212. *Phthalocyanines and Associated Compounds.*[*] *Part XIII. Absorption Spectra.*

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The absorption spectra in the visible region of phthalocyanine, fifteen of its metallic derivatives, and a number of associated compounds containing the tetrazaporphin (porphyrazine) ring have been measured. The spectrum of phthalocyanine is composed of a system of at least seven bands, the main absorption occurring between 6000 and 7000 A. The relationships between the various spectra are discussed, and they are correlated with the spectra of porphyrins and azaporphyrins.

THE data in this paper have been accumulated during a number of years, and represent a general preliminary survey of the field. The results fall into two sections : (i) Determination of the position of the absorption maxima, without absolute intensity measurements, for a large number of compounds, in order to find the general characteristics, the influence of a central metal, and of attached rings. (ii) Quantitative measurements of the extinction curve of a few selected compounds.

EXPERIMENTAL.

(i) *Position of Maxima.*—The spectra were first measured photographically up to about 6400 A., a prism grating spectrograph with a dispersion of 35 A. per mm. at 6000 A. being used. A 500 watt tungsten-filament lamp was employed as a source of light, and the wave-lengths of the edges of the absorption bands were interpolated from a superimposed iron or copper arc spectrum. This method was particularly useful for the study of the weaker bands in the orange to green region, but there were at our disposal no instruments suitable for the extension of photographic measurements above 6400 A. Measurements were therefore made visually, a Hilger constant-deviation wave-length spectrometer being used, up to the limit of the visible region. It seems probable that the various metal-free compounds mentioned below and chloro-aluminium phthalocyanine possess further bands in the near infra-red, and an extension of the measurements into this region would be interesting.

The very low solubilities of most of the compounds was a constant difficulty. Saturated or supersaturated solutions in chloronaphthalene or bromonaphthalene, of the order of 0·00001M were generally used. A few compounds (cobalt, chloroaluminium, and chloroferric phthalocyanines) were conveniently soluble in pyridine, quinoline or ethyl alcohol. Lithium phthalocyanine forms only colloidal solutions in chloronaphthalene and was examined in dry acetone.

(ii) *Intensity Measurements.*—In order directly to compare the extinction coefficients and relative band intensities, quantitative measurements were made on three representative compounds with a Hilger sector photometer. As a light source the continuum from a Pointolite lamp was used, as no sufficiently rich line spectrum is available in the region concerned. Practical difficulties have so far limited the measurements to the stronger bands up to a wave-length of 6450 A. Solutions were prepared by the direct dissolution of weighed amounts of the compound; the concentrations ranged from 5 to 40 mg. per l. and were therefore approximately $M \times 10^{-6}$ to $M \times 10^{-5}$. To cover the wide range of intensities it was necessary to use a corresponding range of concentrations for each substance. We have therefore determined for each maximum the molecular extinction coefficient, ε, related to the observed extinction coefficient, K, by the relationship $\varepsilon = K/c$, where c is the concentration in g.-mols. per l. For since K is defined by $I_0/I = 10^{Kl}$, where l is the cell thickness in cm., and the quantity directly measured on the sector photometer is the density d (where $d = \log_{10} I_0/I = Kl$), then $\varepsilon = \log_{10} I_0/I. 1/cl$ or $d = \varepsilon cl$, the validity of Beer's law being assumed. The introduction of ε is necessary to permit of a comparison between the extinction curves of the different compounds. The values for log ε are liable to error in that only a part of the compound was in true solution and solid tended to separate on standing, so that the concentration is not certain. Stern and Pruckner (*Z. physikal. Chem.*, 1937, **178**, 435), in their work on the absorption spectra of azaporphyrins (imidoporphyrins), made some measurements on metal-free phthalocyanine and experienced the same difficulty.

[*] Continuing the series of papers on " Phthalocyanines," Part XII of which appeared in J., 1937, 933. A broader title has now become necessary.

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Results.—The quantitative results are in Table I. The absorption maxima of phthalocyanine and its metallic derivatives are in Table II, and those of other tetrazaporphins in Table III. In Tables II and III, the relative intensities of the bands are indicated in the last column.

TABLE I.

Phthalocyanine in bromonaphthalene $\{\lambda$	6,320	6,000	5,750	5,490
ϵ	72,000	46,000	11,500	7,000
$\log \epsilon$	4·857	4·663	4·061	3·845
Cobalt phthalocyanine in $\{\lambda$ .... chloronaphthalene ϵ	6,420 64,000	6,040 59,000	— —	— —
Tetrapyridinotetrazaporphin $\{\lambda$ .... in chloronaphthalene ϵ	6,340 54,500	6,080 29,000	5,760 26,000	5,540 21,500

TABLE II.

Maxima (λ) in Absorption Spectra of Phthalocyanine and its Metallic Derivatives.

Compound.	Solvent.[1]	a_1.	a_2.	b.	c.	d.	e.	f.	Order of intensities.
Metal-free	C	7000	[6750]	6640	6325	6000	5760	5500	Weaker bands at 5280(g) and 5040(h) $a_1 > b > d > c > e > f > g > h$
Beryllium [3] (dihydrate)...	C	6920	6815	6550	6305	6140	5910	5700	$a_1, a_2 > d > b > c > e > f$
Dilithium	Ac	—	6880*	6280	5950	5690	5500	—	$a > c > b > d > e$
Magnesium [3] (dihydrate)	C	7045	6780	6625	6490	6305	6125	5970	Weaker band at 5750(g) $a_1, a_2, b > e > c > d > f > g$
Chloroaluminium [3] ...... $\{$C		—	6910*	6650	6220	5970	[5760]	—	$\}a > c > b > d > e$
$\{$Alc		—	6700	6430	6040	5825	[5590]	—	
Vanadyl	C	[7190]	6950	6680	6330	6035	5810	—	$a > c > b > d, e$
Chromium	C	—	6940*	6600	6210	5980	5760	—	$a > c > b > d > e$
Ferrous [4] .... $\{$C		—	6600	—	—	5950	—	—	$a > d$
$\{$Q		—	6600	—	6320	5930	—	—	$a > d > e$
Chloroferric [4] .... $\{$C		—	6590	—	—	5950	—	—	$a > d$
$\{$Q		—	6600	—	6280	5910	—	—	$a > d > e$
Cobalt [3] .... $\{$C		—	6720*	6420	6040	5800	5610	—	$a > c > b > d > e$
$\{$P		—	6550	—	5930	—	—	—	$a > c$
Nickel	C	—	6760*	6410	6025	5800	5580	—	$a > c > b > d > e$
Copper	C	—	6800	6480	6090	5850	5650	—	$a > c > b > d > e$
Zinc	C	—	6800*	6490	6160	5875	5650	—	$a > c > b > d > e$
Silver	C	—	6750*	6425	6050	5800	5600	—	$a > c > b > d > e$
Platinum	C	—	6520	6240	5880	5645	5450	—	$a > c > b > d > e$
Lead	C	—	6850	6420	6150	5910	—	—	$a > b > c > d$

* Broad band, indefinite maximum. [1] Solvents : C = chloronaphthalene; Ac = acetone; Alc = alcohol; Q = quinoline; P = pyridine. [3] Traces of metal-free compound, formed during dissolution, are possible. [3] Note effect of solvation. See p. 1156.

TABLE III.

Maxima (λ) in Absorption Spectra of Compounds with Similar Ring System.

Solvent : Chloronaphthalene.

Compound.*	a.	b.	c.	d.	e.	f.	Order of intensities.
Phthalocyanine	7000	6640	6325	6000	5760	5500	$a > b > d > c > e > f$. For weaker bands see Table II.
α-Naphthalocyanine	7200	6770	6450	6060	[5840]	—	$a > b > d > c > e$ $\}$ Practically
β-Naphthalocyanine	7200	6780	6500	6060	[5840]	—	$a > b > d > c > e$ $\}$ identical.
Octaphenyltetrazaporphin	6750	—	—	6050	5600	—	$a > d > e$
Magnesium octaphenyltetrazaporphin	6450	—	—	5850	—	—	$a > d$
Magnesium octa-(p-nitrophenyl)tetrazaporphin	6650	—	—	5980	—	—	$a > d$
Copper octaphenyltetrazaporphin	6285	—	—	6040	5700	—	$a > d > e$
Tetrapyridinotetrazaporphin	7000	6730	6340	6080	5760	5540	$a > b > c > d > e > f$
Copper tetrapyridinotetrazaporphin	—	6490	6200	5870	—	—	$b > d > c$. Probably another band of longer wave-length.
Copper tetrathiophenotetrazaporphin	>7050	6600	6310	5930	—	—	$a > b > d > c$
Magnesium tetrathionaphthenotetrazaporphin	—	6780	6410	6040	—	—	$b > d > c$
Copper tetrathionaphthenotetrazaporphin	>7050	6750	—	6000	—	—	$a > b > d$

* For the preparation of these substances, see Bradbrook and Linstead, *J.*, 1936, 1744; Cook and Linstead, *J.*, 1937, 929; Linstead, Noble, and Wright, *ibid.*, p. 911. The nomenclature has been revised to correspond with that of Helberger (*Annalen*, 1937, **529**, 205).

DISCUSSION.

The absorption maxima of phthalocyanine in quinoline solution determined by Stern and Pruckner (*loc. cit.*) were 6980, 6750, 6640, 6330, 6020, 5790, 5580, 5280 A. These are in satisfactory agreement with our results. We are doubtful about the small band at 6750 A., which may be due to a trace of metallic phthalocyanine as impurity. Many metallic phthalocyanines have their main bands in this region. Our curves for metal-free phthalocyanine show only a slight flattening at this point. As far as the measurements

of intensities can be compared, the agreement is satisfactory. The influence of solvent on the absorption spectrum of free phthalocyanine is very slight (although some of the metallic derivatives show evidence of solvation; see below). This has also been noticed in the porphyrin series by Stern and co-workers (see, for example, *Z. physikal. Chem.*, 1936, **177**, 42).

The stronger bands in the phthalocyanine spectrum are found but little altered in that of tetrapyridinotetrazaporphin (pyridinoporphyrazine; Linstead, Noble, and Wright, J., 1937, 911). The spectra of the metallic phthalocyanines differ in some respects from that of the metal-free compound and among themselves, but certain general characteristics appear in common. These are : (1) there are one or two intense bands (a and b) in the region 6600—7000 A. and a fairly strong band (c or d) near 6000 A.; and (2) the intensity of the absorption increases fairly regularly with increasing wave-length, except that the band at about 6000 A. is nearly always more intense than that next to it of longer wave-length.

In contrast are the spectra of the porphyrins which have been fully studied by Fischer, Stern, and their colleagues. The general characteristics are that there are four bands in the region from 4950 to 6150 A. and that the absorption decreases with increasing wave-length. Fischer has recently discovered various azaporphyrins (imidoporphyrins) in which nitrogen atoms to some extent replace the methin groups which link together the pyrrole rings in the porphyrin molecule (*Annalen*, 1936, **521**, 122; 1936, **523**, 154; 1937, **527**, 1; 1937, 528, 1). Stern and Pruckner's study (*loc. cit.*) of the absorption spectra of these compounds brings out the fact that the introduction of the nitrogen atoms produces little change in the position of the bands, but a considerable alteration of the intensities, the bands of longer wave-length being greatly intensified. The data of the present paper enable the analysis to be taken a stage further and the general outlines can be summarised as follows :

FIG. 1.

(1) The introduction of nitrogen atoms in place of methin groups in the porphin system leads to a great increase in intensity of the absorption bands of longer wave-length, but all the bands remain below about 6300 A. On the other hand, the introduction of four nitrogen atoms in laterally fused rings, as in the change from phthalocyanine to tetrapyridinotetrazaporphin, has no substantial 'effect.

(2) The introduction of aromatic rings either fused to the $\beta\beta'$-positions, as in phthalocyanines, or substituted as β-phenyl groups, as in octaphenyltetrazaporphin (Cook and Linstead, J., 1937, 929), leads to the development of intense bands in the red region, between 6600 and 7000 A. With the further study of the tetrabenzazaporphin group it will be possible to take this comparison further.

The central conjugated azaporphin ring system is regarded as the chromophore of the phthalocyanine molecule and the fused benzene rings (or substituted phenyl groups) as enhancing the selective absorption by lengthening the conjugated chain. The group provides an example of the effect observed by Kuhn in the polyenes, namely, that an increasing number of conjugated double bonds results in a displacement of the absorption bands towards longer wave-lengths, high extinction coefficients, and a multiple band system. As an example of the first effect, we may compare the maximum of the main band of phthalocyanine, at 7000 A., with that of α- and β-1 : 2-naphthalocyanines, which lies at 7200 A. in the same solvent.

Effect of Metals.—In Figs. 1, 2, and 3, the positions of the band maxima are plotted on a wave-number scale to bring out certain interesting relationships. The introduction of metals into the phthalocyanine molecule has a variable effect on the intensity and spacing, but on the whole does not alter the general type. The weakest absorption bands of the metal-free compound can no longer be detected and the whole spectrum is shifted towards
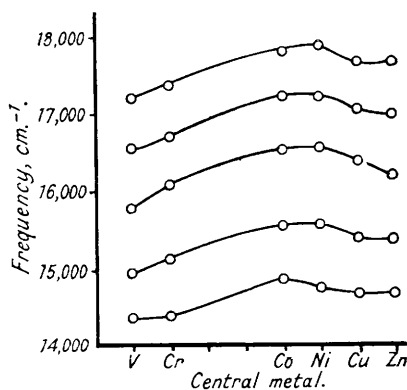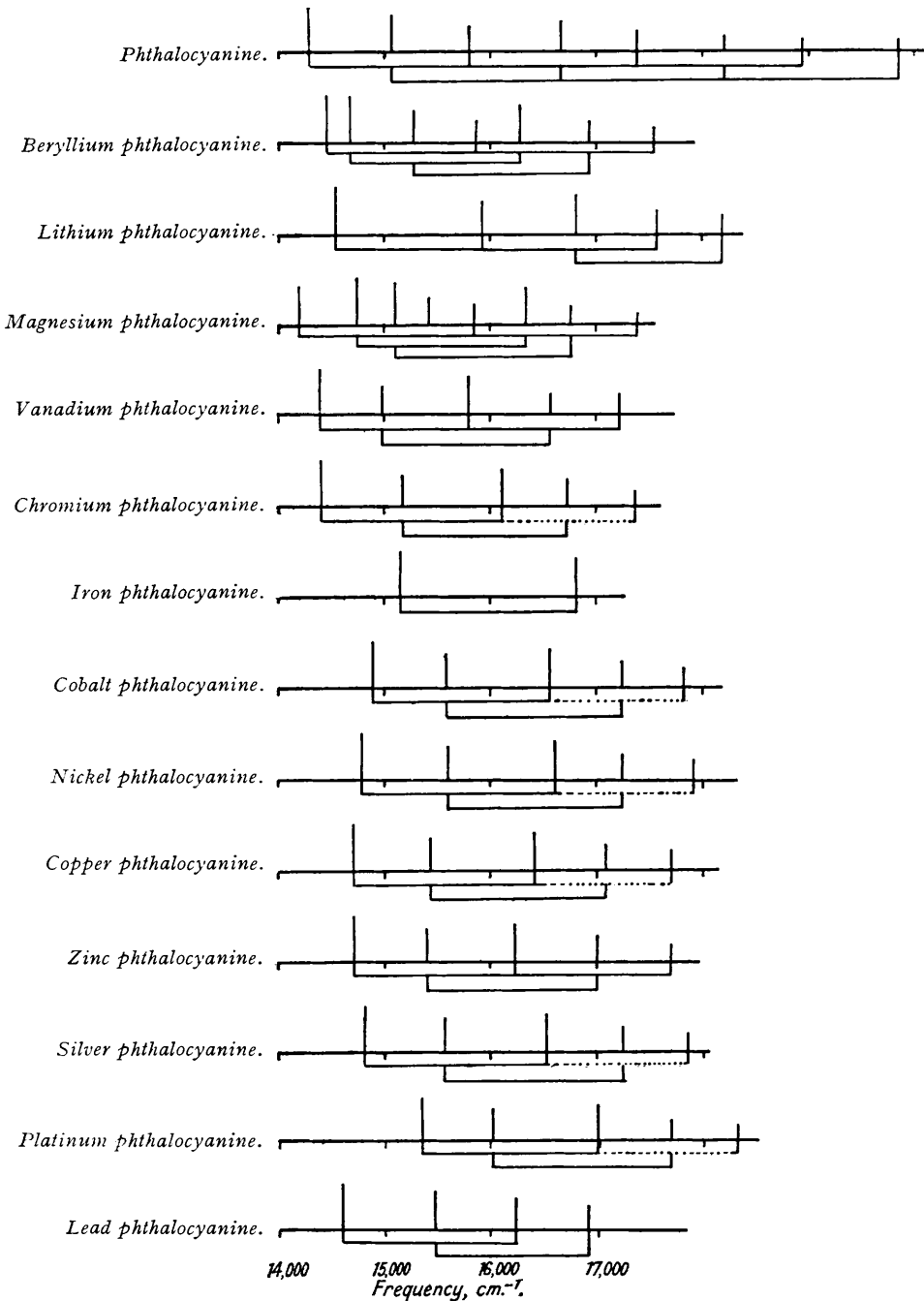
higher frequencies. The amount of displacement increases with the atomic number of the central atom, as is shown by the following comparisons of corresponding bands :

			Diff.		Diff.
(Copper phthalocyanine	....	14,710	} 105 cm.$^{-1}$	15,435	} 125 cm.$^{-1}$
\ Silver ,,	....	15,815		15,560	
(Nickel ,,	....	14,850	} 500 cm.$^{-1}$	15,600	} 425 cm.$^{-1}$
\ Platinum ,,	....	15,350		16,025	

FIG. 2.

Phthalocyanine.

Beryllium phthalocyanine.

Lithium phthalocyanine.

Magnesium phthalocyanine.

Vanadium phthalocyanine.

Chromium phthalocyanine.

Iron phthalocyanine.

Cobalt phthalocyanine.

Nickel phthalocyanine.

Copper phthalocyanine.

Zinc phthalocyanine.

Silver phthalocyanine.

Platinum phthalocyanine.

Lead phthalocyanine.

14,000   15,000   16,000   17,000
Frequency, cm.$^{-1}$.

Superimposed on this mass effect, there appears to be a second periodic effect. The compounds of vanadium, chromium, iron, cobalt, nickel, copper, and zinc cover the most important part of the first transition series. If the positions of the main bands of each of the phthalocyanine derivatives of these metals, in chloronaphthalene, are plotted against the atomic number of the metal, the values fall on a smooth curve (Fig. 1), the displacement reaching a maximum with nickel. In view of the fact that the tendency to form

FIG. 3.
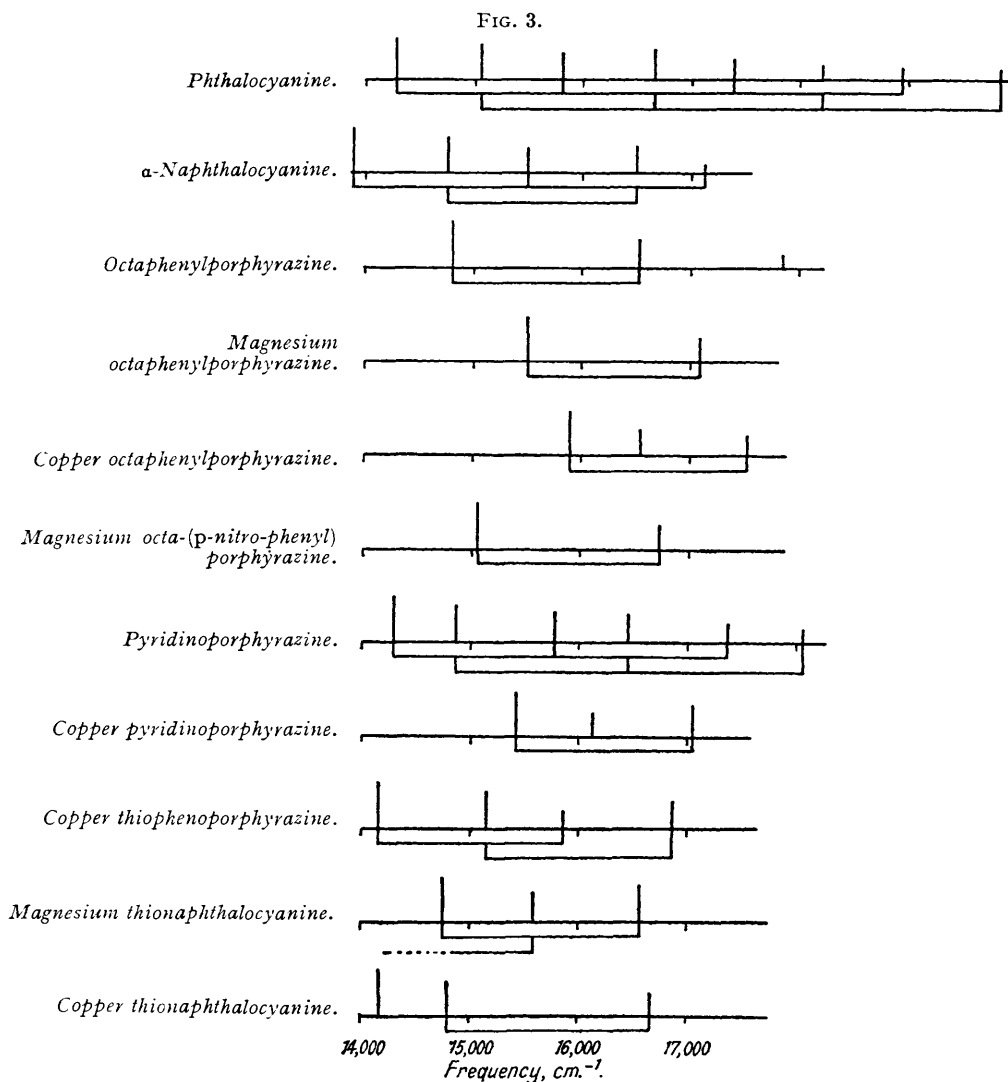
planar four-co-ordinate compounds reaches its maximum with nickel, palladium, and platinum, it is possible that the magnitude of the shift in the absorption spectra can be correlated with the strength of the co-ordinate links of the central atom. A similar displacement of absorption towards higher frequencies with the introduction of metal occurs with octaphenyl- and heterocyclic tetrazaporphins.

Frequency Differences.—Fig. 2 indicates that the eight main bands of the phthalocyanine spectrum fall into two groups, in each of which the intensity diminishes regularly with increasing frequency. Within each group the bands are separated by a frequency difference which is practically constant within the experimental error.

Spacings in the absorption spectrum of phthalocyanine.

a_1—c	1520	b—d	1610 ⎫	
c—e	1570	d—f	1550 ⎬	Mean, 1585 cm.$^{-1}$
e—g	1560	f—h	1620 ⎭	

Essentially the same spacing is to be found in the spectra of the metallic derivatives (Fig. 2), although the frequency difference tends to increase as the atomic weight of the central metal rises. Especially significant is the fact, shown in Fig. 3, that the same factor and band spacing are to be found in the spectra of octaphenyltetrazaporphin, its *p*-nitro-derivative, tetrapyridinotetrazaporphin, and α- and β-naphthalocyanines. With a slight augmentation the same interval appears also in the spectra of the tetrathionaphtheno-tetrazaporphin derivatives.

This regularity indicates the identity of the principal vibrating system. The mean frequency, 1585 cm.$^{-1}$, in the phthalocyanine (tetrazaporphin) spectrum may be compared with the 1560 cm.$^{-1}$ term identified by Hellström (*Arkiv Kemi, Min. Geol.*, 1936, **12**, *B*, no. 13) in the spectrum of the porphyrins. These are of the same order as the known Raman frequencies : for C=C, 1600 cm.$^{-1}$, for C=N, by interpolation between C=C and C=O, about 1640 cm.$^{-1}$.

There is strong evidence, both physical and chemical, that the central azaporphin nucleus of the phthalocyanine molecule constitutes a benzene-like resonance hybrid. We therefore identify the oscillating system responsible for the 1585 cm.$^{-1}$ band spacing with this central conjugated system. The corresponding 1560 cm.$^{-1}$ frequency of the porphyrins may similarly be assigned to the corresponding central ring system. On this basis the observed absorption bands in the spectrum of phthalocyanine correspond with the vibrational levels of two excited electronic states, the excitation being associated with the great ring. The band maxima are represented by the two series :

$$\nu_1 = 14{,}290 + 1585\,n_1 \text{ cm.}^{-1} \quad \text{and} \quad \nu_2 = 15{,}060 + 1585\,n_2 \text{ cm.}^{-1}$$

The two band systems are regarded as derived from different electronic levels, rather than, following Hellström's views on the porphyrin system, from ground-states of differing vibrational energy, because (i) no 890 cm.$^{-1}$ band progression has been identified, (ii) it may readily be calculated that the populations of energy levels differing, as in this case, by about 2·5 Cals., are far too disparate to account for the observed roughly equal intensity of the bands.

Finally, a few minor points may be dealt with. The absorption spectra of ferrous and of chloroferric phthalocyanine are indistinguishable both in chloronaphthalene and in quinoline (Table II). Hence during the process of dissolution there has been either oxidation or reduction, so that the final state of oxidation is independent of the initial state. It seems most reasonable to suppose that the absorption spectra actually measured are those of chloroferric phthalocyanine in chloronaphthalene and of hydroxyferric phthalocyanine (or a base compound) in quinoline. The effect of solvation appears in the spectra of cobalt phthalocyanine in pyridine and of chloroaluminium phthalocyanine in ethyl alcohol, the spectra being displaced to shorter wave-lengths.