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meso-Tetrapyridylporphins and Their Metal Complexes. Syntheses and Physico-Chemical Properties

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Three isomers of *meso*-tetrapyridylporphins, *i.e.* tetra(2-pyridyl)- (**2**), (3-pyridyl)- (**3**), and (4-pyridyl)- (**4**), porphin have been synthesized. They were soluble in acetic acid, chloroform and acidic aqueous solvents. Solubilities in chloroform, dimethylformamide and pyridine were in the order **3**>**2**>**4**. Comparison of the visible spectra indicated that the intensities of the bands due to 0–0 transitions decreased (**3**>**4**>**2**) with an increase of the electron-withdrawing character of the pyridyl substituent. The copper(II) and zinc(II) complexes of **2** and **3** have been prepared. Infrared and nuclear magnetic resonance spectra and their assignments of the porphins and/or the metal complexes were described.

Keywords——*meso*-tetra(2-pyridyl)porphin; *meso*-tetra(3-pyridyl)porphin; *meso*-tetra(4-pyridyl)porphin; copper porphyrin; zinc porphyrin; visible spectra of porphyrins; solubility of porphyrins

meso-Tetraarylporphins have been widely used as models for naturally occurring porphyrins. We have been working for mechanisms of metal ion incorporation into porphyrins.[2] Kinetic studies on copper(II)-tetraphenylporphin (**1**) reaction in aqueous dimethylformamide provided valuable data for the mechanistic interpretation. Low solubility of this porphin, however, prevented the investigation in the solvent with a water content exceeding 10%.

In an attempt to obtain porphyrins soluble in both dimethylformamide (DMF) and water, we have synthesized the three isomers of *meso*-tetrapyridylporphins (**2**, **3**, **4**).

Since first synthesized by Fleischer,[3] tetra-(4-pyridyl)porphin (**4**) has been used in a number of studies. In contrast to this situation is paucity of reports on **2** and **3**. Three reports dealing with **2** and/or **3** have been appeared so far, *viz.* mössbauer studies on iron(III) complexes,[4] electrochemical reactions[5] and a synthetic method of **3** with identification with a nuclear magnetic resonance (NMR) datum.[6] Their complexes with metal ions other than Fe(III) have not been described in the literature.

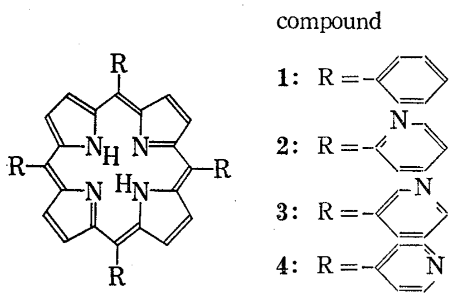

Chart 1

A report on syntheses and some physical properties of **2** and **3** is presented here with a view to comparing the properties of the three isomers. We have also investigated Cu(II) and Zn(II) complexes of **2** and **3**.

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[2] *a*) S. Sugata and Y. Matsushima, *J. Inorg. Nucl. Chem.*, 39, 729 (1977); *b*) *Idem, ibid.*, "in press."

[3] E.B. Fleischer, *Inorg. Chem.*, **1**, 493 (1962).

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

[5] B.P. Neri and G.S. Wilson, *Anal. Chem.*, **45**, 442 (1973).

[6] R.G. Little, J.A. Anton, P.A. Loach, and J.A. Ibers, *J. Heterocyclic Chem.*, **12**, 343 (1975).

Results and Discussion

Syntheses

For the syntheses of **2**, **3**, and **4** was employed the Rothemund method,[7] the direct condensation of pyrrole and a corresponding aldehyde. Use of propionic acid as a solvent, developed by Longo, *et al.*,[8] enhanced the yields. Crude products contained a small amount of chlorin. Treatment with 2,3-dichloro-5,6-dicyanobenzoquinone[9] was successful in obtaining chlorin-free porphins. Purified **3** and **4** were obtained in satisfactory yields (15.6 and 18.6%, respectively). That of **2** was less than 1%.

Copper(II) and zinc(II) complexes were prepared in good yields by the method of Adler, *et al.*,[10] in which porphins and excess metal perchlorates were allowed to react in boiling DMF.

Solubilities

Solubilities of the porphins and their Cu(II) and Zn(II) complexes are tabulated (Table I). Three tetrapyridylporphins are soluble in acidic media, whereas practically insoluble in aqueous solution with pH value of above 4.0.

TABLE I. Solubilities of *meso*-Tetrapyridylporphins and Their Metal Complexes[a]

Solvents	Compounds						
	2	3	4	2-Cu	2-Zn	3-Cu	3-Zn
Acetic acid	sol	sol	sol	sol	m	sol	m
1 N HCl	sol	sol	sol	sol	dec	sol	dec
H_2O	i	i	i	i	i	i	i
Methanol	sl	sl	sl	sl	sl	sl	sl
Ethanol	sl	sl	sl	sl	sl	sl	sl
Pyridine	m	sol	sl	m	m	sol	sol
$CHCl_3$	sol	sol	m	m	sl	sl	i
DMF	m	m	i	sl	sl	m	sl
Benzene	sl	m	sl	i	i	sl	sl
CCl_4	i	sl	i	i	i	i	i
DMSO	m	m	i	sl	sl	m	m
Ether	i	i	i	i	i	i	i
Acetone	sl	sl	i	i	i	sl	i
Ethyl acetate	i	sl	i	i	i	sl	sl
Dioxane	sl	m	i	sl	sl	sl	sl
n-Hexane	i	i	i	i	i	i	i
CH_3CN	i	i	i	i	i	i	i

a) abbreviations: sol, soluble; m, moderately soluble; sl, slightly soluble; i, insoluble; dec, decomposition

Solubilities in organic solvents followed in the order **3**>**2**>**4**. This was most remarkable with DMF and pyridine. From the fact, **2** and **3** seem to be more suitable in the mechanistic studies of metal complex formation in these media.

Cu(II) and Zn(II) complexes are generally less soluble than the parent porphins.

Visible Absorption Spectra

Table II lists wavelengths and extinction coefficients of absorption bands of the three porphins in various solvents. Fleischer[3] described spectral data of **4** in $CHCl_3$, 1.0N HCl and pH 2.3 aqueous solution, which agreed well with those in the present study. Only spectral

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[7] P. Rothemund, *J. Am. Chem. Soc.*, **61**, 2912 (1939).

[8] F.R. Longo, M.G. Finarelli, and J.B. Kim, *J. Heterocyclic Chem.*, **6**, 927 (1969).

[9] G.H. Barnett, M.F. Hudson, and K.M. Smith, *J. Chem. Soc. Perkin I*, **1975**, 1401.

[10] A.D. Adler, F.R. Longo, F. Kampas, and J. Kim, *J. Inorg. Nucl. Chem.*, **32**, 2443 (1970).

TABLE II. Electronic Absorption Bands of *meso*-Tetrapyridylporphinsa)

Solvents	Compounds 2	3	4
$CHCl_3$	417(352)	417(340)	417(369)
	514(17.5)	516(19.1)	513(19.5)
	547(4.2)	551(7.3)	547(5.4)
	588(5.4)	590(5.8)	588(5.9)
	644(1.4)	646(2.8)	645(1.3)
DMF	416(354)	418(427)	
	512(16.9)	515(18.4)	
	545(4.3)	549(7.3)	
	587(4.9)	590(5.4)	
	642(1.8)	645(3.7)	
Pyridine	420(359)	421(415)	419(399)
	514(18.2)	518(19.0)	514(20.3)
	548(4.8)	552(8.0)	548(5.8)
	589(5.5)	592(5.6)	589(5.9)
	644(1.9)	647(3.4)	645(2.1)
Acetic acid	416(214)	417(296)	419(188)
	511(15.2)	513(17.3)	514(13.5)
	546(3.8)	547(4.7)	549(4.5)
	585(5.6)	588(5.6)	589(4.6)
	642(2.0)	643(2.0)	645(1.1)
Water (pH 2.3)	415(192)	416(237)	420(226)
	514(10.4)	515(9.8)	519(13.6)
	548(4.2)	552(5.6)	555(5.9)
	583(6.5)	586(8.7)	586(7.6)
	634(4.3)	639(7.9)	638(2.7)
1.0N HCl	440(234)	434(412)	443(332)
	586(10.4)	585(13.0)	590(14.3)
	633(7.4)	633(23.0)	639(18.2)

a) Wavelengths for bands are given in nm. Numbers in parentheses are $\varepsilon \times 10^{-3}$.

data published to this date on **2** and **3** were those in 1.0N HCl.5) These are in good agreement with ours except for the longest band of **2**.

Spectra of the porphins were similar in DMF, $CHCl_3$ and pyridine. The porphins may be in free base form in these solvents. **3** exhibited a typical etio spectrum in close resemblance to **1**.11) Absorption peaks of **3** showed slight red shifts from the corresponding peaks of **2** and **4**.

Reduced intensities of bands I and III12) are noted in the spectra of **2** and **4**. They are quite similar to each other and may be classified as phyllo-type, which is shown by unsubstituted porphin.11)

Ratios of intensities of band III and II ($\varepsilon_{III}/\varepsilon_{II}$) are in the order $\mathbf{3}>\mathbf{4}>\mathbf{2}$. Electron-withdrawing character of the pyridyl group should increase in the order $\mathbf{3}<\mathbf{4}<\mathbf{2}$. Kim, Leonard and Longo13) found that when there is an electron-withdrawing substituent in the ortho position of phenyl groups of **1**, the extinction coefficients of bands I, III and Soret are diminished with respect to the unsubstituted **1**. Meot-Ner and Adler14) reported that bands

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11) A.I. Scott, "Interpretation of the Ultraviolet Spectra of Natural Products," Pergamon Press, Oxford, 1964.

12) The visible bands of porphyrins are usually numbered I, II, III, IV, starting from the low-energy end. Bands I and III are ascribed to 0–0 forbidden transitions and bands II and IV to 0–1 allowed vibrational bands.

13) J.B. Kim, J.J. Leonard, and F.R. Longo, *J. Am. Chem. Soc.*, **94**, 3986 (1972).

14) M. Meot-Ner and A.D. Adler, *J. Am. Chem. Soc.*, **97**, 5107 (1975).

I and III are intensified in derivatives of **1** with an electron-donating substituent in the para position of the phenyl group. The present finding conforms to these previous results and leads to the conclusion: the electron-withdrawing character of the substituent in meso-tetraarylporphins reduces the absorption intensities due to 0—0 transitions, whereas the electron-donating character increases them.

In weakly acidic water (pH 2.3), Soret bands became less intense and the longest band showed blue shift with a slight intensification. The porphins are supposed to be in free base form with protonated pyridine nitrogens. Spectra in acetic acid were similar to those in weakly acidic water and the porphins should be present as the same species.

TABLE III. Electronic Absorption Bands of the Metal Complexes

Compounds	Solvents	Wavelength in nm ($\varepsilon\times10^{-3}$)			
2-Cu	$CHCl_3$	415(461)	502(4.0)	539(21.6)	572(3.5)
	DMF	414(516)	502(4.2)	539(22.8)	573(3.7)
2-Zn	$CHCl_3$	425(474)	523(4.2)	562(21.2)	598(3.3)
	DMF	424(455)	520(2.6)	557(18.0)	596(3.5)
3-Cu	$CHCl_3$	416(490)	502(3.5)	540(21.5)	575(2.5)
	DMF	416(437)	504(3.2)	541(18.5)	578(2.3)
	pyridine	423(340)	509(3.3)	549(17.5)	590(3.1)
	acetic acid	415(406)	501(3.4)	540(20.7)	575(3.2)
	water (pH 2.3)	418(256)	506(2.7)	545(14.6)	577(2.9)
	1.0N HCl	419(315)	505(3.0)	545(17.9)	578(3.7)
3-Zn	DMF	427(521)	522(3.1)	560(18.9)	599(6.5)
	pyridine	431(375)	526(4.8)	564(14.7)	603(8.2)
	acetic acid	431(324)	520(2.7)	559(18.5)	594(2.8)

TABLE IV. Infrared Spectra of Tetrapyridylporphins and Their Metal Complexes[a]

2	3	4	2-Cu	2-Zn	3-Cu	3-Zn	Assignments
3310 w	3320 w	3310 w					N-H stretch.
1585 s	1587 w	1593 s	1586 s	1585 s	1588 w	1587 w	pyridine skeletal stretch.
1568 m	1569 w	1545 w	1568 m	1565 m	1568 w	1569 w	C=C (pyrrole) str.
			1539 vw	1529 w	1538 vw	1521 w	
1460 m	1470 m	1470 w	1465 m	1464 m	1472 w	1471 m	C=N (pyrrole) str.
1430 m	1410 m	1403 m	1429 m	1425 m	1408 m	1408 m	pyridine skel. str.
1352 w	1354 w	1351 w	1347 w	1338 w	1349 m	1343 m	C=N(pyrrole) str.
1230 m	1230 w	1230 w	1253 w	1247 w			
1193 w	1186 m	1188 w	1207 w	1204 w	1207 w	1207 w	
					1187 m	1188 m	
1152 w	1155 w	1156 w	1151 w	1148 w			
1115 w	1114 w	1113 w	1113 vw	1113 m	1111 w	1107 w	
	1077 w	1070 w	1071 w	1068 w	1076 w	1074 w	
1053 w	1047 vw		1055 w	1051 vw	1052 w	1049 w	
1008 m	1027 m		1029 w	1022 w	1027 w	1029 m	C-H rock. (pyrrole)
1000 w		1004 vw		1007 sh	1014 w	1007 w	
989 w	989 sh	990 vw	1006 s	997 s	997 s	994 s	porphin ring deformation
980 w	980 m	979 w	990 w				
971 s	966 s	970 s	972 w				
883 w	880 w	883 m	897 w	886 vw		885 w	
792 s	793 s	798 s	792 s	789 s	792 s	792 s	pyrrole ring deform.
759 s	781 s	786 s	762 s	776 s			CH out of plane deform. (pyridine).
	733 m	748 sh	728 w	730 w	746 vw	746 vw	
727 s	715 s	728 s	715 s	714 s	716 s	716 s	pyridine skeletal deform.

[a] Band frequencies are given in cm^{-1}.
intensities: vw, very weak; w, weak; sh, shoulder; m, medium; s, strong

Aqueous 1.0N HCl solutions were green and the porphins are in the diacid form, in which eight nitrogens are fully protonated.

Spectral properties of the metal complexes are listed in Table III. Difference in porphins had little influence on the spectra. Cu(II) complexes showed somewhat different spectra in pyridine from those in $CHCl_3$ and DMF. The result may reflect axial coordination of pyridine molecules. The difference in the spectra was smaller in Zn(II) complexes. **3**-Zn(II) complex decomposed almost instantly in 1.0 N HCl, giving rise to the spectrum of the diacid form of **3**. With **2**-Zn(II) complex, the spectral change in 1.0 N HCl was slower with a life-time of several hours.15)

Infrared Spectra

Table IV is a list of infrared (IR) absorption of the tetrapyridylporphins and their metal complexes with the band assignments.16) IR data of **4** and its metal complexes were described by Fleischer.3)

The weak N–H stretching vibrations above 3310 cm^{-1} for the porphins are absent in the metal complexes, since the acidic hydrogens are replaced by the metal ion. The differences in the three isomers were most prominent in 715—790 cm^{-1}, where C–H out of plane deformation and skeletal deformation of the pyridyl group were located.

In studies on IR spectra of metal complexes of *p*-substituted derivatives of **1**, Thomas and Martell16a) concluded that the strong absorption band near 1000 cm^{-1} possibly due to a ring deformation vibration is sensitive to the nature of the metal ion and is directly related to the strength of the metal-nitrogen bonds in the metal complexes. In the metal complexes of the tetrapyridylporphins, the metal sensitive bands shift to the higher frequencies in the order Cu(II)>Zn(II). The order indicates the relative strengths of the metal-ligand bonds and conforms to the order of stabilities of the complexes.17) The order **2**-Zn(II)>**3**-Zn(II) in IR frequencies is also in accord with the rate of decomposition in 1.0 N HCl solution.

TABLE V. NMR Spectra of Tetrapyridylporphins[a)]

Assignments	Compounds		
	2	3	4
Pyrrole N-H	−2.82 (2H, s)	−2.78 (2H, s)	
Pyrrole β-H	8.82 (8H, s)	8.88 (8H, s)	8.85 (8H, s)
	[8.88]	[8.99]	[9.06]
Pyridyl-H	7.70 (4H, dd, C_5-H)	7.76 (4H, dd, C_5-H)	8.16 (8H, d, C_3-H)
	[8.09]	[8.21]	[8.66]
	8.13 (4H, dd, C_4-H)	8.54 (4H, d, C_4-H)	9.06 (8H, d, C_2-H)
	[8.48]	[9.02]	[9.31]
	8.66 (4H, d, C_3-H)	9.08 (4H, d, C_6-H)	$J_{2,3}=5.3$
	[8.52]	[9.27]	
	9.08 (4H, d, C_6-H)	9.46 (4H, s, C_2-H)	
	[9.26]	[9.62]	
	$J_{3,4}=6.2$	$J_{4,5}=7.6$	
	$J_{4,5}=8.0$	$J_{5,6}=5.0$	
	$J_{5,6}=5.0$		

a) The chemical shifts in $CDCl_3$ are given in ppm with tetramethylsilane as the internal standard and coupling constants are in Hz.
Numbers in bracket are the chemical shifts in acetic acid.

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15) This phenomenon was described more quantitatively in P. Hambright, T. Gore, and M. Burton, *Inorg. Chem.*, **15**, 2314 (1976), which was published after the submission of the present paper.

16) Assignments of the bands are made according to the following references and to the literature cited therein; *a*) D.W. Thomas and A.E. Martell, *J. Am. Chem. Soc.*, **81**, 5111 (1959); *b*) H. Ogoshi, N. Masai, Z. Yoshida, J. Takemoto, and K. Nakamoto, *Bull. Chem. Soc. Japan*, **44**, 49 (1971).

17) J.E. Falk, "Porphyrins and Metalloporphyrins," Elsevier, Amsterdam, 1965, p. 34.

NMR Spectra

The NMR data of the three porphins in $CDCl_3$ and in acetic acid are summarized in Table V. They clearly indicate the structure of the compounds. The NMR spectrum of **3** in $CDCl_3$ was described by Little, *et al.*[6] and is in good agreement with ours.

Peaks due to pyridyl hydrogens showed down field shifts in acetic acid. This may reflect protonation of pyridine nitrogens in this solvent. In the higher field than tetramethylsilane (TMS) was a signal of N–H of pyrrole, which was not observed with **4** probably due to low solubility of this compound to chloroform. The N–H resonances were not visible in acetic acid.

Experimental

Synthesis of 3——**3** was synthesized by the method of Longo, *et al.*[8] with a modification. A propionic acid solution of 12.4 g 3-formylpyridine and 7.8 g pyrrole was refluxed for 45 min. The yield of crude **3** as obtained by evaporation of the solvent and followed washing by DMF was 2.8 g. A spectrum of the crude product showed the presence of chlorin. Crude **3** was dissolved in ethanol-free $CHCl_3$ and 700 mg 2,3-dichloro-5,6-dicyanobenzoquinone in benzene was added. The mixture was refluxed for 2 hr and, then, chromatographed on alumina using $CHCl_3$ as the eluant. Purple crystals of purified **3** was obtained by addition of methanol to the eluate.

2 and **4** were prepared by the analogous method. The analytical results are presented in Table VI.

Table VI. Analytical Data

Compounds	Formula	Analysis (%)					
		Calcd.			Found		
		C	H	N	C	H	N
2	$C_{40}H_{26}N_8$	77.65	4.24	18.11	77.60	4.19	18.08
3	$C_{40}H_{26}N_8$	77.65	4.24	18.11	77.57	4.05	17.78
4	$C_{40}H_{26}N_8$	77.65	4.24	18.11	76.57	4.39	17.79
2-Cu	$C_{40}H_{24}N_8Cu$	70.63	3.56	16.47	70.73	3.81	16.03
3-Cu	$C_{40}H_{24}N_8Cu$	70.63	3.56	16.47	70.52	3.52	16.30
2-Zn	$C_{40}H_{24}N_8Zn$	70.44	3.55	16.43	69.48	3.47	16.01
3-Zn	$C_{40}H_{24}N_8Zn$	70.44	3.55	16.43	69.05	3.59	15.83

Preparation of Cu(II) and Zn(II) Complexes——DMF solutions containing porphin and two equimolar copper perchlorate or ten equimolar zinc perchlorate were refluxed for 1 hr. Then, twice amounts of water was added and allowed to stand several hours. Precipitate was filtered, washed, dried and, then, purified by chromatographing on alumina. Eluants were DMF for **3**-Cu(II), pyridine for **3**-Zn(II), and $CHCl_3$ for **2**-Cu(II) and **2**-Zn(II) complexes. Complexes were crystallized from DMF and dried over P_2O_5 at 110°. Yields: **3**-Cu(II), 78.5%; **3**-Zn(II), 65.4%; **2**-Cu(II), 81.5%; **2**-Zn(II), 67.3%. Cu(II) complexes were redish-purple and Zn(II) complexes purple crystals. The analytical results are presented in Table VI.

Spectral Measurements——The electronic absorption spectra were recorded at room temperature with a Union-Giken Model SM-202 spectrophotometer. Infrared spectra were taken in KBr pellets on a JASCO DS-701G spectrometer. NMR spectra were obtained with a JEOL PS-100 spectrometer at 100 MHz.

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