[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY OF WASHINGTON UNIVERSITY AND THE UNIVERSITY OF CALIFORNIA]

Spectra of the Metallo-derivatives of $\alpha,\beta,\gamma,\delta$-Tetraphenylporphine

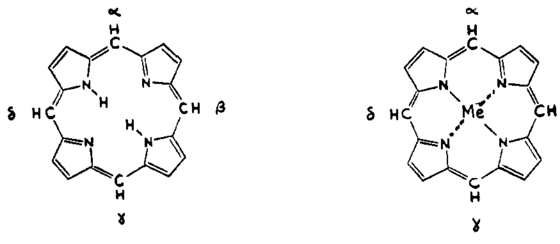
BY G. D. DOROUGH,[1a] J. R. MILLER[1b] AND FRANK M. HUENNEKENS[1c]

The absorption spectra of seventeen of the metallo-derivatives of $\alpha,\beta,\gamma,\delta$-tetraphenylporphine are correlated with the nature of the bonding between the central metal substituent and the nitrogen atoms of the porphine ring. The oscillator strengths for the first two electronic transitions in these spectra have been calculated, and the results are discussed. Included in the experimental section are methods of preparation and details of certain chemical properties of the metallo-tetraphenylporphines, and a few emission and acid salt spectra of tetraphenylporphine compounds.

Porphines[2] and their metal derivatives (see Fig. 1) possess as one of their most striking physical properties a series of well defined and intense absorption bands in the visible region of the spectrum. These spectra have not only been of practical use in the characterization and analysis of porphine compounds, but have also been the subject of many theoretical discussions and interpretations.[3] Recent interest in porphine spectra has centered about attempts to calculate from molecular orbital and free electron models a set of energy levels consistent with the observed spectra.[4,5,6] Although quantum mechanics probably offers the greatest hope for a real understanding of the nature of porphine spectra, the methods applied to date do not readily treat of the effect of the central metal substituent, and it is this effect which perhaps is of greatest interest to chemists. The present paper contains quantitative absorption spectra of various metal complexes of a simple porphine, $\alpha,\beta,\gamma,\delta$-tetraphenylporphine.[7] These spectra, together with the oscillator strengths for the electronic transitions involved, permit an evaluation of the effect of the central metal substituent on porphine spectra.

Experimental

Preparation of Tetraphenylporphine (Free Base).—The free base was prepared from pyrrole and benzaldehyde and purified by methods which have been described previously.[8]



a. b.

Fig. 1.—a, The porphine ring (all porphine structures with two center hydrogens are termed porphine "free bases"); b, a metalloporphine (divalent metal).

Preparation of Metallo-tetraphenylporphines.—All the metalloporphines used in this study were prepared from the free base. A general procedure which is applicable to the preparation of most metalloporphines is as follows:

A 2.0- to 5.0-ml. aliquot (*ca.* 10^{-4} *M*) of the free base in an appropriate reaction solvent (see below) is boiled gently with about 50 mg. of the metal acetate. If the acetate is not available, a mixture of 250 mg. of sodium acetate and 50 mg. of the nitrate or chloride of the metal often may be substituted. After conversion to the metalloporphine is complete (usually within 5 min.) as indicated by the absence of free base absorption bands in a visual spectroscope, the solution is transferred to a small separatory funnel with about 5 cc. of benzene. Water is added to the separatory funnel, and the resulting benzene layer is washed several times with water to completely remove the reaction solvent and inorganic salts. A final wash of 1 *N* NH_4Cl is sometimes necessary to break emulsions. The benzene layer is dried over anhydrous sodium sulfate, and diluted to 10 ml. in a volumetric flask. The resulting benzene solution is of an appropriate concentration to use in the Beckman Spectrophotometer for measuring absorption spectra down to about 4500 Å.; below 4500 Å. a dilution of the order of 1 to 10 is required.

The reaction solvents most frequently employed are glacial acetic acid for tin(II), copper(II), silver(II), cobalt(II), nickel(II) and iron (III), and pyridine for zinc(II), cadmium(II), mercury(II) and lead(II). Pyridine also may be used for copper and tin, and water-soluble organic solvents such as acetonitrile, dioxane, and acetic anhydride are exemplary of additional solvents which may be substituted in some cases.

If it is desired to prepare the solid salts, the above procedure is modified to the extent of employing larger amounts of solvents and free base. The resulting benzene solution is evaporated to dryness under vacuum to yield the solid metalloporphine. Recrystallization of the solid often may be accomplished by slowly adding methanol to a concentrated chloroform solution of the metalloporphine.

Special comment is necessary on the iron salt. Ferrous acetate, prepared by dissolving iron wire in glacial acetic acid, is used rather than ferric acetate. The resulting ferrous metalloporphine is very rapidly oxidized by air to the ferric stage, the appended anion being an acetate. The FeOH compound is formed by shaking a benzene solution of the acetate with aqueous NaOH. The FeCl compound is formed by shaking the FeOH porphine with concentrated HCl. The FeCl and FeOAc compounds are very similar in spectra.

Special preparative methods are needed for the synthesis of the other metalloporphines. The magnesium derivative is prepared by means of the Grignard reagent as previously

---

[1] (a) Washington University, St. Louis; (b) du Pont Fellow in Chemistry, Washington University, 1950–1951; (c) University of California Fellow in Chemistry, 1947–1948. Present address: Institute for Enzyme Research, University of Wisconsin, Madison, Wisconsin.

[2] The nomenclature used in this article follows the trend of recent years in which the name porphyrin is reserved as a general name for all tetrapyrrole pigments embodying the basic configuration shown in Fig. 1, and the terms porphine, chlorin (dihydroporphine), and tetrahydroporphine are used to denote the reduction level of the ring system. The porphine ring has none of the double bonds in the β,β'-positions of the pyrrole groups reduced, the chlorin has one, and the tetrahydroporphine has two. See reference 3, footnote 2.

[3] A review article which cites many of these references is Aronoff, *Chem. Revs.*, **47**, 175 (1950).

[4] Simpson, *J. Chem. Phys.*, **17**, 1218 (1949).

[5] Longuet-Higgins, Rector and Platt, *ibid.*, **18**, 1174 (1950).

[6] Kuhn, *ibid.*, **17**, 1198 (1949).

[7] This porphine differs from the structures of Fig. 1 by the substitution of four phenyl groups for the hydrogens at the positions labeled α, β, γ and δ. No steric interference is present in the molecule if the planes of the phenyl rings are at right angles to the plane of the porphine ring; considerable steric interference would be present if the phenyl rings were coplanar. Since quinoidal type resonance forms which would require the coplanar structure are of very high energy due to a disruption of the porphine ring conjugation in such forms, it seems reasonable that the plane of the phenyl rings are always at right angles to that of the porphine ring, and that the effect of the phenyl substitution on the porphine system is limited almost solely to a minor electrostatic effect. It is thus our belief that the easily accessible tetraphenylporphine compound is a satisfactory model for a study of this kind. It is a model unlike any naturally occurring porphine, however, in that the latter never carry four methine carbon substituents.

[8] Ball, Dorough and Calvin, THIS JOURNAL, **68**, 2278 (1946).

described.[9] The barium salt is prepared by the addition of 0.1–0.2 cc. of a saturated methanolic solution of barium oxide to 10 cc. of a dry benzene solution of the free base. Centrifugation removes the excess barium methylate which precipitates from benzene solution. The disilver salt is prepared by the addition of silver acetate to a pyridine solution of the free base. The salt forms rapidly, requiring only a slight warming. Vigorous boiling of the green disilver salt converts it slowly to the reddish-orange monosilver divalent salt by the novel reaction: $PAg_2 \rightarrow PAg + Ag^\circ$. The metallic silver often precipitates as a mirror on the wall of the test-tube. According to Haurowitz,[10] the precipitation of the silver is quantitative. In acetic acid as a solvent the reaction proceeds directly to the monosilver salt without the formation of a silver precipitate. To accompany the oxidation of the silver from +1 to +2 in this case, it seems likely that a reduction of +1 hydrogen is involved. The reaction might be written

$$PH_2 + Ag^+ \xrightarrow{\text{acetic acid}} PAg + H^+ + {}^1/_2H_2$$

The disilver salt is not stable in acetic acid solution, in fact, water is sufficient to hydrolyze it.

The alkali salts are prepared as follows: 3.5 cc. of a solution of free base in anhydrous pyridine (*ca.* 10^{-5} *M*) is placed in a 1-cm. square Pyrex cuvette capped with a standard taper joint. 0.1 cc. of a solution of the alkali metal hydroxide in absolute methanol (*ca.* 10^{-1} *M*) is added with mixing, and the cuvette sealed. The resulting green salt is stable toward hydrolysis for many hours in the case of lithium, sodium and potassium. The alkali salts also may be prepared free of all other substances by the use of high vacuum technique.[11] Solutions of material prepared in this way can be kept indefinitely in sealed tubes without any apparent degradation. The spectra of the alkali porphines in pure pyridine prepared by vacuum technique agree to within 5% of the corresponding spectra obtained from solutions prepared as above in pyridine–methanol mixtures. This would indicate that the equilibrium, $PH_2 + 2CH_3OM = PM_2 + 2CH_3OH$, is practically complete to the right under the conditions employed in the latter solutions.

The rubidium and cesium alkali porphines may be prepared in pyridine by the addition of the corresponding hydroxide in methanol, but such solutions are very unstable and rapidly revert to the free base. The spectra of such solutions when freshly made indicate that the spectra of these two alkali derivatives are rather unlike those of the first three members of the group.

It should be remarked that the magnesium, cadmium, mercury and lead derivatives gradually deteriorate if their benzene solutions are exposed to light. Such solutions are stable in the dark indefinitely, however.

The amphoteric nature of the porphine molecule permits the formation of acid salts (involving the addition of protons to the center of the porphine), as well as metal derivatives (involving the loss of protons from the center). The spectra of these salts are influenced by the nature of the acid as illustrated in Fig. 3. The salts are prepared by dissolving an appropriate quantity of free base in the desired solvent: 98% sulfuric acid, glacial acetic acid, or benzene containing HCl (benzene shaken with concd. HCl and dried over anhydrous sodium sulfate). The spectra in sulfuric acid change slowly with time, due to sulfonation. The sulfate curve in Fig. 3 represents essentially a zero time curve.

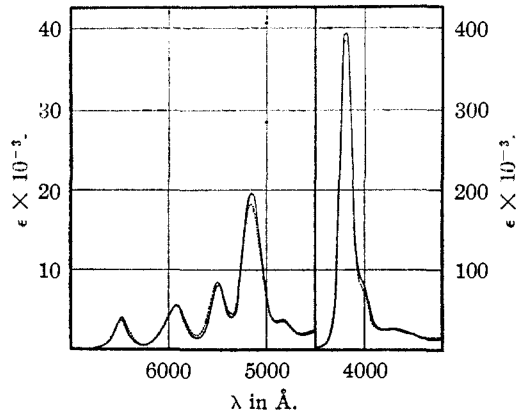


Fig. 2.—Absorption spectra of the free base: solid line, benzene; dashed line, pyridine.

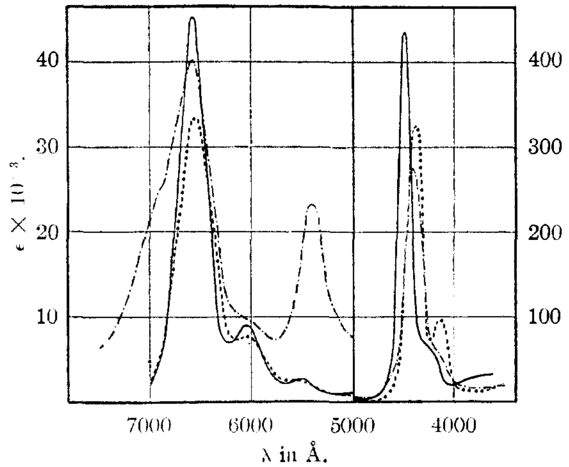


Fig. 3.—Absorption spectra of acid salts: solid line, hydrochloride in benzene; dashed line, acetate in glacial acetic acid; dashed-dotted line, sulfate in 98% sulfuric acid.

Absorption Spectra.—All the absorption spectra[12] shown in Figs. 2–10 were measured on a Beckman model DU Spectrophotometer, taking readings of optical density every 50 Å. The absorption curves represent smooth lines drawn through these points.

The extinction coefficients were calculated from the optical densities and the concentration of the solution by the equation, $\log_{10} I_0/I = \epsilon cd$, where $\log_{10} I_0/I$ is the optical density at a particular wave length (or increment of wave lengths), ϵ is the extinction coefficient at that wave length, c is the concentration in moles/liter, and d is the thickness of the absorbing medium in cm. The concentrations of the metalloporphine solutions were determined in three ways: (1) By weighing a given sample of the solid metallo-derivative, and dissolving it in a known volume of solvent.

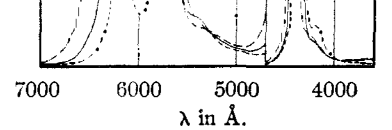


Fig. 4.—Absorption spectra of group I metalloporphines: solid lines, disodium; dashed line, dilithium; dashed-dotted line, dipotassium; solvent, from 7000–4700 Å., pyridine; below 4700 Å., pyridine–3% methanol (see experimental).

---

[9] Huennekens and Calvin, This Journal, **71**, 4025 (1949).

[10] Haurowitz, *Ber.*, **68**, 1795 (1935).

[11] Barnes and Dorough, This Journal, **72**, 4045 (1950).

[12] Many of these spectra agree qualitatively with those given by Knorr and Albers, *J. Chem. Phys.*, **9**, 497 (1941). There are differences of ϵ values, however, and some differences due to the fact that the free base material used by these authors in the preparation of the metallo-derivatives apparently contained some free base chlorine. (Compare the free base curve of Knorr and Albers with the free base curves of tetraphenylporphine and tetraphenylchlorin given in reference 7.)

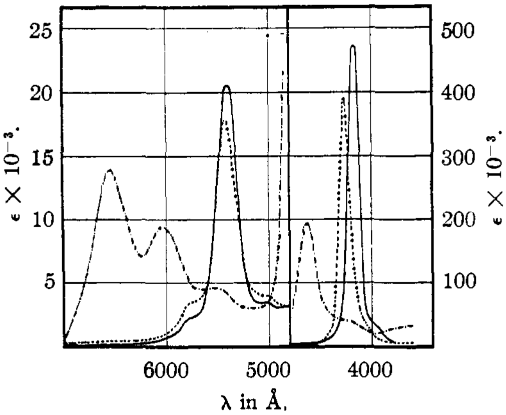


Fig. 5.—Absorption spectra of sub-group I metalloporphines: solid line, copper(II); dashed line, silver(II); dashed-dotted line, disilver(I); solvent, benzene for copper(II) and silver(II), pyridine for disilver(I).

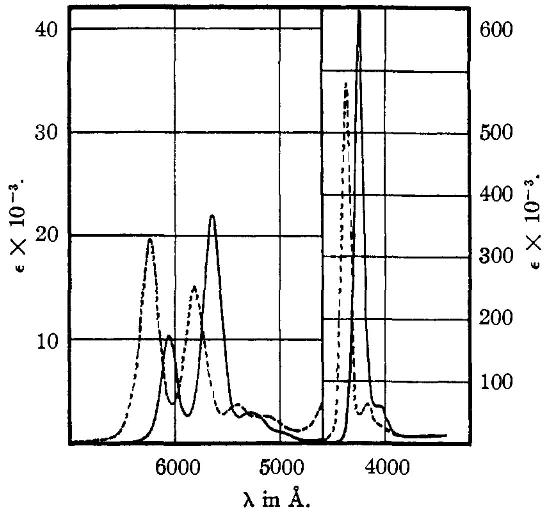


Fig. 6.—Absorption spectra of group II metalloporphines: solid line, magnesium (in benzene); dashed line, barium (in benzene-2% methanol).

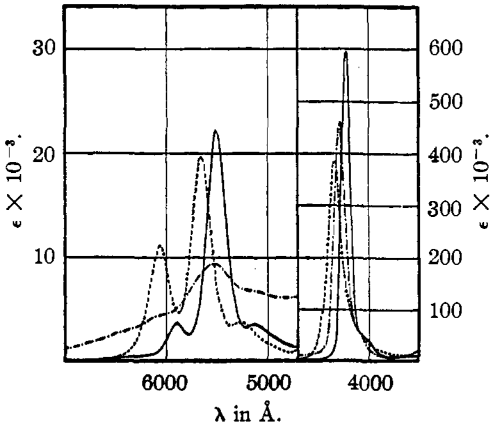


Fig. 7.—Absorption spectra of sub-group II metalloporphines: solid line, zinc; dashed line, cadmium; dashed-dotted line, mercury(II); solvent, benzene.

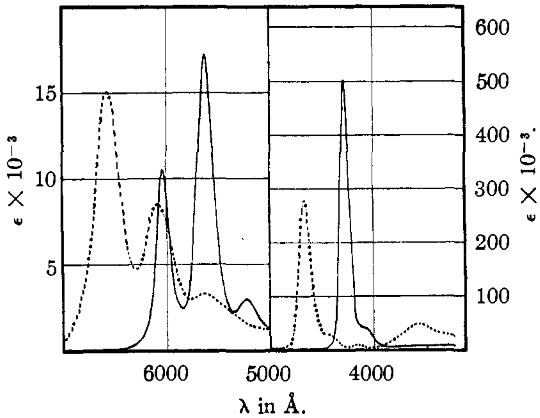


Fig. 8.—Absorption spectra of group IV metalloporphines: solid line, tin(II); dashed line, lead(II); solvent, benzene.

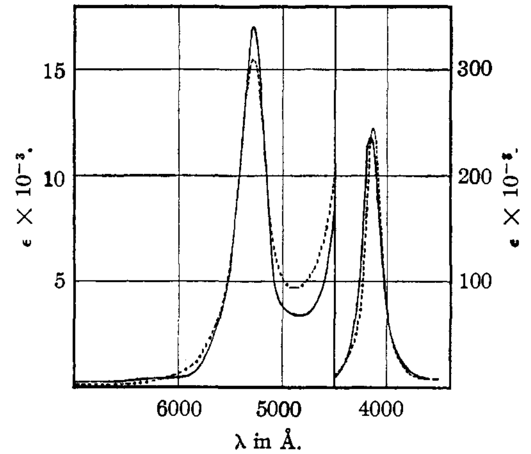


Fig. 9.—Absorption spectra of the transition group metalloporphines: solid line, nickel(II); dashed line, cobalt(II); solvent, benzene.

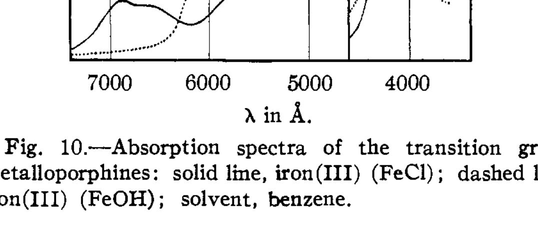


Fig. 10.—Absorption spectra of the transition group metalloporphines: solid line, iron(III) (FeCl); dashed line, iron(III) (FeOH); solvent, benzene.

(2) By carrying out quantitatively the transfers involved in the general procedure for the preparation of metalloporphines given in the previous section. If this is done, the concentration of the final benzene solution will be $V/10 \times C_0$, where V is the volume in ml. of the aliquot of free base, and C_0 is the concentration of the free base solution.

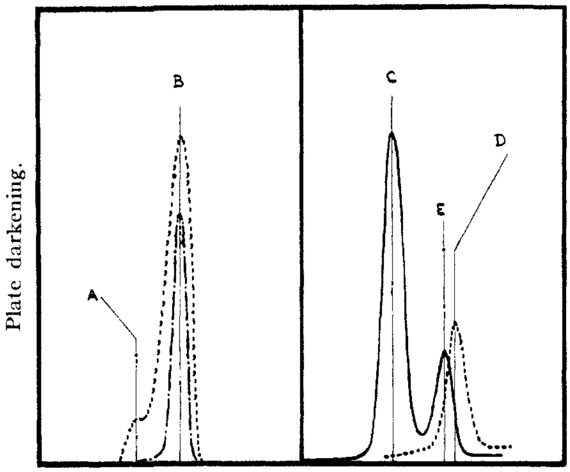
(3) By quantitatively hydrolyzing the metalloporphine and determining the concentration of the resulting free base solution from known ε values. The hydrolysis is carried out by shaking a benzene solution of the metalloporphine with water or HCl solution. After hydrolysis, the benzene solution is separated and dried over anhydrous sodium sulfate. (If an HCl solution has been used, the drying must

be preceded by neutralization with 6 N NH_4OH and several washings with water in order to convert to the free base any porphine hydrochloride which may have been formed.) This method is applicable to the silver (using 12 N HCl), zinc (using 6 N HCl), magnesium and cadmium (using 3 N HCl), barium, mercury and lead (using 1 N HCl), and the alkali and disilver derivatives (using water). These acid concentrations do not necessarily represent minimum values required for hydrolysis.

As a check, all three methods have been applied to zinc tetraphenylporphine, giving results which agreed to within 2%.

The solvent, if it does not interact chemically with the porphine, has relatively little effect on the absorption spectra (see Fig. 2). If complexing occurs with the solvent, as is often the case with pyridine, very marked differences in the spectra are noted. This is particularly true of the magnesium and sub-group II derivatives.[13] For this reason, as many as possible of the absorption spectra have been measured in the inert solvent benzene.

Emission Spectra.—The phosphorescence spectra were determined in E.P.A. solvent (ether, isopentane, alcohol, 5:5:2) using the apparatus described by Lewis and Kasha.[14] The fluorescence spectra were determined in benzene solution on the same apparatus, modified to permit side illumination and with the phosphoroscope removed. The spectra were photographed on hypersensitized Eastman Kodak Plates I-N or I-L. The plates were traced on a Zeiss Recording Microphotometer, and the curves in Fig. 11 are direct reproductions of these tracings. The general shape of the emission bands and their locations are valid; however, the relative heights of even two peaks belonging to the same substance are not absolute since the sensitivity of the photographic plates varies with the wave length. No systematic investigation of the emission spectra has been undertaken in this study, but the examples of Fig. 11 have been included for general reference.



Phosphorescence (in EPA) Fluorescence (in benzene)

Fig. 11.—Emission spectra: solid line, free base; dashed line, zinc; dashed-dotted line, magnesium; (peak heights are not relative as shown—see experimental); wave lengths in Å.: A-8800, B-7900, C-7300, D-6500, E-6600.

Oscillator Strengths.—The calculation of the oscillator strength depends only upon a determination of the integral $\int \epsilon \, dv$. The value of this integral was obtained by measuring the area under the absorption curves shown in Figs. 2-11. Since these curves are plots of ϵ *versus* λ, the areas were taken in segments of wave length over which the frequency did not change appreciably, and an average value of the frequency was used for that segment. In the red region segments of 500 Å. may be used without appreciable error; at shorter wave lengths somewhat smaller segments must be used (200–300 Å.). The areas were measured with a Keuffel and Esser Compensating Polar Planimeter. The oscillator strengths were calculated from these areas by the equation[15]

$$f = \frac{2303\ Mc}{N\ \pi\ e^2}\,\eta_0\left(\frac{3}{\eta_0^2 + 2}\right)^2 \int \epsilon \, dv$$
$$= 1.44 \times 10^{-19}\,\eta_0\left(\frac{3}{\eta_0^2 + 2}\right)^2 \int \epsilon \, dv$$

where M is the mass of the electron in g., c is the velocity of light in cm./sec., N is the Avogadro number, e is the charge of the electron in e.s.u., η_0 is the index of refraction of the solvent, v is the frequency of light, and ϵ is defined in the experimental section on absorption spectra.

Discussion

It has previously been shown that the metalloporphines differ widely in the ease with which they undergo exchange, replacement, and hydrolysis reactions.[11] They also differ widely in the ease with which they can be formed from the parent free base porphine, and in a number of physical properties. Despite these many differences, the absorption spectra of the free base porphine and all the metallo-derivatives have certain obvious resemblances. The absorption bands appear in two sets, the first in the region of 7000 to about 4500 Å., the second from about 4500 to 4000 Å. The latter set, commonly called the Soret bands, have approximately ten- to twenty-fold larger extinction coefficients at the peak maxima. It has been assumed for a number of years that each of these sets represents a separate electronic transition (with the individual bands of each set being vibrational terms), the assumption[16] being based on qualitative evidence such as the following: the spacing of the bands in the first electronic set is generally uniform[17] and of an energy value (1200–1500 cm.$^{-1}$) which could be reasonably associated with a vibrational term; the spacing between the nearest bands of the two sets bears little relation to this fundamental vibrational difference, or any multiple thereof; the change from the free base to a metalloporphine, or from one metalloporphine to another, often results in marked changes in the appearance of the bands of the first set, but in only minor changes in the Soret bands.

The quantum mechanical approaches[4,5] to porphine spectra lead to sets of energy levels which give the expected two electronic transitions, and add some new information concerning polarization and the degeneracy of the levels. However, these π-electron calculations provide no information concerning vibrational transitions which accompany the electronic ones. Unfortunately, one of the main effects of the center metal substituent is an alteration of the vibrational pattern of the spectra, particularly of the first electronic transition. Since the effect of the metal on the main porphine system is transmitted through the four nitrogens to which the metal is attached, it is reasonable that correlations should exist between

---

[13] Dorough and Miller, in preparation.

[14] Lewis and Kasha, This Journal, **66**, 2100 (1944).

[15] Bonhoeffer and Harteck, "Grundlagen der Photochemie," Theodor Steinkopff, 1933; Kuhn, *Helv. Chim. Acta*, **32**, 2247 (1949).

[16] Suggested as early as 1935 by Haurowitz (ref. 8).

[17] The uniformity is in no way exact, however, for the spacing in the free bases of both tetraphenylporphine and porphine decreases 200-300 cm.$^{-1}$ in going from the long to the short wave length bands. In the metallo-derivatives of tetraphenylporphine this trend is often in the reverse direction. In contrast, Anderson, *et al.*, *J. Chem. Soc.*, 1151 (1938), have shown for the closely related phthalocyanine a uniform band spacing with an average deviation of only 33 cm.$^{-1}$.

the kind of spectra given by a particular metalloporphine and the nature of the metal to nitrogen bonding. A number of such correlations are evident as follows: Although most of the divalent metalloporphines have rather similar spectra, there are quite definite differences which depend on whether or not a *d* metal oribital is available for covalent bonding. Those metals which have such an orbital[18] have spectra which are shifted to the blue and characterized by a very depressed first band in the first electronic transition (*cf.* copper, silver, nickel and cobalt in Figs. 5 and 9). The divalent metals in which covalent bonding is limited to *s* and *p* orbitals of the metal have spectra which are shifted to the red compared to the *d* group, and which are characterized by a much more intense first vibrational band (*cf.* magnesium, barium, zinc, cadmium and tin in Figs. 6, 7 and 8). Of an entirely different nature are the spectra of the metalloporphines which are completely ionic in character (*cf.* the dialkali, acid and disilver salt spectra).[19]

Since the metals of a given group in the periodic table present the same electronic configuration to the porphine, similar spectra for metalloporphines derived from such metals should be anticipated. In addition, the changes in the spectra experienced in going down a series of metals in a group should be approximately the same for all groups, since the changes induced in the metal are relatively the same, *i.e.*, an increase in the electropositive character of the metal. These expectations are borne out, but with some limitations. The curves of dilithium, disodium and dipotassium (Fig. 4), copper and silver(II) (Fig. 5), magnesium and barium (Fig. 6), and zinc and cadmium (Fig. 7) form sets in which the curves are similar within a periodic group. In each of these sets, the following changes are observed as one proceeds down the group: the entire spectrum shifts to the red; the first peak of the first electronic transition is enhanced; the maximum ϵ of the Soret peak decreases.

Metalloporphine spectra which have little resemblance to the other representatives of their groups are those of the mercury and lead derivatives. The chemical properties of mercury and lead porphines are also somewhat anomalous, and the suggestion has been advanced that these anomalies are related to the large size of mercury and lead which prevents them from assuming a normal position in the center of the ring. If size is the only factor, however, it is difficult to explain the quite normal spectrum of the barium porphine, for barium is larger than either lead or mercury. The spectral abnormality may be an effect of having the 4f shell filled in mercury and lead; certainly there are other rather unexpected properties (*e.g.*, their high ionization potentials and lessened electropositive character) which are a direct result of this feature of their electronic structure. For those chemical properties in which size plays an important factor, the properties of the barium porphine are in line with those of the lead and mercury derivatives.[20]

Of a somewhat different type of metalloporphine are those derived from trivalent metals. Only one representative of this type has been included, that of iron(III). From Fig. 10 it is seen that the anion which occupies the third valence of the iron atom quite markedly affects the nature of the metalloporphine spectra.

In Table I are summarized the oscillator strengths of the first two electronic transitions for tetraphenylporphine and various of its metal derivatives. The oscillator strength is a characteristic constant which measures the total absorption of an electronic transition. Inspection of the values in Table I reveals an interesting relation: In any group of the periodic table in which the bonded metals are at the same oxidation level, and thus presumably bonded in a similar manner, there is an increase in oscillator strength for the first transition and a decrease in the second as one proceeds down the group.

TABLE I

Porphine derivative	Oscillator strength	
	1st transition	2nd transition
Free base	0.12	1.51
Dilithium	.11	1.45
Disodium	.14	1.28
Dipotassium	.17	1.25
Magnesium(II)	.079	1.66
Barium(II)	.10	1.34
Zinc(II)	.088	1.39
Cadmium(II)	.099	1.38
Mercury(II)	.12	1.36
Copper(II)	.086	1.28
Silver(II)	.089	1.13
Disilver(I)	.10	1.02
Tin(II)	.070	1.10
Lead(II)	.085	0.617[a]
Iron(III)(FeCl)	.10	0.995[b]
Iron(III)(FeOH)	.092	1.14[b]
Nickel(II)	.079	1.26
Cobalt(II)	.074	1.15
Acid salt(HCl)	.16	1.41
Acid salt (HOAc)	.16	1.55
Acid salt (H_2SO_4)	.37	1.42

[a] This value excludes the broad peak at about 3600 Å.
[b] Indicates an incomplete value, the ultraviolet tail of the peak not being included (see Fig. 10).

An interpretation of such an effect is offered by the assumption of "configurational interaction" between the excited states. Using the set of energy levels derived by Longuet-Higgins and coworkers[5] as an example (Fig. 12), it is seen that all the excited states have the same symmetry (*Eu*). Perturbation interaction should thus occur between these states, that is, the wave function representative of the first excited state should not be

---

[18] For nickel it is certain that a *d* orbital is used in the metal-nitrogen bonding since nickel ion is paramagnetic but nickel porphines are diamagnetic. Haurowitz and Klemm, *Ber.*, **68**, 2312 (1935).

[19] This comparison must be somewhat limited, for some porphines such as etioporphine II have sodium and hydrochloride salt spectra which resemble the *s* − *p* groups.

[20] For example, unlike the metalloporphines of the smaller divalent metals, the metalloporphines of lead and mercury readily show numerous replacement reactions.[11] Among themselves, mercury ion replaces the larger lead in a porphine, but the reverse does not occur. It should follow, then, that barium in a metalloporphine, should be replaced by both lead and mercury ions. This is so, the reactions occurring almost instantaneously in pyridine solution.

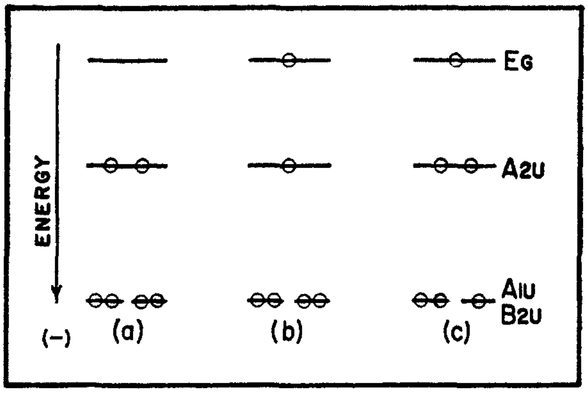


Fig. 12.—Schematic representation of molecular orbitals in porphine according to Longuet-Higgins, Rector and Platt (twenty π electrons in lower molecular orbitals are not shown): a, ground state; b, first excited state ($A_2u \rightarrow Eg$); d, second excited state (A_1u or $B_2u \rightarrow Eg$).

solely that of the state shown in Fig. 12, but should be a sum of the wave functions of all the excited states, each such wave function being multiplied by an appropriate coefficient. The same would be true of the wave function for the second excited state, but with different coefficients. It then turns out, assuming certain normalization and orthogonality requirements, that if the effect of changing the metal in a given group is merely to change the relative values of the coefficients, an increased transition probability for one transition will result in a decreased transition probability for the other. The oscillator strengths, which differ from the transition probabilities only by an energy term, should qualitatively follow the same pattern.

This interpretation is obviously not an explanation of the effect; it is merely a mechanical picture of how the effect might come about. The real explanation would have to reveal how the central metal affects the coefficients in the wave functions for the excited states. Since the change in going down a group of metals in the periodic table is accompanied by an increase in electropositive character of the metal (that is, the valence orbitals of the same azimuthal quantum number become increasingly less stable), the bonding of the metals in a given group in the periodic table should become more ionic in character as one proceeds down the group. This change in bonding would not directly affect the π electron system responsible for the various electronic levels, but it would result in differences in the negative charge on the four center nitrogens. Longuet-Higgins and co-workers calculated the effect of changes in electron density of the four center nitrogens on the electronic energy levels of the porphine ring in attempting to correct for the greater electronegativity of nitrogen as compared to carbon, and by a similar approach it might be possible to calculate the effect of the metal on the oscillator strength. It is perhaps of interest that there is a noticeable trend in which the more electronegative metals, irrespective of their periodic group, have lower oscillator strengths for the first electronic transition than metals of low electronegativity. There is by no means an exact correspondence of electronegativity and oscillator strength, however; nickel and magnesium provide two examples of metals which seem far out of line.

Incidentally, it is seen from Fig. 12 that there are two possible transitions to account for the Soret peaks, an $A_{1U} \rightarrow Eg$, or a $B_{2U} \rightarrow Eg$. It was assumed in our oscillator strength calculations that the small hump which is always present on the short wave length side of the large Soret peak is a vibrational term, but it might be that it is the other of these two possible electronic transitions. The fact that the small hump may correspond to an independent electronic transition would not materially affect the above conclusions regarding the oscillator strengths.

Acknowledgment.—The preparation of this article has been greatly facilitated by helpful discussions with Professors S. I. Weissman and W. T. Simpson, and Mr. Max Wolfsberg. The authors are also deeply indebted to the interest of Professor Melvin Calvin in whose laboratory this investigation was initiated.

ST. LOUIS 5, MO. RECEIVED FEBRUARY 23, 1951