4-pyridyl)-porphine, which is water soluble (Fig. 1). This porphyrin is a new member of the α,β,γ,δ-tetraphenylporphine series.[4]

The free base porphyrin can complex with metal ions to form metalloporphyrin complexes. The pyridines on α,β,γ,δ-tetra-(4-pyridyl)-porphine can pick up protons in acid solution; this property accounts for the porphyrin's water solubility.

In this communication we report the synthesis of α,β,γ,δ-tetra-(4-pyridyl)-porphine and some of its metalloporphyrin complexes and the spectral properties of these molecules.

Experimental

Synthesis.—Literature methods were used to make the α,β,γ,δ-tetra-(4-pyridyl)-porphine.[4] For the preparation of the zinc salt, 50 ml. of pyridine, 15 g. of zinc acetate, 25 ml. of pyrrole, and 35 ml. of 4-pyridine carboxaldehyde were mixed in a 250-ml. all-glass pressure bomb. The bomb was flushed with nitrogen and sealed. The reaction mixture was heated in an oil bath at 110° for 48 hr. Purple crystals of zinc-α,β,γ,δ-tetra-(4-pyridyl)-porphine were collected, washed with alcohol and ether, and dried in an oven at 110°. The yield was about 10%. There was more product dissolved in the reaction mixture but recovery was not attempted. The zinc derivative was purified on an alumina column (Fisher Alumina) using chloroform as a solvent and 5% methanol–chloroform as an eluent. The product was recrystallized from chloroform–methanol.

The porphyrin was prepared by removal of the zinc ion from the zinc porphyrin complex. The zinc derivative was dissolved in chloroform. To remove the zinc ion from the zinc porphyrin complex 6 *N* HCl was added to the chloroform solution. The porphyrin went into the acid layer as the diacid porphyrin. The free base porphyrin was extracted into chloroform after neutralization

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(1) J. F. Taylor, *J. Biol. Chem.*, **135**, 569 (1940).

(2) E. S. G. Barron, *ibid.*, **121**, 285 (1937).

(3) W. M. Clark, "Oxidation-Reduction Potentials of Organic Systems," Williams and Wilkins Company, Baltimore, Maryland, 1960, pp. 448–460.

(4) D. W. Thomas and A. E. Martell, *J. Am. Chem. Soc.*, **81**, 5111 (1959).

of the HCl. This free base porphyrin was purified on a talc column. Another method of preparation and purification of the free base consists in dissolving the zinc porphyrin in 10 *N* HCl and heating at 70–80° for 2 hr. The green precipitate that results is the salt α,β,γ,δ-tetra-(4-pyridyl)-porphine·6HCl. If this salt is dissolved in distilled water the free base results. It then can be extracted into chloroform. The metal complexes were prepared by refluxing the α,β,γ,δ-tetra-(4-pyridyl)-porphine with the metal acetate in acetic acid. The metalloporphyrins so formed were extracted into chloroform and purified on alumina columns.

All the porphyrins prepared were very stable compounds. They did not melt or sublime at temperatures up to 300°.

Spectra.—The visible spectra were taken in 10.00-mm. matched cells in either a Cary Model 14 or a Bausch and Lomb Model 505 spectrophotometer. The extinction coefficients were determined by measuring the spectra of three different solutions of the porphyrin. The average deviations of the extinction coefficients were all less than 2%.

Infrared.—The infrared spectra were taken with a Beckman Model IR-7 spectrometer using KBr pellets. The strongest peaks are listed with each compound.

X-Ray.—X-Ray powder patterns were taken on the porphyrins with a Norelco X-ray machine and a recording diffractometer. Copper radiation was used with a nickel foil filter. The two θ values of the strongest peaks are listed with each compound.

α,β,γ,δ-Tetra-(4-pyridyl)-porphine is a deep purple compound.

Anal. Calcd. for $C_{40}N_8H_{26}$: C, 77.7; N, 18.1; H, 4.2. Found: C, 77.5; N, 18.1; H, 4.4. Infrared peaks in cm.$^{-1}$: 800, 882, 970, 1003, 1400, 1592. X-Ray peaks: 19.85°, 21.10°, 26.24°.

Zinc-α,β,γ,δ-tetra-(4-pyridyl)-porphine is a bright purple compound.

Anal. Calcd. for $ZnC_{40}N_8H_{24}$: Zn, 9.6; C, 70.4, N, 16.3; H, 3.6. Found: Zn, 9.1; C, 70.4; N, 16.4; H, 3.8. Infrared peaks in cm.$^{-1}$: 787, 887, 990, 1400, 1583. X-Ray peaks: 17.65°, 19.52°, 30.40°, 39.70°.

Copper-α,β,γ,δ-tetra-(4-pyridyl)-porphine is a reddish purple compound.

Anal. Calcd. for $CuC_{40}N_8H_{24}$: Cu, 9.3; C, 70.6; N, 16.5; H, 3.6. Found: Cu, 9.2; C, 69.7; N, 16.2; H, 3.9. Infrared peaks in cm.$^{-1}$: 802, 892, 990, 1003, 1403, 1592. X-Ray peaks: 8.50°, 19.92°, 20.93°, 26.10°.

Nickel-α,β,γ,δ-tetra-(4-pyridyl)porphine is a deep red compound.

Anal. Calcd. for $NiC_{40}N_8H_{24}$: Ni, 8.7; C, 71.1; N, 16.6; H, 3.6. Found: Ni, 8.1; C, 70.1; N, 16.5; H, 3.9. Infrared peaks in cm.$^{-1}$: 795, 872, 988, 1004, 1402, 1589. X-Ray peaks: 12.00°, 19.90°, 20.70°, 25.95°.

α,β,γ,δ-Tetra-(4-pyridyl)-porphine·6HCl is a bright green compound.

Anal. Calcd. for $C_{40}N_8H_{26}\cdot6HCl$: Cl, 25.4. Found: Cl, 23.5. This substance was very hydroscopic and also lost HCl on heating, making the analysis difficult and uncertain.

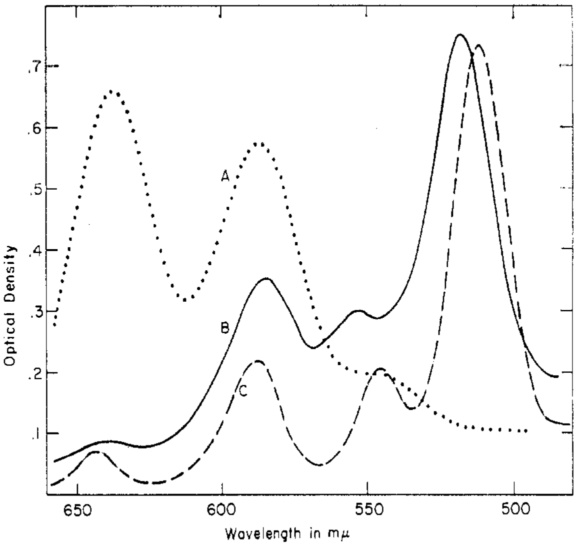

Fig. 2.—A, 3.5 × 10^{-5} *M* α,β,γ,δ-tetra-(4-pyridyl)-porphine in 1.0 *N* HCl; B, 5.7 × 10^{-5} *M* α,β,γ,δ-tetra-(4-pyridyl)-porphine in aqueous, pH 2.3; C, 4.0 × 10^{-5} *M* α,β,γ,δ-tetra-(4-pyridyl)-porphine in $CHCl_3$.

Absorption Spectra.—The α,β,γ,δ-tetra-(4-pyridyl)-porphine is soluble both in chloroform and acidic aqueous solvents. The absorption spectrum of α,β,γ,δ-tetra-(4-pyridyl)-porphine in $CHCl_3$, Fig. 2C, shows a typical four-band free base porphyrin spectrum in the visible region.

The spectrum of this porphyrin in water at pH 2.3 is very similar to the spectrum in chloroform, Fig. 2B. These solutions both are orange in color. In 1.0 *N* HCl the spectrum changes to that of Fig. 2A. The color of this solution is bright green. The green solution constitutes the porphyrin in the "diacid" type of porphyrin. The diacid porphyrin has four protons in the center of the porphyrin ring. Also, the α,β,γ,δ-tetra-(4-pyridyl)-por-

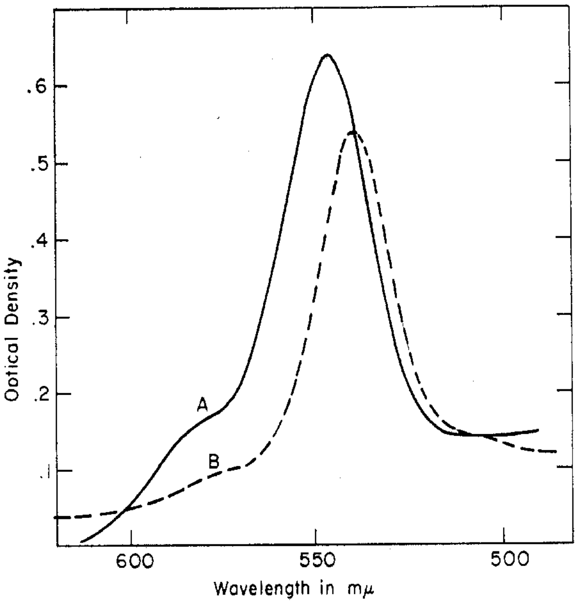

Fig. 3.—A, 4.4 × 10^{-5} *M* copper-α,β,γ,δ-tetra-(4-pyridyl)-porphine in 1.0 *N* HCl; B, 3.7 × 10^{-5} *M* copper-α,β,γ,δ-tetra-(4-pyridyl)-porphine in $CHCl_3$.

phine in 1.0 *N* HCl has four other protons on the pyridine nitrogens. The pK_a of the inner protons is about 1.0. This low pK is due to the high charge of the molecule caused by the presence of the pyridine protons. The 6HCl salt of this compound has been isolated (see Synthesis section). The fact that the spectrum of the $\alpha,\beta,\gamma,\delta$ tetra-(4-pyridyl)-porphine in $CHCl_3$ is very similar to that in aqueous solution (pH 2.3) indicates that the protons on the pyridine nitrogens do not interact greatly with the porphyrin system.

If one replaces the two protons of the free base porphyrin by a metal ion the visible spectrum changes considerably. Fig. 3 shows the spectra of copper-$\alpha,\beta,\gamma,\delta$-tetra-(4-pyridyl)-porphine in both $CHCl_3$ and 1.0 *N* HCl.

TABLE I

Compound	Solvent	Absorption maxima, mμ	Extinction coefficient × 10^{-3}
Free base	$CHCl_3$	417	425
		513	19.6
		547	5.4
		588	5.9
		643	1.7
Free base	Aqueous pH 2.3	420	201
		518	13.5
		553	5.3
		585	6.2
		638	1.3
Free base	1.0 *N* HCl	442	287
		588	12.5
		639	15.8
Zinc complex	$CHCl_3$	442	512
		559	19.4
Copper complex	$CHCl_3$	413	517
		538	21.1
Copper complex	1.0 *N* HCl	423	539
		549	16.6
Nickel complex	$CHCl_3$	412	220
		528	14.9
Nickel complex	1.0 *N* HCl	415	130
		534	10.8
		562	9.5

The spectra of the copper complex are similar in both solvents. Table I lists the main absorption maxima and extinction coefficients of $\alpha,\beta,\gamma,\delta$-tetra-(4-pyridyl)-porphine free base and its metal derivatives.

In the case of the nickel complex, the spectrum in aqueous solution shows that one of the shoulders that existed in $CHCl_3$ solutions had developed into a full-sized band (Fig. 4).

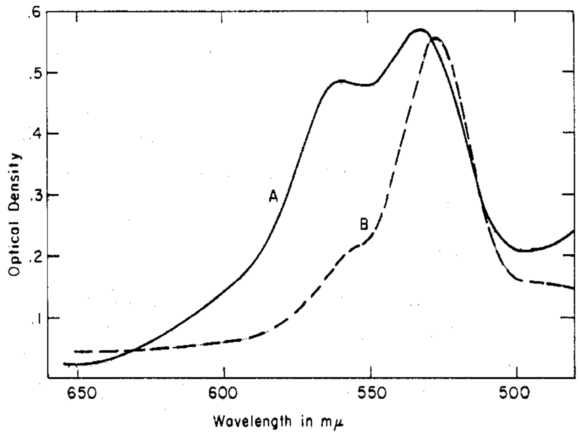

Fig. 4.—A, 5.0 × 10^{-5} *M* nickel-$\alpha,\beta,\gamma,\delta$-tetra-(4-pyridyl)-porphine in 1.0 *N* HCl; B, 3.6 × 10^{-5} *M* nickel-$\alpha,\beta,\gamma,\delta$-tetra-(4-pyridyl)-porphine in $CHCl_3$.

A study of the effects of the solvent on the porphyrin absorption bands should help in the theoretical interpretation of the absorption spectra of the porphyrin system.[5]

Inspection of Table I shows that the absorption maximum shifts to the red in changing from $CHCl_3$ to 1.0 *N* HCl. Also the extinction coefficients are smaller in 1.0 *N* HCl. The Soret band, the band that occurs in the 410-mμ region, is affected most by the solvent change. Its extinction coefficient is reduced by almost 50% on solvent change. The visible bands also are affected but by a much smaller amount. The reason for these effects is not yet understood.

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[5] M. Gouterman, *J. Mol. Spectr.*, **6**, 138 (1960).