THE PHTHALOCYANINES

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I. Introduction

In 1928, at Grangemouth, Scotland, at the works of Messrs. Scottish Dyes Ltd., traces of a dark blue insoluble complex were noticed in the iron vessels used to prepare phthalimide from phthalic anhydride and ammonia (*65, 221*). This product was subsequently shown to be ferrous phthalocyanine. Since then literally thousands of patents and publications concerning the phthalocyanines have appeared. It is probable that the phthalocyanines have been the subject of more physical studies than any other single class of compound, partly as a result of their unique structure and partly because of their high thermal and chemical stability.

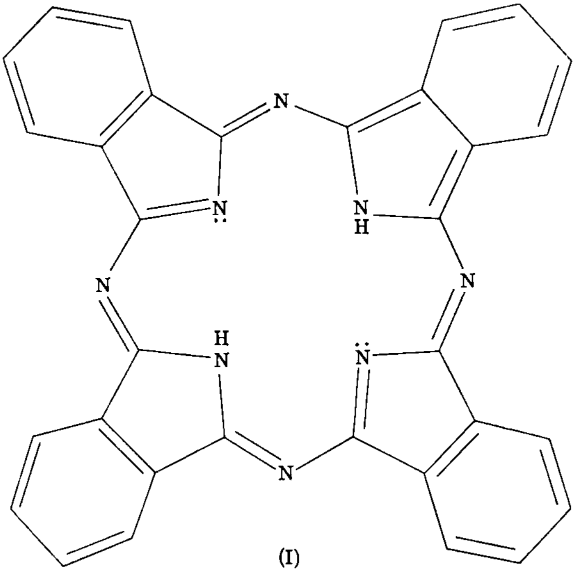
In this review the physical and inorganic chemistry of the phthalocyanines will be discussed in detail. The review will be limited to nuclear unsubstituted derivatives, except where mention of a substituted derivative is pertinent to the discussion. The organic chemistry of the complexes, e.g., chlorination (*12*), will not be discussed. There have been many articles and books reviewing the industrial uses of the phthalocyanines (*39, 64, 129, 133, 232, 304, 321, 365, 369, 382*), and hence this aspect will not be touched upon here. A more general review has also appeared recently (*251*). Polymeric phthalocyanines (*79, 241–243*) will not be covered.

II. Methods of Preparation and Molecular Structure

A. GENERAL

The classic studies elucidating the structure of the phthalocyanines were carried out at Imperial College in the early 1930's under the direction of Sir Patrick Linstead. Linstead and his colleagues (*5, 10, 11, 40, 73, 74, 221–224, 226*) showed that phthalocyanine (I) (abbreviated Pc) contained a ring system of four isoindole units linked by aza nitrogen atoms (Fig. 1). It is therefore closely related to the naturally occurring porphyrins, but having aza rather than methine corner links. The analogy to the porphyrins makes the understanding of the chemical and physical behavior of the phthalocyanines especially important in the long-term investigation of natural life processes. The two central hydrogen atoms of structure (I) are replaceable by a wide range of metals and metalloids. The compounds so obtained are usually insoluble in common solvents, but have some slight solubility in higher boiling aromatic solvents such as quinoline, chlorobenzene, and chloronaphthalene. The complexes are all intensely colored—purple, blue, or green compounds with a beautiful red reflex. Most of them are thermally very stable and many will sublime unchanged at 400°C/10^{-6} mm. Copper phthalocyanine has been shown (*210*) to be stable at 900°C *in vacuo*.

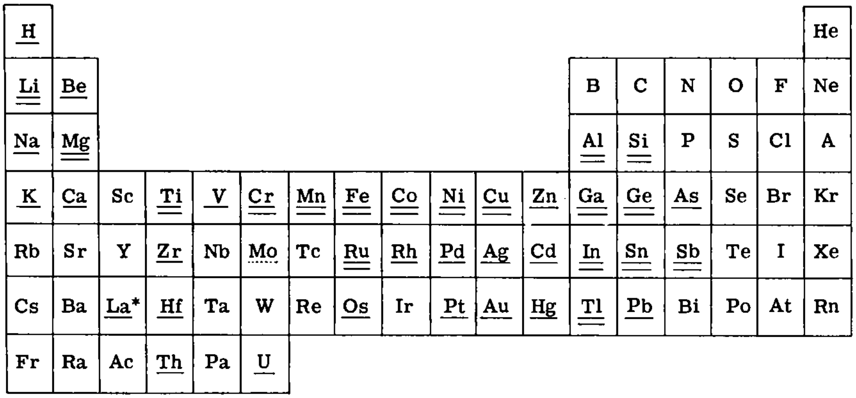
The phthalocyanines often exist in two or more polymorphic modifications, which may be distinguished by infrared and X-ray diffraction techniques (see Section D). Although phthalocyanines in which the central metal ion has an oxidation state of 2 are the most common, complexes are known in all oxidation states from 0 to 6. Phthalocyanine manganese complexes, for example, are known in oxidation states 0, 1, 2, 3, 4, (*10, 88, 93, 339*). Figure 2 illustrates the occurrence of metal phthalocyanines through the periodic classification.



(I)

FIG. 1. Structure (I), metal-free phthalocyanine.

Phthalocyanines exhibit varying stabilities toward solution in concentrated sulfuric acid. Virtually all the complexes are freely soluble in this acid; but some, such as PcCu and PcNi, are reprecipitated unchanged upon dilution, whereas others, for example, PcCa and $PcNa_2$, are demetallated. The product, metal-free phthalocyanine (abbreviated PcH_2), is itself slowly decomposed in concentrated sulfuric acid. Berezin has studied the behavior in concentrated sulfuric acid in great detail (see Section VI,B). The phthalocyanine unit is moderately stable toward oxidation, but may be broken down to phthalimide or phthalic acid by a two-electron oxidation with ceric or dichromate ions (*74, 227*). Elvidge (*89*) has developed the dichromate oxidation into an elegant method for the quantitative determination of the oxidation state of the central metal ion. Under certain circumstances, a one-electron oxidation product, having the ring system



H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	A
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La*	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac	Th	Pa	U												

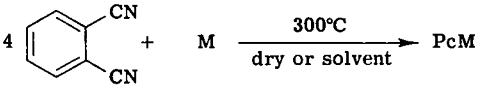
FIG. 2. Phthalocyanine complexes. Single underline, one complex known; double underline, more than one complex known; dotted underline, inadequately characterized. The asterisk indicates that no complexes of Ce, Pr, Pm, or Tb have been characterized.

intact, may be detected. This product is paramagnetic and exhibits an electron-spin resonance spectrum (*128, 130*) (see Section V,C) typical of a free radical.

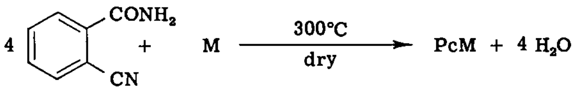
B. METHODS OF PREPARATION

Phthalocyanine metal complexes may be prepared by various methods, the more general methods (*10, 11, 34, 40, 86, 112*) being illustrated in the following equations:

$$\mathrm{PcH_2 + MX_2 \xrightarrow[\text{B.Pt.}]{\text{solvent (e.g., quinoline)}} PcM + 2\,HX} \qquad \text{(II)}$$

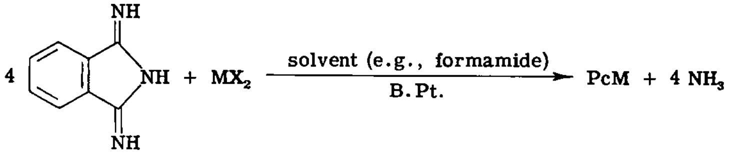


(III)



(IV)

Reactions (III) and (IV) may also be carried out with metal salts or metal oxides:

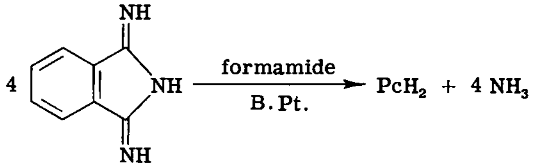


(V)

$$PcLi_2 + MX_2 \xrightarrow[\text{room temp.}]{\text{solvent}} PcM + 2\,LiX \qquad \text{(VI)}$$

Metal-free phthalocyanine may be prepared by a number of routes of which examples are given below.

$$PcNa_2 + 2\,H_3O^+ \longrightarrow PcH_2 + 2\,Na^+ + 2\,H_2O \qquad \text{(VII)}$$



(VIII)

$$PcCa + H_2SO_4 \longrightarrow PcH_2 + CaSO_4 \qquad \text{(IX)}$$

Equations (II) to (IX) illustrate basic methods of preparation, but many variations are used, particularly in industry, to obtain an economic yield. Phthalic acid, phthalamide, phthalimide, and phthalic anhydride, together with urea, are often used instead of phthalonitrile, and catalysts such as ammonium molybdate or zirconium tetrachloride may be employed (*249*, *251*, *269*). The reaction between phthalonitrile and metals (finely divided or acid-etched) is usually very vigorous at 250°–300°C, sufficient heat being generated to maintain the reaction temperature. This is an illustration of the ease with which the phthalocyanine skeleton is formed. Even more surprising are the observations that palladium black (*113*) and gold (*189*) will dissolve in molten phthalonitrile. Reaction (III) between phthalonitrile and a finely divided metal, metal hydride, oxide, or chloride is perhaps the most generally employed. For the unstable phthalocyanine complexes such as that of silver (*11*), the double decomposition reaction

(VI) is to be preferred. Nuclear halogenation often occurs when metal halides are reacted directly with phthalonitrile or *o*-cyanobenzamide; this may be minimized by the addition of urea, use of basic solvents, or carrying out the reaction at a lower temperature.

Purification of the products is best effected by sublimation at 400°C *in vacuo*. However, not all phthalocyanines will sublime; recrystallization from chlorobenzene, quinoline, or chloronaphthalene may then be employed. Certain more soluble phthalocyanines may be Soxhlet-extracted with lower boiling solvents such as acetone or alcohol.

C. STRUCTURE OF METAL PHTHALOCYANINES

1. *X-Ray Investigations*

In a classic series of papers, starting in 1935, Robertson showed that the environment of the metal atom was square planar (*224*, *225*, *300–304*) and moreover, that unlike the situation prevailing in the porphyrins, the entire phthalocyanine molecule was square to within the limits of accuracy of the study. Complete structural studies were carried out with the metal-free derivative (*224*), and the nickel (*302*) and platinum (*303*) complexes. Metal-free phthalocyanine, and beryllium, manganese(II), iron(II), cobalt(II), nickel(II), and copper(II) phthalocyanines are isomorphous (*303*). The phthalocyanines form long flat ribbon-like monoclinic crystals, the surface of the ribbon being the (001) plane and the axis (010). The (207) plane is generally well developed. The space group is $P2_1/a$ (C^5_{2h}), the cell is tetragonal, and the molecular symmetry is centrosymmetric. Table I lists the relevant structural data.

TABLE I

CELL CONSTANTS OF PHTHALOCYANINES[a]

Lattice parameters	PcH_2	Be	Mn	Fe	Co	Ni	Cu	Pt
a (Å)	19.85	21.2	20.2	20.2	20.2	19.9	19.6	23.9
b (Å)	4.72	4.84	4.75	4.77	4.77	4.71	4.79	3.81
c (Å)	14.8	14.7	15.1	15.0	15.0	14.9	14.6	16.9
V (Å^3)	1173	1293	1233	1231	1235	1186	1180	1186
β	122.2°	121.0°	121.7°	121.6°	121.3°	121.9°	120.6°	129.6°

[a] Space group $P2_1/a$; symmetry—centrosymmetric. From reference (*225*).

a. Metal-Free Phthalocyanine. The structure of metal-free phthalocyanine is illustrated in Fig. 3. Identical molecules occur along the b axis at intervals of 4.72 Å. The perpendicular distance between planes is 3.38 Å,

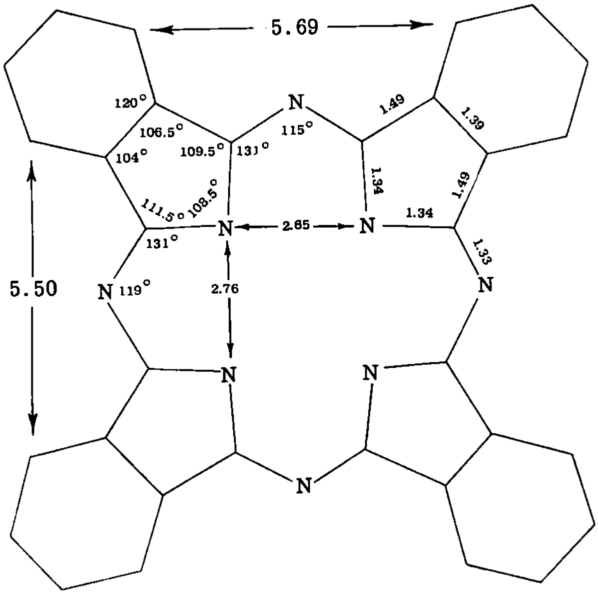


Fig. 3. The structure of metal-free phthalocyanine.

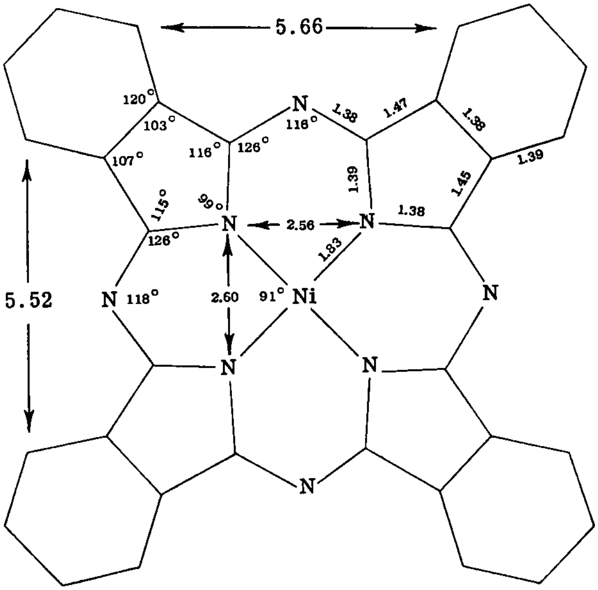


Fig. 4. The structure of nickel phthalocyanine.

close to that observed (3.4 Å) in graphite. The nearest intermolecular approach is 3.35 Å.

b. Nickel Phthalocyanine. The molecules of nickel phthalocyanine (Fig. 4) make an angle of 44.2° to the projection plane (010). The four isoindole nitrogen atoms are shifted 0.09 Å toward the nickel atoms relative to their position in the metal-free ligand, while the angle at the isoindole nitrogen atom has decreased from 108° to 99°. The perpendicular distance between planes along the *b* axis is 3.38 Å. The molecules lie in the crystal in such a way that the nickel atom lies 3.38 Å above (and below) a corner nitrogen atom of an adjacent molecule. There are no other intermolecular contacts. The inclination of the molecular axis to the *b* axis is 45.8°, exactly the same as in metal-free phthalocyanine (*302*).

The environment about the nickel atom, and its isomorphous analogs, may therefore be regarded as six-coordinate D_{4h}, but with two long interactions perpendicular to the molecular plane. This result has important implications in the study of the magnetic (see Section V,D) and electrical (see Section VI,D) properties of the phthalocyanines.

c. Platinum Phthalocyanine. Platinum phthalocyanine is not isomorphous with the other complexes studied. The molecule is inclined at 26.5°, rather than 44.2°, to the (010) plane and hence has a significantly smaller unit cell width. The perpendicular distance between planes is 3.41 Å. The molecules are so staggered that there are no intermolecular contacts, i.e., the platinum atoms do not lie directly above or below nitrogen atoms. The nearest intermolecular distance is 3.55 Å. The inclination of the molecular plane to the *b* axis is 63.9°. Bond angles and bond lengths were cited in this study, but the large size of the platinum atom made the investigation very difficult. The authors (*303*) did not put too much weight upon the accuracy of their data in this particular case. It is now thought (*379*) that no reliance should be placed upon the actual bond length and angle data, although the basic structure is undoubtedly correct. The molecular weight calculated from the X-ray data (*300*) was in good agreement with the calculated value.

d. Other Phthalocyanines. Chromous phthalocyanine is not isomorphous with other first-row transition metal phthalocyanines. Electron diffraction studies showed (*90*) that two of the unit cell dimensions were 3.4 and 42.5 Å (*90, 213*). The small unit cell width implies that the chromous phthalocyanine units are probably stacked on top of one another, i.e., making an angle of 0° with the (010) plane. This conclusion is supported by the magnetic data (see Section V,D).

Oxymanganese(IV) phthalocyanine, which is thought to have a polymeric structure involving O—PcMn—O—PcMn— chains (*88*), has a unit cell width of 7.2 Å as determined from electron diffraction studies (*213*).

This corresponds with exactly four times the expected Mn—O bond distance (1.6 Å). The Mn—O—Mn bond angle is undoubtedly 180°. This manganese complex is not isomorphous with oxyvanadium(IV) phthalocyanine (*214*), which is thought to be a five-coordinate monomer. [Oxytitanium(IV) phthalocyanine is isomorphous with the vanadium analog (*214*) as indicated from powder photographs.] A number of group IVB elements also give phthalocyanines of the type $(PcMO)_x$ where M = Si, Ge, and Sn. The X-ray powder photographs of these complexes (*194*) show lines corresponding to interplanar spacings of 3.32, 3.50, and 3.83 Å, respectively. Assuming a linear arrangement for the M—O—M bonds, this yields M—O bond distances of 1.66, 1.75, and 1.91 Å for the Si—O, Ge—O, and Sn—O bonds. These values are consistent with corresponding M—O bond lengths in other compounds (*336*). X-ray powder photograph data have also been reported for $PcSn(OH)_2$, $PcSnF_2$, $PcSnCl_2$, $PcSnBr_2$, $PcSnI_2$, Pc_2Sn, PcSn, and PcPb (*195*).

2. Electron Microscope Studies

Metal phthalocyanine crystals have been studied with the electron microscope (*98, 146, 207, 246, 247, 259, 332, 333*). Lines are observed whose distance apart corresponds with the interplanar spacings calculated from the X-ray data. However, these are not actual images but may be explained by a dynamical theory of electron diffraction (*146*). The crystal behaves as a two-dimensional diffraction grating, producing a cross-grating diffraction pattern (*246*). The image of the plane is formed as a result of interference between zero-order and the first-order spectrum of the planes concerned. These recombine in the image plane and their mutual interference produces a set of lines of the same spacings as the planes in the crystal from which they arise (*1*).

TABLE II

DATA FROM ELECTRON MICROSCOPY

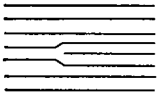
Complex	Plane	d^a (Å)	d^b (Å)	Reference
PcPt	$20\bar{1}$	12.0 ± 0.2	11.94	(*246*)
	$20\bar{1}$	12.0 ± 0.2	11.94	(*98*)
PcCu	$20\bar{1}$	10.3 ± 0.3	9.8	(*246*)
	$20\bar{1}$	9.9 ± 0.2	9.8	(*98*)
	$20\bar{1}$	9.8	9.8	(*333*)
	001	12.6	12.4[c]	(*333*)
	$20\bar{1}$	9.9 ± 0.2	9.8	(*333*)

[a] Electron microscope values.

[b] X-ray data.

[c] Twinned crystal.

The data obtained in this manner (Table II) are in good agreement with those spacings obtained from X-ray studies. An interesting development of this work has been the direct observation (*97, 246, 366*) of crystal dislocations, such as that shown in (X). These dislocations include complex arrays and unit edge dislocations (*333*). Since the image is a projection of the crystal, some kinds of dislocation, such as vacancies, are unlikely to be seen. Helical or screw forms of copper phthalocyanine, with a period of about 2000 Å, have been observed with the electron microscope (*98, 246*). Ubbelohde and Woodward (*353*) have investigated the effect of temperature (90°–600°K) on the lattice spacings of metal-free, nickel, and platinum phthalocyanines. Radiation damage to the crystal planes is discussed in Section VI,E,2.



(X)

D. POLYMORPHIC FORMS

Metal-free phthalocyanine exists in three polymorphic forms (α, β, and γ) (*112, 317*), while most other phthalocyanines exist in two (α and β) (*81, 143, 167, 172, 180, 196, 317, 331, 355*). The polymorphic forms differ in their infrared spectra (see Section VI,A), X-ray diffraction patterns (*81, 144, 172, 317, 377*), reflectance spectra (*317*), conductivity, and resistivity (see Section VI,D).

The X-ray measurements of Robertson and his co-workers were in all cases carried out on the more stable β modification, which is also the more crystalline modification. The α modification is unstable to transition to the β form in aromatic solvents (*335*). Ebert and Gottlieb have published (*81*) detailed methods by which the different polymorphs of copper, nickel, zinc, and metal-free phthalocyanine may be isolated. Phthalonitrile condenses in hydrogen-donor solvents, such as cyclohexylamine, to form metal-free phthalocyanine. The α metal-free phthalocyanine may be obtained from this reaction by milling the product in the dry with sodium chloride, the β form by milling in the presence of xylene. Solutions of metal-free phthalocyanine in sulfuric acid precipitate the α modification upon dilution (*172*). This may be sublimed below 200°C *in vacuo*, but is converted to the β modification above this temperature. Copper phthalocyanine behaves similarly. The β phthalocyanine may be reconverted to the α form by milling in the dry with sodium chloride or sodium sulfate. The γ metal-free phthalocyanine is prepared by demetallating calcium phthalocyanine with dilute hydrochloric acid (*112*).

An X-ray diffraction study of powdered α copper phthalocyanine, prepared by diluting a concentrated sulfuric acid solution of β copper phthalocyanine, has been made (*305*). The space group is probably $P4/m$ (C'_{4h}), containing six molecules per unit cell. The cell constants, a = 17.376 Å and b = 12.790 Å, were determined. The heat of transition of α to β copper phthalocyanine in *o*-chlorophenol at 80°C is 2.57 ± 0.03 kcal/mole (*29*).

Zhdanov and Vorona have made a detailed X-ray study of the effects of temperature upon the various forms of copper phthalocyanine (*381*). If copper phthalocyanine is sublimed between 150° and 250°C, the α modification is observed. Below this temperature range, the α modification is mixed with another unknown form. Heating for 20 minutes at 315°C or evaporation at 280°–300°C produces the β modification. The α and β forms of copper phthalocyanine differ in tinctorial power. The reflectance spectrum of the α form exhibits a fairly broad band at 480–487 mμ while this band occurs at 475–478 mμ in the β form (*317*). An X-ray diffraction curve has been reported (*80*) for a third, γ, form of copper phthalocyanine (*212*). The interplanar spacings for this complex are compared in Table III with those found for the α and β polymorphs. Suito and Ueda (*334*) have studied the rate of transformation of the α to the β polymorph in different solvents. During the transformation an intermediate metastable form similar in appearance to the stable β polymorph, but having different lattice spacings (12.78–13.04, 11.09–12.08, 3.62–3.74 Å), was observed.

TABLE III

d_{hkl} INDICES (Å) FOR POLYMORPHIC FORMS OF COPPER PHTHALOCYANINE

Compound	Indices
α-PcCu	12.90(100),[a] 9.00(13), 5.60(20), 3.71(17), 3.58(17), 3.33(25), 3.25(29)
β-PcCu	12.70(100), 9.70(71), 8.50(8), 7.20(6), 4.84(18), 4.17(11), 3.75(43), 3.41(31), 3.19(15), 2.94(18)
γ-PcCu	13.50(100), 11.95(98), 9.12(22), 8.51(16), 5.57(53), 4.17(8), 3.74(22), 3.57(38), 3.38(62), 2.95(17)

[a] Estimated intensities in parentheses. From references (*80*, *212*, *377*).

III. Phthalocyanine Complexes of the Non-Transition Elements

A. GROUP IA PHTHALOCYANINES

1. *Metal-Free Phthalocyanine*

The parent ligand may be prepared by acid demetallation of the so-called labile metal phthalocyanines. These include the phthalocyanines of

Mg, Be, Ag, Fe(II), Sb(III), Mn(II), Sn(II), alkali metals, alkaline earth metals, rare earths, Cd, Hg, and Pb (*19, 21, 54, 119, 226*). The rate of demetallation varies considerably (*19*) (see Section VI,B). The phthalocyanines of Cu, Zn, Co(II), Ni, Pt, Pd, VO, Al, Ga, and In resist demetallation in concentrated sulfuric acid at room temperature (*10, 21, 56, 57*). Phthalocyanine may also be prepared by the condensation of phthalonitrile or 1,3-diiminoisoindoline in hydrogen-donor solvents (*10, 81, 86, 346*), and by the catalytic condensation of phthalonitrile in the dry with platinum metal (*10*). Processes involving intermediates such as phthalic acid and urea have also been developed (*380*).

Phthalocyanine is slowly decolorized in concentrated sulfuric acid at room temperature (*20*) (see Section VI,B). Boiling in 20% nitric acid also results in decomposition, phthalimide being precipitated (*40*). The two central hydrogen atoms may be replaced by deuterium (*118, 213, 323*) (see Section VI,A). Metal-free phthalocyanine is readily purified by rapid recrystallization from concentrated sulfuric acid (α modification) or by sublimation in vacuum at 400°C (β modification).

The alkali metal phthalocyanines are, with the exception of the dilithium derivative, fairly insoluble in most organic solvents. The dilithium complex is unique in being soluble in a wide range of organic solvents including alcohol and acetone (*11*). All the complexes are readily demetallated by dilute aqueous acid. Dilithium phthalocyanine is rapidly demetallated by cold water (*11*), while disodium phthalocyanine is more resistant to hydrolysis, reacting slowly with hot water. The dipotassium derivative is said to be more readily demetallated than the sodium complex, perhaps because of its larger size (*10*).

2. Dilithium Phthalocyanine

Dilithium phthalocyanine was originally prepared from lithium amyloxide and phthalonitrile in boiling amyl alcohol (*11*), but may also be prepared from lithium hydride (*53*) or lithium metal (*214*) and phthalonitrile. It is readily purified by recrystallization from acetone. A monolithium derivative, presumably lithium hydrogen phthalocyanine, is formed when a deficiency of lithium or lithium salt is used in these reactions. It is a black insoluble compound of unknown structure (*11*). The high solubility of the dilithium complex makes it a very useful intermediate in double decomposition reactions. Many comparatively unstable metal phthalocyanines can be formed by the reaction of dilithium phthalocyanine and the appropriate metal salt in a solvent such as acetone, dimethylformamide, or quinoline (*11, 119, 120*).

The molecular polarizability of dilithium phthalocyanine has been found to be 16 ± 3 $\times 10^{-24}$ cm^3, in contrast to 62 ± 6 $\times 10^{-24}$ for barium and 120 ± 30 $\times 10^{-24}$ cm^3 for copper phthalocyanine (*78*).

3. Disodium Phthalocyanine

Disodium phthalocyanine may be prepared by the reaction of phthalonitrile with sodium amyloxide in amyl alcohol (*10*), or from sodium hydride and phthalonitrile (*52*). It does not sublime, and is readily demetallated by methanol and less readily by the higher alcohols (*75*). The complex reacts with methyl iodide in ethyl alcohol to give only the unmetallated derivative (*10*).

4. Dipotassium Phthalocyanine

This is prepared from potassium amyloxide and phthalonitrile (*10*). Very little work appears to have been done with the complex. Heavier group IA metal phthalocyanines have not been reported.

B. GROUP II PHTHALOCYANINES

1. Beryllium Phthalocyanine

Beryllium metal, previously etched with acid, reacts with phthalonitrile to yield beryllium phthalocyanine, the only square planar derivative of beryllium known (*10*). Both anhydrous beryllium and magnesium phthalocyanines react readily with moisture to form very stable dihydrates. Dehydration may be effected only by sublimation *in vacuo*. Sidorov has studied the interaction of sublimed layers of beryllium and magnesium phthalocyanines with water, by infrared spectroscopy (*325*). Some of the absorption bands arising from the phthalocyanine unit shift when water vapor is introduced. This behavior was not noted with other phthalocyanines (see Section VI,A).

2. Magnesium Phthalocyanine

Prepared from magnesium or magnesium oxide and *o*-cyanobenzamide (*40*), magnesium phthalocyanine has been the subject of much study since it is a synthetic analog of chlorophyll. Perhaps understandably, much of this work has been connected with photosynthesis, luminescence, fluorescence, etc. (see Section V,B). The molecular weight of magnesium phthalocyanine has been measured ebullioscopically in naphthalene (*223*). Because of the very low solubility of the substance, a very accurate platinum thermometer was employed. Nevertheless the successful measurement represents quite an achievement.

In addition to water vapor, sublimed magnesium phthalocyanine also interacts with acetic acid vapor, hydrogen bromide, hydrogen chloride, and deuterium chloride and bromide (*324*). The absorption spectra of these adducts have been interpreted in terms of attack by the protons on peripheral nitrogen atoms, and perhaps also central nitrogen atoms. Magnesium phthalocyanine also forms adducts with aniline, 2,4-lutidine, pyridine, quinoline, *o*-toluidine, acetone, ethanol, methanol, ethyl sulfide, ethylmercaptan, and thiophene (*350*), and with molecular oxygen (*121*, *122*, *124*, *191*).

Magnesium phthalocyanine may also be prepared from phthalonitrile, sodium cyanamide, and magnesium powder (*107*), phthalimide and magnesium (*346*), or phthalamide and magnesium imide (*287*).

3. Calcium Phthalocyanine

This complex may be prepared from quicklime and phthalonitrile (*10*, *38*) or from dilithium phthalocyanine and calcium chloride in ethanol (*11*). It does not sublime.

4. Barium Phthalocyanine

Prepared from baryta and phthalonitrile, barium phthalocyanine does not sublime, and is more readily demetallated by cold hydrochloric acid than is calcium phthalocyanine (*10*). Heavier group IIA phthalocyanines have not been reported.

5. Zinc Phthalocyanine

This complex may be prepared from phthalonitrile and zinc dust (*10*, *50*, *51*) or from dilithium phthalocyanine and zinc chloride in absolute ethanol (*11*). The use of zinc chloride and phthalonitrile leads to nuclear halogenated products (*10*). Zinc phthalocyanine sublimes readily and may be reprecipitated unchanged from concentrated sulfuric acid (*10*, *21*, *23*). The complex is inert toward exchange with 250-day Zn^{65} as zinc acetate in pyridine (*7*). Field emission microscopy has yielded a value of 7.0 ± 0.5 electron volts for its ionization potential (assumed equal to its work function) (*136*). McCartin (*236*) has investigated spectroscopically the interaction of various organic acceptors with zinc phthalocyanine in acetone solution. The absorption peak at 668 mμ is depressed and broadened in the presence of strong Lewis acids. Neglecting solvent competition, the equilibrium constant for complex formation is 2.3, 10, and 345 liters/mole at 25°C for 2,4,6-trinitrotoluene, *sym*-trinitrobenzene, and 2,4,7-trinitro-9-fluorenone, respectively. Picric acid is also shown to form a very strong complex having a new absorption band at 705 mμ. Zinc phthalocyanine is believed to function as an electron donor in the excited state.

6. *Cadmium Phthalocyanine*

Prepared from phthalonitrile and cadmium filings, little is known about cadmium phthalocyanine. It does not sublime, and is reported to be insoluble in all solvents. It is demetallated by concentrated sulfuric acid (*10*).

7. *Mercury Phthalocyanine*

Mercury(II) phthalocyanine is prepared by the interaction of mercuric chloride with dilithium phthalocyanine in absolute alcohol (*11*). It is readily demetallated in concentrated sulfuric acid and in boiling chloronaphthalene, and will not sublime (*111*, *226*).

C. GROUP IIIB PHTHALOCYANINES

No boron phthalocyanines have been characterized.

1. *Aluminum Phthalocyanines*

An extensive series of phthalocyanine derivatives of aluminum have been reported. The reactions of aluminum phthalocyanine are illustrated in Fig. 5 (XI)–(XVIII). Chloroaluminum phthalocyanine (XI) may be prepared from aluminum trichloride and phthalonitrile (*10*, *57*, *268*), *o*-cyanobenzamide, or unmetallated phthalocyanine (*56*), in boiling quinoline; (XI) hydrolyses to a hydroxy derivative (ν_{OH}, 3375 cm^{-1}) (*268*) when dissolved in concentrated sulfuric acid and subsequently reprecipitated with aqueous ammonia (*57*, *268a*) or water (*10*). The complex exists as a mono- and as a trihydrate (*268a*, *10*). Two molecules of water may be removed from the latter quite readily, whereas the third comes off at 110°C/0.1 mm. The monohydrate (XII) is probably six-coordinate in analogy to the corresponding chromium derivative (see Section IV,C). When heated to 400°C, (XII) first loses water to form the very hygroscopic anhydrous derivative, and then condenses forming the oxide (XIII). The oxide, which is presumably a binuclear derivative, is not hydrolyzed by boiling water or by refluxing 15 *N* sodium hydroxide or 0.1 *N* hydrochloric acid. The Al—O—Al link is, however, solvolyzed in concentrated sulfuric acid at room temperature, or by refluxing 6 *N* hydrochloric acid (*268a*). No corresponding chromium complex is known, the hydroxide being stable to sublimation (*90*).

The hydrogen atom of the aquo group of (XII) is acidic; the complex reacts with sodium hydroxide to yield an ill-characterized salt (*10*), and will condense with other acidic hydroxyl groups. Thus Owen and Kenney (*268*) have synthesized a series of aryloxy aluminum derivatives by the condensation of (XII) with various phenols. The complexes formed with phenol, *p*-phenylphenol, and *p*-methoxyphenol—(XIV), (XV), and (XVI)

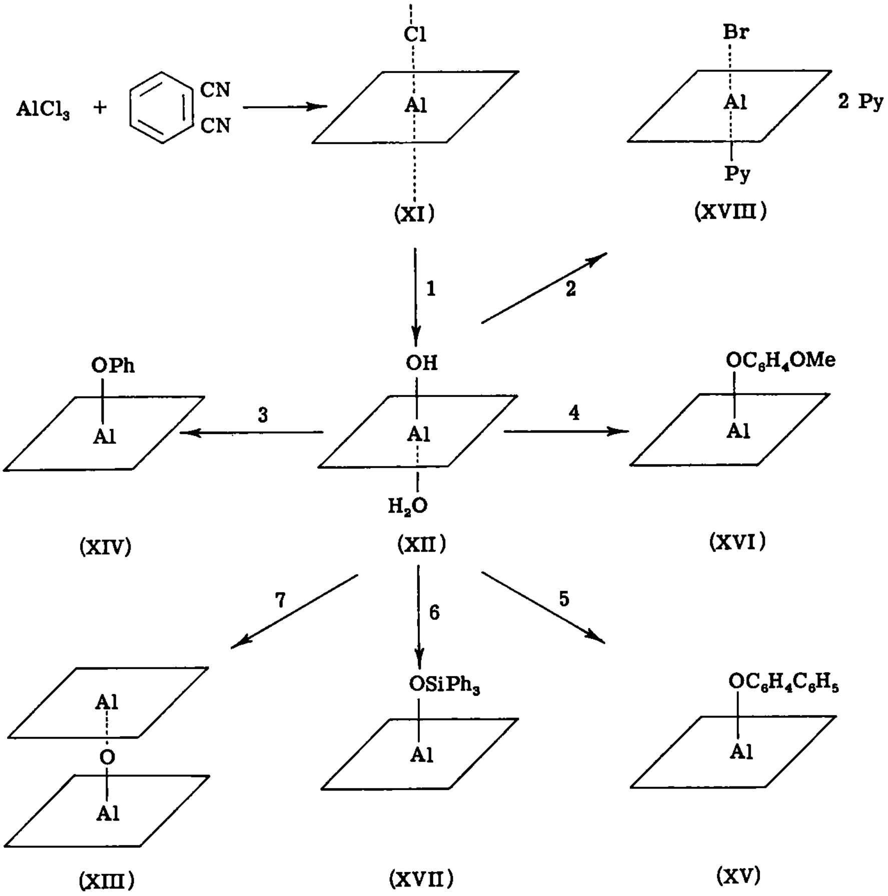


FIG. 5. The chemistry of aluminum phthalocyanines. Reaction pathway (1) H_2SO_4/NH_4OH; (2) Py/HBr; (3) C_6H_5OH; (4) $MeOC_6H_4OH$; (5) PhC_6H_4OH; (6) Ph_3SiOH; (7) 400°C.

—resist hydrolysis by refluxing aqueous ammonia but appear to suffer some decomposition when sublimed. Refluxing 6 *N* sulfuric acid does affect hydrolysis. Triphenylsilanol reacts similarly to form triphenylsiloxy-aluminum phthalocyanine (XVII), which has a Si—O—Al bond system. This complex sublimes readily without decomposition and resists refluxing 12 *N* sulfuric acid, but not concentrated sulfuric acid. The structures of these complexes are not known but, in view of the tendency for the anhydrous hydroxide to achieve six-coordination, it seems likely that they are six-coordinate polymers rather than five-coordinate monomers. Five-coordination would imply a square pyramidal structure, while the only definite example of five-coordinate aluminum is trigonal bipyramidal (*157*). The hydroxide (XII) reacts with hydrogen bromide and pyridine to form bromoaluminum phthalocyanine tripyridinate (XVIII) (*177*), from which the pyridine is readily removed. The infrared spectra of these aluminum phthalocyanine derivatives are characterized by a band near 903 cm^{-1} (*294*). Other aluminum silicon phthalocyanines will be discussed in Section D.

2. Gallium, Indium, and Thallium Phthalocyanines

Chlorogallium, chloroindium, and iodothallium phthalocyanines are formed by the reaction of *o*-cyanobenzamide with the corresponding halides in boiling quinoline (*55–57*). These complexes are *not* isomorphous with one another, nor with chloroaluminum phthalocyanine. Reprecipitation from sulfuric acid leads to the formation of the corresponding hydroxides. Chlorogallium phthalocyanine may also be prepared from gallium trichloride and phthalonitrile in the dry at 300°C (*278*). Dilithium phthalocyanines reacts with thallous hydroxide in absolute alcohol to give an unidentified bright green precipitate (*11*).

D. GROUP IVB PHTHALOCYANINES

Phthalocyanines in which a carbon atom occupies the central site are unknown. The reason for this may involve thermodynamics, but it is just as likely that it is because no serious attempt has been made to prepare them.

1. Silicon Phthalocyanines

Dichlorosilicon phthalocyanine (XIX) is prepared from silicon tetrachloride and phthalonitrile in quinoline at 200°C (*168, 170*). The blue-green crystals, which sublime readily at 430°C *in vacuo*, hydrolyze forming dihydroxysilicon phthalocyanine (XX) when refluxed with equal volumes of pyridine and aqueous ammonia (*200*). The corresponding difluorosilicon phthalocyanine is resistant to hydrolysis. Conversion of the chloride to the corresponding dicyanate, dithiocyanate, and diselenocyanate occurs upon reaction with the appropriate silver pseudohalide (*178*). The complexes are believed to involve nitrogen to silicon bonding in the case of the thiocyanate and selenocyanate.

The dihydroxide (XX) behaves very much as the corresponding aluminum derivative, but is not sufficiently acidic to form a sodium salt (*170*). A band at 3535 cm^{-1} in its infrared spectrum is assigned as the OH stretching vibration, while a possible OH deformation mode is observed at 831 cm^{-1}. The complex polymerizes in the following manner at 400°C, with loss of water:

$$x\text{PcSi(OH)}_2 \rightarrow \text{HO(PcSiO)}_x\text{H} + (x - 1)\text{H}_2\text{O} \qquad \text{(XXI)}$$

From a study of the amount of water formed per molecule of the hydroxide used, Joyner and Kenney concluded that x lies between 10 and 10^2. The siloxane polymer, a blue air-stable powder is thermally very stable, withstanding 520°C *in vacuo* for several hours (without subliming) (*171*). It is also hydrolytically stable, being soluble in concentrated sulfuric acid without decomposition (*268*). A band at 987 cm^{-1} in its infrared spectrum is assigned to the Si—O—Si stretching vibration. Further reactions of the dihydroxide are illustrated in Fig. 6.

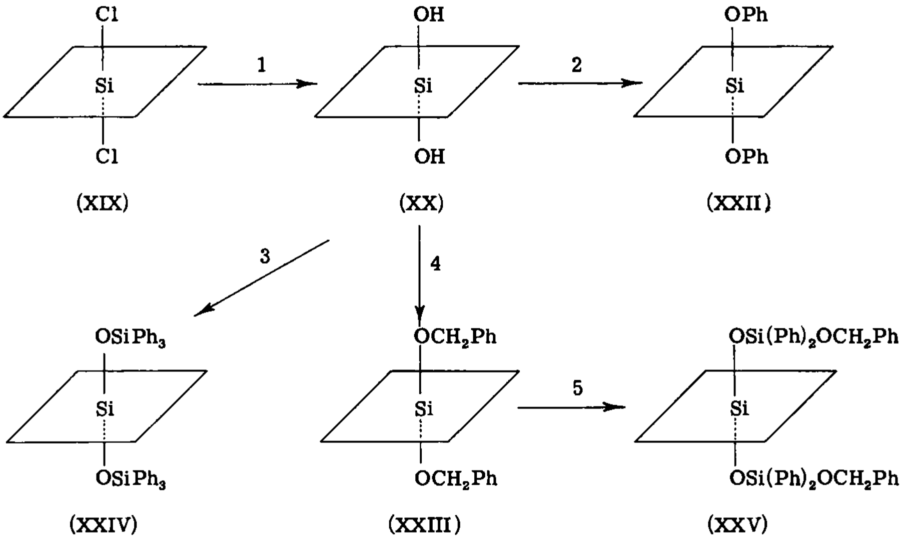


FIG. 6. The chemistry of silicon phthalocyanines. Reaction pathway (1) Py/NH_4OH; (2) Py/$\text{C}_6\text{H}_5\text{OH}$; (3) Ph_3SiOH; (4) $\text{C}_6\text{H}_5\text{CH}_2\text{OH}$; (5) $\text{Ph}_2\text{Si(OH)}_2$.

Thus (XX) reacts with phenol in pyridine to form diphenoxysilicon phthalocyanine (XXII), with benzyl alcohol to form (XXIII), and with triphenylsilanol to form (XXIV) (*168, 170, 200*). These complexes sublime readily without decomposition (cf. corresponding aluminum derivatives). Bis(diphenylmethylsiloxy)silicon phthalocyanine, which melts before subliming, is one of the very few metal phthalocyanines which actually melt (*373*). The siloxy complex (XXIV) may also be prepared in benzyl alcohol, thus implying that the Si—O—Si(Pc)—O—Si backbone is more stable than C—O—Si(Pc)—O—C. The dibenzyloxy derivative (XXIII) reacts with diphenylsilanediol to form bis(benzyloxydiphenylsiloxy)silicon phthalocyanine (XXV).

Alkoxy derivatives may be prepared by the reaction:

$$PcSi(OH)_2 + 2ROH \rightarrow PcSi(OR)_2 + 2H_2O \qquad \text{(XXVI)}$$

The more acidic the alcohol, the more readily does this reaction occur. Diethoxysilicon phthalocyanine, which was prepared in low yield by the reaction of the dihydroxide with ethanol in boiling 1-chloronaphthalene, is more readily obtained by the reaction of dichloro- or dibenzyloxysilicon phthalocyanine with sodium borohydride in ethanol (*200*). It is slightly soluble in ethanol and benzene, and does not melt below 360°C. Higher alkoxides of silicon phthalocyanine do, however, melt; thus complex (XXVI) ($R = C_8H_{17}$) melts with decomposition at 260°C, while (XXVI) ($R = C_{18}H_{37}$) melts at 152°C without decomposition. Trichloroethanol reacts readily with (XX) forming the alkoxide (XXVI) ($R = CH_2CCl_3$), while neopentyl alcohol requires a high reflux temperature to form (XXVI) ($R = C_5H_{11}$). The visible absorption spectrum of a dialkoxide is almost independent of the group R (see Section V,B). The higher alkoxides are quite readily soluble in benzene, a factor which may be related to the flexibility of the side chain attached to the silicon atom. The complexes are, however, thermally unstable and hence cannot be sublimed. They resist 2 *N* sodium hydroxide, but are converted to the hydroxide by hydrochloric acid at 100°C.

Kreuger and Kenney have discussed (*200*) the mechanism by which the dialkoxides are produced. They favor siliconium ions as the most likely intermediates:

$$HOPcSiOH + ROH \rightarrow HOPcSiOH_2^+ + RO^- \qquad \text{(XXVII)}$$
$$HOPcSiOH_2^+ \rightarrow HOPcSi^+ + H_2O \qquad \text{(XXVIII)}$$
$$HOPcSi^+ + RO^- \rightarrow HOPcSiOR \qquad \text{(XXIX)}$$

and argue that silicon can stabilize the siliconium ion by delocalizing the positive charge over the phthalocyanine ring system by means of its d_{xz} and d_{yz} orbitals. This seems reasonable at first sight, but it is difficult to understand why, if this is so, the hydroxide complex is not acidic toward aqueous alkali. The acidity of phthalocyanine hydroxides $PcM(OH)_{1 \text{ or } 2}$ toward alkali decreases qualitatively in the order Cr(III) $\cong$ Mn(IV) $\cong$ Sn(IV) > Al(III) > Si(IV) $\cong$ Ge(IV). The position of silicon seems anomalous (see Section VII).

The condensation of hydroxyaluminum phthalocyanine with dihydroxysilicon phthalocyanine has been studied (*268a*). The reaction proceeds in refluxing 1-chloronaphthalene:

$$PcSi(OH)_2 + 2PcAl(OH)H_2O \rightarrow PcAlOSiPcOAlPc \qquad \text{(XXX)}$$
$$PcSi(OH)_2 + PcAl(OH)H_2O \rightarrow PcAlOSiPcOSiPcOAlPc \qquad \text{(XXXI)}$$

These interesting phthalocyanine aluminosiloxanes are insoluble, thermally stable complexes which sublime unchanged. The backbones, which are presumably linear, are Al—O—Si—O—Al and Al—O—Si—O—Si—O—Al, respectively. Hydrolysis of (XXX) with pyridine and hydrogen bromide gave (XVIII) and dihydroxy silicon phthalocyanine, while hydrolysis of (XXXI) gave the same aluminum derivative but a new silicon derivative:

$$\mathrm{PcAlOSiPcOSiPcOAlPc + HBr + Py \rightarrow PcAlBr{\cdot}3Py + HO(PcSiO)_2H} \qquad \text{(XXXII)}$$

$HO(PcSiO)_2H$ (XXXII) condenses to the polysiloxane (XXI) on strong heating (*171*). The aluminosiloxanes may be regarded as condensed phthalocyanine siloxanes end stopped by aluminum phthalocyanine.

2. Germanium Phthalocyanines

Germanium forms phthalocyanine complexes similar to those produced with silicon and aluminum (*169, 220*). The dichloro complex (XXXIII), which is formed by the reaction of germanium tetrachloride and either *o*-cyanobenzamide or metal-free phthalocyanine, is fairly resistant to hydrolysis by steam or ammonium hydroxide, and may be purified by vacuum sublimation. It may be converted to the hydroxide (XXXIV) by reprecipitation from concentrated sulfuric acid. The chemistry of germanium phthalocyanines is illustrated in Fig. 7. The dihydroxide (OH stretching vibration occurs at 3500 cm^{-1} in the infrared) condenses with phenol, forming diphenoxygermanium phthalocyanine (XXXV). The corresponding di-*p*-phenylphenoxy- and bis(triphenylsiloxy)germanium phthalocyanines have also been reported (*169, 220*) and are stable to sublimation *in vacuo*. With diphenylsilanediol, bis(diphenylhydroxysiloxy)germanium phthalocyanine (XXXVI) (OH stretching vibration at 3545 cm^{-1}) is produced. This is in contrast to the behavior of dihydroxysilicon phthalocyanine, which does not react with diphenylsilanediol (*170*). (XXXVI) is very soluble in dioxane from which it may be recrystallized with two molecules of dioxane. It reacts with benzyl alcohol to form bis(diphenylbenzyloxysiloxy)germanium phthalocyanine (XXXVII), which has the interesting backbone C—O—Si—O—Ge—O—Si—O—C, and condenses with itself at 385°C, forming the polygermanosiloxane $[PcGe(OSi(Ph)_2O)_2]_x$ (XXXVIII), an involatile, insoluble polymer. The polygermanoxane $HO(PcGeO)_xH$ (XXXIX) forms when (XXXIV) is heated. The symmetric Ge—O—Ge vibration occurs in the latter complex at 899 cm^{-1} (*194*). All germanium phthalocyanines exhibit a sharp band in the region 900–906 cm^{-1}, and hence may be distinguished from silicon phthalocyanines where a band is observed some 10 cm^{-1} higher (*220*).

3. Tin Phthalocyanines

The derivatives of tin were first investigated by Linstead and his coworkers (*10*). Both stannous and stannic phthalocyanines were charac-

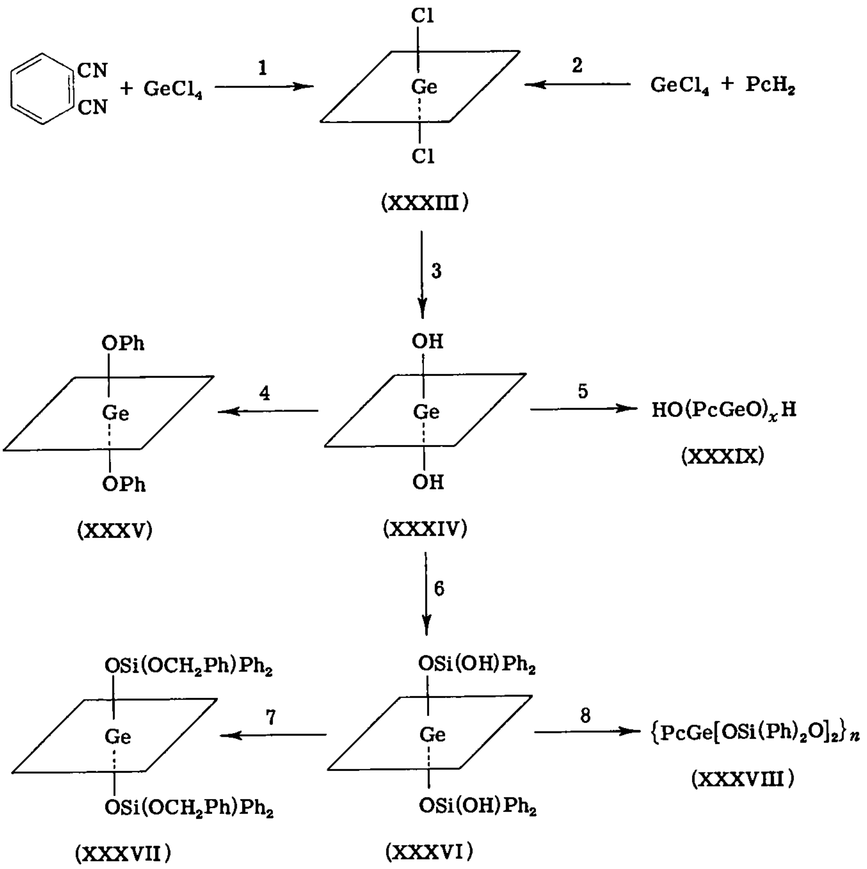


FIG. 7. The chemistry of germanium phthalocyanines. Reaction pathway (1), (2) Quinoline at reflux; (3) Py/NH_4OH; (4) C_6H_5OH/C_6H_6; (5) heat; (6) $Ph_2Si(OH)_2/C_6H_6$; (7) $C_6H_5CH_2OH$; (8) 385°C.

terized. The reaction between phthalonitrile and stannous chloride is violently exothermic and produces the green dichlorostannic phthalocyanines (XLI) (the asymmetric Cl—Sn—Cl stretching vibration occurs at 299 cm^{-1}) (*196*). The same compound may be prepared by the reaction of stannic or stannous chloride with metal-free phthalocyanine (*10*). The chemistry of the tin derivatives is illustrated in Fig. 8. Upon reduction with stannous chloride or hydrogen gas in quinoline, (XLI) gives the square planar stannous phthalocyanine (XL), a blue-black crystalline solid (*10*, *195*). This may also be prepared from metal-free phthalocyanine and metallic tin. Oxidation of stannous phthalocyanine with iodine or bromine leads to the corresponding dihalides (XLII) (X = I and Br), which may be

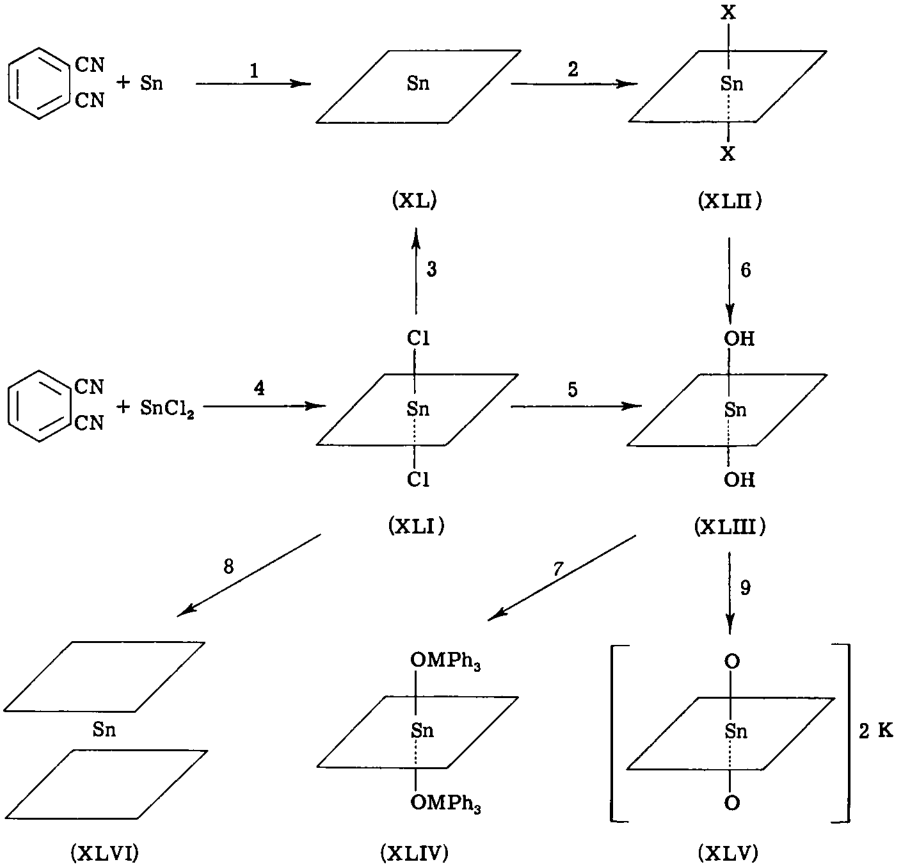


FIG. 8. The chemistry of tin phthalocyanines. Reaction pathway (1) 300°; (2) X (Br_2 or I_2); (3) $SnCl_2$, H_2, or $NaBH_4$; (4) refluxing chloronaphthalene; (5), (6) EtOH/NH_4OH; (7) Ph_3SiOH, Ph_3GeOH; (8) $PcNa_2$; (9) KOH.

hydrolyzed to the dihydroxide (XLIII) (asymmetric O—Sn—O vibration at 563 cm^{-1} and OH stretching vibration at 3510 cm^{-1}) (*196*). (XLIII) reacts with triphenylsilanol and with triphenylgermanol to form the bis(triphenylsiloxy) (XLIV, M = Si), and bis(triphenylgermanoxy) (XLIV, M = Ge) derivatives, respectively. Diiodostannic phthalocyanine (XLII, X = I) reacts with sodium triphenylcarbinol to form bis(triphenylmethoxy)-stannic phthalocyanine (XLIV, M = C) (*179*). Oxidation of (XL) with chlorine leads to a chlorine nuclear substituted derivative of (XLII, X = Cl). The difluoride (XLII, X = F) (asymmetric F—Sn—F stretching vibration occurs at 531 cm^{-1} in the infrared) (*196*) may be prepared from (XLIII) and aqueous hydrofluoric acid (*195*), while aqueous hydrochloric acid yields (XLII, X = Cl). Stannous phthalocyanine is inert to refluxing ethanol, water, glacial acetic acid, and 3 *N* sodium hydroxide, but reacts with dinitrogen tetroxide to give an unidentified green product (*10*). Boiling aqueous potassium hydroxide converts the dihydroxide (XLIII) to its dipotassium salt (XLV), while the action of alcoholic alkali is to break down the pigment.

The halides vary in hydrolytic stability. Thus the fluoride is not hydrolyzed by refluxing aqueous ammonium hydroxide, while the chloride hydrolyzes completely in 45 hours and the iodide in 45 minutes. The complexes increase in solubility in chloronaphthalene in the sequence F < Cl < I, which is interpreted to imply increasing covalent character to the bond, in that sequence (*195*). The variation in hydrolytic stability has also been interpreted in terms of increasing covalent character. The hydrolytic stability of the fluoride may also be due to its low solubility which renders attack by hydroxyl groups kinetically very slow.

Dichlorostannic phthalocyanine undergoes a very interesting reaction with disodium phthalocyanine to form the unique bis(phthalocyanine)-tin(IV) (XLVI) (*10*), which is a distinct homogeneous phase (*374*), and which has been shown to contain quadrivalent tin by quantitative oxidation (*89*). Two polymorphs of (XLVI) are known, α and β. The β form purified by vacuum sublimation is converted to the α form when crystallized from naphthalene or 1,2,4-trimethylbenzene. Their infrared spectra are very similar, but they differ in their X-ray powder photographs. The *d* spacings (Å) of the three strongest lines (visually estimated intensities in parentheses) are (*195*):

αPc_2Sn	12.4(10); 9.69(9); 8.37(8)
βPc_2Sn	12.5(10); 8.02(5); 3.45(3)

A differential thermal analysis study has been made of these complexes and also of a 1-chloronaphthalene adduct (*195*). The complexes decompose above 560°C *in vacuo* with the formation of unmetallated phthalocyanine and stannous phthalocyanine. The infrared spectrum of (XLVI) is not greatly different from that of other phthalocyanines, suggesting very little distortion in the phthalocyanine rings (*195*). Stannic phthalocyanine (XLVI) may have a "sandwich" structure in which the tin atoms lie between the two phthalocyanine units in an eight-coordinate environment (*109*). An X-ray structural determination is in progress (*307*).

4. Lead Phthalocyanine

Lead phthalocyanine, obtained from the exothermic reaction between litharge and phthalonitrile (*10, 195*), is readily demetallated by concentrated acids and is not very stable in organic solvents. It forms pure green crystals when sublimed or when recrystallized from quinoline or chloronaphthalene. No quadrivalent lead derivatives have been reported.

E. GROUP VB PHTHALOCYANINES

No derivatives of nitrogen (!) or phosphorus are known. It can be only a matter of time before complexes of the latter element are synthesized.

1. Arsenic Phthalocyanines

Arsenic trichloride reacts with dilithium phthalocyanine in dimethylformamide to yield chloroarsenic phthalocyanine (*308*), which does not react with silver ions in pyridine. Its absorption spectrum has been recorded (Section V,B), but little else is known of the complex.

2. Antimony Phthalocyanines

Dark green chloroantimony phthalocyanine is prepared from the reaction of metal free phthalocyanine with antimony trichloride in refluxing chloronaphthalene (*11*). The complex, which may be sublimed without decomposition, is demetallated in concentrated sulfuric acid, and in boiling quinoline. Diantimony phthalocyanine ($PcSb_2$) is produced when antimony reacts with phthalonitrile at 300°C. The structure of this unusual complex is not known. The suggestion that it may consist of antimony phthalocyanine units linked together by Sb—Sb chains (*11*) seems unlikely in the light of modern knowledge.

IV. Phthalocyanine Complexes of the Transition Elements

No complexes of scandium or of yttrium are known. The complexes of the lanthanides and of the actinides will be considered in Sections I and J.

A. GROUP IVA PHTHALOCYANINES

1. Titanium Phthalocyanines

Chlorotitanium(III) phthalocyanine is formed by the reaction of titanium trichloride with dilithium phthalocyanine in boiling quinoline in the absence of air. This d^1 complex has a magnetic moment of 1.79 B.M. (see Section VI,D) (*341*). It is stable to air oxidation in the solid state but is oxidized in solution. The oxidation product is oxytitanium(IV) phthalocyanine (titanyl phthalocyanine). This latter diamagnetic complex may also be prepared by the reaction of titanium tetrachloride dipyridinate and phthalonitrile at 270°C followed by sublimation at 400°C/10^{-6} mm (*213*). Titanium tetrachloride reacts with phthalonitrile to yield, after recrystallization from sulfuric acid, dihydroxytitanium(IV) phthalocyanine (*320*).

This is a rather surprising result, and it seems more likely that the complex should be formulated as oxytitanium(IV) phthalocyanine monohydrate. An infrared study would confirm this since oxytitanium(IV) phthalocyanine shows, in addition to the spectrum characteristic of a phthalocyanine, a strong band at 978 cm^{-1} (*341*) (965 cm^{-1}) (*213*), assigned to the Ti=O stretching vibration. The complex may therefore be regarded as five-coordinate and presumably square pyramidal. The complex is slowly decolorized in chlorobenzene solution in air, phthalimide being the final product (*213*) (see also Section VI,C).

2. Zirconium and Hafnium Phthalocyanines

Both zirconium and hafnium tetrachlorides react with phthalonitrile at 170°C to give products which when crystallized from sulfuric acid were formulated as dihydroxyzirconium(IV) and -hafnium(IV) chlorophthalocyanine dihydrates (*284*). Once again their formulation as oxy derivatives, perhaps polymeric, seems more reasonable. A sulfonated hafnium phthalocyanine has also been reported (*119*).

B. Group VA Phthalocyanines

Complexes with niobium and with tantalum are unknown.

1. Vanadium Phthalocyanine

Vanadium pentoxide reacts with phthalonitrile to yield oxyvanadium(IV) phthalocyanine (*10*). This complex may be sublimed and is recovered unchanged from concentrated sulfuric acid upon dilution. Its infrared spectrum has been studied by several workers. All report a strong band assigned to the V=O stretching vibration. The frequencies reported are 1017 (*341*), 1004 (*213*), and 1003 (*311*). The magnetic moment of this d^1 complex is 1.71 B.M. (*312*). It is isomorphous (*214*) with its titanium analog. The d line spacings are as follows (principal lines only), d_{hkl} (Å):

OTiPc	9.14*s*; 6.69*w*; 5.48*w*; 3.10*w*; 2.84*m*; 2.72*m*; 2.45*m*
OVPc	9.14*s*; 6.84*w*; 5.46*w*; 3.10*w*; 2.88*m*; 2.76*m*; 2.47*m*

C. Group VIA Phthalocyanines

Molybdenum phthalocyanine has been mentioned in the literature a number of times (*142, 226, 250, 356*) but has not been adequately characterized. However, molybdenum dioxide is reported to react with phthalonitrile, at 260°C, to yield a polymeric oxymolybdenum phthalocyanine (*252*). An early attempt to prepare tungsten phthalocyanine failed (*11*). There has been no mention of the complex since.

1. *Chromium Phthalocyanines*

Chromium phthalocyanines were mentioned several times in the early literature before they were adequately characterized (*5, 10, 61, 106, 110, 226, 296, 297*). The formation of mixtures when phthalonitrile is heated with chromic salts held up the early investigation of these compounds. The chemistry of the chromium phthalocyanines, as elucidated by Elvidge and Lever (*87, 90*), is illustrated in Fig. 9.

Chromic acetate reacts exothermically with phthalonitrile, at 270°C, to yield a mixture of acetatochromium(III) phthalocyanine (XLVII) and chromium(II) phthalocyanine (XLVIII). The mixture, when washed with organic solvents, is extensively hydrolyzed to chromium(III) phthalocyanine hydroxide (XLIX). Repeated sublimation at 400°C/10^{-6} mm affords the pure hydroxide, the chromous component being oxidized. The ready formation of the dimethanolate (L, R = R′ = MeOH), when the hydroxide is warmed with methanol, suggests that the hydroxide should be regarded as involving a four-coordinate cationic species. A diaquo cation (L, R = R′ = H_2O) may be prepared from aqueous ethanolic acetic acid. The mixed complex (L, R = MeOH, R′ = H_2O) is also known. The cationic nature of these complexes was demonstrated electrophoretically, the colored spot moving to the cathode. When heated at 180°C/20 mm, both (L, R = R′ = H_2O) and (L, R = MeOH, R′ = H_2O) yield the six-coordinate hydroxoaquochromium(III) phthalocyanine (LI). The dimethanolate desolvates to the hydroxide (XLIX) under these conditions.

The aquo group in (LI) is very tenaciously held and conversion to (XLIX) can be effected only by sublimation. Mild treatment of (LI) with acetic anhydride and with propionic anhydride gave, respectively (LII) (R = OAc, R′ = H_2O), and (LII) (R = O·CO·Et, R′ = H_2O). The presence of terminally bound acid residues in these complexes was indicated by the observation of ketonic absorption in the infrared spectrum at 1715 cm^{-1} (w) in both cases. Both complexes withstand 180°C/20 mm. The complex (LIII) (ν_{CO}, 1718 cm^{-1}) is obtained when the hydroxoaquo complex (LI) is refluxed with acetic anhydride. With methanolic acetic acid the hydroxide (XLIX) affords (LII) (R = OAc, R′ = MeOH) (ν_{CO}, 1715 cm^{-1}). This is, however, unstable at 180°C/20 mm and yields (XLVII), which may also be prepared from (XLIX) and acetic anhydride in the cold. This latter involatile complex was formulated as a six-coordinate polymer involving acetate bridges. This is perhaps difficult to rationalize with the asymmetric CO_2^- vibration occurring at 1709 cm^{-1}, since bridged acetate groups generally absorb near 1610 cm^{-1} (*216*).

A dichloride formulated as (LIV) is obtained when dry hydrogen chloride is passed into a boiling methanolic suspension of (XLIX). This

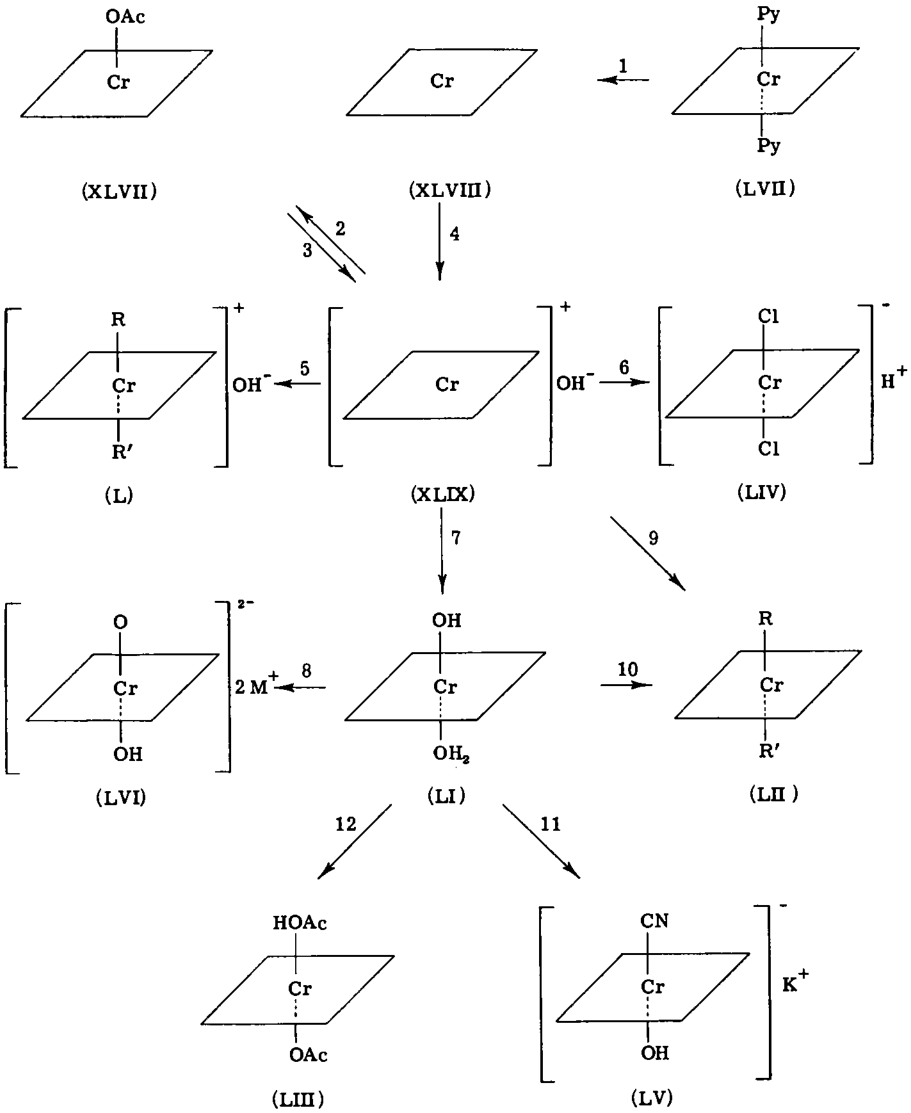


FIG. 9. The chemistry of chromium phthalocyanines. Reaction pathway (1) sublime; (2) CH_3COOH; (3) H_2O; (4) O_2/H_2O; (5) alcohol; (6) HCl/MeOH; (7) H_2O/EtOH/CH_3COOH; (8) alkali; (9) acid; (10) acid anhydride; (11) KCN/EtOH; (12) reflux acetic anhydride.

complex is thermally stable but hydrolytically very unstable. Potassium cyanide reacts with (LI) to form potassium phthalocyanine hydroxocyanochromate(III) (LV) (ν_{CN}, 2137 cm^{-1}), which hydrolyzes in the absence of excess cyanide ion. In concentrated cyanide solutions, dicyano species are believed to be formed. There is some evidence for the formation of thiocyanates and selenocyanates in solution in the presence of the appropriate potassium salts.

The hydroxoaquo complex (LI), which is only slightly soluble in ethanol, is readily soluble in the presence of sodium hydroxide forming the disodium salt (LVI, M = Na). Diammonium (LVI, M = NH_4) and dipyridinium (LVI, M = C_5H_5NH) salts are also known. Whereas the hydroxoaquo complex (LI) reacts with pyridine to yield (LVI, M = C_5H_5NH), the hydroxide (XLIX) undergoes a very interesting reduction forming dipyridinechromium(II) phthalocyanine (LVII). Acid-free pyridine must be employed; even the traces of acid picked up from the laboratory atmosphere are sufficient to prevent this reduction, an old sample of pyridine giving only the pyridinium salt. Sublimation of this chromous derivative in a vacuum line previously flushed with nitrogen yields chromium(II) phthalocyanine (XLVIII). This complex is fairly stable to air in the solid state and in pure pyridine solution, but is oxidized in other solvents (*87, 90, 213*). There appears to be extensive chromium-chromium interaction occurring in chromium(II) phthalocyanine (*215*) (see Section V,D), the complex being similar in this respect to the only other formally square planar chromous derivative, chromous acetate.

D. Group VIIA Phthalocyanines

Complexes of technetium and of rhenium are unknown.

1. *Manganese Phthalocyanines*

Manganese is unique in forming phthalocyanine complexes in five oxidation states from 0 to 4 inclusive. The general chemistry is illustrated in Fig. 10. Manganese metal reacts with phthalonitrile or *o*-cyanobenzamide to yield (*10*) a product of uncertain composition, which sublimes as manganese(II) phthalocyanine (LVIII). Alternatively it may be prepared from manganous acetate and phthalonitrile (*308*). Manganous phthalocyanine, which is demetallated in sulfuric acid (*21*), is readily oxidized in organic solvents to tri- or quadrivalent species, depending upon the solvent and conditions. The absorption spectra and magnetic properties have been used extensively to characterize the different oxidation states (see Section V,B and D). Divalent manganese derivatives exhibit intense absorption near 880 mμ, trivalent near 720 mμ (*93*), and quadrivalent near 620 mμ (*88, 213*). Manganous phthalocyanine dissolves slightly in methanol (*93*) to form

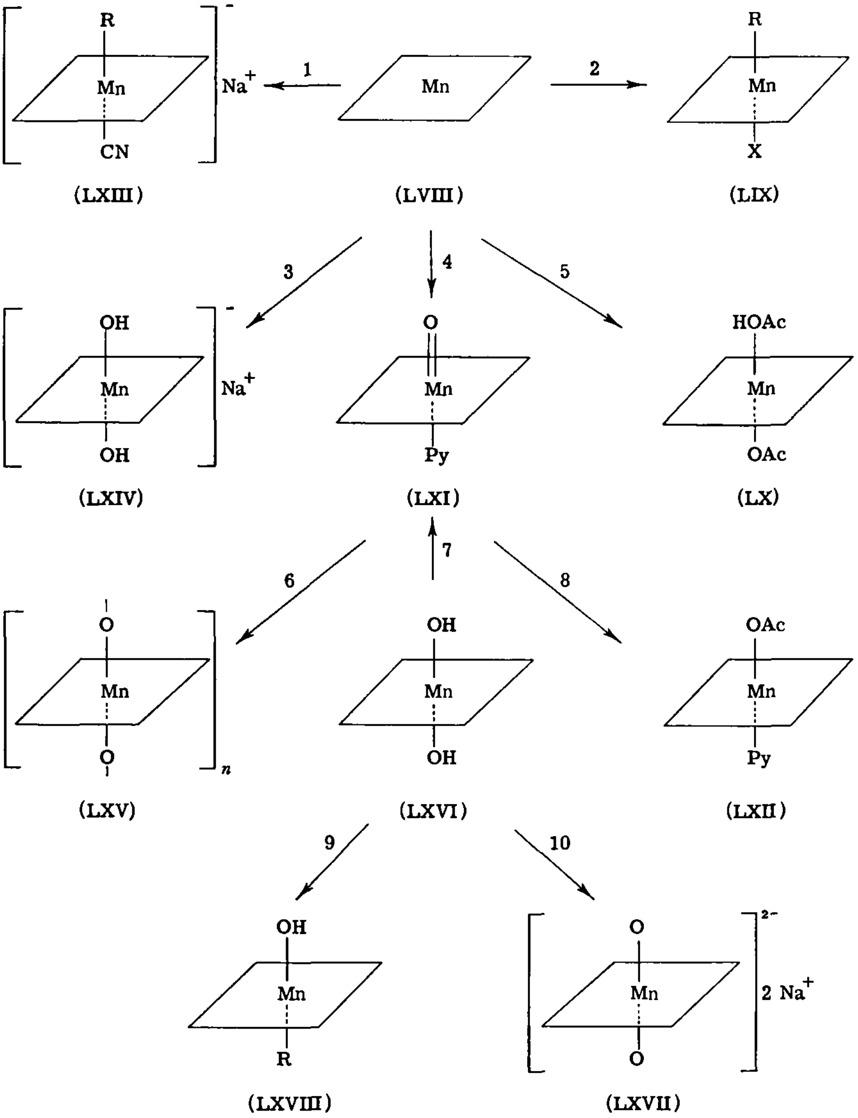


FIG. 10. The chemistry of manganese phthalocyanines. Reaction pathway (1) NaCN/EtOH/N_2; (2) alcohol; (3) EtOH/NaOH; (4) Py/O_2; (5) CH_3COOH; (6) heat; (7) Py; (8) CH_3COOH; (9) MeOH/KCN, KCNS, KCNSe; (10) EtOH/NaOH.

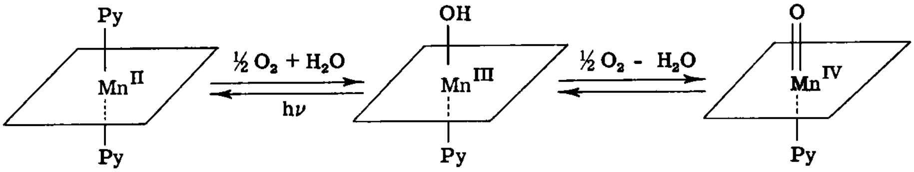
hydroxomethanolmanganese(III) phthalocyanine (LIX, R = MeOH, X = OH) (λ_{max} 716 mμ). The corresponding ethanol derivative (LIX, R = EtOH, X = OH) is also known. In the presence of sodium chloride and a trace of hydrochloric acid, the methanol solutions yield the chloro complex (LIX, R = MeOH, X = Cl), which reacts with pyridine to form (LIX, R = pyridine, X = Cl), (λ_{max} 716 mμ). Extraction of manganous phthalocyanine with glacial acetic acid leads to (LX), analogous to the corresponding chromic complex (LIII), while reaction with pure acid-free pyridine in the presence of air gives oxypyridinemanganese(IV) phthalocyanine (LXI) (λ_{max} 620 mμ). The reaction with oxygen is reversible (*88*). Addition of water to this solution precipitates a product which has been formulated (*288*) as a hydrated peroxide of manganous phthalocyanine, but is better formulated as a hydrated form of (LXI). The magnetic moment quoted for this complex, 1.79 B.M. (*288*), agrees with that predicted for (LXI), namely, that arising from one unpaired electron. The infrared spectrum (*88*) of (LXI) has a band at 1096 cm^{-1} assigned to the Mn═O stretching vibration. When acid is added to a pyridine solution of (LXI), reduction to the trivalent stage occurs, e.g., (LXII) (λ_{max} 713 mμ) being obtained (*93*) when acetic acid is used, and chloropyridinemanganese(III) phthalocyanine (λ_{max} 716 mμ) when pyridinium hydrochloride is used (*93*).

In the absence of air, manganese(II) phthalocyanine reacts with cold ethanolic sodium cyanide to form sodium phthalocyanine cyanoethanolmanganate(II) (LXIII, R = EtOH). At reflux temperatures, in the presence of air, the trivalent sodium phthalocyanine dicyanomanganate(III) (LXIII, R = CN) is formed (*93*). This is photoreduced to the divalent product *in vacuo*. The corresponding quadrivalent derivative is also known (*213*) (see below). Manganous phthalocyanine dissolves in ethanolic sodium hydroxide (*93*) to yield sodium phthalocyanine dihydroxymanganate(III) (LXIV) (λ_{max} 716 mμ). In very concentrated alkaline solution, a quadrivalent derivative is formed (*213*).

When (LXI) is heated it loses pyridine, forming oxymanganese(IV) phthalocyanine (LXV), formulated (*88*) as a polymer ($\nu_{\text{Mn-O-Mn}}$ 820 cm^{-1}) analogous to the corresponding silicon and germanium derivatives. Quadrivalent manganese derivatives are best prepared from (LXVI) obtained by the reaction of 1,3-diiminoisoindoline with manganous formate in dimethyl sulfoxide (*213*). The structure of this complex is not known for certain, as it has an anomalous magnetic moment (μ_e = 4.51 B.M., see Section V,D). It dissolves in alcoholic sodium hydroxide to yield disodium phthalocyanine dioxomanganate(IV) (LXVII), whose magnetism (*215*) (Section V,D) is consistent with its formulation as a quadrivalent derivative. (LXVI) reacts with pyridine in the presence of air to form the previously encountered (LXI), with methanolic sodium cyanide to form cyanohydroxymanganese(IV) phthalocyanine (LXVIII, R = CN) (ν_{CN} 2128 cm^{-1}), and with potassium cyanate in *n*-butanol to form (LXVIII, R = NCO) (ν_{NCO} 2188 cm^{-1}) (*213*).

As has already been pointed out, the stable oxidation state of manganese phthalocyanine in alcoholic alkaline media is pH dependent (*93*, *213*), the oxidation of manganese(III) to manganese(IV) being easier at higher pH.

The fact that manganous phthalocyanine, when dissolved in pure acid-free pyridine, absorbs oxygen reversibly was first pointed out by Elvidge and Lever (*88*), and was developed subsequently by Engelsma *et al.* (*93*). The oxidation proceeds from oxidation state 2 to 3 to 4 in successive stages (*93*). The mechanism suggested by Engelsma and co-workers, illustrated in Fig. 11, supersedes that of Elvidge and Lever, suggested on the basis of their early investigation (*88*). The complex (LXIX) is assumed to be present when manganous phthalocyanine is dissolved in air-free pyridine; it cannot be isolated (*93*, *213*). When air is introduced, oxidation to the trivalent species (LXX) takes place. This also could not be isolated. The complex (LXX) is photosensitive, intense light causing reduction to (LXIX), while in the dark disproportionation to (LXIX) and (LXI) occurs. In the presence of oxygen, (LXX) slowly oxidizes to (LXI), a process which is accelerated by light. In the absence of air, (LXI) is reduced to (LXIX) apparently without the intermediate formation of the trivalent (LXX). This process is rapid in sunlight but slow in the dark. Boiling a pyridine solution of (LXI) leads rapidly to (LXX). Some evidence was presented (*93*) for a further transient trivalent species. Aerial oxidation of manganese(II) phthalocyanine is also reported to occur in pyridine containing sodium hydroxide (*93*).



λ_m 880, 660 | 716 | 620 mμ

(LXIX) (LXX) (LXI)

FIG. 11. The oxygen-breathing mechanism of manganese phthalocyanine.

A polarographic study of a pyridine solution of the quadrivalent (LXI), using 0.05 *M* lithium bromide as a carrier electrolyte, showed two reduction steps with half-wave potentials at −0.76 and −0.94 volt, ascribed to the processes (LXI)–(LXX)–(LXIX) (*88*). In a later study (*288*), using lithium chloride as a carrier electrolyte, a single wave at −0.88 volt was observed.

In conclusion, it is seen that the stable oxidation state of manganese phthalocyanine in weakly donor solvents such as methanol, ethanol, chloroform, and chloronaphthalene, and in strong donors containing a trace of acid, is 3. Slow oxidation occurs when manganese(II) phthalocyanine is dissolved in these solvents, whereas slow reduction occurs when oxymanganese(IV) phthalocyanine is employed. In strongly donor solvents such as pyridine, dimethyl sulfoxide, diethylamine, quinoline, or strongly alkaline alcohol, the stable oxidation state in the presence of oxygen is 4 (*88*, *93*, *213*).

Lower oxidation states of manganese phthalocyanine have been investigated by Taube and co-workers (*339*, *340*). Lithium benzophenone reacts with manganese(II) phthalocyanine in dry tetrahydrofuran to give the air-sensitive lithium phthalocyanine manganate(I) and dilithium phthalocyanine manganate(0) as tetrahydrofuran solvates. The manganese(0) derivative is unique in phthalocyanine chemistry in being spin-free (see Sections V,D and VII).

E. Complexes of Iron, Ruthenium, and Osmium

1. *Iron Phthalocyanines*

o-Cyanobenzamide reacts with iron wire at 250°C to yield ferrous phthalocyanine (LXXI), being the compound which was first observed at Grangemouth in 1928. Some reactions of the complex, which is readily purifiable by sublimation (*10*, *11*, *40*), are illustrated in Fig. 12. Ferrous phthalocyanine is, like most phthalocyanines, virtually insoluble in organic solvents and is certainly insoluble in water, yet undergoes the extraordinary reaction of being readily soluble in water, and in alcohols, in the presence of cyanide ions. With potassium cyanide, the diamagnetic dipotassium phthalocyanine dicyanoferrate(II) (LXXII) is produced. This complex, which hydrolyzes rapidly in the absence of cyanide ions, has been the subject of a nuclear magnetic resonance study in alcoholic cyanide solution (*92*) (see Section V,C,2). Neither manganese nor cobalt(II) phthalocyanines are soluble in aqueous cyanide solutions (*213*). Ferrous phthalocyanine is also soluble in alcohols in the presence of sodium hydroxide, but no products appear to have been isolated (*48*). Many organic bases, such as pyridine, quinoline, imidazole, and substituted derivatives thereof, react with ferrous phthalocyanine forming diamagnetic six-coordinate complexes, e.g., dipyridine ferrous phthalocyanine (LXXIII) (*11*, *132*, *208*). 2-Substituted aromatic amines and 4-substituted imidazole derivatives do not appear to react, presumably for steric reasons (*208*). Aniline and *o*-toluidine form hexaamine derivatives (*11*). Sublimed layers of the complex (LXXI) reversibly absorb hydrogen chloride and bromide (*324*) but do not absorb water vapor (*325*).

The resonant nuclear γ-ray absorption (Mössbauer effect) spectrum of ferrous phthalocyanine has been determined (*96*). A doublet splitting, ΔE, of 2.62 ± 0.01 mm/sec was observed. This quadrupole splitting arises from interaction of the excited Fe^{57} nucleus with the electric field gradient surrounding it. The isomer shift, δ, of 0.49 ± 0.01 mm/sec is much smaller than that observed in most other ferrous derivatives. This isomer shift is related to the *s* electron density at the nucleus (*368*), and hence the low isomer shift implies a high degree of covalency in the iron-nitrogen bonds.

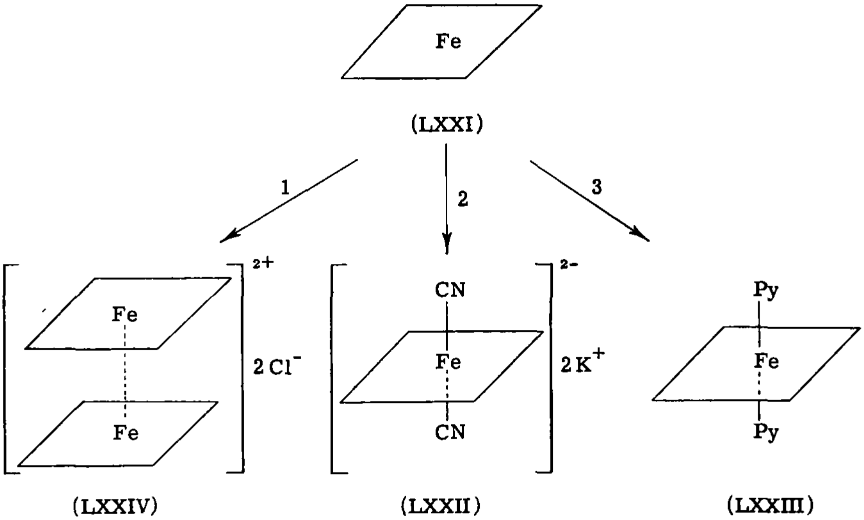


FIG. 12. The chemistry of iron phthalocyanines. Reaction pathway (1) HCl/100°C; (2) KCN/H_2O, EtOH; (3) Py.

Ferrous phthalocyanine is aerially oxidized in concentrated hydrochloric acid suspension to chloroferric phthalocyanine (LXXIV) (*11*). The ease with which this is formed suggests that it might be a simple hydrochloride, but this possibility was eliminated by quantitative oxidation (*89*), which indicated the presence of ferric ion. The magnetic behavior is quite different from that of ferrous phthalocyanine (*215*) (see Section V,D), and is interpreted in terms of a dimer involving metal-metal bonds. An X-ray structural analysis is really required to prove this point, however. The complex (LXXIV) sublimes almost quantitatively, ferrous phthalocyanine and hydrogen chloride being formed (*10, 213*). The source of the hydrogen is a mystery and further work is required.

Change of oxidation state upon sublimation is not uncommon in phthalocyanine chemistry, e.g., the quadrivalent manganese derivative (LXV) sublimes in poor yield to form manganese(II) phthalocyanine (*213*), and stannic phthalocyanine (XLVI) sublimes to stannous phthalocyanine (*195*).

The ferric complex (LXXIV) is reduced in solution, since its visible absorption spectrum is identical with that of ferrous phthalocyanine (*5*). Attempts to prepare hydroxyferric derivatives were unsuccessful (*10, 213*), as were attempts to prepare other ferric phthalocyanines from ferric starting materials. Ferric chloride is reported to form a molecular complex with metal-free phthalocyanine in chloronaphthalene (*134*). A new absorption peak appears at 750 mμ when the reactants are mixed. Stannous chloride and ferrous chloride form similar complexes, also with an absorption band at 750 mμ, whereas hydrogen chloride gives a band at 740 mμ. If water is admitted, or if the solution is degassed with argon, the spectrum of metal-free phthalocyanine reappears. The complex is formed only when the metal-free phthalocyanine is allowed to come into contact with air before solution. If the ligand is degassed, and then dissolved, no molecular complex is formed, even if air is subsequently admitted.

The reduction of ferrous phthalocyanine with lithium benzophenone in tetrahydrofuran yields the solvated lithium phthalocyanine ferrate(I) (having one unpaired electron) and dilithium phthalocyanine ferrate(0) (diamagnetic) (*340*). The reduction of (LXXI) with alkaline sodium borohydride in methanol has also been studied (*48*).

2. Ruthenium Phthalocyanine

Ruthenium(II) phthalocyanine has been reported by Kreuger and Kenney (*193*). It is formed by the reaction of ruthenium trichloride and *o*-cyanobenzamide, and sublimes with difficulty. It is presumably square planar, although no magnetic data were recorded, and like ferrous phthalocyanine it forms adducts with aniline and *o*-toluidine containing six molecules of base. It is stable in concentrated sulfuric acid but is not oxidized in hydrochloric acid suspension. There is obviously much scope for further study, particularly with regard to higher oxidation state complexes.

3. Osmium Phthalocyanine

Osmium tetroxide was heated with phthalonitrile to form an osmium derivative which was crystallized from concentrated sulfuric acid as the diamagnetic sulfato-osmium(IV) phthalocyanine (*25*). A six-coordinate sulfato-bridged structure was proposed, but no infrared data were cited in support of this idea. The complex is extremely soluble in concentrated sulfuric acid. The diamagnetism is unexpected. Osmium(IV) has a d^4 configuration, and a moment above 2.0 B.M. might have been predicted. The lower symmetry, D_{4h} rather than O_h, would lead to an increase rather than a decrease in the moment. Berezin and Sosnikova suggest that π-bonding from osmium to phthalocyanine is very important, and hence that the energy of the d_{xz} and d_{yz} pair of orbitals is sufficiently low for the four electrons to pair up in them. In view of the fact that osmium(IV) derivatives often do have very low moments in complexes where such π donation would be impossible (*217*), it is probably not necessary to invoke π-bonding to explain the diamagnetism. In any case it is doubtful that π-bonding, from metal to phthalocyanine, is particularly important in higher oxidation state complexes, because there would be too great a dissimilarity in the energies of the relevant orbitals.*

F. COMPLEXES OF COBALT, RHODIUM, AND IRIDIUM

No iridium complexes have been reported.

1. Cobalt Phthalocyanines

Cobalt phthalocyanine is formed when etched massive cobalt metal is heated with phthalonitrile (*10*). It is soluble without decomposition in concentrated sulfuric acid and may be sublimed to dark blue needles with a reddish purple luster. It is not particularly soluble in alcoholic alkali or cyanide solutions (cf. ferrous phthalocyanine). Whereas iron(II) and the higher oxidation states of manganese readily form six-coordinate phthalocyanine derivatives, cobalt is reluctant to do so. The seventh electron is presumably in the d_{z^2} orbital (*131*, *139*) and this seems to prevent the close association of any further ligands. Cobalt phthalocyanine is readily soluble in pyridine, and the electron-spin resonance spectrum (*139*) being different from that of the crystal implies that there is some interaction between solvent and complex. The visible absorption spectrum in pyridine differs from that in chloronaphthalene, again implying some sort of interaction. Recrystallization from pyridine gives only a very loosely bound monopyridinate; desolvation can be effected simply by washing with ether (*10*). Cobalt phthalocyanine does not exchange with radiocobalt (Co^{60}) in pyridine solution, nor does the tetrasulfonated derivative in aqueous solvent (*372*).

Attempts to oxidize cobalt phthalocyanine to a cobalt(III) derivative in neutral or basic solvent were unsuccessful (*213*). However, it is reported (*30*) that cobalt phthalocyanine is oxidized to nitratocobalt(III) phthalocyanine by nitric acid in nitrobenzene at 10°–20°C. Unfortunately no data were presented which excluded the alternative formulation of the complex as a nitric acid adduct of cobalt(II) phthalocyanine, which seems more likely.

* The complex is now believed to contain Os(VI) [Keen, I. M., *Platinum Metals Rev.* **8**, 143 (1964)].

Cobalt(II) phthalocyanine is reduced by lithium benzophenone in tetrahydrofuran to lithium phthalocyanine cobaltate(I) (diamagnetic) and dilithium phthalocyanine cobaltate(0) (having one unpaired electron) (*340*).

2. Rhodium Phthalocyanine

Chlororhodium(III) phthalocyanine is prepared from rhodium trichloride and phthalonitrile (*28, 160*). It is stable in concentrated sulfuric acid and may be precipitated therefrom as the bisulfate. The oxidation state of the metal was proved by quantitative oxidation (*28*). Bisulfatorhodium(III) phthalocyanine is reasonably soluble in common organic solvents.

G. Complexes of Nickel, Palladium, and Platinum

1. Nickel Phthalocyanines

Nickel phthalocyanine is conveniently prepared by heating etched nickel foil in *o*-cyanobenzamide at 270°C (*10*). An alternative preparation involves phthalic anhydride, urea, nickel chloride hexahydrate, and ammonium molybdate in trichlorobenzene at 200°C (*81*). It is stable to concentrated sulfuric acid, sublimes readily, and shows no tendency to form six-coordinate derivatives (*10, 213, 325*).

The monovalent and zerovalent phthalocyanines may be prepared as their lithium salts as previously described. The former has one unpaired electron and the latter is diamagnetic (*340*). No other nickel phthalocyanines are known.

2. Palladium Phthalocyanine

Palladium chlorophthalocyanine is formed when phthalonitrile is heated with palladous chloride. Like other nuclear halogen-substituted phthalocyanines, it will not sublime (*11, 278*). The unsubstituted derivative may be prepared by the dehydrogenation of tetracyclohexenotetrazaporphin with palladium black (*113*), or by the action of palladous chloride on lithium phthalocyanine in absolute alcohol (*11*). It is also possible to prepare the complex by dissolving palladium black in boiling phthalonitrile, a really remarkable reaction.

3. Platinum Phthalocyanine

Platinum phthalocyanine may be prepared from platinous chloride and phthalonitrile (*10*). The reaction of phthalonitrile with platinum metal gives only the metal-free derivative. Both these reactions are in contrast to the behavior of palladium. Platinum phthalocyanine is particularly stable toward oxidizing agents (*89*) and resists cold nitric acid.

H. Complexes of Copper, Silver, and Gold

1. Copper Phthalocyanines

In 1927 de Diesbach and von der Weid reported a blue precipitate formed when *o*-dibromobenzene was heated with cuprous cyanide in pyridine at 200°C (*76*). This unidentified material was almost certainly copper phthalocyanine. Although as yet unidentified, copper phthalocyanine was mentioned in the earliest patent reference to this class of compound (*65*). Copper(II) phthalocyanine is best prepared (*73*) by the action of copper bronze on phthalonitrile at 270°C in the absence of a solvent or in boiling quinoline, chloronaphthalene, or pyridine. The complex may also be prepared by the action of copper salts upon phthalonitrile. The reaction of cuprous chloride with phthalonitrile has been studied in detail; copper(II) phthalocyanine is formed below 200°C but, above this temperature, halogenated phthalocyanines are produced (*73*). Copper metal and cuprous salts are reported not to react with phthalonitrile in the absence of air (*211*). Copper(II) phthalocyanine is stable to concentrated sulfuric acid, molten potassium hydroxide, and boiling hydrochloric acid, but is decomposed by nitric acid to phthalimide and copper salts. It shows no tendency to add further ligands forming six-coordinate complexes, although sublimed layers will absorb hydrogen bromide, but not hydrogen chloride, presumably via the peripheral nitrogen atoms (*324*). Copper phthalocyanine is oxidized reversibly to solids of low tinctorial power by oxidizing agents such as peroxides, hydroperoxides, organic hypochlorites, and *N*-halogen compounds (*279*). The complex was obtained in a very high degree of purity for radiochemical work by sublimation in a moving stream of argon at 590°C (*316*). The dielectric constant of air-packed copper phthalocyanine is 4.85 (*367*).

The zerovalent dipotassium phthalocyanine cuprate(0) may be prepared by the reduction of the cupric complex with potassium in liquid ammonia. It was not possible to isolate a copper(I) derivative (*370*). Like other low oxidation state metal phthalocyanines, this complex is air- and water-sensitive.

2. Silver Phthalocyanine

Silver phthalocyanine may be prepared by the action of silver nitrate on dilithium phthalocyanine in absolute alcohol at room temperature, or by the action of silver sulfate upon lead phthalocyanine in boiling chloronaphthalene (*11*). It is rapidly decomposed by sulfuric acid (*11, 26*), and cannot be recrystallized or sublimed without suffering some loss of silver. It is of some interest that the original sample prepared by Linstead's group was found, some twenty years later, to have decomposed into metal-free phthalocyanine and silver metal (*91*).

The original investigators were not able to distinguish between the formulations silver(II) and hydrogen silver(I) phthalocyanine. To clarify this point, electron-spin resonance studies have been carried out by two groups of workers. Kholmogorov and Glebovsky (*181*) found a narrow line (4.8 gauss) at $g = 2.0023$, ascribed to a paramagnetic impurity (*182*), in an otherwise diamagnetic material, thus implying that the oxidation state of the silver is 1. MacCragh and Koski (*237*) in addition to finding a line at $g = 2.003$ (6 gauss), which they were able to remove by repeated washing of the sample with ethanol and benzene, noted additional lines characteristic of silver in oxidation state 2 (see Section V,C). No magnetic data are available. It is still an open question whether silver phthalocyanine, as normally prepared, is truly a divalent silver complex, or whether it is a monovalent complex containing only a small amount of divalent oxidized material.

3. *Gold Phthalocyanine*

Aurous bromide reacts with 1,3-diiminoisoindoline to form a gold-containing phthalocyanine of uncertain formula, having an electron-spin resonance spectrum characteristic of a gold(II) species (*189*). If properly substantiated, this will be the first divalent gold derivative to be synthesized.

I. Complexes of the Lanthanide Elements

Sulfonated derivatives of lanthanum, neodymium, samarium, europium, gadolinium, dysprosium, holmium, erbium, thulium, ytterbium, and lutetium have been briefly reported (*119*). Chloroerbium(III) phthalocyanine dihydrate may be prepared from erbium trichloride and phthalonitrile at 150°C (*318*). It is demetallated by concentrated sulfuric acid. Formatosamarium(III) phthalocyanine, prepared from samarium formate and phthalonitrile, decomposes in boiling 1-bromonaphthalene (*319*). Cerium phthalocyanine has been mentioned in the literature (*181*) but has not been characterized. Europium, gadolinium, and ytterbium phthalocyanines have been prepared from *o*-cyanobenzamide and the corresponding trichlorides at 250°C. They are remarkably soluble in common solvents such as acetone and ethanol. The gadolinium complex has a magnetic moment of 8.2 B.M. (*140*).

J. Complexes of the Actinide Elements

A quinoline-soluble thorium phthalocyanine is formed in the reaction of thorium tetrachloride with phthalonitrile at 260°C (*378*), but no analytical data were reported. An ill-characterized sulfonated derivative has also been recorded (*119*). Uranyl phthalocyanine (UO_2Pc) has been observed as the product of the reaction of bis(dimethylformamide)uranyl acetate with dilithium phthalocyanine (*119*, *120*), and of the reaction of uranyl acetate with phthalic anhydride (*187*, *233*). Recently, however, Bloor *et al.* (*31*) reported that uranyl phthalocyanine formed by the reaction of uranyl chloride and phthalonitrile in dimethylformamide at 180°C has different infrared and visible absorption spectra from those originally quoted (*187*, *233*) and they conclude, on the basis of infrared data, that the uranyl phthalocyanine obtained by previous workers was essentially a mixture of α metal-free phthalocyanine and inorganic uranium salts.

Uranyl phthalocyanine (*31*) has a linear O—U—O bond system whose asymmetric stretching frequency occurs at 920 cm^{-1}. A band observed at 278 cm^{-1} in the far infrared is assigned to the O—U—O bending vibration. The electronic spectrum of uranyl phthalocyanine in 1-chloronaphthalene is unique in having no absorption in the 500–800 mμ region. All other phthalocyanines exhibit bands in this region (see Section V,B). The complex may be purified by sublimation, but is demetallated in sulfuric acid.

V. Electronic Structure and Spectra

A. Molecular Orbital Studies

The conjugated ring system of phthalocyanine comprises 40 atoms. The metallated phthalocyanines belong strictly to D_{4h} symmetry, whereas unmetallated phthalocyanine, by virtue of the two replaceable hydrogen atoms, belongs to D_{2h}. However, the two hydrogen atoms represent but a small perturbation and the latter may also be regarded as having D_{4h} symmetry, to a first approximation, as was assumed for porphin by Longuet-Higgins *et al.* (*230*, *283*). Group theory then shows that there will be 10 e_g, 4 a_{1u}, 6 a_{2u}, 5 b_{1u}, and 5 b_{2u} π orbitals. The shapes of the molecular orbitals are illustrated in Fig. 13. The a_{2u} orbital has no nodes, except of course in the plane of the phthalocyanine unit, while the a_{1u} orbital has nodes passing through all the nitrogen atoms. The b_{2u} orbital has nodes passing through the corner nitrogen atoms, while in the b_{1u} orbital the nodal plane passes through the central four nitrogen atoms. Each of the components of the doubly degenerate e_g orbital has a nodal plane through a pair of opposite central nitrogen atoms.

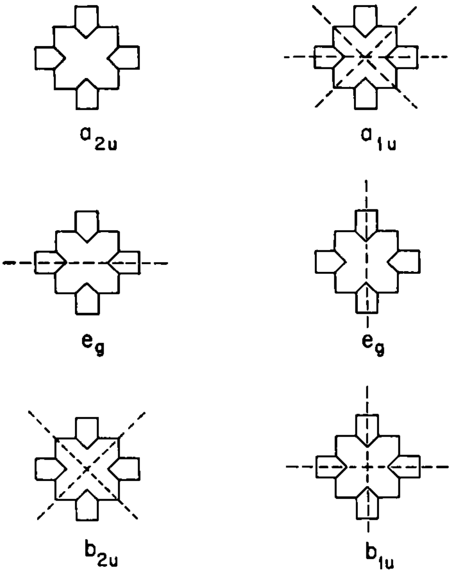


FIG. 13. Molecular orbital symmetries.

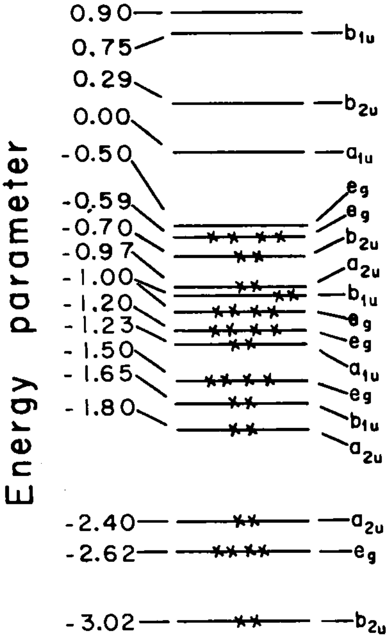


FIG. 14. The molecular orbital energies of phthalocyanine.

A number of LCAO calculations have been reported (*49*, *186*, *265*, *289*), but perhaps the most detailed study has been that of Basu (*14*), who used a simple Hückel treatment.

The relative energies of the lowest 18 molecular orbitals are illustrated in Fig. 14. These are only approximate since configurational interaction has been ignored. The electron densities and mobile bond orders are shown in Fig. 15, assuming different coulombic integrals for the carbon and nitrogen atoms. The electron densities were correlated with the reactivity of the phthalocyanine ring toward chlorination, sulfonation, etc., and toward its mode of degradation (*14*). The molecular orbitals are further discussed below.

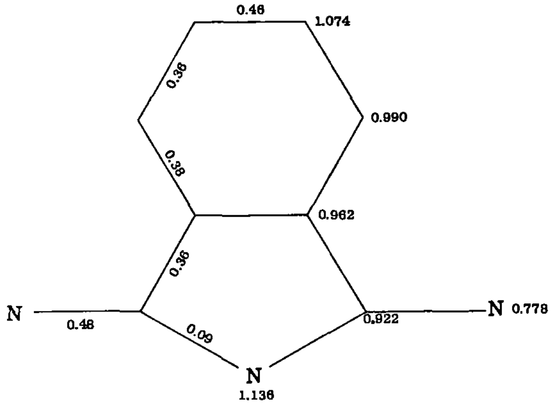


FIG. 15. Mobile bond orders and electron density in phthalocyanine. A single bond has a mobile bond order of zero, and a double bond has a mobile bond order of one.

B. ELECTRONIC SPECTRA

1. *Absorption and Reflectance Spectra*

In Table IV are listed all the available electronic absorption data for the phthalocyanines with the exception of some of the earlier work (*330*, *337*). Table V lists the spectra of some phthalocyanines in the solid state, and Fig. 16 illustrates the spectra of metal-free phthalocyanine and of the zinc derivative.

All normal oxidation state phthalocyanines are characterized by an intense band near 28,000 cm^{-1} (Soret band), and another intense band near 14,000–15,000 cm^{-1}. Metal-free phthalocyanine differs in having an intense doublet near 14,000–15,000 cm^{-1}. The intensities are of the order of 10^5 (dipole strength 1–2 Å^2) (*138*). Films as thin as 30 Å are reported, by virtue of their color, to be visible to the naked eye (*165*). Because of the 14,000–

TABLE IV
ELECTRONIC ABSORPTION SPECTRA

Complex	Solvent[a]	Visible and ultraviolet absorption spectra[b,c,d]	Reference
PcH_2	ClN	698(5.21), 665(5.18), 638(4.62), 602(4.43), 554(3.57), 350(4.74)	(*374, 5, 12a, 23, 31, 204, 318*)
	Q	698, 675, 664, 633, 602, 558, 528	(*330*)
	Py	672, 644	(*374*)
	SA(17.44)	840, 775, 690, 430, 305, 232	(*18, 23, 28*)
$PcLi_2$	Ac	688, 628, 595, 569, 550	(*5*)
PcCu	ClN	678(5.34), 648(4.51), 611(4.56), 588(4.06), 567(3.91), 526(3.57), 510(3.56), 350(4.76)	(*374, 5, 12a 237, 318*)
	SA(17.88)	794(5.36), 704(4.56), 440(4.32), 305(4.73), 290(4.56), 225(4.82)	(*18, 28*)
	SA(15.75)	792(5.38), 704(4.56), 440(4.36), 306(4.75), 287(4.61), 224(4.86)	(*18*)
	SA(13.80)	792(5.39), 700(4.49), 440(4.28), 305(4.72), 291(4.58), 224(4.83)	(*18*)
PcAg	ClN	677, 649, 611, 348	(*237, 5*)
	ClN	810(3.21), 698(4.37), 666(4.44), 608(3.85), 345(4.15)	(*23*)
PcAu	ClN	662, 633, 601, 348*	(*189*)
PcBe[e]	ClN	692, 681.5, 655, 630.5, 614, 591, 570	(*5*)
PcMg[e]	ClN	702(4.15), 680(4.93), 648(4.08), 611(4.08)	(*12a, 5, 23, 26*)
	Py	674.5(4.94), 647(4.39), 610(4.45), 587(3.79), 568(3.59), 347(4.73)	(*374*)
	ET	667(5.28), 606(4.56), 340(4.83), 270(4.92), 230(4.93)	(*23*)
PcZn	ClN	681(5.35), 649(4.48), 611(4.54)	(*12a, 5, 318*)
	Py	672(5.45), 646(4.56), 607(4.59) 347.5(4.81)	(*374*)
	SA(17.44)	788(5.32), 700(4.50), 440(4.26), 310(4.83), 229(4.95)	(*18, 24*)
	SA(14.00)	784(5.28), 698(4.46), 440(4.12), 310(4.78), 230(4.86)	(*18, 24*)
PcCd	ClN	700(4.16), 664(4.12), 612(3.64), 430(3.55), 340(3.91)	(*23*)
PcAlCl	ClN	691, 665, 622, 597, 576	(*5, 318*)
	ET	670, 643, 604, 582.5, 559	(*5*)
$PcAl{\cdot}HSO_4$	ET	675(5.20), 608(4.49), 350(4.79), 238(4.5)	(*23*)
	SA(17.88)	810(5.29), 720(4.52), 460(4.36), 312(4.95), 225(4.76)	(*18*)
	SA(15.27)	802(5.07), 765(4.98), 435(4.41), 315(5.20), 222(4.76)	(*18*)

TABLE IV (*Continued*)

Complex	Solvent[a]	Visible and ultraviolet absorption spectra[b,c,d]	Reference
PcAl·HSO_4	SA(13.75)	794(4.99) 760(4.98), 683(4.39), 430(4.32), 307(4.72), 221(4.78)	(*18*)
PcAlOPh	Py	680, 652, 614	(*268*)
$PcAlOC_6H_4Ph$	Py	678, 651, 612	(*268*)
$PcAlOC_6H_4OCH_3$	Py	678, 649, 612	(*268*)
$PcAlOSi(Ph)_3$	Py	679, 649, 612	(*268*)
PcAlBr	Py	682, 650, 612	(*177*)
PcGaCl	D	684, 655, 616, 594, 573	(*55*)
	ClN	700(4.93), 668(4.25), 629(4.15), 605(3.57), 585(3.40), 365(4.50), 342(4.94)	(*55*)
$PcSm(HCO_2)$	BrN	674, 609, 463–464	(*319*)
PcEuCl	ClN	674	(*140*)
PcGdCl	ClN	671	(*140*)
PcErCl	BrN	667, 602, 461–462	(*318, 319*)
PcYbCl	ClN	670(5.36)	(*140*)
$PcUO_2$	ClN	914.5(4.62), 810sh, 420(4.7)	(*31*)
$PcSi(OCH_2CCl_3)_2$	B	679, 650, 612	(*200*)
$PcSi(OC_6H_{11})_2$	B	673, 643, 606	(*200*)
$PcSi(OC_8H_{17})_2$	B	674, 645, 606	(*200*)
$PcSi(OC_8H_{37})_2$	B	674, 644, 606	(*200*)
PcSn	ET	682, 616, 359, 302, 238	(*23*)
Pc_2Sn	CB	774(4.57), 626(5.06), 575.5(4.33), 338(5.11)	(*374*)
PcPb	ClN	714(5.11), 664(4.55), 430(4.08), 342(4.85)	(*23*)
	ClN	685, 642, 615, 591	(*5*)
PcTiO	CB	690(5.39), 662.5(4.50), 622.5(4.58), 346(5.34)	(*213*)
PcAsCl	Py	580, 340	(*308*)
PcVO	CB	695(5.25), 665(4.63), 619(4.58), 346(4.96)	(*213, 5*)
$PcCr(Py)_2$	Py	687(4.85), 632(4.20), 560(3.70), 525(3.86), 500(3.70), 345(4.59)	(*90*)
PcCrOH	CB	689(4.92), 621(4.14), 502(3.91), 347(4.62)	(*90*)
$PcCr(H_2O)_2OH$	MT	676(5.17), 610(4.48), 502(4.05), 477(3.99), 344(4.60), 268(4.48)	(*90*)
$PcCr(MeOH)_2OH$	MT	670(5.11), 605(4.40), 505(3.82), 475(3.79), 340(4.55)	(*90*)
$Na_2[PcCrO(OH)]$	MTA	669(5.25), 604(4.47), 475(3.56), 337(4.71), 278(4.59), 268(4.63)	(*90*)
K[PcCrCN(OH)]	MT	677, 611, 515, 345, 321, 308, 271	(*90*)
$K[PcCr(CN)_2]$	MTC	675, 615, 518, 490, 380, 345, 322, 309, 258	(*90*)

TABLE IV (*Continued*)

Complex	Solvent[a]	Visible and ultraviolet absorption spectra[b,c,d]	Reference
$K[PcCr(SCN)_2]$	MTT	682, 617, 511, 349, 298, 270	(*90*)
$HPcCrCl_2$	MTH	682(5.15), 615(4.30), 507(4.03), 495(3.93), 355(4.70), 347(4.71), 282(4.57)	(*90*)
PcMn	Py(N_2)	880, 835, 660, 643, 467, 323, 300	(*93*)
	ClN(N_2)	878, 682, 654, 598, 532, 494, 473, 440	(*93*)
	C_2B	1350, 1090, 850	(*70*)
PcMnOH	ClN	726, 654, 520, 365	(*93*)
	Py	712.5(4.77), 337(4.53)	(*213, 93*)
Na[PcMnCN·EtOH]	ETC	824, 660, 598, 533, 464, 373	(*93*)
Na[PcMnCN·Py]	PyC	816, 660, 598, 537, 473	(*93*)
$Na_2[PcMn(CN)_2]$	ETC	752, 669, 636, 614, 557, 385	(*93*)
PcMnO·Py	Py(O_2)	620(4.62), 570i(3.82), 325(4.49)	(*213, 93*)
PcFe	C_2B	656(4.84), 595(3.95), 330(4.68)	(*374*)
	ClN	658(4.70), 632(4.26), 597(4.2)	(*12a, 5*)
	Q	660, 632, 593	(*5*)
$PcFePy_2$	Py	654(5.03), 593(4.47), 414(4.29), 329.5(4.88)	(*374, 12a*)
PcRu	B	645, 584	(*193*)
$PcRu{\cdot}6PhNH_2$	B	632, 580, 378	(*193*)
$PcRu{\cdot}6CH_3C_6H_4NH_2$	B	632, 582sh, 379	(*193*)
$PcOs{\cdot}SO_4$	SA(15.00)	768(4.31), 700(4.44), 415(4.47), 280(4.93)	(*28*)
	SA(18.00)	805(4.11), 720(4.32), 280(4.74)	(*25*)
	Ac	675, 608, 301, 271	(*25*)
PcCo	Py	657.5(5.07), 596.5(4.51), 330(4.86)	(*374, 5*)
	ClN	672(5.19), 606.5(4.53), 348(4.65)	(*374, 5, 317*)
	ET	750, 660, 330, 238	(*23*)
	SA(17.88)	790(5.12), 700(4.48), 427(4.27), 291(4.72), 222(4.65)	(*18*)
	SA(15.00)	782(5.09), 700(4.48), 422(4.32), 298(4.84), 222(4.79)	(*18*)
	SA(13.80)	780(5.82), 700(4.37), 420(4.37), 300(4.81), 222(4.82)	(*18*)
$PcRh{\cdot}HSO_4$	SA(18.00)	768(4.56), 692(4.28), 437(4.07), 312(4.55), 269(4.55), 224(4.66)	(*28*)
	SA(16.00)	768(4.57), 698(4.28), 439(4.07), 308(4.50), 269(4.57), 224(4.72)	(*28*)
PcNi	ClN	671(5.10), 643(4.47), 603(4.51), 580(3.82), 560(3.75), 351(4.57)	(*374, 5*)
	SA(17.44)	778(4.57), 690(4.18), 302(4.61), 226(4.77)	(*18, 24*)
	SA(14.00)	774(4.51), 700(4.10), 300(4.51), 224(4.68)	(*18, 24*)

TABLE IV (*Continued*)

Complex	Solvent[a]	Visible and ultraviolet absorption spectra[b,c,d]	Reference
PcNi	SA(13.40)	774(4.42), 700(3.95), 300(4.50), 223(4.66)	(*18*)
PcPd	ClN	660.5(5.32), 633(4.51), 595.5(4.57) 576.5(4.07), 557(3.98), 347(4.69)	(*374*)
	SA(17.44)	771(5.17), 702(4.44), 444(4.19), 262(4.73)	(*24*)
	SA(15.00)	768(4.97), 744(4.89), 429(4.29), 261(4.71)	(*24*)
	SA(14.00)	768(4.91), 740(4.88), 430(4.19), 259(4.59)	(*24*)
PcPt	ClN	652, 624, 588, 564.5, 545	(*5*)
	SA(17.44)	772(5.18), 686(4.47), 438(4.26), 271(4.93)	(*24*)
	SA(15.00)	760(4.95), 664(4.36), 427(4.19), 276(4.84)	(*24*)

[a] Solvents: ClN, 1-chloronaphthalene; Q, quinoline; Ac, acetone; ET, ethanol; MT, methanol; Py, pyridine; SA, sulfuric acid, molarity in parentheses; BrN, 1-bromonaphthalene; B, benzene; CB, chlorobenzene; C_2B, dichlorobenzene; MTA, methanol plus alkali; MTH, methanol plus trace of HCl; D, dioxane; C, after a solvent, signifies the presence of sodium cyanide.

[b] mμ (log ε).

[c] The data are taken from the first reference cited, which is generally the most recent; subsequent references deal with measurements in the same solvent, carried out by other workers. Where there is disagreement, both sets of measurements are cited.

[d] (*) Broad band, indefinite maximum; (sh) shoulder; (i) inflection.

[e] Hydrated species.

15,000 cm^{-1} absorption, phthalocyanines generally give deep blue or green solutions. Reduced metal phthalocyanines normally give red or purple solutions but little quantitative data are available. Shablya and Terenin have reported, however, the spectrum of the magnesium phthalocyanine negative ion in tetrahydrofuran solution, by reduction with sodium, over the range 400–1000 mμ (*314*, *315*).

Although there has been much theoretical study of the spectra of porphin and its metal derivatives (*137*, *138*, *230*, *283*), comparatively little has been said about the metal phthalocyanines. It has been generally assumed that the theory developed for porphin will apply equally to the phthalocyanines. Two general approaches have been used to interpret the spectra of the phthalocyanines. In the Free Electron Gas model, developed by Kuhn (*201–206*, *309*) in a manner similar to that of Simpson (*327*), the phthalocyanine unit is regarded as a polyene in which the π electrons are constrained to move in a closed ring-shaped path, in a field of constant

TABLE V
ELECTRONIC SPECTRA—SOLID STATE

Complex	Method[a]	Electronic spectrum[b] (cm^{-1} log ϵ)				Reference
PcH_2	SC	9597vw	8032w	3817w		*(115)*
	SC-ac*	15,750	13,900			*(235)*
	SC-b	14,440	15,350			*(235)*
	NaCl	16,300				*(299)*
PcCu	RpB	15,870	13,980			*(68)*
	NaCl	16,420				*(299)*
	SC	10,989(2.5)	9890(2.3)	9178(2.73)		*(115)*
	SC-ac*	13,114				*(115)*
	SC-b*	13,280				*(115)*
PcZn	NaCl	15,900	14,580			*(299)*
	RpB	15,740	13,510			*(68)*
PcGaCl	Tp	27,000	14,700	13,330		*(55)*
	Rp	31,250	17,230			*(55)*
PcSn	NaCl	13,920				*(299)*
PcPb	NaCl	14,050				*(299)*
PcCr	NaCl	15,950	14,500			*(299)*
PcFe	NaCl	15,200				*(299)*
PcCo	NaCl	16,300				*(299)*
	RpB	16,000	14,190			*(68)*
	SC	9804vw	9174vw	5376w		*(115)*
	SC-ac*	13,586				*(115)*
	SC-b*	14,044				*(115)*
PcNi	NaCl	16,300				*(299)*
	RpB	16,130	14,540			*(68)*
	SC	8803w	7974vw	7663vw	6410(25°)w 6337(−175°)w	*(115)*
	SC-ac*	13,577				*(115)*
	SC-b*	13,976				*(115)*

[a] NaCl, reflectance of powder diluted 0.1% in sodium chloride; SC, single crystal; SC-ac, single crystal, polarized light in ac plane; SC-b, single crystal, polarized light along b axis; Tp, powder, transmission; Rp, powder, reflection; RpB, powder, reflection, using black background.

The asterisk indicates that from these data, factor group splittings may be determined (Davydov). The following values of ΔD result: PcH_2 1750, 1450; PcCo 458; PcNi 399; PcCu 166 cm^{-1}.

[b] Abbreviations: w, weak; vw, very weak.

potential energy (Fig. 17). The energy difference between the highest occupied and the lowest empty state is expressed in terms of L, the circumference of the path, m, the mass of the electron, h, Planck's constant, and N the number of π electrons involved:

$$\lambda_m = \frac{8mc}{h}(L^2/N + 1) \qquad \text{(LXXV)}$$

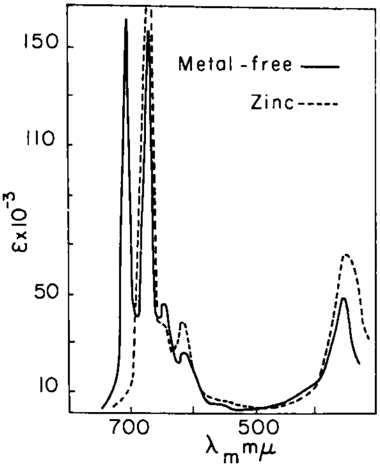


FIG. 16. The electronic spectra of metal-free and zinc phthalocyanines.

A parameter may also be introduced to correct for the difference in the electronegativities of carbon and nitrogen. The electrons can be considered to set up a series of standing waves whose half-wave length corresponds to L/n where n takes all values from 1 to N. These correspond to the N energy levels, the lower $N/2$ levels being filled. In the case of metal-free phthalocyanine, there is reasonably good agreement between the predicted band

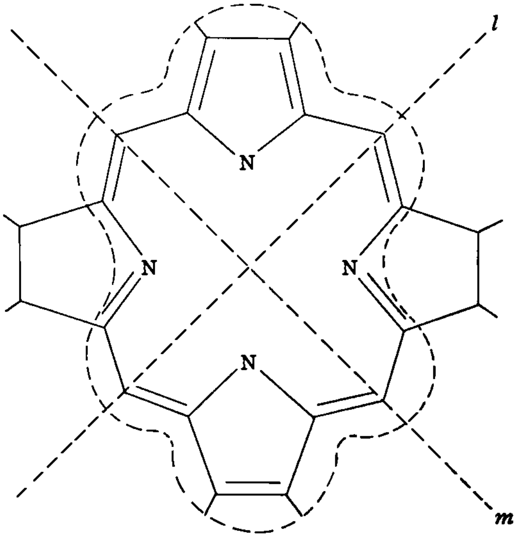


FIG. 17. The 18π electron system of phthalocyanine.

energies and oscillator strengths and the experimentally observed spectrum (*205*).

The second theoretical approach considers the electronic spectra to arise through transitions from one molecular orbital level to another, and may therefore be discussed in terms of the treatment developed by Basu (*14*). The high intensity and relatively low energy of the observed bands imply that they arise through π—π^* transitions (*282*). In D_{4h} symmetry the excited states concerned are doubly degenerate and of symmetry E_u (*235*), hence configurational interaction is likely to be important. In D_{2h} symmetry E_u transforms as B_{1u} and B_{2u} (or B_{2u} and B_{3u}, depending upon the convention employed), thus leading to a splitting of the degenerate states. The splitting which is observed in the spectrum of metal-free phthalocyanine is a measure of the departure from D_{4h} symmetry (*235*).

Using the molecular orbital diagram (Fig. 14), the lowest energy electronically allowed transitions probably involve the configurations $(b_{2u}e_g)$, $(a_{2u}e_g)$, and $(b_{1u}e_g)$. However, transitions from filled orbitals of e_g symmetry to some of the higher singly degenerate odd orbitals cannot be excluded. Basu (*14*) concluded that the lowest energy absorption near 15,000 cm^{-1} arose from the transition $e_g \leftarrow b_{1u}$ $(E_u \leftarrow A_{1g})$, and the band near 28,000 cm^{-1} (Soret band) from $e_g \leftarrow b_{2u}$ $(E_u \leftarrow A_{1g})$. There is another double band at slightly higher energies still, which may involve a transition from the a_{2u} level. Because of configurational interaction, these assignments cannot be assumed to be necessarily correct. Indeed, consideration of Fig. 14 would lead one to suggest that the latter assignment belongs to the lower energy band.

Lyons *et al.* (*234*, *235*) have studied the polarized crystal spectrum of metal-free phthalocyanine at 90° and 300°K. The B_{1u} and B_{2u} components of the E_u state in D_{2h} symmetry are polarized along the *m* and *l* directions, respectively (Fig. 17). In metal-free phthalocyanine the *l* axis is slightly shorter than the *m* axis. All the doublet bands observed in the spectrum are polarized in this manner, thus supporting their assignments in D_{2h} as being the B_{1u} and B_{2u} components of the E_u (D_{4h}) state.

The metallated derivatives have only one principal band in the red and can be assumed to be of D_{4h} symmetry. The oscillator strength of this band is approximately twice that of each of the metal-free absorption bands ($f = 0.52$) (*235*). In addition to the main absorption bands, phthalocyanines exhibit weaker satellite bands. In metal-free phthalocyanine the absorption maxima (in 1-chloronaphthalene) of these satellite bands are given by the relationship

$$\nu_1 = 14{,}290 + 1585n_1 \qquad \nu_2 = 15{,}060 + 1585n_2 \text{ cm}^{-1} \qquad \text{(LXXVI)}$$

where n_1 and n_2 are integers (*5*). The interval 1585 cm^{-1} corresponds to one of the principal vibrational frequencies observed in the infrared spectrum. The additional structure is therefore assigned as transitions to higher vibrational levels of the particular electronic state concerned. Personov (*280*) has studied the spectrum of metal-free phthalocyanine in frozen paraffins at 77°K. A very sharp spectrum was observed, in octane, consisting of seventy absorption lines between 699.5 and 589.7 mμ. The spectrum in each paraffin consists of several identical vibrational series with origins at corresponding lines of the $(O - O')$ multiplet, and shifted relative to one another by the amount of the splitting in the multiplet. A similar fluorescence spectrum was also observed.

In considering the metallated derivatives, it is revealing to compare the phthalocyanines with the porphyrins. The two highest filled orbitals of porphin are of symmetry a_{2u} and a_{1u}, and the principal absorption bands are assigned as $e_g \leftarrow a_{2u}$ and $e_g \leftarrow a_{1u}$ (Soret) (*137*, *138*). Despite the close similarity in structure, some variation in behavior may be expected in the light of the differing assignments. Gouterman (*137*) has pointed out that two types of metal porphin interaction may be expected: the inductive effect and the conjugative effect. The former arises from a change in potential at the coordinating nitrogen atoms due to the differing metal ions. This may affect the energies of the e_g, a_{2u}, and b_{2u} orbitals, but will not affect the a_{1u} and b_{1u} orbitals since they have nodes at these nitrogen atoms. The conjugative effect arises through π interactions between metal and porphin. From the small dependence of the spectrum upon the central metal ion, it was concluded that, in the case of the porphins, π-bonding involving d orbitals was negligible, but that involving the $p_\pi(a_{2u})$ orbital was significant (*137*). This conclusion rests partly upon the observation that there is a linear relationship between the electronegativity of the central metal ion (for ns and ns^2 ions) and the absorption maximum of the red band.

With a few exceptions, the variation in the absorption spectrum with central metal ion is even less marked in the phthalocyanine series. This is particularly true of the position of the red band, which is almost independent of the central metal ion. There appears to be no obvious relationship between the electronegativity of the metal ion and the absorption maxima in the phthalocyanine series (*214*). This is readily understood since there is no metal orbital of b_{1u} or b_{2u} symmetry, and the metal e_g orbitals will, in general, have too low an energy to interact with the phthalocyanine e_g orbital involved in the transition. The small variations which do occur in the red band are therefore probably inductive rather than conjugative. The Soret band, in the blue, does vary slightly with metal ion, and it seems probable that the transition involves the a_{2u} orbital admixed by configurational interaction (see also Section VII).

Riggleman and Drickamer (*296*) have investigated the effect of high pressure upon the low energy absorption maximum. The pressure shifts are relatively modest, but are very sensitive to the metal involved. In all cases there is a red shift which is interpreted as a van der Waal's (dispersion) interaction between neighboring molecules, particularly between the metal ion and the π electron levels of the adjacent molecules. The excited state would consequently be lowered in energy more than the ground state. At relatively low pressures (50 kbar), the order of increasing shift is (for divalent ions) Cu < Zn < Fe < metal-free < Ni < Co < Cr (-300 to -700 cm^{-1}), while at higher pressures (140 kbar) it is Pb < Zn < Fe < Sn < Cr. This is roughly the order of increasing polarizability of the central metal ion. It is suggested that the large shift observed with chromous phthalocyanine is due to the high polarizability of the chromous ion. The observed frequency shift increases with increasing pressure but, in the case of lead, levels off at higher pressures, perhaps because there is a limit to the extent to which the lead atom can be compressed. Phthalocyanine triplet-triplet transitions have been recorded (*229*).

In Table V are listed the spectroscopic data from single crystal and from powder studies. The origin of the low energy near infrared absorption is in doubt. Fielding and MacKay (*115*) note that the 6410 cm^{-1} band in nickel phthalocyanine shifts to lower energy with decreasing temperature, and suggest that it arises through a $d - d$ transition within the nickel atom. This conclusion has been questioned by Day *et al.* (*70*). The other low energy bands are ascribed tentatively to spin-allowed symmetry-forbidden transitions (*115*) or to spin-forbidden singlet-triplet transitions (*70*).

Chadderton (*47*) has discussed the absorption spectra of platinum, copper, and metal-free phthalocyanines as sublimed films and also in the vapor state (not platinum). In general two main absorption bands were observed in the red region. The spectra of single crystals were also recorded. At low temperature (−90°C) the spectrum of a single crystal of copper phthalocyanine includes a series of sharp peaks attributed to phonon-assisted transitions, i.e., to the stimulation of lattice vibrations. Fielding and MacKay (*115*), using polarized light, observed four bands in the crystal spectrum, comprising two pairs of oppositely polarized components. The long wavelength components were reported (Table V). Day *et al.*, who originally reported two bands in the reflection spectrum of metal phthalocyanines (*68*), later amended this to four (*70*). The data were interpreted in terms of Davydov theory (*67*), which supposes that the splitting ΔD (Fig. 18) arises from interactions between nonequivalent molecules, and that X is related to interactions between equivalent molecules in the unit cell, where such molecules are represented by point dipoles. This would imply that both X and ΔD should have a similar dependence upon the central metal ion, which is contrary to that observed (X, Co > Ni < Cu, ΔD, Co > Ni > Cu) (*70, 115*). It is suggested (*70*) that out-of-plane

π-bonding (between the metal ion and the nitrogen atom of an adjacent molecule) (*47*), which reduces the symmetry from D_{4h} to D_2 (and splits the E_u state into B_1 and B_2, Fig. 18), is partly responsible for the values

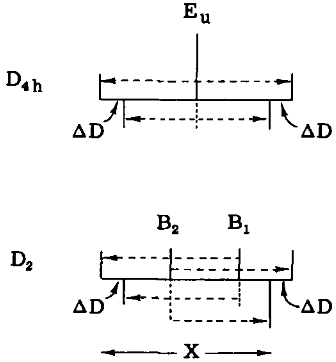


FIG. 18. Davydov splitting diagram.

of X observed. This conclusion is derived on the basis that we might intuitively expect the importance of out-of-plane π-bonding to follow the sequence Co > Ni < Cu.

Lyons *et al.* (*235*) have made a theoretical study of the polarized spectrum of metal-free phthalocyanine crystals, using a similar approach.

2. Fluorescence Spectra

The phenomenon of fluorescence is of interest in connection with the mechanism of photosynthesis. Both chlorophyll and magnesium phthalocyanine fluoresce in alcohol, the latter with emission near 675 mμ, about 5 mμ beyond that of the former. The fluorescence of magnesium and of other phthalocyanines has been extensively investigated, primarily by Russian workers (*4, 15, 77, 99–103, 121–125, 140, 173, 187, 191, 192, 228, 229, 233, 263, 280, 294, 313, 329, 344*). Zinc phthalocyanine is reported to fluoresce at 673.1 mμ, and metal-free phthalocyanine at 691.8 mμ (*4, 15*). No phosphorescence was observed. The fluorescence spectrum is due to light emitted when electrons in excited triplet states fall back into the ground singlet state. The excited states have lifetimes of approximately 10^{-9} sec (*77, 313*). At low temperatures the vibrational fine structure is observed (*280*). Oxidizing molecules such as oxygen, quinone, and hydroquinone have a strong quenching effect upon the fluorescence, whereas reductants have little effect. The strong quenchers do not, on the other hand, have much effect upon the absorption spectrum, while weak quenchers, such as iodine and *m*-dinitrobenzene, influence the absorption spectrum markedly (*101, 192*). Monomolecular layers of magnesium phthalocyanine, adsorbed onto magnesium oxide, fluoresce in the presence of donors such as oxygen, water, hydrogen sulfide, chlorine, iodine, ether, and ethanol. The emission wavelength is determined by the donor molecule (principal bands: EtOH, 673; Et_2O, 668; H_2O, 679; O_2, 659, 697 mμ). In addition, two or three further bands occur on the long wavelength side, separated from one another by 500–900 cm^{-1}. These bands correspond to transitions from excited triplet states to different vibrational levels of the ground state. Above 400°C the fluorescence spectrum disappears but may be restored by addition of one of the donors. Presumably donor acceptor complexes are formed (*122*, *123*). Experiments have shown that, whereas ethanol can replace oxygen in the complex, the reverse replacement will not occur (*124*). Systematic studies of the changes in fluorescence and absorption spectrum of magnesium phthalocyanine dissolved in toluene, in the presence or absence of air, have been carried out. The intensity of the band at 672 mμ decreases upon evacuation and increases again when air is readmitted (*103*). The luminescence of rare-earth phthalocyanines has been investigated. Europium phthalocyanine fluoresces strongly, gadolinium phthalocyanine weakly, and the ytterbium complex not at all (*140*); the relationship between the fluorescent yield and the electronic structure of the metal is discussed.

C. RESONANCE SPECTRA

1. *Electron-Spin Resonance Spectra*

There has been much interest in the electron-spin resonance spectra of metal phthalocyanines, because information relating to the relative energies of the metal d orbitals, and to the presence or absence of σ and π-bonding, can often be deduced therefrom.

The metal orbitals transform in D_{4h} symmetry as follows:

$$\begin{array}{rr} s, d_{z^2} \leftrightarrow a_{1g} & p_x,\ p_y \leftrightarrow e_u \\ d_{x^2-y^2} \leftrightarrow b_{1g} & p_z \leftrightarrow a_{2u} \\ d_{xy} \leftrightarrow b_{2g} & d_{xz},\ d_{yz} \leftrightarrow e_g \end{array}$$

It therefore follows from Section A, and the fact that σ orbitals on the nitrogen atoms span a_{1g}, e_u, and b_{1g}, that the d_{z^2} and $d_{x^2-y^2}$ orbitals will be σ antibonding, the latter strongly so, the d_{xy} orbital formally nonbonding, and the d_{xz} and d_{yz} orbitals π antibonding.

The molecular orbitals of especial interest have the form (numbering the coordinating nitrogen atoms 1 to 4):

$$b_{1g} \qquad \alpha d_{x^2-y^2} \pm \alpha'/2[-\sigma^1 x + \sigma^2 y + \sigma^3 x - \sigma^4 y] \qquad \text{(LXXVII)}$$

$$b_{2g} \qquad \beta_2 d_{xy} \pm \beta'_2/2[p_y{}^1 + p_x{}^2 - p_y{}^3 - p_x{}^4] \qquad \text{(LXXVIII)}$$

$$e_g \begin{cases} \beta_1 d_{xz} \pm \beta_1'/2[p_z{}^1 - p_z{}^3] \\ \beta_1 d_{yz} \pm \beta_1'/2[p_z{}^2 - p_z{}^4] \end{cases} \qquad \text{(LXXIX)}$$

Although with the simple treatment above the d_{xy} orbital appears nonbonding, it is possible to visualize it being involved in in-plane π-bonding, as indicated in (LXXVIII) (*260*).

Table VI lists all the published electron-spin resonance data pertaining to paramagnetic metal phthalocyanines. In addition to the g values, the most commonly recorded datum is the α^2 value; $\alpha = \alpha^2 = 1$ refers to purely ionic bonding (LXXVII) and values of α^2 less than 1 imply some delocalization of the $d_{x^2-y^2}$ electron onto the phthalocyanine ligand. Thus the value of $\alpha^2 = 0.54$ for silver phthalocyanine may be interpreted to mean that the $d_{x^2-y^2}$ electron spends 46% of its time on the phthalocyanine ligand. The comparatively low values of α^2 reported for copper and silver phthalocyanine (*131*, *139*, *145*, *237*, *260*, *298*, *347*) suggest a high degree of covalency in these complexes.

Most authors have assumed that out-of-plane π-bonding (intramolecular) is unimportant ($\beta_1 = \beta_1{}^2 = 1$) (LXXIX). Recently Harrison and Assour (*145*) have concluded that such π-bonding is important in copper phthalocyanine (see also Section VII). In-plane π-bonding seems intuitively unlikely, and the original suggestion (*260*) that it was in fact important in copper phthalocyanine ($\beta_2{}^2 = 0.65$) (LXXVIII) was later refuted by Harrison and Assour (*145*).

The most probable order of d levels in copper phthalocyanine is illustrated in Fig. 19 (*131*, *145*). The calculated energies (*131*) are appended. The relative order of the e_g and b_{2g} orbitals is the inverse of that found for copper acetylacetonate (*238*). Although the data for cobalt phthalocyanine (*139*) cannot be assigned unambiguously, the orbital levels are probably in the same relative order. The hole would then be in the d_{z^2} orbital rather than in the $d_{x^2-y^2}$ (as in copper phthalocyanine) and this is in accord with the observation that the electron-spin resonance spectrum of cobalt phthalocyanine is solvent dependent, while that of copper phthalocyanine is not (*131*, *139*). The alternative assignment of the cobalt data places the hole in the d_{xy} orbital lying some 16,000 cm^{-1} above the d_{xz},d_{yz} pair, which seems unlikely.

Several authors have measured the copper and cobalt hyperfine interaction constants, A and B (Table VI), arising from coupling between the electronic spin and the nuclear spin of the central metal ion. Four lines are seen in the case of copper phthalocyanine due to interaction between the electron and the nuclear spin of Cu^{63} ($I = \frac{3}{2}$); single crystals of cobalt phthalocyanine diluted in zinc phthalocyanine gave eight components due to interaction with the nucleus of Co^{59} ($I = \frac{7}{2}$) (*167*).

The relatively low values found for α^2 suggest that it should be possible to see splitting due to a hyperfine interaction between the electron spin and the nuclear spin of the coordinating nitrogen atoms. This was not observed in the early crystal investigations, but was later detected in solution studies of both copper and silver phthalocyanines (*145*, *237*, *239*). This observation offers direct proof that metal electrons are delocalized onto the phthalocyanine unit by a σ mechanism. Harrison and Assour conclude that delocalization involving a π mechanism is also important (*145*).

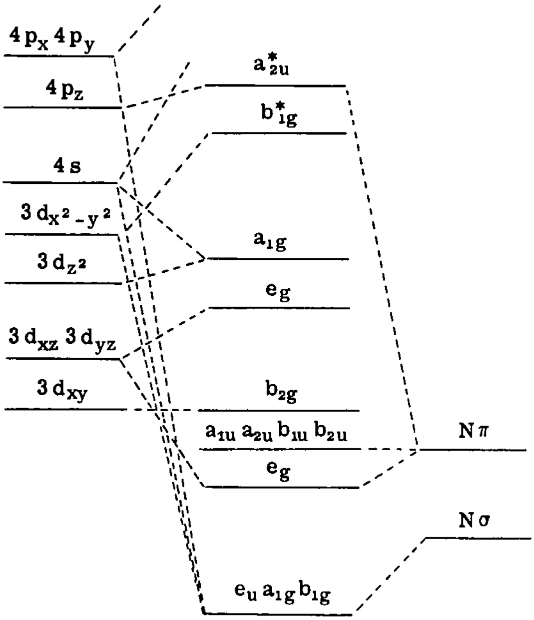


FIG. 19. A molecular orbital scheme for copper phthalocyanine.

It is pertinent to remark when considering electron-spin resonance data that, although the various studies of copper phthalocyanine (*16*, *131*, *139*, *140*, *210*, *239*, *260*, *261*, *299*) have yielded essentially the same parameters, the detailed interpretation of these parameters has often been strikingly different.

Electron-spin resonance signals have also been detected in unmetallated phthalocyanine, and in many "diamagnetic" metal phthalocyanines including nickel, magnesium, aluminum, lead, zinc, sodium, potassium, beryllium, tin, platinum, and cerium (*166*, *181*, *262*, *347*). In most cases the lines are narrow and centered at the free spin value of $g = 2.0023$, implying the presence of a radical species. Repeated washing with organic

TABLE VI
Electron-Spin Resonance Data

Complex	$\bar{g}$[a]	$g_\perp$	$g_\parallel$	α^2	Method[b]	Additional data[c]	Reference
PcCu	2.1(40*g*)	—	—	—	PW	—	(*181, 209, 347*)
	—	2.045 ± 0.003	2.165 ± 0.003	0.79	Xtal	$A = 0.022 \pm 0.001$ $B = 0.003 \pm 0.001$	(*131*)
	—	2.045	2.165	0.78	SA(77°K)	$\beta_2^2 = 0.65$	(*260*)
	—	2.045	2.165	—	FS	$A = 0.022$, $B = 0.003$, $P = 0.035$	(*239*)
	—	2.037	2.180	0.72	SA(136°K)	$\alpha' = 0.57$; $C = 1.39$, $D = 1.47 \times 10^{-3}$	(*237, 299*)
	—	2.050	2.179	0.85	Xtal	$A = 0.0202$, $B = 0.0019$, $C = 1.45$, $D = 1.79 \times 10^{-3}$, $\alpha' = 0.6$, $Q = 6 \times 10^{-4}$	(*145*)
PcVO	2.0(500*g*)	—	—	—	PW	—	(*166*)
PcMn	2.0(500*g*)	—	—	—	PW	—	(*166*)
PcFeCl	2.5(1900*g*)	—	—	—	PW	—	(*181*)
PcCo	2.4(1000*g*)	—	—	—	PW	—	(*181*)
	—	2.2	2.05	—	Py	—	(*139*)
	—	2.92	1.92 ± 0.01	—	Xtal(20°K)	$A = 0.017 \pm 0.01$	(*131,139*)
	—	2.88	—	—	—	$B = 0.027 \pm 0.01$	
PcAg	—	2.016	—	—	PW	—	(*237*)
	—	2.017	2.093	0.54	ClN(77°K)	$\alpha' = 0.71$; $C = 2.14$, $D = 2.32 \times 10^{-3}$	(*237*)
PcAg	2.0023(4.82)				PW		(*189*)
PcAu	2.065	1.996			ClN(77°K)	$D = 1.58 \times 10^{-3}$	(*181*)

[a] Width in gauss in parentheses.

[b] PW, powder; Xtal, single crystal; FS, frozen solution; Py, pyridine solution; ClN, chloronaphthalene; SA, concentrated sulfuric acid.

[c] A,B are metal, and C,D are nitrogen hyperfine interaction constants in wave numbers. Q is a quadrupole interaction constant in wave numbers. For other parameters, see text.

solvents, or repeated recrystallization from concentrated sulfuric acid, decreases the intensity of the signal. Moreover, when such samples are sublimed the signal is more intense in the residue than in the sublimate. Kholmogorov concluded (*182*) that the radical species was an impurity, there being one unpaired spin per 10^2 to 10^4 molecules (*181*). More recently the centers responsible for the radical resonance were found to be oxygen impurities adsorbed by the compounds. The experimental evidence was not able to distinguish between the electrons being on the surface or in the bulk of the complex. Metal-free phthalocyanine single crystals were found to contain some 10^{17} unpaired electrons/cm^3 (*145a*). Electron-spin resonance signals are also generated when metal-free phthalocyanine is pyrolyzed at 400°C (*166*, *376*). Stannous phthalocyanine is anomalous in having a four-line spectrum of varying width with g values somewhat less than 2.002 (*262*).

Electron-spin resonance technique has been used to study the nature of the one-electron oxidation products formed when metal-free phthalocyanine, and some metallated derivatives, are oxidized by one equivalent of ceric ion (*41*, *128*, *130*). Although phthalocyanine normally oxidizes in a two-electron process to phthalimide, under controlled conditions it is possible to stop the oxidation at the one-electron stage, a radical cation being formed. Besides ceric ion, other oxidizing agents such as potassium permanganate and dichromate, and perchloric acid may be employed (*41*). The radical cation, which is relatively stable in syrupy phosphoric acid at low temperature, may be reduced back to phthalocyanine by ferrous or stannous ions. The cation disproportionates on standing to phthalocyanine and two-electron oxidation products. The g value was still 2.0023 in the metallated derivatives(Al, Cu, and Co), indicating that the unpaired electron was in an orbital not associated with the central metal ion.

2. Nuclear Magnetic Resonance Spectra

The proton magnetic resonance spectrum of dipotassium phthalocyanine dicyanoferrate(II) and of an analogous methyl-substituted derivative has been recorded at 60 mc/sec in methanolic potassium cyanide with tetramethylsilane as an internal calibrant (*92*).

a. Dipotassium Phthalocyanine Dicyanoferrate(II). The spectrum shows only two kinds of proton (indicated by AA′ and BB′ in Fig. 20a), having origins at $\tau = 0.85$ and 2.17, respectively. The low field values result from the strong de-shielding of the secondary field induced in the 18-membered phthalocyanine ring. The latter is assumed to be aromatic and sustain a considerable ring current, as found for porphyrins (*2*, *3*, *45*). The spectrum comprises two bands of equal intensity, each of six lines symmetrically disposed about the band center (proton resonance origin). Analysis of the pattern as arising from an AA′XX′ spin-coupled system, gave the following coupling constants:

$$J_{AB} = J_{A'B'} = 7.0; \quad J_{BB'} = 7.8; \quad J_{AB'} = J_{A'B} = 1.2; \quad J_{AA'} = 0.4 \text{ c/sec}$$

These parameters, after allowance for line width (0.3 c/sec) and overlap, gave a calculated spectrum which matched that observed in both line positions and intensities.

(a) (b)

FIG. 20. The protons responsible for the nuclear magnetic resonance spectrum of phthalocyanine.

b. Dipotassium Tetra-4-methylphthalocyanine Dicyanoferrate(II). The spectrum shows that the macrocyclic ring is centrosymmetric. The four methyl groups are equivalent, giving rise to a single line at $\tau = 7.16$, and the ring protons provide only three signals. The latter comprise two doublets at $\tau = 2.38$ and 1.05 assigned (as in Fig. 20b) to protons X and A, with $J_{AX} = 8.4$ c/sec, and a singlet at $\tau = 1.10$ from proton M. The lines were not very well resolved but it was suggested that J_{MX} and J_{AM} were very small and together less than 1 c/sec.

D. MAGNETIC SUSCEPTIBILITY DATA

Many transition metal phthalocyanines are paramagnetic owing to the presence of unpaired electrons in the *d* orbital levels. Although many authors have included magnetic measurements in their studies, only four publications have appeared devoted entirely to magnetic behavior: Klemm (*185*, *312*) studied the magnetic properties of vanadyl, manganous, ferrous, cobaltous, nickel, and copper phthalocyanines; Havemann *et al.* (*147*) studied ferrous, cobaltous, and copper phthalocyanines; and in a recent publication Lever (*215*) correlated the magnetic behavior of 21 square planar, five-coordinate, and octahedral metal phthalocyanines (from titanium to copper inclusive) with their electron configuration.

Table VII lists all the available magnetic susceptibility data. In most cases there is good agreement between the magnetic behavior predicted on the basis of electron configuration and the observed behavior, and only those complexes of especial interest will be discussed here.

TABLE VII
THE MAGNETIC MOMENTS OF TRANSITION METAL PHTHALOCYANINES[a]

Complex	Oxidation state	Coordination number	Number of unpaired electrons	$\mu_e(25°\mathrm{C})^b$ (B.M.)	Θ^c (°K)	Reference
PcTiCl	3	6?	1	1.79	—	*(341)*
PcVO	4	5	1	1.71	4	*(312)*
PcCr	2	6	4	3.49	306	*(215)*
$\mathrm{PcCrPy_2}$	2	6	2	3.16	35	*(215)*
$\mathrm{[PcCr]^+OH^-}$	3	4	3	4.03	15	*(215)*
$\mathrm{PcCr(H_2O)(OH)}$	3	6	3	3.69	0	*(215)*
$\mathrm{[PcCr(OH)(O)]^{2-}2Na^+}$	3	6	3	3.91	155	*(215)*
$\mathrm{[PcCr(OH)(O)]^{2-}2PyH^+}$	3	6	3	4.06	15	*(215)*
$\mathrm{[PcMn]^{2-}2Li^+6THF}$	0	4?	3	4.13	—	*(339)*
$\mathrm{[PcMn]^-Li^+6THF}$	1	4?	2	2.86	—	*(339)*
PcMn	2	4	3	4.34	−6	*(215)*
	—	—	—	4.33	—	*(93)*
	—	—	—	4.55	—	*(312)*
PcMn(MeOH)(OH)	3	6	4	4.87	—	*(93)*
PcMn(OAc)(Py)	3	6	4	4.76	—	*(93)*
$\mathrm{[PcMn(O)_2]^{2-}2Na^+}$	4	6	3	4.00	49	*(215)*
$\mathrm{PcMn(OH)_2}$	4?	6?	3?	4.51	15	*(213)*
PcMn(OH)(CN)	4	6	3	3.88	5	*(215)*
PcMnO	4	6	3	3.77	46	*(215)*
$\mathrm{[PcFe]^{2-}2Li^+6THF}$	0	4?	0	0	—	*(339)*
$\mathrm{[PcFe]^-Li^+5THF}$	1	4?	1	1 spin^d	—	*(340)*
PcFe	2	4	2	3.85	9	*(215)*
	—	—	—	3.96	—	*(312)*
	—	—	—	4.51	—	*(147)*
$\mathrm{PcFe(Py)_2}$	2	6	0	0^e	—	*(312)*
PcFeCl	3	5?	3?	3.32	53	*(215)*
$\mathrm{[PcCo]^{2-}2Li^+6THF}$	0	4?	1	1 spin^d	—	*(340)*
$\mathrm{[PcCo]^-Li^+5THF}$	1	4?	0	0	—	*(340)*
PcCo	2	4	1	2.72	60	*(116)*
	—	—	—	2.66	—	*(147)*
	—	—	—	2.14	—	*(312)*
$\mathrm{[PcNi]^{2-}2Li^+6THF}$	0	4?	0	0	—	*(340)*
$\mathrm{[PcNi]^-Li^+4THF}$	1	4?	1	1 spin^d	—	*(340)*
PcNi	2	4	0	0^f	—	*(312)*
$\mathrm{[PcCu]^{2-}2K^+4NH_3}$	0	4?	1	1.74	—	*(370)*
PcCu	2	4	1	1.73	—	*(244, 295, 312)*
	—	—	—	1.75	—	*(147)*

---

[a] All the data are calculated on the basis of a diamagnetic correction for the phthalocyanine ligand of 290 × 10^{-6} c.g.s.

[b] From $\mu_e = 2.839\,(\chi_m T)^{\frac{1}{2}}$.

[c] Curie-Weiss constant (the negative of the intercept on the temperature axis in a plot of $1/\chi_m$ versus T°K).

[d] Exact moments not recorded in the publication.

[e] $\chi_G = -0.3 \times 10^{-6}$ c.g.s.

[f] $\chi_G = -0.4 \times 10^{-6}$ c.g.s.

1. Square Planar Complexes

Square planar complexes of chromium(III) and manganese(II) are unknown outside the phthalocyanine series; their magnetic moments are in accord with that predicted on the basis of putting three and five electrons, respectively, into the four lower energy *d* orbitals (Fig. 19). The magnetic behavior and small unit cell width of chromous phthalocyanine are interpreted (*215*) in terms of a metal-metal interaction extending throughout the lattice. The phthalocyanine units are presumably stacked on top of one another, with a fairly short chromium-chromium distance. The coupling of the chromium atoms gives rise to a number of spin states $S = 0$ to $S = 4$, whose energies depend upon the exchange integral J. From a study of the temperature variation of the magnetic susceptibility, J was evaluated as $-38.2°$. The moment of ferrous phthalocyanine, which had at one time been tentatively interpreted in terms of a spin-free–spin-paired equilibrium (*267*), arises from a spin-paired ground state with an appreciable orbital contribution (*215*). Chloroiron(III) phthalocyanine has an abnormal temperature dependence interpreted in terms of dimerization of phthalocyanine iron(III) cations (LXXIV). The iron-iron interaction will give rise to spin states from $S = 0$ to $S = 3$. The g value was evaluated as 1.77 and the exchange integral J as $-10.4°$. The temperature variation of the magnetic susceptibility of cobalt phthalocyanine is anomalous (*116*). A high temperature-independent paramagnetic term may be involved. The magnetic moment of dilithium phthalocyanine manganate(0) cannot be readily interpreted in terms of a spin-paired structure, irrespective of whether one assumes that it is a genuine manganese(0) derivative or a complex containing a reduced phthalocyanine unit. The magnetic moment corresponding to three unpaired electrons appears to follow from the spin-free arrangement $b_{2g}^2 e_g^3 a_{1g}^1 b_{1g}^1$. Where it is possible to distinguish between the two possibilities, all other metal phthalocyanines are spin-paired (see also Section VII). It is certainly logical, however, that if we are ever to observe spin-free metal phthalocyanines, then we may expect them among the low oxidation state complexes.

2. Six-Coordinate Metal Phthalocyanines

The six-coordinated complexes belong to the point group D_{4h}, and deviations in behavior from that expected for the group O_h are marked. Thus the temperature variation of the susceptibility of dipyridinechromium(II) phthalocyanine can be explained in terms of D_{4h} symmetry, in which the ground state is $^3A_{2g}$, rather than in O_h symmetry in which the ground state is $^3T_{1g}$ (*215*).

The sodium salt of the phthalocyanine hydroxyoxychromate(III) anion has an anomalously high Curie-Weiss constant (155°). The corresponding pyridinium salt has a Curie-Weiss constant of only 15° (*90*). Apparently the cation perturbs the anion in some manner. A similar but less marked effect operates in the manganese(IV) analogs. The polymeric oxymanganese(IV) phthalocyanine has a discontinuity in its magnetic behavior at about 200°, which may be due to a phase change in the crystal (*215*). The complex Py(O)MnPc·$2H_2O$, originally formulated as a dimeric peroxy manganese(II) derivative (*288*), has a magnetic moment consistent with its reformulation as pyridineoxymanganese(IV) phthalocyanine dihydrate. Because of the presence of the double bond to the oxygen atom, the three electrons of the Mn(IV) ion are fed into the remaining two *d* orbitals, giving rise to one unpaired electron.

The calculated diamagnetic anisotropy of metal-free phthalocyanine is fifteen times as great as that of benzene (*148, 231*).

VI. Physical Studies

A. INFRARED SPECTRA

In view of the large size and complexity of the phthalocyanine ligand, it is perhaps not surprising that no attempt has been made to assign in detail the infrared spectra of phthalocyanine and its metal derivatives. However, infrared studies have figured prominently in the investigation of metal phthalocyanines because of the characteristic "fingerprint" of the ligand. Proof of the formation of a new metal phthalocyanine has often been based entirely on a close correlation of the infrared spectrum with that of an authentic phthalocyanine derivative. Many groups (*30, 44, 81, 90, 118, 170, 177, 180, 193, 196, 220, 268, 268a, 322, 323, 342, 352*) have studied the infrared spectra of these complexes. Some of the data relating to the simpler derivatives are listed in Table VIII. It will be seen that the infrared spectrum depends markedly upon the particular polymorph involved, and indeed this technique may be used to distinguish between the various polymorphic forms.

Because of the limited solubility of metal phthalocyanines, the spectra are limited to the solid state. Most authors have used Nujol or halocarbon mulls, but Sidorov and Kotlyar (*323*) sublimed the complexes onto potassium chloride or bromide disks. The disks and samples were maintained at a temperature of about 100°C, as a result of which thin layers of the α modification were always produced. The β polymorphs were obtained by taking the disks and subjecting them to a temperature of 280°–300°C *in vacuo* for several hours, whereupon the $\alpha \rightarrow \beta$ transformation took place. The infrared spectra were then remeasured. The spectral characteristics of the α and β forms are almost independent of the central metal ion. In-

TABLE VIII
INFRARED SPECTRA (3500–450 CM^{-1})[a]

	PcMg		Fe		H_2		Li_2	SnF_2
No.	α	β	α	β	α	β		
1	435	437	435	436	434	434	432	435
2	505		518		492	489 496	480	497
3	575		575		557		525 572	531 573
4	642	644	644	645	620	616	632	643 688
5	728	731	726	734	714	720	732	726
6	752	754	756		730 736		750	750
7						753		
8	776	—	771	—	766	771	770	774
9	—	781	—	780	778	779		783
10	801	801	804	803				
11	872	—	868	—	870	—		
12	—	877	—	877	—	880		
13	890		910		874	873	890	892
14	949	949	948 940	948 —	946	952	945	
15	—	957	—	957	—	958		963
16					1007		1002	
17	1060	1059	1072	1073			1052	1060
18	1086	1078	1089	1086	1094	1094	1090	1088
19	—	1100	—	1098				
20	1116	1118	1121	1123	1119	1119	1117	1120
21	1163	1162	1165	1164	1160	1156	1165	1164
22	—	1173	—	1173	—	1163		
23	1283		1290		1277		1283	1284
24					1304			
25					1321	1323		
26	1333	1335	1333		1336	1334	1336	1346
27	1408	1407	1422	1422	1439	1437		1412
28	1454	1451	1468	1468	1461	1459		
29			1484		1478		1484	1475
30	1481	1478 1482	1516	1514	1503	1502		
31	1586	1584	1592	1592	1600 1610	1600 1605	1585	
32	1609	1608	1611	1609	1617	1613	1606	1610
33					3292	3273		3030

[a] The data are taken from references (*31*, *196*, *323*), the numbering system from (*323*). Data for the first three complexes are taken from sublimed films, and for the last two from Nujol mulls. The references cited also include data for $PcSnCl_2$, $PcSnBr_2$, $PcSnI_2$, $PcSn(OH)_2$, Pc_2Sn, PcSn, PcPb (*196*), PcZn, PcCu, PcCo, PcNi (*31*, *323*). The infrared spectra of chromium phthalocyanines are considered in (*90*).

deed, most metal phthalocyanines have closely similar spectra, although silver and uranyl phthalocyanines are exceptions (*31*, *323*). The β modification is much richer in spectral absorption than the α modification, perhaps owing to the more compact packing of the molecules in the former case resulting in stronger intermolecular interactions. In this way lines, which were forbidden in the α form, may become allowed in the β form (*323*). The lower symmetry of metal-free phthalocyanine (D_{2h} rather than D_{4h}) probably accounts for the greater complexity of the metal-free ligand spectrum.

Certain of the absorption bands are central ion-sensitive (lines 13, 17, 23 and 27–31). These all follow approximately the same sequence, namely, $\text{Mg} \cong \text{Zn} < \text{Cu} < \text{Fe} < \text{Co} < \text{Ni}$. There appears to be no especial significance to this order. A similar effect is observed in the Nujol mull spectra, but it is probably not valid to compare the two sets of data in view of the different manner in which they were obtained. Using band number 13, the Nujol mull data follow the order $\text{Pb} < \text{Sn(II)} < \text{Sn(IV)} < \text{UO}_2 < \text{Al(III)} < \text{Ge(IV)} < \text{Ru(II)} < \text{Si}$ (*170*, *177*, *195*, *196*, *220*, *295*). This order is not especially significant either, except for a tendency for the more covalent ions to give higher frequencies. It is probably not worthwhile to rely too much on solid state infrared data. The intense absorption band near 714 cm^{-1} (line 5) is assigned as a C—H out-of-plane deformation (*118*, *323*), the 1610 and 1475 cm^{-1} bands to C—C benzene-ring skeletal vibrations, and the 3030 band to the C—H stretching vibration (*196*). The infrared spectrum of *N*-deuterated metal-free phthalocyanine has been studied (*118*, *323*). The data are listed in Table IX. A sample containing at least 70% PcD_2 was used. The band near 3298, assigned as the N—H stretching vibration by Sidorov and Kotlyar, has been observed in copper phthalocyanine

TABLE IX

ASSIGNMENTS OF NH AND ND VIBRATIONS IN METAL-FREE PHTHALOCYANINE AND ITS *N*-DEUTERATED DERIVATIVES[a]

Absorption due to NH		Absorption due to ND		
α	β	α	β	Assignment
3292	3273	2466	2456	Stretching vibrations in PcH_2 and PcD_2
3317	3297	~2480	2467	Stretching vibrations in PcHD
1539		1144		Deformational frequencies
1250		962		
		976		
		1076		

[a] From reference (*323*).

(*115*) and as a result it was suggested (*118*) that the assignment was incorrect. However, in a later study of copper phthalocyanine (*31*), the band was not observed. The assignment is almost certainly correct. The far infrared spectra (100–300 cm^{-1}) of metal-free, copper, and uranyl phthalocyanines have been recorded (Table X). The UO_2 bending vibration was observed at 278 cm^{-1}.

TABLE X
LOW FREQUENCY INFRARED ABSORPTION[a]

PcH_2	PcCu[b]	$PcUO_2$
340	345	—
—	304	306
280	283	—
—	—	278 (UO_2 vibration ?)
266	267	—
256w	258	258
233	230	244
227	—	—
155vw	154	164ms
—	122	147ms

[a] Absorption at 350–100 cm^{-1}, Nujol. Abbreviations: w, weak; vw, very weak; ms, moderately strong. From reference (*31*).

[b] Generally weak spectrum.

B. THERMODYNAMIC AND KINETIC STUDIES

By far the most detailed thermodynamic studies have been made by Berezin, who has looked at the equilibria existing in concentrated sulfuric acid. Linstead's group were the first to observe that some of the metal phthalocyanines were demetallated in concentrated sulfuric acid, whereas others appeared indefinitely stable (*10*). It was shown that all phthalocyanines which resisted attack were of metals whose radii were of the right size to fit nicely into the space available at the center of the ligand. Berezin has since put these observations on a more quantitative basis (*19, 21, 26*). Labile complexes (i.e., those which are demetallated instantly or fairly rapidly in concentrated sulfuric acid) include those of the alkali metals, alkaline earth metals, Be, Mg, Cd, Hg, Sb(III), Pb, Sn(II), Mn(II), and Fe(III). Stable complexes (demetallated very slowly in acid) include those of Zn, Al, $Cl_2Sn(IV)$, OV(IV), Co(II), Rh(II), Os(IV), Ni(II), Pd(II), Pt(II), and Cu(II). The actual rates of decomposition vary widely; thus, while calcium and magnesium phthalocyanines are demetallated very rapidly, silver and lead phthalocyanines react fairly slowly (*19*). The rates of decomposition in 1 *M* sulfuric acid increase in the sequence (*19*) Fe(III)

$<$ Ag $<$ Mn $<$ Pb $<$ Cd $\lesseqgtr$ Hg $<$ Ca. The position of the ferric complex should be regarded as uncertain, since the method of preparation used would not have yielded a pure ferric product, but rather ferrous. Berezin (*18*, *19*, *21*, *23*, *26–28*) studied the reaction.

$$\mathrm{MPcH^+ + 2H_3O^+ \rightleftarrows M^{++}_{(aq)} + H_2PcH^+} \tag{LXXX}$$

in sulfuric acid. The kinetics of dissociation were studied by absorbance at 450 and 680 mμ at concentrations of about 10^{-4} M (some of the spectroscopic data obtained in concentrated sulfuric acid are included in Table IV). The rate of hydrolysis is given by:

$$\frac{-d(\mathrm{MPcH^+})}{dt} = k_v(\mathrm{MPcH^+})(\mathrm{H_3O})^2 \tag{LXXXI}$$

Values for the rate constant k_v are listed in Table XI. The constant k_v is independent of the concentration of sulfuric acid within the range 15–18 M, and the reaction is irreversible.

TABLE XI

RATE CONSTANTS, k_v, FOR HYDROLYTIC CLEAVAGE OF "STABLE" METAL PHTHALOCYANINES (LXXXI)[a]

Metal ion	$T°$	$k_v \times 10^3$ (hr^{-1} liter^2 mole^{-2})
Rh(III)	120	0.253 ± 0.030
Rh(III)	138	1.02 ± 0.10
Os(IV)	120	0.136 ± 0.012
Pt(II)	120	0.452 ± 0.023
Pd(II)	120	0.450 ± 0.030
Cu(II)	136	61.0 ± 5.0
Cu(II)	120	10.2 ± 1.2
Cu(II)	25	0.2 (13.8 M acid)
Al(III)	120	1.10 ± 0.07
Al(III)	25	0.5 (10.7 M acid)
Zn(II)	25	0.3 (15.8 M acid)
Co(II)	25	0.7 (13.8 M acid)

[a] From reference (*19*, *23*, *28*).

Metal-free phthalocyanine itself undergoes further decomposition in concentrated sulfuric acid (*20*, *26*) according to the reactions:

$$\mathrm{H_2Pc + H_2SO_4 \rightleftarrows H_2PcH^+ + HSO_4^-} \tag{LXXXII}$$

$$\mathrm{H_2PcH^+ + 3H_3O^+ \rightleftarrows H_2PcH_4^{4+} + 3H_2O} \tag{LXXXIII}$$

The conjugation in the ring is destroyed at this stage.

$$\mathrm{H_2PcH_4^{4+} + 8H_2O \rightarrow 4C_8H_5O_2N + 4NH_4^+ + H_2} \tag{LXXXIV}$$

The rate law is

$$\frac{-d(H_2Pc)}{dt} = 1.12 \times 10^{-4}(H_2Pc)(H_3O)^4 \qquad \text{(LXXXV)}$$

Most of the labile metal phthalocyanines react at a similar rate, indicating that demetallation occurs rapidly by reaction (LXXX) which is followed more slowly by reactions (LXXXII)–(LXXXIV). There is some evidence that silver and chloroferric phthalocyanines may undergo some ring cleavage prior to demetallation. From the variation of rate constant with temperature (*23*, *26*) the activation energy for hydrolysis was found to be 19.5 kcal/mole for metal-free phthalocyanine, and 21.7 kcal/mole for the dichlorostannic derivative. The acid concentrations were 17.7 and 17.18 *M*, respectively.

TABLE XII
SOLUBILITY OF METAL PHTHALOCYANINES IN SULFURIC ACID; p*K* VALUES (LXXXVI)[a]

Metal ion	Acid concentration (moles/liter)	p*K*
Co(II)	16.7	2.35
	13.8	2.45
Rh(III)	16.5	1.03
	14.5	1.03
Ni(II)	17.7	1.46 ± 0.03
	14.52	1.43
	12.33	1.49
Pt(II)	17.7	1.50
	15.5	1.57
Os(IV)	15.5	0.60
$Sn(IV)(HSO_4)_2$	16.0	3.59
Al(III)	16.0	2.60
V(IV)	17.7	1.92
Cu(II)	17.7	1.84 ± 0.1
	16.7	1.81
	14.52	2.02
	14.20	1.94
	14.00	1.95
	13.8	1.91
	12.6	1.74, 1.71
	12.06	1.67, 1.69
Zn(II)	17.7	2.31 ± 0.04
Metal-free	17.7	1.65

[a] Only a selection of the available data is tabulated here. From references (*17*, *20–22*, *24*, *28*).

The solubility of metal phthalocyanines in concentrated sulfuric acid has been studied (*17*, *19–21*, *24*, *28*). The p*K* values for the reaction

$$\mathrm{MPc_{solid}} + \mathrm{H_2SO_4} \rightarrow \mathrm{MPcH^+} + \mathrm{HSO_4^-} \qquad \text{(LXXXVI)}$$

are listed in Table XII. In Table XIII are listed the ΔG, ΔH, and ΔS values derived (*22*) from a temperature study of reaction (LXXXVI). Berezin has linked both solubility and dissociation rate with bond type (see Section VII). Radiochemical methods have been used to study the solubility of metal phthalocyanines in sulfuric acid. Radiocobalt does not exchange with cobalt, nickel, zinc, or aluminum phthalocyanine in 17.2 *M* sulfuric acid (*19*).

TABLE XIII
THERMODYNAMIC PARAMETERS FOR REACTION (LXXXVI)[a]

Metal ion	ΔH°_{298} (kcal/mole)	ΔG	ΔS (e.u.)
Cu(II)	5.7 ± 0.6	2.235 ± 0.04	11.6 ± 2.1
Zn(II)	5.23	3.06	2.76
Al(III)Cl	−9.9	2.605	−42 (17 *M*)
Al(III)Cl	4.22	3.542	2.26 (16 *M*)

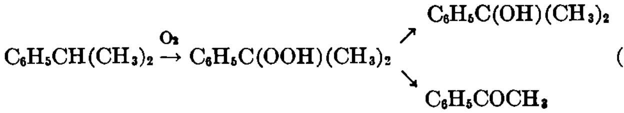
[a] Sulfuric acid 83–99%. From reference (*22*).

C. CATALYTIC BEHAVIOR

The metal phthalocyanines behave as heterogeneous catalysts in many reaction systems. Calvin and associates have shown that both metal-free and copper phthalocyanines undergo atomic exchange with molecular hydrogen (*42*), catalyze atomic exchange between hydrogen (and deuterium) and water vapor (activation energy 6 kcal/mole), and catalyze the combination of hydrogen with oxygen at temperatures of 250°–370°C (activation energy 18 kcal/mole). These phthalocyanines also appear to catalyze the conversion of parahydrogen into normal hydrogen with an activation energy of 5–7 kcal/mole (*43*, *82*), although there is some uncertainty relating to this work (*285*).

Certain metal derivatives, particularly the ferrous and chloroferric complexes, catalyze the decomposition of hydrogen peroxide. They are themselves destroyed in the process (*58*, *127*, *371*). Paquot and his coworkers have extensively investigated the catalytic properties of the phthalocyanines (*71*, *270–277*). Nickel phthalocyanine is a useful catalyst for the autoxidation of α-carbon atoms of ethylenic molecules. Thus nickel phthalocyanine (0.4%) catalyzes the aerial oxidation of cyclohexene to cyclohex-1-ene-1-one and cyclohex-1-ene-3-one at 65°C (*271*), whereas at 120°C ethylbenzene is converted to acetophenone in 18% yield. Under similar conditions toluene yields 3% of benzaldehyde. α-Pinene is catalytically oxidized by iron, cobalt, or nickel phthalocyanines to verbenone in 10–25% yield (*270*). The nickel complex also catalyzes the oxidation, at 120°–130°C, of saturated ketones, such as cyclohexanone and 2-octanone, to α-diketones and aldehydic and acidic scission products (*273*). The oxidation of saturated fatty acids was also investigated by Paquot (*275*). The aerobic oxidation of unsaturated fatty acids was investigated by Uri (*354*). Iron and cobalt phthalocyanines speeded up the reaction some ten times.

Kropf (*161*, *197–199*) has studied the autoxidation of cumene, *p*-nitrocumene, toluene, ethylbenzene, diphenylmethane, *p*-xylene, *p*-cymene, *m*-diisopropylbenzene, phenylcyclopentane, and phenylcyclohexane. The autoxidation proceeds in most cases via the formation of a hydroperoxide, for example,



$$C_6H_5CH(CH_3)_2 \xrightarrow{O_2} C_6H_5C(OOH)(CH_3)_2 \begin{matrix} \nearrow C_6H_5C(OH)(CH_3)_2 \\ \searrow C_6H_5COCH_3 \end{matrix}$$

(LXXXVII)

Table XIV illustrates how the reaction products and yield depend upon the particular metal phthalocyanine employed as catalyst. The mechanism of catalysis varies with temperature. Below 100°–105°C copper phthalocyanine catalyzes the formation of the hydroperoxide, but above this temperature catalyzes its decomposition. Other metal phthalocyanines behave similarly (save vanadium, see below). Above the critical tempera-

TABLE XIV

INFLUENCE OF THE METAL CATALYST UPON REACTION PRODUCTS OF (LXXXVII) (DIVALENT METAL PHTHALOCYANINES)[a]

Catalyst	Uncatalyzed reaction	Mn	Fe	Co	Ni	Cu	Zn	Mg
Hydroperoxide	1.5	17.9	12.4	5.8	31.7	12.9	14.2	10.3
Carbinol	0	31.8	40.8	50.0	9.0	0	0	0
Acetophenone	0	13.4	17.1	21.3	1.5	0	0	0
Hydroperoxide in total product	>98	28.4	7.6	7.5	75.0	>98	>98	>98
Carbinol in total product	0	70.4	70.1	70.1	86.0	0	0	0

[a] Conditions: 1 mole cumol, 0.5 mmole catalyst; 10.0 mmoles added hydroperoxide, temperature 80°C, reaction time 10 hours. Values given as per cent. From reference (*197*).

ture, the frequency factor increases with increasing catalyst concentration and correspondingly the activation entropy decreases, while the empirical activation energy is the same as in the uncatalyzed reaction. Below this temperature, the activation energy decreases with rising catalyst concentration (12 kcal/mole at a catalyst concentration of 0.1 millimole per mole of cumene, and 9 kcal/mole at 0.75 mmole/mole, compared with 15.8–16.3 kcal/mole for the uncatalyzed reaction). The low temperature mechanism probably involves the activation of molecular oxygen by chemisorption on the catalyst (*197*). Vanadyl phthalocyanine also acts as a catalyst, but the same mechanism was observed over all the temperature range studied (*199*). Kropf points out that, as an oxygen atom is already attached to the vanadium atom, a chemisorption process is unlikely in this case. The behavior of oxytitanium(IV) phthalocyanine, which is oxidized in air in chloronaphthalene solution (*213*) presumably via the intermediate formation of a molecular oxygen complex, indicates that the presence of a coordinated oxygen atom does not inhibit the absorption of molecular oxygen.

Iron and copper phthalocyanines catalyze the isomerization of dimethyl maleate to dimethyl fumarate in the vapor phase at 300°C. No catalytic activity was observed in solution (*338*). Magnesium and zinc phthalocyanines catalyze the polymerization of methyl methacrylate when illuminated (λ_m 600 mμ) (*197*). Manganous phthalocyanine (*88*) and ferrous phthalocyanine (*59*) catalyze the aerial oxidation of benzyl alcohol to benzaldehyde. The catalytic oxidation of ascorbic acid, using magnesium and copper derivatives, is light-sensitive (*190, 310*). α-Tetralin is catalytically oxidized, in the presence of the magnesium, zinc, or iron complexes, to α-tetralone, the reaction being chemiluminescent (*60, 61, 158, 159, 371*). The oxidation of luminol to 5-aminophthalazine-1,4-dione, catalyzed by iron phthalocyanine, is also chemiluminescent (*61, 345, 351*).

D. ELECTRICAL PROPERTIES

1. *Electrical Conductivity* (*Dark Current*)

A compound whose electrical conductivity follows the law.

$$\sigma = \sigma_0 e^{-E/2kT} \qquad \text{(LXXXVIII)}$$

(where σ = specific conductivity at T°K; σ_0 is a constant, intrinsic conductivity; k is the Boltzmann constant, and E is an energy gap) is known as a semiconductor. Semiconductors are expected to be rectifiers (see Section D,2), to exhibit a Hall effect (see Section D,3), to produce thermoelectric power (this section), and to exhibit photovoltaic phenomena (see Section D,4).

The semiconductor properties of the phthalocyanines were first ob-

TABLE XV

THE ELECTRICAL CONDUCTIVITY OF PHTHALOCYANINES[a]

Complex[b]	Resistivity (Λ/cm)	E_g (eV)	E_{opt} (eV)	SE[c]	Method[d]	Reference
αH_2	790×10^7	1.42	0.42	1250	PC.P/N_2	*(143, 219)*
	—	0.50	—	—	PC.P/N_2	*(375)*
βH_2	42.7×10^{13}	1.74	—	670	PC.P/N_2	*(143)*
	$\sim 10^{12}$	—	—	—	SC/N_2	*(68, 150)*
	—	1.9	—	—	PC.P/N_2	*(219)*
	—	1.8	—	—	PC.P/N_2	*(375)*
	—	1.7 ± 0.05	—	50	SC/N_2	*(114)*
	—	—	0.34	—	SC/N_2	*(219)*
H_2	$\sim 10^{13}$	1.4–2.0	—	—	SC/He	*(69, 184)*
	2×10^7	—	—	—	RQ	*(358)*
	—	1.7	—	—	SC	*(149)*
	—	1.9	0.34	—	PC.P	*(218)*
	—	—	0.24	—	PC.P	*(9)*
	—	1.44–1.87	—	—	SC-SF	*(183)*
	—	1.73	—	—	SF/O_2-free	*(360, 364)*
	—	1.3	—	—	SF/vacuum	*(9)*
	—	1.49	—	—	Summary of work	*(86)*
βCu	$3.0 \pm 0.1 \times 10^{11}$	—	—	—	SC	*(68)*
	—	1.64 ± 0.03	—	50	SC/N_2	*(114)*
	—	2.06(1.62)[e]	—	—	SC/vacuum	*(153)*
	—	2.04(1.44)[e]	—	—	SC/air	*(153)*
	—	1.62(1.62)[e]	—	—	SC/O_2	*(153)*
	—	2.14(2.14)[e]	—	—	SC/H_2	*(153)*
Cu	2×10^{11}	—	—	—	SC	*(69)*
	2×10^7	—	—	—	RQ	*(358)*
	—	1.85	—	—	SC.SF	*(183)*
Cu	10^{12}–10^{13}	1.64	—	—	SF/O_2-free	*(360, 364)*
	—	—	0.43	—	PC/P	*(9)*
	10^{13}–10^{14}	1.87	—	—	SC	*(63)*
	—	1.19	—	—	SC/I_2	*(63)*
	—	1.3	—	—	PC.P	*(66)*
	—	1.79	—	—	PC/N_2	*(108)*
Mg	10^6	—	—	—	RQ	*(358, 359)*
	—	1.2	—	—	F.SF	*(360, 364)*
Fe	4×10^9	—	—	—	SC	*(69)*
Mn	4×10^6	—	—	—	SC	*(69)*
βCo	$9.9 \pm 7.5 \times 10^9$	—	—	—	SC	*(68, 69)*
	—	1.60 ± 0.025	—	—	SC/N_2	*(114)*
αNi	14×10^7	1.20	—	970	PC.P/N_2	*(143)*
βNi	40×10^7	2.28	—	1280	PC.P/N_2	*(143)*
βNi	$6.3 \pm 3.1 \times 10^{10}$	—	—	—	SC	*(68, 69)*
αZn	4.7×10^7	0.86	—	960	PC.P/N_2	*(143)*
βZn	$2.8 \pm 1.0 \times 10^9$	—	—	—	SC	*(68, 69)*
	4.3×10^5	1.44	—	1750	PC.P/N_2	*(143)*

TABLE XV (*Continued*)

Complex[b]	Resistivity (Λ/cm)	E_g (eV)	E_{opt} (eV)	SE[c]	Method[d]	Reference
Zn	—	1.51	—	—	F/O_2-free	(*360, 364*)
Pt	—	1.52	—	—	PC.P/N_2	(*108*)

[a] Where several authors have obtained similar results, the composite data are tabulated and both references cited.

[b] Where the polymorph is not explicitly defined, the β polymorph may in most cases be assumed.

[c] Seebeck effect.

[d] PC, polycrystalline powder; P, under pressure; SC, single crystal; F, film (deposited); SF, sublimed film; RQ, rubbed on quartz.

[e] The first value applies to above, and the second below, 373°K.

served by Eley (*83–85*) and by Vartanyan (*358*). Following this discovery, there has been intense interest in the behavior of the metal phthalocyanines, and many measurements have been reported. Experimentally it is very difficult to ensure good contact between the electrodes and the sample, and much of the earlier work has been criticized; in particular the use of compressed samples to reduce intercrystalline resistance is believed to be only qualitatively effective (*163*). Bradley *et al.* (*37*) have in fact discussed the effect of pressure upon the conductivity of metal phthalocyanines; there is little change above a pressure of 80 kg/cm². Table XV lists the various values of E_g (LXXXVIII) reported, under the conditions cited. A number of the earlier less reliable measurements have been omitted. Replacement of the two central hydrogen atoms by a metal atom has little effect upon the energy gap (*114*) which lies between 1.5 to 1.7 eV, and is sensitive to the atmosphere (or lack of it) surrounding the sample (*32, 63, 143, 153, 162, 357, 359–363*). There is a close similarity between E_g and the energy of the intense absorption band in the red (Table XVI) (*47, 114,*

TABLE XVI

RELATIONSHIP OF E_g TO OPTICAL ABSORPTION[a] (*46*)

	PcH_2	PcCu	PcPt
Optical absorption (single crystal data)	1.55 ± 0.01[b]	1.58 ± 0.01	1.57 ± 0.02 eV
	2.61 ± 0.03[b]	2.81 ± 0.04	2.81 ± 0.03
	1.64 ± 0.03[c]	1.67 ± 0.03	1.7 ± 0.05
	2.76 ± 0.06[c]	3.10 ± 0.15	2.95 ± 0.07
E_g (single crystal)	1.7	1.64	1.52

[a] E_g values from Table XV.

[b] Calculated from central point on linear part of low energy absorption edge.

[c] Calculated at top of absorption band when intensity begins to fall.

229, 360, 362, 363), which suggests that the conduction mechanism involves excitation to the first excited state of the molecule (for a full discussion of the mechanism, see subsection 5).

2. Rectification

Haak and Nolta (*141, 142*) have observed rectifying phenomena when polycrystalline samples of metal-free or metal phthalocyanines are compressed between different metal electrodes. A small amount of a liquid polar impurity was found to be essential for rectification to occur. The rectification ratio (ratio of conductance in forward and reverse directions, the forward direction being movement of electrons from the least noble electrode to the sample) varies from 25 to 500. The latter value is obtained when copper phthalocyanine is sandwiched between either platinum and silver, or silver and aluminum, electrodes. Kleitman (*183*) has also demonstrated that metal-free phthalocyanine can act as a rectifier.

3. Hall Effect

If a conductor carrying a current is placed in a magnetic field such that the field is perpendicular to the current, then an e.m.f. may be produced across the conductor, perpendicular to both field and current. This is known as the Hall effect. The e.m.f. produced is often so small that very specialized electronic techniques must be used to detect it. Its importance relies on the fact that a study of the Hall effect can provide a great deal of information about the mechanism of conduction.

Studies of the Hall effect have been made on metal-free phthalocyanine (*149*), on copper phthalocyanine (*72, 153*), and on polymeric phthalocya-

TABLE XVII
THE HALL EFFECT IN METAL-FREE AND COPPER PHTHALOCYANINES

Complex	T°K	μ_H(cm^2/V sec)[a]	ρ(cm^{-3}, carriers)[b]	Reference
PcCu	322.5	−75	—	(*153*)
	322.5	−52	—	(*153*)
	337	−31	—	(*153*)
	357	−16	—	(*153*)
	396	+18	—	(*153*)
	410	+215	10^8	(*72*)
	480	120–140	2×10^9	(*72*)
	520	50–75	4×10^9	(*72*)
	580	100	10^{11}	(*72*)
	630	40	7×10^9	(*72*)
PcH_2	—	0.1–0.4	$2\text{–}12 \times 10^6$	(*149*)

[a] Hall mobility.

[b] Number of carriers per unit volume.

nines (*94*, *95*). The experimental results are listed in Table XVII. The majority carriers in metal-free phthalocyanine were found to be negatively charged, i.e., were electrons. This is in contradiction with earlier studies (*175*) where positive holes were assumed to be the majority carriers. The Hall mobility of copper phthalocyanine is considerably greater than that of metal-free phthalocyanine (*72*, *153*). There is evidence for a two-carrier mechanism with a change in sign of the Hall mobility at about 100°. Discussion of these data will be deferred to subsection 5.

4. Photoconductivity

The photovoltaic effect was first observed in the phthalocyanines in 1948 by Putseiko (*291*). Since then the photoconductivity of polycrystalline samples and of sublimed films has been extensively investigated (*32*, *33*, *66*, *69*, *104*, *115*, *184*, *218*, *292*, *294*, *343*, *358*, *360–364*). The majority carriers are assumed to be holes (*174*). *In vacuo* the steady state photocurrent is related to the activation energy ΔE for photoconductivity by:

$$i_{ph} = i_0 e^{-\Delta E/kT} \qquad \text{(LXXXIX)}$$

ΔE is found to be of the order of 0.2 to 0.45 eV (see Table XVI) (*9*, *174*, *218*, *360*). The photocurrent is proportional to the light intensity I, according to

$$i_{ph} = KI^n \qquad \text{(XC)}$$

The value of n generally cited is 1 for oxygen-free films, decreasing toward $\frac{1}{2}$ as the oxygen pressure is increased (*8*, *32*, *360*, *362*, *364*). Recently, however, Harrison and Assour report a value of $n = \frac{1}{3}$ for single crystals of metal-free phthalocyanine; the theoretical implications of this result were discussed (*155*). The variation of the photoconductivity with wavelength follows the optical absorption spectrum (*32*, *47*, *361–363*). Day and Williams (*68*) have shown that metal-free, nickel, and copper phthalocyanines, in addition to being photosensitive in the visible region, have appreciable photosensitivity in the infrared, exhibiting a maximum photocurrent when irradiated with light of wavelength 0.9–1.1 μ. Fielding and MacKay (*115*), however, while confirming the infrared sensitivity of the metal-free and copper complexes, were unable to detect the infrared sensitivity of the nickel derivative. Manganese(II) phthalocyanine has also been shown to be photosensitive in the infrared region (*69*). Metal-free phthalocyanine shows a strong photoresponse in the ultraviolet region (*152*).

Since the mechanism of conduction involves an electron transfer by some means, several authors have investigated the effect of deliberately adding electron acceptor or electron donor impurities (*174*, *175*, *294*, *349*). The addition of donors such as *N*,*N*,*N*′,*N*′-tetramethyl-*p*-phenylenediamine or phenothiazine decreases both dark conductivity and photoconductivity by a factor of 6 and 25, respectively. *o*-Chloranil, on the other hand, being an electron acceptor, increases the dark conductivity by as much as 10^7, and the photoconductivity by up to 10^5. The spectral response of the doped samples still follows the absorption spectrum. At low temperatures (−100°C) the dark current of the doped sample is 10^{14} times higher than of the undoped sample, while the photoconductivity is not appreciably altered by temperature. The activation energy for the dark current is reduced, in doped samples, from the normal values of 1.5–2.0 eV to 0.2 eV. The activation energy for the photocurrent remains unchanged at about 0.2 eV. In the undoped samples thermal energy is required to produce carriers, while in the doped (e.g., *o*-chloranil) samples, carriers are already present from the process:

$$\mathrm{Pc} + \mathrm{A} \xrightarrow{\text{dark}} \mathrm{Pc}^+ + \mathrm{A}^- \qquad \text{(XCI)}$$

where A is the acceptor. Doping with an electron acceptor thus eliminates the requirement of thermal energy to produce charge carriers. The activation energy of 0.2 eV is interpreted as the energy required to migrate the carriers after their formation (*188*); hence it is approximately the same as the photoconductivity activation energy. The photomechanism in doped samples is thought to follow (*174*) the following process:

$$\mathrm{Pc} + h\nu \xrightarrow{\text{light}} \mathrm{Pc}^* \qquad \text{(XCII)}$$

then from (XCI)

$$\mathrm{Pc}^* + \mathrm{A}^- \xrightarrow{\text{light}} \mathrm{Pc}^+ + \mathrm{A}^- \qquad \text{(XCIII)}$$

Putseiko (*294*) has observed that the addition of quinone to amorphous magnesium phthalocyanine increases the latter's photoelectric sensitivity by 10^2 to 10^3 times. The same complex deposited on a zinc oxide surface also shows enhanced sensitivity, the majority carriers now being negative (*292*, *343*). The mechanism may involve energy transfer by excitons from the phthalocyanine to the zinc oxide surface.

5. Mechanism of Conductivity

Space precludes a detailed discussion of the various mechanisms proposed for the conduction of charge through a phthalocyanine lattice. However, some of the more salient points will be mentioned. The conductivity is undoubtedly associated with the mobile π electrons of the phthalocyanine ring (*86*). Eley proposed (*84*, *85*) that the conductivity arose through thermal or optical excitation of π electrons from the highest filled to the lowest empty π orbital. Using the Free Electron Gas approach developed by Kuhn (Section V,B), a value of E_0, the energy difference between the filled and empty orbitals mentioned above, was calculated. The electrons in the excited state are now presumed to tunnel through the intermolecular barrier with negligible energy requirement, provided the molecules are in close contact. Alternatively, it may be possible for the hole in the lower orbital to migrate in a similar manner. Garrett (*126*) has pointed out, however, that there is no *a priori* reason to associate E_0 with any term separation in an individual molecule.

The presence of a free surface seems to be a necessity for detection of a photocurrent, and the surface conditions greatly affect the magnitude of the photocurrent while having little effect upon the absorption spectrum. It is known that, when light is absorbed in the fundamental absorption band, excitons are created and may diffuse a considerable distance through the crystal (*264, 326*). Photoconductivity may then be caused by the arrival of the excitons at the surface and decomposition thereon to a pair of charged carriers (*126*). The excitons in this case are excitations of a lattice of molecules in which the electronic excitation of one molecule is shared to some degree among neighboring molecules. Such a state is itself nonconducting (*67*). Heilmeier *et al.* (*153, 154*) do not accept the exciton mechanism but prefer a band model. Thus the photoconductivity of metal-free phthalocyanine is ascribed (*151, 152*) to the direct formation of carriers by suitable radiation, the effective lifetime of a photoexcited carrier in a crystal being approximately 0.9×10^{-8} sec. Using this lifetime and the Hall mobility, a diffusion length of 5×10^{-6} cm was calculated. Assuming radiation of wavelength 730 mμ, this implies that the carriers are produced further away from the surface than one diffusion length. The migration involves a number of conducting bands, the lowest of which consists of discrete levels of width 0.014 eV and separation 0.05 and 0.12 eV. The bottom of this band is located 1.68 eV above the highest filled band. A second conducting band exists 3.2 eV above the filled band (*154, 156*). Liang and Scalco find that the band gap in α and β metal-free phthalocyanine is 0.6 and 1.2 eV, respectively (*219*).

The mechanism and kinetics of photoconductivity have been studied by high-intensity low-duration light pulse techniques (*174, 175, 293, 348*). The decay of the photocurrent in the bulk is a result of a diffusion-limited bimolecular recombination of electrons and holes with a recombination radius of approximately one molecular diameter (*174*).

The very high Hall mobility of copper phthalocyanine relative to that of the metal-free ligand has been discussed. The mobility is proportional to the width of the conduction band (*145*) and is also related to conductivity and activation energy (*240*). In copper phthalocyanine there is presumed to be overlap of the π-orbitals of the ligand with the 3*d* orbitals on the metal (Section V,C). Moreover, there is evidence for an interaction of these 3*d* orbitals with the π-orbitals of *neighboring* phthalocyanine units, thus providing a pathway for charge carriers (*145, 153*), not present in the metal-free ligand.

In a very recent article (*145a*) it is suggested that the absorbed oxygen may be associated with the electronically active centers in phthalocyanine semiconduction, it having previously been observed that, in the strict absence of oxygen, the activation energy for the dark current may be as high as 2 eV (*153*).

E. RADIOCHEMISTRY

1. *Szilard-Chalmers Process*

The Szilard-Chalmers process is a method of manufacturing isotopes by neutron bombardment of a complex. The recoiling isotopes of higher mass number are isolated while the parent isotope remains complexed. Several conditions must be fulfilled to obtain a good enrichment E (defined as the factor by which the specific activity of the product is enhanced relative to that of a simple target) (*316*). After the chemical bond in the target molecule has been ruptured, the recoiling radioactive atom must not recombine with the original target fragments nor undergo thermal exchange with inactive target molecules in a time comparable to that of irradiation. The new chemical form of the active atoms must be easily separable from the target species without inducing decomposition or exchange with the latter. Finally, the target species must not decompose appreciably in the radiation field to yield inactive atoms of the same chemical form as the Szilard-Chalmers product. The metal phthalocyanines having high thermal and chemical stability are particularly suitable targets (*6, 62, 160, 257, 258, 278, 281, 316*). The phthalocyanines of iron, cobalt, copper, zinc, rhodium, sodium, gallium, and palladium have been used as targets. The yields Y (fraction of radioactivity produced in the target in high specific activity), which are often very high, are generally independent of the time of exposure to the neutron flux. The enrichment E tends to decrease with increasing exposure.

After irradiation the radioactive isotope is separated from the unchanged complex by dissolution in concentrated sulfuric acid, reprecipitation of the complex by dilution, and filtration. In this way yields of 12-hour Cu^{64} of over 70%, and enrichments of greater than 350, have been obtained with a neutron flux of 2×10^{14} n.v.t. For 14-hour Zn^{69m}, Y is greater than 50% and E greater than 35 with a flux of 2×10^{16} n.v.t. (*316*). $Rhodium^{103}$ phthalocyanine was employed (*160*) to separate 42-second Rh^{104} and 4.3-minute Rh^{104}. The isotope Co^{60} was obtained in 95.5% purity by using cobalt phthalocyanine as a target (*257, 258*).

2. Radiation Damage

The effect of a high radiation flux upon the structure of metal phthalocyanines has been investigated. Intensities of 10^{20} thermal neutrons/cm^2 tend to convert crystalline copper phthalocyanine to an amorphous state (*306*). Bowden and Chadderton (*35, 36*), using the electron microscope, have discussed the disorder in the molecular array caused by fission damage. Tracks and dislocations due to the passage of individual fission fragments could be seen.

F. FIELD EMISSION MICROSCOPY

Because of their large size, the metal phthalocyanines were one of the first classes of molecules to be studied with the field emission microscope (*13, 135, 136, 245, 246, 253–256*). The images produced were in many cases roughly square and made up of four well-defined quadrants. It would appear that single molecules of phthalocyanine give rise to individual "images" having the molecular symmetry of the compound. Only diffraction patterns might have been expected, since the resolving power of the technique is at best only about 20–30 Å while a phthalocyanine molecule is only some 10 Å broad. The images are actually formed by electrons coming from π orbitals of the phthalocyanine, rather than from the Fermi sea of substrate. These electrons suffer considerable field enhancement in the vicinity of the molecule, and will be emitted most readily from the four corners of the molecule where the field is highest. The emerging electrons will therefore acquire considerable velocity components directed away from the molecular center giving rise to 10–20 times extra enlargement (*135, 136*). The actual theory is complex and many molecules give similar patterns, since the pattern is a function of the electron distribution rather than the molecular geometry.

The field emission microscope has been used to determine the polarizabilities of copper, barium, and dilithium phthalocyanines, which are 120 ± 30, 62 ± 6, and $16 \pm 3 \times 10^{-24}$ cm^3, respectively (*78, 135*).

G. MISCELLANEOUS STUDIES

The X-ray absorption edge spectra of iron, cobalt, and nickel phthalocyanines have been recorded. When a compound absorbs X-rays, a 1s electron is considered to make a transition to some unoccupied orbital of the K-electron excited atom (i.e., an atom having a hole in the K shell). Nickel phthalocyanine showed absorption at 7 and 18.5 eV (*248*), iron phthalocyanine at 18 eV, and cobalt at 25 eV (*117*). The second maximum may be due to a second order plasma interaction (i.e., transition from a

1*s* orbital to a 3*d* orbital of the K-excited atom, with simultaneous emission of a plasmon) (*328*).

The energy required to remove an electron from the surface of a phthalocyanine crystal to infinity (surface ionization energy) has been measured by Pope (*286*) by an electrostatic method, and by Kearns and Calvin (*176*) by the photoelectric threshold method. The surface ionization energy is 5 eV and is independent of the presence or absence of the central metal ion.

Cobalt phthalocyanine has recently been employed as a catalyst to activate oxygen in a fuel cell (*167a*). Phthalocyanines have been used to develop a photographic method of Fourier synthesis (*46*) and have also been used in qualitative analysis (*164*).

VII. The Metal-Ligand Bond

Metal phthalocyanines were originally classed as covalent on the basis of their low spin magnetic behavior. Although the supposition that low spin complexes are "covalent" while high spin complexes are "ionic" is an overgeneralization, it is still normally assumed that in low spin complexes covalent bonding is probably important. Moreover, Mössbauer experiments with ferrous phthalocyanine (Section IV,E,1) also indicate a high degree of covalent character. Contrary to this suggestion is the observation by Whalley (*374*) that metal-free phthalocyanine dissolved in pyridine exhibits a "metallated phthalocyanine" type of spectrum in the visible region. Presumably the species in pyridine is the phthalocyanine dianion; since its spectrum is similar to that of most metallated derivatives, the inference is that the metal ion has little influence upon the molecular orbital energies of the ligand. Of course it should be borne in mind that the orbitals responsible for the spectra and those responsible for the σ-bonding have different symmetries, so the effect of one upon the other will be mainly inductive. Covalent σ-bonding must certainly play some part in the phthalocyanines, but is perhaps not so important as in the metalloporphyrins (*105*, *266*, *290*).

There is also the question of π-bonding and of bonding interaction between neighboring molecules. The large Hall mobility of copper phthalocyanine relative to that in the metal-free ligand (Section VI,D,3) is interpreted in terms of an interaction between copper orbitals and the π orbitals on a neighboring phthalocyanine molecule (3.38 Å distant) (*145*, *153*). There is also evidence for this type of interaction from solid state visible spectra studies (*69*, *70*).

Berezin has correlated the stability, and solubility in sulfuric acid, with σ- and π-bonding. As π-bonding from the metal to the ligand increases, the basicity of the ring, and hence solubility of the complex in acid, increases. σ-Bonding operates in the reverse sense. On this basis Rh(III) is thought to be a better π donor than Pd(II) or Pt(II), and Os(IV) better than Rh(III) (*22*, *28*). The diamagnetism of the Os(IV) complex is interpreted in terms of strong π-bonding from metal to ligand, the four electrons pairing up in the metal e_g orbitals, stabilized by back-donation. As Os(IV) complexes often have low moments even in complexes where π back-donation is impossible (*217*), it is perhaps not necessary to invoke such bonding to explain the diamagnetism. π-Bonding in high oxidation state complexes such as Rh(III) and Os(IV) is not normally thought to be important, because the energies of the orbitals concerned are likely to be too different from appropriate orbitals on the ligand. Also, since such π-bonding presumably involves the empty low-lying phthalocyanine e_g orbital, it should be reflected in the visible spectrum of the complexes, which does not appear to be the case.

Berezin has also used the kinetics of hydrolysis as a guide to metal-ligand bond strength (*19*). The order of stability found was Fe(III) > Ag >Mg > Pb > Cd, Hg > Ca. However, kinetic slowness may be due to a high activation energy rather than a low bond energy.

In general, π-bonding may take several forms:

(*a*) In-plane π-bonding utilizing the metal d_{xy} orbital. This has already been discussed (Section V,C,1) and, although there is some evidence to the contrary, is probably unimportant.

(*b*) Interaction between the empty metal $a_{2u}(p_z)$ orbital (in square planar complexes) and the filled a_{2u} π orbital on the ligand. The variation of the Soret band in the ultraviolet spectrum, with metal, is quite marked (in the lanthanide series, the band in the 400–450 mμ region may be the Soret band), and may be due to admixture of the metal a_{2u} orbital, i.e., to ligand to metal π-bonding.

(*c*) Interaction between the filled metal e_g orbitals and the filled ligand e_g orbitals. Harrison and Assour (*145*) have provided evidence from electron-spin resonance that this type of out-of-plane bonding is important. If this is so, one may have expected that the electron-spin resonance spectrum of the radical cation of copper phthalocyanine (*40*) would have given a g value other than 2.0023, owing to interaction of the odd electron with the copper atom via π-bonding of this nature. Of course it is possible that the oxidation does not involve loss of an electron from the highest filled (e_g) level, but from a lower lying level.

(*d*) Interaction between the filled metal e_g orbitals and the empty ligand e_g orbitals, i.e., metal to ligand π-bonding. Since transitions to this ligand level are thought to be responsible for the visible and ultraviolet spectrum, the spectrum should be very sensitive to π-bonding and hence to the metal ion, whereas in fact it is not. For metals in their normal oxidation states, the metal e_g and ligand e_g orbitals are probably too dissimilar in energy. For low oxidation states, however, the situation should be more favorable. Such an interaction will lead to an increase in the energy of the ligand orbital and hence to a shift in the absorption spectrum to the blue. The red color of low oxidation state metal complexes in solution (e.g., the zero and monovalent complexes of iron, cobalt, nickel, etc.) may be an indication of π back-donation of this type. As the oxidation state decreases, we may in any case expect an increase in π back-donation and a decrease in σ-bond strength. The decrease in σ-bond strength is probably responsible for the low spin nature of the zerovalent manganese derivative. Extensive back-donation in the low oxidation state complexes leads in the limit to their formulation as quadrinegative phthalocyanine salts of normal oxidation state metals. Clearly they exist as a resonance mixture of the two extremes.

Finally, there is the question of the acidity of hydroxy or aquo groups attached to the central metal ion. Phthalocyanine hydroxy complexes of Cr(III), Mn(IV), Sn(IV), and Al(III), but not Si(IV) and Ge(IV), will react with alkali to form salts. This is to some extent the reverse of the normal situation, since chromic hydroxide will not react with alkali under normal conditions whereas silicic acid will. The acidity of the chromium and manganese derivatives has been explained (*87*) in terms of electron withdrawal from the hydroxyl group by the phthalocyanine ligand via the metal atom in a form of perpendicular conjugation (π-ligand, d metal, p oxygen orbital overlap). The silicon and germanium complexes ought to be acidic in their own right; the fact that they are not (other than the condensation reactions) suggests that electron density is being fed onto the oxygen rather than withdrawn from it. Perhaps the d orbitals of the silicon and germanium atoms are not of suitable energy to take part in any conjugation, while the high base strength of the ligand renders the silicon and germanium atoms less positive than usual.

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