182. *Conjugated Macrocycles. Part XXXII.* Absorption Spectra of Tetrazaporphins and Phthalocyanines. Formation of Pyridine Salts.*

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Metal-free tetrazaporphins in pyridine solution give absorption spectra similar to those of their metal derivatives. This is apparently because pyridinium salts are formed. The electronic absorption spectra of a number of metal phthalocyanines have been redetermined. The composition of the unusual stannic phthalocyanine has been confirmed.

THE absorption spectra of metal-free tetrazaporphins in, *e.g.*, chlorobenzene or 1-chloronaphthalene normally show two bands of high intensity in the visible region.[1] However, solutions of these compounds in pyridine (free from metal ions) can show spectra similar to those of the metal tetrazaporphins, *i.e.*, with a single intense band in the visible region. The metal derivatives of tribenzotetrazaporphin show two intense peaks in the visible region,[2] but again there is a close similarity between their spectra and that of the metal-free pigment in pyridine. The conditions under which these pyridine solutions with anomalous absorption spectra are formed, together with their absorption maxima in the visible region, are given in Table 1. The tetrazaporphin product was the only one isolated. It seems

TABLE 1. *Light absorptions of tetrazaporphin pyridinium salts in pyridine.*

Pyridinium salt from	Method	$\lambda_{max.}$ (mμ)
Tetrazaporphin	*a*	576, 530, 332 ($E^{1\%}_{1\,cm.}$ 547, 93, 336)
Tetramethyltetrazaporphin	*a*	581, 546
Octamethyltetrazaporphin	*a*	595, 547
Tetracyclohexenotetrazaporphin	*a*	595, 548
Tribenzotetrazaporphin	*b*	663, 626, 590
Phthalocyanine	*c*	672, 644

Methods: *a*, Anærobic irradiation of a pyridine solution with collimated light from a " Pointolite " lamp at 25 cm. *b*, Keeping a pyridine solution in the absence of air for 7 days. *c*, Extraction into pyridine in a Soxhlet apparatus.

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* Part XXXI, *J.*, 1958, 3879.

[1] Linstead and Whalley, *J.*, 1952, 4839; Ficken and Linstead, *J.*, 1952, 4846; Baguley, France, Linstead, and Whalley, *J.*, 1955, 3521; Brown, Spiers, and Whalley, *J.*, 1957, 2882; Elvidge and Linstead, *J.*, 1955, 3536.

[2] Elvidge, Golden, and Linstead, *J.*, 1957, 2466.

likely that the tetrazaporphins form pyridinium salts because the two central hydrogen atoms of the macrocycles are known to be weakly acidic. These salts, which would be expected to show spectra of the metal tetrazaporphin type, would readily dissociate into their components. Dissociation indeed occurs on dissolution in solvents such as chlorobenzene, except for the tetrazaporphin product which is surprisingly stable.

Good evidence for the pyridinium salt structure comes from the infrared absorption characteristics of the tetrazaporphin–pyridine compound, given in Table 2. Also listed for comparison are the data for tetrazaporphin and magnesium tetrazaporphin. The spectrum of the pyridinium salt shows a doublet at 2012, 1953 cm.$^{-1}$ ascribed[3] to pyridinium $^{+}$N–H and a peak at 1709 cm.$^{-1}$ which may be due to C=NH^{+}.[4] Further, it shows a broad region of absorption at 1755—1575 cm.$^{-1}$, as in the spectrum of magnesium tetrazaporphin.

TABLE 2. *Infrared absorptions in* KBr *disc* (*principal max. in cm*$^{-}$

Tetrazaporphin pyridinium salt	Tetrazaporphin	Magnesium tetrazaporphin	Assignment
	3236w		N–H stretch
3067w, 2915s, 2841s	3044	3067, 2915, 2849m	C–H
2012, 1953d			$^{+}$N–H [3]
1755—1575b		1755—1560b	
1709			C=NH^{+} [4]
1529w, 1464	1550, 1504, 1477	1572w, 1512s, 1463	C=C, C=N
1403w, 1377w, 1260, 987, 800	1424w, 1339w, 1244w, 1225w, 1182w, 1033s, 939s, 825s, 789s, 718s	1412, 1406w, 1316 1240s, 1045s, 968s, 793s, 746s	Skeletal vibrations

s = strong, w = weak, d = doublet, b = broad (medium intensity unspecified).

Previous determinations of the electronic absorption spectra of phthalocyanines involved visual instruments[5] or unusual solvents.[6] The results of recent redeterminations made with photoelectric instruments on carefully purified samples are now recorded. These data, assembled in Table 3, are considered to be accurate and replace those previously published. Quantitative spectral details for palladium and cobalt phthalocyanine are given for the first time. The spectrum of metal-free phthalocyanine and those of its metal derivatives, here examined, all showed the single band at *ca.* 350 mμ which is characteristic of tetrazaporphins. The visible spectra of the phthalocyanine complexes of bivalent Cu, Ni, Co, Fe, Zn, Pd, and Mg were very similar to one another, having a single, narrow, intense band in the 650—675 mμ region. The spectrum of magnesium phthalocyanine is thus different from that reported earlier by Barrett *et al.*[5] The positions of the additional peaks then found correspond to those of metal-free phthalocyanine which may have been formed by traces of hydrochloric acid in the solvent (1-chloronaphthalene). I find that magnesium phthalocyanine which has been crystallised from pyridine, contrary to a previous report,[7] is not contaminated with metal-free pigment.

Stannic phthalocyanine is unusual in containing two phthalocyanine residues for each atom of tin.[8] It would be expected that the spectrum of such a compound would differ from those of the typical metal phthalocyanines but this had not been measured. Stannic phthalocyanine was obtained as before[8] by reaction of dichlorostannic phthalocyanine with disodium phthalocyanine, and the partially purified product was then chromatographed on alumina to remove small amounts of metal-free and dichlorostannic phthalocyanine. The chromatography established that the stannic phthalocyanine was

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[3] Lord and Merrifield, *J. Chem. Phys.*, 1953, **21**, 166.

[4] Cf. Leonard and Gash, *J. Amer. Chem. Soc.*, 1954, **76**, 2781.

[5] Anderson, Bradbrook, Cook, and Linstead, *J.*, 1938, 1151; Barrett, Linstead, Rundall, and Tuey, *J.*, 1940, 1079.

[6] Evstigneev and Krasnovskii, *Doklady Akad. Nauk S.S.S.R.*, 1947, **58**, 1399.

[7] Evstigneev and Krasnovskii, *Doklady Akad. Nauk S.S.S.R.*, 1947, **58**, 417.

[8] Barrett, Dent, and Linstead, *J.*, 1936, 1719.

homogeneous and not a mixture or molecular complex of stannous phthalocyanine and phthalocyanine. Elementary analysis and quantitative oxidation [9] of the crystallised pigment agreed with the constitution reported previously.[8] The light absorption is, indeed, unusual: the spectrum shows a strong band at 626 mμ and a weaker one at the very end of the visible region, at 774 mμ. The nature of the bonding in this unique compound, about which speculation can be made, should become clear from the results of an *X*-ray or electron-diffraction crystallographic examination

TABLE 3. *Visible and ultraviolet absorptions.*

Phthalocyanines		$\lambda_{max.}$ (Å) (and $\log_{10}\varepsilon$)										
Metal-free	*a*	3500				5540		6020	6380	6650	6980	
		4·74				3·57		4·43	4·62	5·18	5·21	
* Cu	*a*	3500		5100	5260	5670	5880	6110	6480	6780		
		4·76		3·56	3·57	3·91	4·06	4·56	4·51	5·34		
Ni	*a*	3510				5600	5800	6030	6430	6710		
		4·57				3·75	3·82	4·51	4·47	5·10		
Co	*a*	3480						6065		6720		
		4·65						4·53		5·19		
* Co	*b*	3300						5965		6575		
		4·86						4·51		5·07		
Fe·2py	*b*	3295	4140					5930		6540		
		4·88	4·29					4·47		5·03		
Fe	*c*	3300						5950		6560		
		4·68						3·95		4·84		
Zn·py	*b*	3475						6070	6460	6720		
		4·81						4·59	4·56	5·45		
* $Mg{\cdot}H_2O$	*b*	3470				5680	5870	6100	6470	6745		
		4·73				3·59	3·79	4·45	4·39	4·94		
* Pd	*a*	3470				5570	5765	5955	6330	6605		
		4·69				3·98	4·07	4·57	4·51	5·32		
Sn diphthalocyanine	*d*	3380						5755		6260		7740
		5·11						4·33		5·06		4·57
Tetrazaporphin												
* Co tetracyclohexeno	*c*	3515						5395		5890		
		4·72						4·17		4·95		

a, 1-Chloronaphthalene; *b*, pyridine; *c*, *o*-dichlorobenzene; *d*, chlorobenzene.
* With Dr. G. E. Ficken.

Lead phthalocyanine is too readily demetallated in dilute solution for accurate spectral details to be obtained. Thus in 1-chloronaphthalene the spectrum is that of metal-free phthalocyanine, and, in pyridine, bands corresponding to phthalocyanine and the pyridinium salt were obtained.

An improved method for the preparation of cobalt tetracyclohexenotetrazaporphin (cf. Ficken *et al.*[1]) is described, and spectral details are included in Table 3.

EXPERIMENTAL

Tetrazaporphin–Pyridine Salt.—A freshly boiled solution of tetrazaporphin (30 mg.) in pyridine (500 c.c.) containing a trace of quinol or pyrogallol was irradiated (in portions) in completely filled 2-cm. cells in the light-path of a Hilger–Nutting visual spectrophotometer: the change was followed spectroscopically and required 1—10 hr./cell-full. The combined products were evaporated to dryness and the blue solid was washed several times with methanol and then crystallised extractively from chlorobenzene to give the pyridine salt (2·6 mg.) (for the infrared spectrum see Table 2).

Purification of Phthalocyanines.—The pigments (see Table) were prepared by methods previously described [1,8,10] and were purified by extractive crystallisation from 1-chloronaphthalene (A), *o*-dichlorobenzene (B), or pyridine (C), with the exception of ferrous phthalocyanine which was obtained pure by sublimation at 350°/10^{-6} mm. of the dipyridine solvate.

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[9] Elvidge, following paper.

[10] Barrett, Frye, and Linstead, *J.*, 1938, 1157.

Phthalocyanine		Found				Calc.			
		C	H	N	Metal	C	H	N	Metal
Metal-free	(A)	74·3	3·9	21·6	—	74·7	3·5	21·8	—
Cu	(A)	66·7	3·1	19·25	11·3	66·7	2·8	19·5	11·0
Ni	(A)	67·1	3·1	19·5	10·2	67·3	2·8	19·6	10·3
Co	(B)	67·4	3·1	19·8	10·1	67·3	2·8	19·6	10·3
Fe,2py *	(C)	69·3	3·8	18·9	7·7	69·4	3·6	19·3	7·7
Fe		68·0	2·9	19·7	9·95	67·6	2·8	19·7	9·8
Zn,py	(C)	67·7	3·5	19·3		67·6	3·2	19·2	
Mg,H_2O	(C)	69·6	3·7	19·5	4·5	69·3	3·3	20·2	4·4
Pd	(B)	61·7	2·8		17·0	62·1	2·6		17·2
Pb	(C)	53·9	2·25	15·6	27·9	53·4	2·2	15·6	28·8

* py = pyridine.

Solutions for spectroscopic examination were prepared by boiling the pigment (0·4—0·6 mg.) with solvent for 5—10 min., cooling the solution, and making the volume up to 100 c.c. Determinations, made with Unicam S.P. 500 and S.P. 600 spectrophotometers, were then completed within 1 hr.

Stannic Phthalocyanine (cf. ref. 8).—Dichlorotin(IV) phthalocyanine (250 mg.) and disodium phthalocyanine (200 mg.) were refluxed in 1-chloronaphthalene (50 c.c.) for 1·5 hr. and the hot solution was filtered from sodium chloride. When the solution had cooled, the metal-free phthalocyanine (140 mg.) which had separated was filtered off. Concentration of the filtrate under reduced pressure afforded a solid, mainly stannic phthalocyanine, which was extracted into benzene (*ca.* 500 c.c.), and the solution was chromatographed on alumina (Spence, type H; 8 × 4·5 cm.). Traces of metal-free phthalocyanine were strongly adsorbed at the top of the column. Dichlorotin phthalocyanine formed a slow-moving green band, and stannic phthalocyanine a blue band which was rapidly eluted with benzene–methanol (20 : 1). The blue solid from evaporation of the eluate was crystallised extractively four times from benzene, the hot solution being filtered each time under gravity through Whatman no. 50 paper to remove traces of alumina. Stannic phthalocyanine was obtained as minute dark blue prisms (Found: C, 67·4; H, 3·1; N, 19·6; Sn, 9·9. Calc. for $C_{64}H_{32}N_{16}Sn$: C, 67·2; H, 2·8; N, 19·6; Sn, 10·4%).

Cobalt Tetracyclohexenotetrazaporphin (with Dr. G. E. Ficken).—Magnesium tetracyclohexenotetrazaporphin monohydrate monopyridine solvate (Ficken *et al.*[1]) (152 mg.) was extracted into a solution of anhydrous cobalt acetate (157 mg.) in dry 2-ethoxyethanol. The solid which separated from the cooled solution was filtered off, washed with hot dilute hydrochloric acid, water, and ethanol, and dried. Extractive crystallisation from *o*-dichlorobenzene gave cobalt tetracyclohexenotetrazaporphin (133 mg., 93%) (Found: C, 65·45; H, 5·7; N, 19·3; Co, 9·9. Calc. for $C_{32}H_{32}CoN_8$: C, 65·4; H, 5·5; N, 19·1; Co, 10·0%).

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