Coordination Chemistry Reviews, 32 (1980) 67–95

SOME NEW DEVELOPMENTS IN THE CHEMISTRY OF METALLOPHTHALOCYANINES

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(Received 8 June 1979)

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A. INTRODUCTION

Like many of the great moments in science, the chemistry of phthalocyanine and metallophthalocyanines began by an accidental discovery. In 1907, Braun and Tcherniac heated an alcoholic solution of *o*-cyanobenzamide in order to study some of its properties [1]. After cooling, small amounts of a blue compound precipitated. The precipitate turned out to be phthalocyanine. This was the first time phthalocyanine was synthesized. In 1927, de Diesbach and von der Weid attempted to prepare *o*-xylenedicyanide from a mixture of *o*-dibromobenzene and cuprous cyanide by heating in pyridine at 200°C. However, they obtained a blue compound containing copper [2]. Later this blue compound was identified as copper(II) phthalocyanine. Thus,

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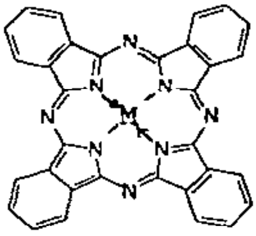


PcM

Fig. 1. Metallophthalocyanine. Pc = phthalocyanine dianion, M = metal(II) ion.

the preparation of the first metallophthalocyanine was also an accident. In the early 1930's, Linstead and his co-workers synthesized many metallophthalocyanines and reported that a phthalocyanine ligand consists of four units of isoindole and has a highly conjugated system [3]. In 1933, for the first time, he used the term "phthalocyanine", which comes from the Greek naphtha (rock oil) and cyanide (dark blue). Later Robertson and co-workers [4—7] elucidated the structures of phthalocyanine and nickel(II), copper(II), and platinum(II) phthalocyanines using single crystal X-ray diffraction analysis (Fig. 1). Since that time, many studies have been done on semiconductivity, photoconductivity, photochemical reactivity, photosynthetic activity, luminescence and fluorescence which are based on the highly conjugated system of phthalocyanine and metallophthalocyanines [8,9]. Many bioinorganic interests have centered on these compounds because metallophthalocyanines have much the same general structures as the naturally occurring metalloporphyrins. Of significance are a few studies on the reversible addition of dioxygen to iron(II) phthalocyanine in an aqueous solution [10—13]. More advances in this area are expected. Furthermore, metallophthalocyanines show a strong blue-green color and have high thermal and chemical stabilities so that they are extensively used as pigments. Figure 2 compares the metal ions complexed to phthalocyanines listed by Lever [8] and Moser and Thomas [9] with metals complexed since their reports. References are given to the synthesis of these new compounds. Since the review of Lever [8], and the book of Moser and Thomas [9] were published, progress in the chemistry of phthalocyanine and metallophthalocyanines has been distinctive. Over 5,000 papers and patents have been reported during this time as is shown in Fig. 3.

During this period, metallophthalocyanines of *f* elements (sandwich-type metallophthalocyanines and uranylsuperphthalocyanine) have been synthesized and characterized [16,17,29,30,31]. Some new methods of studying the nature of phthalocyanine and metallophthalocyanines have been reported, e.g., X-ray photoelectron spectroscopy (ESCA) was used to study the nature of the bonding in some of these new compounds [32—35].

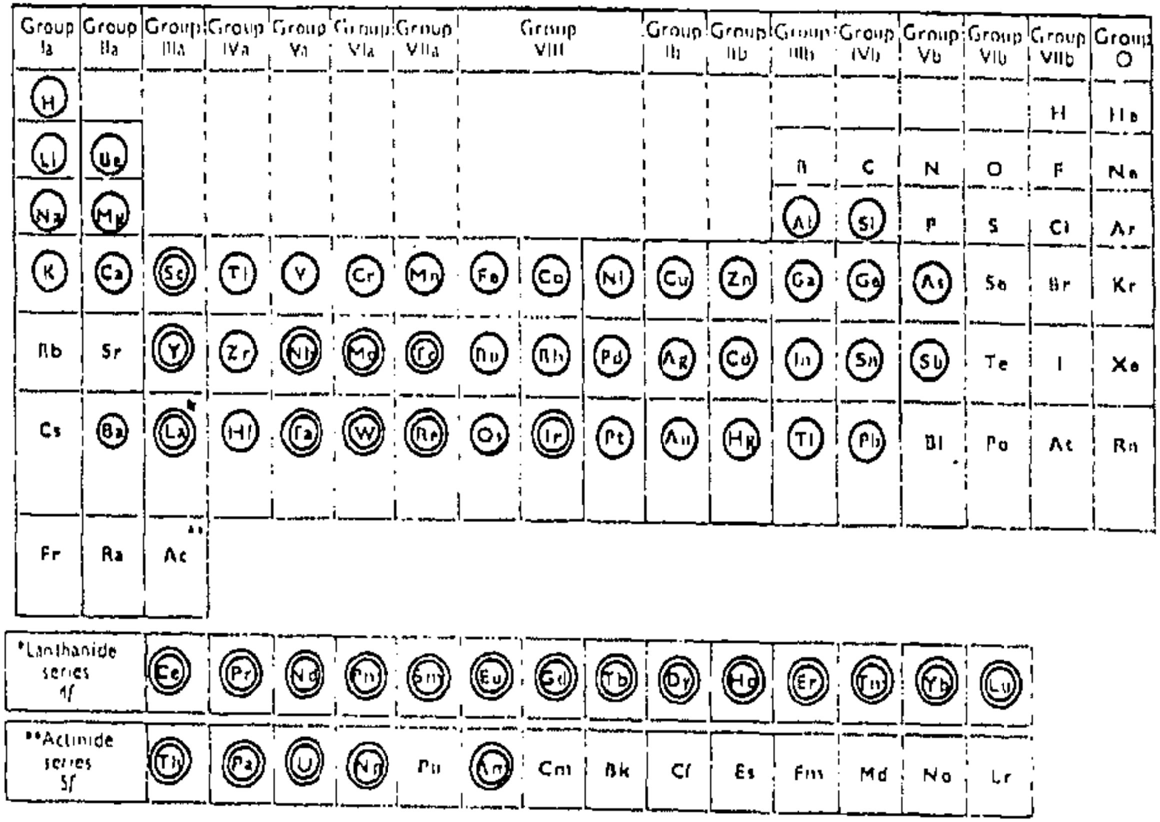


Fig. 2. Metals for which phthalocyanine complexes have been made: ○, metallophthalocyanines mentioned by Lever [8], ◎, more recent metallophthalocyanines. Some of the lanthanide and actinide phthalocyanines were mentioned by Lever, but the characterization of these compounds was not complete. References for the new metals are as follows: Sc[14], Y[15], La[16,17], Nb, Mo, Ta[18], W[19], Re[20,21,22], Tc[22], Ir[23], Th[24], Pa[25], U[26], Np[27] and Am[28].

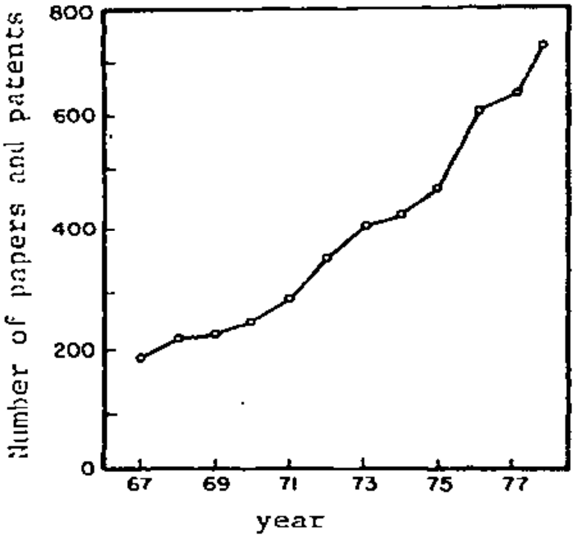


Fig. 3. Number of papers and patents published during the past decade. From Chemical Abstracts.

Several reviews concerning the application of metallophthalocyanines as catalysts, polymers and pigments have been published during this period [36,41]. In addition, the interesting books of photovoltaic effects and photoconductivity have also been reported [42,43].

To summarize the attractive results which have been developed since the review of Lever [8] and the book of Moser and Thomas [9], the synthesis and properties of new-type complexes (sandwich-type and superphthalocyanine) which can be synthesized only with *f*-transition metals and spectroscopic results such as IR, visible, NMR and ESCA, will be presented in this review.

B. SYNTHESIS

(i) General synthesis

Metallophthalocyanines can be prepared by various methods. The most general methods are illustrated in the following equations [8,9] where

Pc = phthalocyanine dianion, M = metal(II)

$$\text{M} + 4\ \text{phthalonitrile} \xrightarrow[\text{dry or solvent}]{300^\circ\text{C}} \text{PcM}$$

$$\text{M} + 4\ \text{phthalic anhydride} + 4\ \text{urea} \xrightarrow[\text{heat}]{300^\circ\text{C}} \text{PcM} + 2\ \text{H}_2\text{O} + \text{CO}_2$$

$$\text{MX}_2 + \text{PcLi}_2 \xrightarrow[\text{solvent}]{\text{room temp.}} \text{PcM} + 2\ \text{LiX}$$

The use of catalysts with metal salts and phthalic anhydride has proved successful for the synthesis of metallophthalocyanines [44—46]. For instance, copper(II) phthalocyanine is prepared from phthalic anhydride, urea, boric acid, and copper chloride in the presence of ammonium molybdate in trichlorobenzene at 195—200°C with excellent yield (>70%) and fewer imine impurities [44]. The synthesis of soluble metallophthalocyanine complexes has also been of recent interest. For instance water-soluble metallophthalocyanine complexes are synthesized as follows [10,47]. A mixture of the monosodium salt of 4-sulfophthalic acid, ammonium chloride, urea, ammonium molybdate and metal(II, III) salt is heated for several hours at 180°C in nitrobenzene. The crude product is treated with hydrochloric acid, sodium hydroxide and finally washed with aqueous ethanol. After being refluxed for a few hours in absolute methanol, the blue, pure product is obtained (yield ca. 80%). On the other soluble derivatives, Russian chemists have reported systematic studies [48—51]. Tetra-nitro, -chloro, -amino and -hydroxy phthalocyanine complexes of cobalt(II), for instance, are prepared from the respective phthalic acid derivatives and anhydrous cobalt(II) chloride in the presence of urea and ammonium molybdate in nitrobenzene at 180—190°C.

In general, the stability of metallophthalocyanine complexes depends on both the charge and size of the metal ions. Thus, metals with a high charge: size ratio form complexes which resist replacement by protonic acids and thermal decomposition (Al(III), Cu(II) etc.). For those complexes, sublimation in vacuo and reprecipitation from concentrated sulfuric acid and water can be effectively employed. While those complexes with a lower charge: size ratio deposit significant amounts of free phthalocyanine by the sublimation and reprecipitation methods unless great care is taken.

(ii) Sandwich-type derivatives

Linstead and co-workers [52—54] and Robertson [55] showed that the composition and structure of most metallophthalocyanines can be expressed by the formula PcM, PcMX and $PcMX_2$ for bi-, tri- and quadrivalent metals.

The first complex of unusual geometry was synthesized by Barrett et al. [53] in 1936. This complex, a tin(IV) phthalocyanine containing two phthalocyanine ligands (Pc_2Sn), was prepared by the reaction of $PcSnCl_2$ with $PcNa_2$ in chloronaphthalene. The absorption of this complex is shifted to a longer wavelength compared to those of normal metallophthalocyanines. Recently, the structure of this complex was elucidated by an X-ray diffraction study which will be described later [56]. Though many kinds of metallophthalocyanines have been synthesized, compounds having this unusual composition were not reported until sandwich-type complexes of *f*-elements were prepared [16,17,24—28]. The synthesis of *f*-element phthalocyanines has played an important role in advancing the chemistry of metallophthalocyanines with the preparation of sandwich-type complexes and superphthalocyanines.

Kirin et al., in attempting to prepare neodymium phthalocyanine, separated two compounds from an N,N-dimethylformamide (DMF) solution by chromatography on an alumina column [16]. The most easily eluted compound has an absorption maximum at 634 nm, giving a blue solution, while the other has one at 679 nm, giving a green solution. From elemental analysis, Kirin et al. found that the blue compound is a diphthalocyanine complex [57]. No consistent analysis figures were obtained for the green compound, but because its optical spectrum is similar to that of a monophthalocyanine complex, they have suggested a formula, PcNdCl.

Misumi and Kasuga also prepared some lanthanide diphthalocyanine complexes which were characterized by elemental analysis and visible spectra [17]. They also found the green complex, which they presumed to be the monophthalocyanine complex, was difficult to isolate from solution. In an electrochromatographic separation of the crude reaction products in DMF, the blue diphthalocyanine complex moves to the anode whereas the green monophthalocyanine complex moves to the cathode. The magnetic moment of cerium diphthalocyanine complex is 1.80 B.M. (room temp.), and this compound moves to the anode in the electrochromatographic separation in DMF. They suggested the oxidation state is 3+ for the cerium ion of this compound. In a solution of 1-bromonaphthalene, the spectrum of the diphthalocyanine complex changes to that of the monophthalocyanine complex. This was explained by the reaction of the complex with trace amounts of free bromine present in the solvent by which one of the ligands was removed and PcNdBr was formed. The same shift of spectrum also occurs in 1-chloronaphthalene, DMF + acetic acid, DMF + hydrochloric acid, and DMF + nitric acid.

On the other hand, MacKay et al. reported that the green compound of gadolinium phthalocyanine is also the diphthalocyanine type complex according to analytical, ESR and magnetic susceptibility measurements [58]. They explained the behavior of the blue and green complexes by an equilibrium between the two forms in a non-aqueous solvent

$$\underset{\text{(green)}}{\mathrm{Pc_2GdH}} \rightleftharpoons \underset{\text{(blue)}}{\mathrm{Pc_2Gd^-}} + \mathrm{H^+} \tag{1}$$

where the formation of the green complex is favored under acidic conditions and the formation of the blue complex, which is an anionic form, under basic conditions. This result is different from those of Kirin et al. [57] and Misumi and Kasuga [17] who concluded that their green complex was monophthalocyanine because the visible spectrum resembles those of normal monophthalocyanines. MacKay et al. [58] concluded that the color changes observed can be due to changes in a π-electron distribution on formation of anion, cation or neutral species rather than due to a change from diphthalocyanine to monophthalocyanine.

They mentioned, however, the existence of ytterbium monophthalocyanine (PcYX) [58]. We may consider, therefore, that the green compounds consist of two types of complexes; the protonated type of the sandwich complex and the monophthalocyanine complex, while the blue compound is the ionized sandwich-type compound. Recently, Corker et al. also reported that the color of lutetium phthalocyanine is changed as a result of formation of an organic-free radical (see Section C (ii)) [59].

Moskalev and Kirin also prepared water-soluble sulfonated ammonium salts, $NH_4[(SO_3NH_4)_4Pc_2M]$ with M = Y, Gd, Lu [60]. They reported that the solution color of these salts changes according to the pH of the solution (green with a low pH, and blue with a high pH).

Reaction of AnI_4 (An = Th, Pa, U) with phthalonitrile at 250°C yielded actinide diphthalocyanine complexes [24–26]. Pc_2Pa was also formed from PaI_5, and Pc_2Np was prepared from NpI_3 [27]. The dark violet Pc_2An complexes can be sublimed without decomposition at 550°C and 10^{-5} Torr. These complexes are stable to air. The molecular weights of these compounds were determined by mass spectrometry [24]. The electronic spectra are characteristic for diphthalocyanine complexes. Americium phthalocyanine was also prepared from americium acetate and phthalonitrile [28]. Comparison of the properties of americium phthalocyanine with those of trivalent lanthanides indicates that the americium ion in this compound is in the trivalent state and its structure can be described by a sandwich-type model. As Kirin and Moskalev mentioned, formation of these diphthalocyanine complexes must require a minimum of an accessible 3+ or 4+ oxidation state of central metals and ionic radii for these oxidation states which are greater than the phthalocyanine radius [61]. The crystal and molecular structure of $Pc_2U(IV)$ was determined from three-dimensional X-ray data [62]. The uranium atom is coordinated eight-fold by the isoindole nitrogen atoms of the two phthalocyanine rings. One ligand is rotated by 37° past the eclipsed configuration. The phthalocyanine ligand in this compound is not planar but convex. The distance between the N_4 (the central isoindole nitrogen atoms) planes of the two macrocycles is 2.81 Å. This structure is almost the same as that of $Pc_2Sn(IV)$. In Pc_2Sn, one ligand is rotated by 42° past the eclipsed configuration and the distance between the N_4 planes of the two mac-

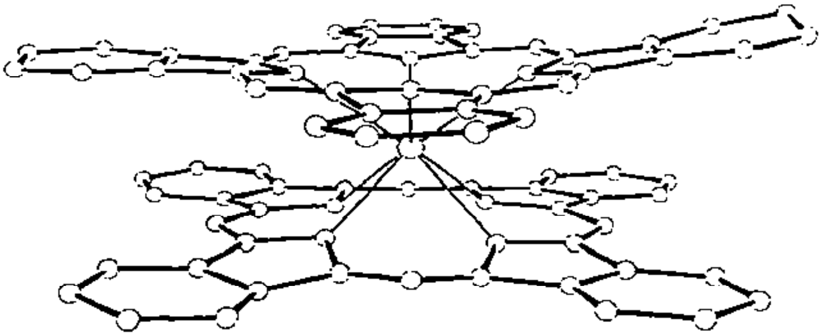


Fig. 4. Elevation view of bisphthalocyaninatoneodymium(III) [63].

rocycles is 2.70 Å [56]. The degree of shift from the staggered orientation of Pc_2U is larger than that of Pc_2Sn because the distance between the two N_4 planes of Pc_2U is longer than that of Pc_2Sn so that the benzene rings of the two phthalocyanine rings in Pc_2U need to be closer than those of Pc_2Sn to make an effective interaction between them (3.35 Å). Furthermore, the structure of Pc_2NdH was elucidated by Kasuga et al. [63]. This compound has an exactly staggered orientation and phthalocyanine ligands do not show the degree of convexity that Pc_2U and Pc_2Sn show (Fig. 4). The distance between the N_4 planes of the two macrocycles is 2.96 Å.

(iii) Superphthalocyanines

Baumann and Binert prepared phthalocyanine containing 6 units of phthalonitrile per one atom of cobalt when cobalt salts were heated with phthalonitrile, phthalic acid or phthalic anhydride and urea at 160—170°C [64]. Such phthalocyanine complexes of copper and nickel were also prepared by Barnhart and Skiles who proposed the following structure for these complexes (Fig. 5) [65]. Perkins and Whelen also synthesized novel copper and nickel phthalocyanine complexes which have 5 phthalonitrile units [66]. The compounds containing 5 or 6 phthalonitrile units are considered to be the phthalocyanine precursors. While the detailed structures are not known, these unusual metallophthalocyanine compounds have bright colors and may be useful as dyes [66].

A uranyl phthalocyanine complex was also prepared from uranyl salts and phthalonitrile but no structure was suggested until experiments by Friedel et al. [67]. Lux [29] suggested a structure of the uranyl complex of cyclopentakis(2-iminoisoindolenin) (superphthalocyanine, $SPcH_2$, Fig. 6) based

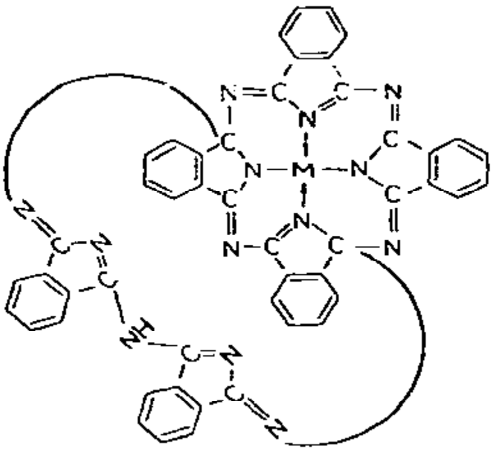


Fig. 5. Proposed metallophthalocyanine precursors. M = Ni(II) or Cu(II).

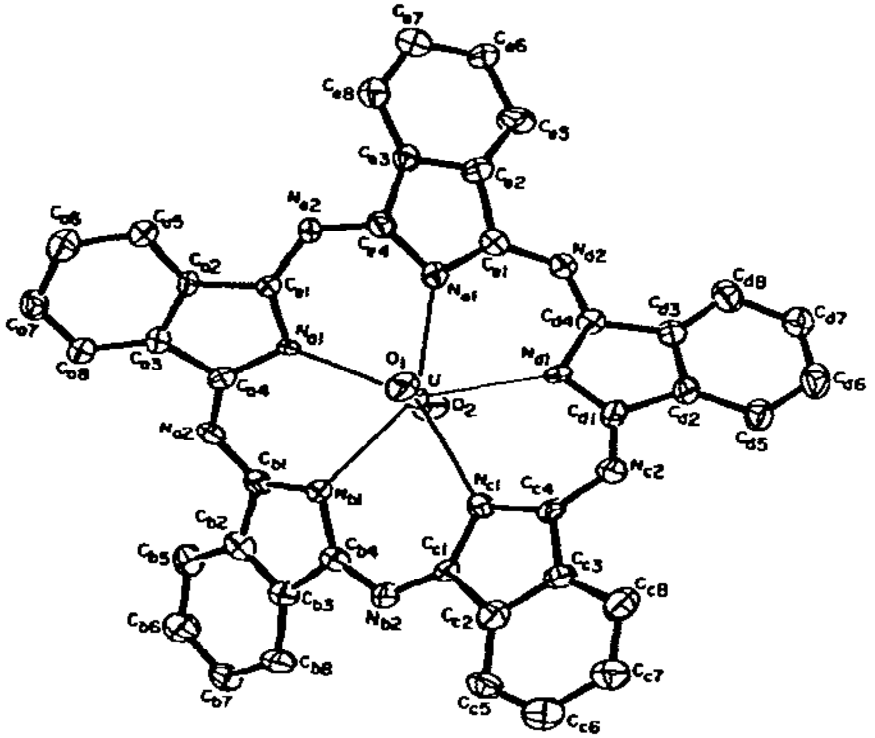


Fig. 6. Structure of uranylsuperphthalocyanine [30].

on the following evidence: the compound sublimes at 400—500°C and 10^{-5} Torr without decomposition, the mass spectrum has a molecular ion at *m/e* 910 and is consistent with the proposed structure. The electronic spectrum can be well explained by the electron-gas model of Kuhn (Table 1) [68]. This ligand is probably the first 20-annulene with a π-electron system to be realized. This structure was determined from an X-ray diffraction study by

TABLE 1

A comparison of absorption spectra of phthalocyanine and superphthalocyanine compounds [29]

Compound	*L*	λ_{max} (nm)	
		Calc.	Exp.
Pc_2U	16—annulene 21.6 Å	645	643
$SPcUO_2$	20—annulene 27 Å	910	915

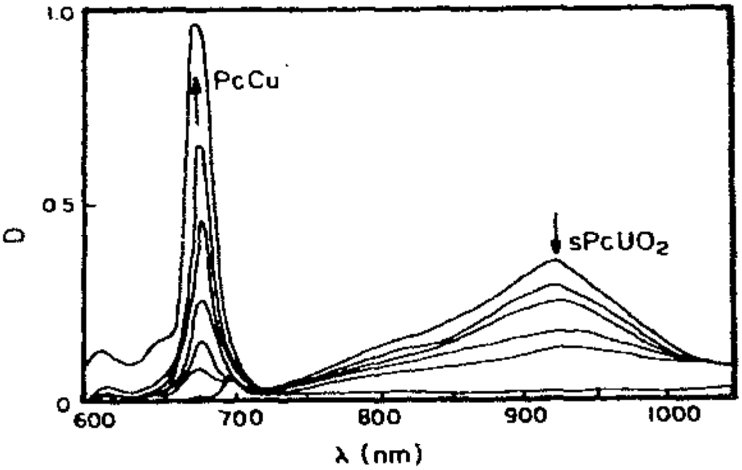


Fig. 7. The reaction of uranylsuperphthalocyanine with $CuCl_2$ in 300/1 = 1-chloronaphthalene/DMF at 75°C [31].

Marks and co-workers [30] who confirmed the structure proposed by Lux [29].

Marks and Stojakovic [31] also reported that the replacement of the uranyl ion in $SPcUO_2$ by other metal ions produces the corresponding four-subunit transition metal complex in high yield

$$SPcUO_2 + MX_2 \rightleftharpoons PcM + UO_2X_2 + \text{phthalonitrile} \qquad (2)$$

where M is Co, Ni, Cu, Zn, Sn or Pb.

The mechanistic features of the transmetallation reaction were investigated in most detail for the $CuCl_2$ system. As shown in Fig. 7, the contraction proceeds smoothly. Figure 7 shows an interesting optical characteristic of $SPcUO_2$, e.g. very strong absorption ($\log \epsilon = 4.82$ at 914 nm) in the near IR.

C. PROPERTIES

(i) Visible and IR spectra

It has been known that IR absorption spectra of phthalocyanine and metallophthalocyanine compounds show differences between α- and β-polymorphic forms [69]. Infrared spectra of the α- and β-polymorphic forms suspended in Nujol are similar in the 3,000–8,000 nm range. However, there are noticeable differences at 12,500–14,500 nm.

In the visible region, it was reported that transmission spectra of sublimed thin films of the α-crystalline forms of PcH_2, PcCu, PcNi, PcCo and PcZn in the 500–900 nm region change sharply as a result of the α to β transforma-

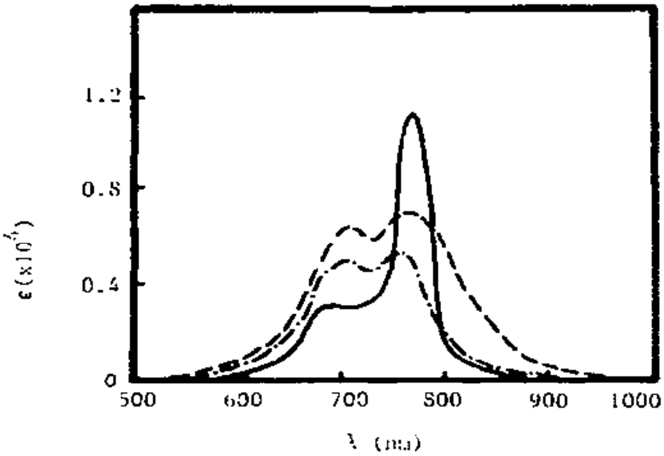


Fig. 8. Absorption spectra of X_4—PcCu: ———, monomer molecule in benzene; · — · — ·, dimer molecule in benzene, - - - - - -, solid phase [73]. X = octadecylsulfonamide.

tion induced by heating to above 300°C [70]. In the β crystal of the metal complex, an intramolecular distortion or site symmetry should split the *Ea* molecular states. These in turn should also be red shifted and split by the crystal environment. Therefore, the changes in the visible spectra are observed [70].

The electronic spectra of monomeric and dimeric phthalocyanine complexes are also different. Hush and Woolsey interpreted the spectral differences of monomeric and dimeric silicon phthalocyanine in terms of exciton coupling of neutral-excitation transitions of the two phthalocyanine rings of the dimer [71].

Abkowitz and Monahan studied the degree of molecular association of copper-4,4′,4″,4‴-tetraoctadecylsulfonamidophthalocyanine (X_4—PcCu, X = octadecylsulfonamide) in benzene and tetrahydrofuran by electronic and ESR spectra [72]. Electronic spectra in the visible region demonstrate the existence of the monomer—dimer equilibrium. Self-association is manifested principally in the appearance of new absorption bands as the complex concentration in solution is increased. Figure 8 shows the resolved monomer and dimer solution spectrum of X_4—PcCu in benzene [72].

A comparison of the resolved solution dimer spectrum with that of the solid shown in Fig. 8 strongly suggests that the solid phase of the phthalocyanine complex (X_4—PcCu), like the liquid phase, is also composed of dimeric pairs of phthalocyanine complexes.

$$2\,X_4\text{—PcCu} \overset{K}{\rightleftharpoons} (X_4\text{—PcCu})_2 \qquad (3)$$

In the 10^{-6}—10^{-3} M concentration range, the dimerization constants, K, are $(1.58 \pm 0.09) \times 10^4\ M^{-1}$ and $(1.41 \pm 0.50) \times 10^2\ M^{-1}$ at room temperature in benzene and tetrahydrofuran, respectively.

ESR measurements involving water-dimethylformamide solutions of the copper(II) and vanadyl tetrasulfophthalocyanine complexes carried out at room temperature and 77 K also provide good evidence for the formation of the dimer [73]. The ESR spectrum of an aqueous solution of the copper derivative at room temperature consists of a weak isotropic line at g ca. 2. At 77 K the isotropic signal is also obtained at g ca. 2. The addition of dimethylformamide to form solvent mixtures containing up to 50% (v/v) of DMF has little effect on the signal observed at 77 K in the g ca. 2 region though a signal can be detected at g ca. 4. The low-field component of the spectrum (at $\delta 4$) is attributable to $\Delta M = \pm 2$ transitions arising from the triplet state formed by coupling of the copper(II) ions in a dimeric form of the copper(II) derivative while the signal at g ca. 2 indicates that the corresponding $\Delta M = \pm 1$ transition may also be observed. In solutions containing still greater amounts of DMF (90% v/v), the spectrum in the g ca. 2 region shows the presence of a highly resolved spectrum, similar to that observed by Rollman and Iwamoto [101] in dimethylsulfoxide, due to monomeric species though a very weak $\Delta H = 2$ transition is still present. The study of dimeric-tetrasulfophthalocyanine and its metal derivatives shows the equilibrium constants for dimer formation [74]. From this study, the stability of the dimers is found to be Cu(II) > H_2 > Fe(II) > VO^{3+} ~ Zn(II) > Co(II). The role of the metal ion in determining the instability of the dimer is thought to be due to competition between water molecules and phthalocyanine molecules for other phthalocyanine molecules such that the water molecules bond to the metal ion in the axial sites. On the basis of a simple electrostatic model, the separation between the two parallel planes in the activated complex is estimated to be ca. 5 Å [73].

The IR and far IR spectra of phthalocyanine and its metal derivatives were systematically studied by Kobayashi et al. [75,76]. All of the divalent metallophthalocyanine complexes are usually taken to belong to D_{4h} point group, whereas metal-free phthalocyanine has D_{2h} symmetry. The E_u mode of vibration, which is IR active for complexes with D_{4h} symmetry, is known to split into two other IR active modes, B_{2u} and B_{3u}, without too much change in the peak position when the compounds happen to assume D_{2h} symmetry as a result of minor substitution. Such an effect of splitting is shown for those in the lower frequency region. In the higher frequency region, the characterization of doublets is difficult because of the overlapping of a greater number of peaks which make the spectra in that region much more intricate. In the case of metallophthalocyanines, the absorption bands apparently corresponding to those which appear as the doublets for metal-free phthalocyanines are detected as singlets which exhibit considerable shifts to higher frequencies as shown in Table 2.

The corresponding absorption peaks are always shifted in the same order

$$\mathrm{Ni} > \mathrm{Co} > \mathrm{Fe} > \mathrm{Cu} > \mathrm{Zn} > \mathrm{H_2} \qquad (4)$$

TABLE 2

Absorption frequencies showing the splitting behavior of H_2 phthalocyanine (cm^{-1}) [75]

D_{2h}	D_{4h}						
H_2	Fe	Co	Ni	Cu	Zn	Pd	Pt
489 498	518	519	521	509	512	514	516
552 559	574	574	578	575	575	578	581
617	642	642	645	640	637	648	645

This strongly indicates that the absorption bands are affected by the complexed metal ion.

In the far IR region, three remarkable metal dependent bands exist in each spectrum of metallophthalocyanines [76]. Two of these bands are also obtained in metal-free phthalocyanine, one being at 342 cm^{-1} and the other at 259 cm^{-1} and 289 cm^{-1} as a doublet. On the basis of the same criterion concerning the splitting behavior, the 342 cm^{-1} series (5) are assigned to be out-of-plane vibrations associated with the isoindole ring which is closely coordinated to the metal ion. The frequencies of these metal dependent bands shift in the order

$$H_2 > Cu > Zn > Pd > Fe > Co > Ni > Pt \quad (5)$$

The frequencies of the other metal dependent bands (6) around 300 cm^{-1} also shift in the order

$$Zn > H_2 > Cu > Fe > Pd > Co \simeq Ni > Pt \quad (6)$$

The third group of metal dependent bands (7) which appears with high intensities in the region 150—200 cm^{-1} for Fe-, Co-, Ni-, and Cu-phthalocyanines is assigned to the metal—ligand vibrations, because these strong bands are not observed in the spectrum of metal-free phthalocyanine. The frequencies of the metal—ligand vibrations in the derivatives shift to higher frequency in the order

$$Zn > Pd > Pt > Cu > Fe > Co > Ni \quad (7)$$

(ii) Electrochromism

Lutetium(III) diphthalocyanine deposited as a thin film on the electrode surface exhibits electrochromism and was investigated by Moskalev and Kirin [77]. Three main types of absorption spectra of the lutetium(III) diphthalocyanine film, corresponding to the electrode potentials of 0.0, —0.8, and 1.0 V may be distinguished in Fig. 9.

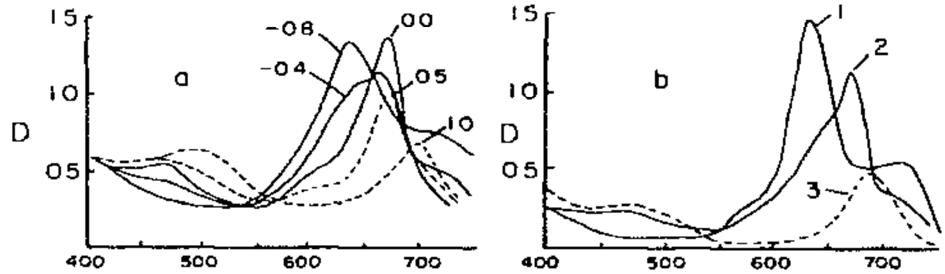


Fig. 9. (a) Absorption spectra of a film of lutetium-diphthalocyanine on the electrode at different electrode potentials in 0.1 M potassium chloride solution (the numerals against the spectral curves denote the electrode potential in volts relative to the saturated silver/-silver chloride electrode). (b) Absorption spectra of sulfonated lutetium-diphthalocyanine in aqueous solution: (1) ionized form $[Pc_2Lu]^-$ at pH 11.5; (2) protonated form Pc_2LuH at pH 4; (3) absorption spectrum of a film of the molecular complex $[Pc_2LuH]I_2$ on glass [77].

The transition from one type of spectrum to another gives rise to isosbestic points on the optical density plots, giving evidence of a direct conversion of one form of diphthalocyanine into another as the electrode potential is varied.

The absorption spectra of the protonated and ionized forms of lutetium-(III) diphthalocyanine in an aqueous solution and the absorption spectrum of a film of the molecular complex with iodine on a glass support are presented in Fig. 9. Comparison of the spectra in Figs. 9a and 9b reveals a profound similarity between the spectrum of the protonated form, Pc_2LuH, in solution (Fig. 9b, curve 2) and the absorption spectrum of the film on the electrode at a potential of 0.0 V (Fig. 9a), and similarity also exists between the spectrum of the ionized form, $[Pc_2Lu]^-$, in solution (Fig. 9b, curve 1) and the spectrum of the film at a potential of −0.8 V (Fig. 9a). Hence, judging from the absorption spectra, at negative electrode potentials there is a reversible transition between the protonated and ionized forms of lutetium-(III) diphthalocyanine in the film via a reaction of the type:

$$[Pc_2Lu]^- + H^+ \rightleftharpoons [Pc_2Lu]H \qquad (8)$$

Comparison of the absorption spectrum of the diphthalocyanine film at an electrode potential of 1.0 V (Fig. 9a) with the absorption spectrum of the film of the molecular complex, $[Pc_2LuH]\cdot I_2$, on glass (Fig. 9b) also reveals a similarity. Moskalev and Kirin suggested that in the region of positive electrode potentials, a molecular complex is formed by the diphthalocyanine complex with acceptor species in the electrolyte, which may be O_2 and H_2O molecules. The formation and decomposition of the molecular diphthalocyanine complex at positive electrode potentials may be represented by eqn. (9)

$$\begin{tikzcd} A + Pc_2LnH \arrow[r] & A + [Pc_2LuH]^* \arrow[r] & A\cdot[Pc_2LuH] \arrow[ll, dashed, bend left] \end{tikzcd} \qquad (9)$$

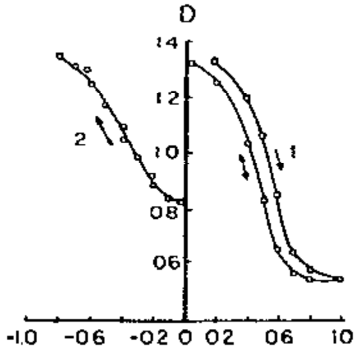


Fig. 10. Variation of the steady-state optical density of the lutetium-diphthalocyanine film with electrode potential: (1) at 673 nm; (2) at 640 nm. The arrows against the curves indicate the direction of measurements on the potential scale [77].

In this equation the asterisk denotes the diphthalocyanine complex which is in an activated state due to high potential and is therefore capable of interaction with the electron acceptor, A. The continuous arrows in the equation denote the direction of the reaction involving the formation of the complex as the electrode potential is increased, and the dashed arrow shows the pathway for the decomposition of the complex as the potential is reduced. The validity of eqn. (9) is confirmed by the presence of a loop in the curves relating the optical density at the 673 nm absorption band to the electrode potential (Fig. 10, curve 1), which is probably due to a difference between the pathways for the formation and decomposition of the molecular complex. In contrast, curve 2 in Fig. 10 does not show a hysteresis, in agreement with the complex identity of the forward and reverse pathways in the ionization of the diphthalocyanine at negative electrode potentials (reaction (8)).

Moskalev and Kirin also observed electrochromism for the diphthalocyanine complexes of other lanthanides and also yttrium and scandium, which demonstrates that this interesting phenomenon is common to this class of phthalocyanine complexes [77]. The possibility of applying the property of electrochromism in diphthalocyanine complexes was studied by Nicholson and Galiardi [78]. They prepared a display in which $Pc_2Lu^{III}H$ was coated on the surface of an electrode. Pc_2LuH undergoes a remarkable series of color changes when subjected to direct-current signals up to about 1 V while in contact with an aqueous electrolyte. A full spectral range of colors is generated by adjustments of the applied voltage. As they mentioned, with further developments this system may become useful for full color imaging and graphic displays, as well as alphanumerics.

Corker et al. also investigated the electrochromic behavior of the lutetium complex in DMF solutions using ESR and optical techniques to characterize the species giving rise to different colors [59]. Electrolysis of a DMF solution yields reversibly four different colors: violet, blue, green, and yellow-red. Two of these, the violet and the green, exhibit ESR signals indicative of organic-free radicals. They attributed these results to oxidation and reduction of phthalocyanine ligands as follows

$$[Pc_2Lu^{III}H]^- \underset{e}{\overset{e}{\rightleftharpoons}} [Pc_2Lu^{III}H] \underset{e}{\overset{e}{\rightleftharpoons}} [Pc_2Lu^{III}H]^+ \underset{e}{\overset{e}{\rightleftharpoons}} [Pc_2Lu^{III}H]^{2+} \qquad (10)$$

one-electron reduction		one-electron oxidation	two-electron oxidation
violet	blue	green	yellow-red

In eqn. (10), the blue species is $Pc_2Lu(III)H$ and the green is $[Pc_2Lu(III)H]^+$, as opposed to other groups' results [16,17,48]. Corker et al. [59] also interpreted the pH effect as follows

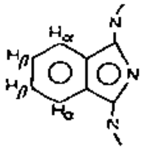
$$Pc_2Lu^{III}H \rightleftharpoons Pc_2Lu^{III}H_2^+ \qquad (11)$$

(blue: high pH) (green: low pH)

Protonation to form the green species occurs at one of the nitrogen bridge atoms of the phthalocyanine ligand. With this interpretation, the cation formed at the low pH would not be a radical. However, the positive charge created upon protonation of the bridge nitrogen would move into the π-system of the ligand. Thus, the protonated species should have the same optical spectrum as that of the cation radical in eqn. (11). Even though their work is somewhat crude on characterization of an initially prepared green complex and measurement of electrical potentials, their explanation of the electrochromism of the lutetium phthalocyanine complex is valuable and attractive. (See Section vi for further studies on radical phthalocyanine species.)

(iii) NMR spectra

In the PMR spectrum of $PcGe(OSi(C_2H_5)_3)_2$, multiplets are centered at δ (ppm) 9.70, 8.38, −1.24 and −2.42 [79]. On the basis of Lever's work, the low-field multiplets (9.70 and 8.38) can be assigned to the α and β ring protons (see scheme below) [80]. The remaining triplet and quartet (−1.24 and −2.42) can then be assigned to the methyl and methylene protons of the triethylsiloxy group.



The macro-rings of these compounds have a ring current which shifts the proton signals of α and β protons of the rings toward a low magnetic field and shifts those of methyl and methylene groups of the axial ligands toward a high magnetic field.

The metal complexes having the ring current and vacant coordination sites

TABLE 3

^{1}H NMR data for PcM derivatives *, ** [31]

Compound	^{1}H NMR
PcZn	9.50 (8 H,m), 7.94 (8 H,m)
$(\beta\text{-CH}_3)_4$PcZn	9.19 (8 H,d, J = 8.8 Hz), 7.69 (4 H,d, J = 8.0 Hz), 2.76 (12 H,s)
SPcUO$_2$	9.06 (10 H,m), 7.68 (10 H,m)
$(\beta\text{-CH}_3)_5$SPcUO$_2$	8.96 (10 H,m), 7.46 (5, H,d, J = 7.2 Hz), 2.46 (15 H,s)
PcLi$_2$ ***	9.38 (8 H,m), 8.04 (8 H,m)

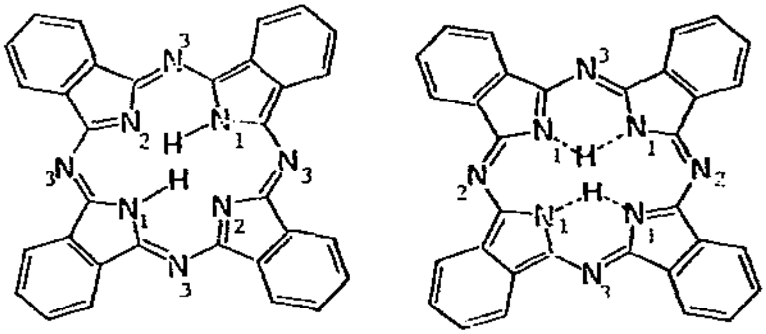
* FT data in δ (ppm). ** All data in C_6D_6 at 30°C. *** 2% $Me_2SO\text{-}d_6$ added to enhance solubility. Key: s = singlet; d = doublet, m = multiplet.

are potential chemical shift reagents. Dichlorogermanium(IV) and iron(II) phthalocyanines were regarded as possible shift reagents [31]. However, their use as shift reagents is limited by solubility problems. Using Fourier transform techniques, Marks and Stojakovic [31] reported NMR studies of lithium, zinc, and uranyl phthalocyanines (Table 3). The high field multiplets were assigned to the β ring protons (e.g., 7.94 for PcZn, 7.09 for $(\beta\text{-CH}_3)_4$PcZn). On the other hand, metalloporphyrins are more soluble than metallophthalocyanines and are useful for NMR shift reagents. A few papers have presented more detailed discussions on NMR studies of metalloporphyrins [81,82]. The smaller shielding ability of the phthalocyanine ring relative to the porphine ring can be ascribed mainly to the result of perturbations of the central porphine-like ring by the azo nitrogen atoms and the benzo rings and to effects from the anisotropy of the benzo rings [81].

(iv) X-ray photoelectron spectroscopy

The location of acidic protons in metal-free phthalocyanine has been the subject of long debate. Proposed structures are the bonded structure and the bridged structure as shown in Fig. 11.

Niwa et al. presented evidence for the bonded structure utilizing X-ray photoelectron spectroscopy (ESCA) [32,33]. In the bonded structure of phthalocyanine, there are three chemically different nitrogens, namely, two pyrrole nitrogens (N_1), two aza nitrogens (N_2), and four *meso*-bridging aza nitrogens (N_3) (Fig. 11a). The 1*s* binding energies of the aza nitrogens in both structures are so close that they cannot be observed as two separate peaks (a limitation due to the resolution of spectrometer). On the other hand, the 1*s* binding energy of the nitrogen bonding with the central hydrogen atom is higher than the energies of the aza nitrogens. Two nitrogen 1*s* peaks with a relative intensity ratio of 0.33 [2 N_1 : (2 N_2 + 4 N_3)] (see Fig. 11a) should be observed for the bonded structure. In the bridged structure, on the other hand, a ratio of 1.0 [4 N_1 : (2 N_2 + 2 N_3] (see Fig. 11b) should be observed.



(a) (b)

Fig. 11. The molecular structures of PcH_2 : (a) bonded PcH_2 ; (b) bridged PcH_2.

The observed nitrogen 1*s* spectrum indicates that the bonded structure of phthalocyanine predominates (Fig. 12).

In the nitrogen 1*s* spectrum of copper phthalocyanine, a single sharp peak was observed accompanied by a weak satellite. The profile of the single sharp peak indicates a small energy separation between four equivalent central nitrogens and four equivalent *meso*-bridged nitrogens. This separation indicates a small difference in the charge densities on the two different kinds of nitrogens [33].

He I photoelectron spectra of metal-free and metallophthalocyanines (Mg, Fe, Co, Ni, Cu and Zn) were also obtained for the gaseous molecules [83].

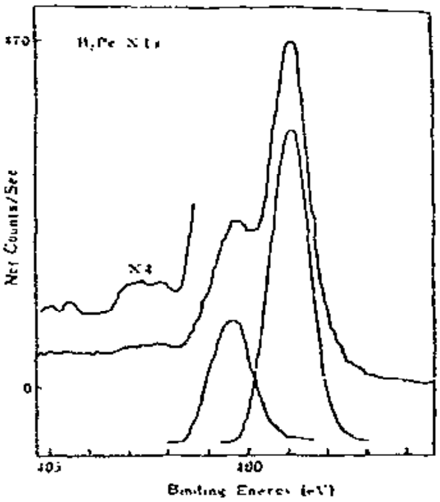


Fig. 12. The nitrogen 1*s* spectrum for PcH_2 using Mg $K\alpha$ X-ray. The spectrum is deconvoluted into overlapping Gaussians [32].

Comparison of these spectra reveals that the uppermost occupied orbitals are ringlike, and not metal $3d$-like, in all cases. The experimental results and inferences were compared with recent ab initio calculations, and indicated that the X_α local density method is a promising one for describing the electronic structure of these large molecules.

Tsutsui and co-workers also investigated the ESCA of diphthalocyanine-lanthanides, Pc_2LnH (Ln = La, Ce, Pr, Nd and Ga) and -actinides, Pc_2An (An = Th and U) [34,35,84]. As in copper(II) phthalocyanine, the nitrogen 1s spectra of these sandwich-type complexes show a single sharp peak [84]. This indicates that the central metal is equivalently surrounded by eight central nitrogen atoms and that the charge density of the central nitrogen atoms is accidently the same as that of the outer-bridging aza nitrogen atoms. They also examined the satellites accompanying lanthanide $3d_{5/2}$ and actinide $4d_{5/2}$ signals [35]. In the case of Pc_2LnH, a shake-up satellite was not observed in the $Pr^{III}(f^2)$ and $Nd^{III}(f^3)$ compounds which have sufficient vacant f-orbitals to receive electrons from ligands, whereas $La^{III}(f^0)$ and $Ce^{III}(f^1)$ compounds showed satellites. Analyzing the data carefully, they concluded that f-orbitals play an important role in the core-ionization process to give a sharp variation in intensity of the satellites.

(v) Conductivity

The superconductivity of organic or inorganic polymers (especially the polymers of one-dimensional stacks) has come of interest. In general, the stacked material consists of electron donors and acceptors. From theoretical models, the high conductivity is known to occur if the donor is planar and is highly polarizable. The phthalocyanine compounds are easily oxidized, and therefore are candidates for donors.

Marks and co-workers did an intensive study of the conductivity of partially oxidized phthalocyanine complexes [30]. The oxidation of Fe, Co, Ni, Cu, Zn, Pt and metal-free phthalocyanines by iodine vapor or solution results in darkly colored solids with a range of stoichiometries (eqn. 12). The exact composition obtained depends on the conditions and hence is a direct measure of the degree of partial oxidation.

$$\mathrm{PcM} + \frac{x}{2}\ \mathrm{I_2} \xrightarrow[\mathrm{M\,=\,Fe,\ Co,\ Ni,\ Cu,\ Zn,\ Pt\ or\ H_2}]{} \mathrm{(PcM)(I)}_x \qquad (12)$$

The reaction is reversible, and iodine can be removed by heating the solids in vacuo. The fact that these materials exhibit truly mixed or partial valency is supported by Raman, iodine-129 Mössbauer and X-ray powder studies [85,86]. Electrical conductivity measurements were performed on pressed pellets using a locally designed four-probe apparatus. The powder data can be fitted to eqn. (13), where E_a is the activation energy for conductivity

$$\sigma = \sigma_0\, e^{E_a/RT} \qquad (13)$$

TABLE 4

Conductivity data * [30]

Compound	x	Room temperature conductivity (Ω^{-1} cm^{-1})	E_a (eV)
(PcCu)I_x	1.71	4.2	0.021
(PcPt)I_x	0.96	2.4	0.016
(PcCo)I_x	2.20	2.3	0.040
(PcNi)I_x	0.56	0.7	0.024
	1.0	0.7	0.036
	1.74	0.8	0.021
	0.60	0.1	0.065
	1.0	0.06	0.082
(PcFe)I_x	1.93	4×10^{-3}	0.127
	2.74	2×10^{-3}	0.070
	3.85	1×10^{-4}	0.254
(Quinolinium) (TCNQ)$_2$		4.0	0.03
Quinolinium	(single crystal)	100	~0
PcNi		1×10^{-11}	1.6
PcCo		2×10^{-10}	1.6
PcFe		2×10^{-10}	

* All measurements employed compressed pellets except as noted.

Values of E_a derived from a least-squares fit are given in Table 4 together with room temperature conductivity values and data for unoxidized phthalocyanines. For all values of x, the conductivities are dramatically increased by iodine oxidation. In particular for $x < 3$, the increases are roughly nine to ten orders of magnitude. In these cases the activation energies are nearly zero (roughly 50-fold less than the parent complex). As shown in Table 4, the pressed pellet conductivities of (PcCu)(I)$_{1.71}$ and (PcPt)(I)$_{0.93}$ are comparable to those of quinoline (TCNQ)$_2$ and have even lower activation energies for conduction. These conductivity results, along with structural and spectroscopic data, indicate that the partial iodine oxidation of phthalocyanines indeed produces a new class of molecular metals. A single crystal of PcNiI exhibits metallic electrical conductivity isotropically [87]. A single crystal EPR study of PcNiI provides evidence that the partial oxidation is predominantly ligand-centered, rather than metal-ion centered.

(vi) Electrochemistry

Redox processes have an important role in biological systems. Studies of the redox processes in metalloporphyrins and metallophthalocyanines which mimic biological systems are important in elucidating the mechanism of dioxygen transport in hemoglobin and myoglobin.

Lever and Wilshire have shown that the potential of a Fe(III)/Fe(II) couple is tuned by such factors as the nature of the porphyrin and its side chains, the axial ligands, ion pairing, solvation and oligomerization of the metalloporphyrin, etc., and that metallophthalocyanines are more sensitive to these factors than metalloporphyrins so that the former system is useful to study such factors [88,89].

Many kinds of reduced species of metallophthalocyanines were reported by Taube and co-workers [90—92]. Some of these species were used in catalytic reactions as EDA (electron donor and acceptor) complexes, e.g. ammonia synthesis [93—96], Fischer—Tropsch synthesis [97,98], and hydroformylation reactions [99]. Lever and co-workers also synthesized oxidized species of first row transition metal phthalocyanines, and the isolated (cation) radical species were characterized by electronic and IR spectra, magnetism, ESR and Mössbauer spectral methods, and oxidative titrations [100]. These compounds were prepared by the reaction of oxidizing agents with PcM(II) complexes (M is a first row transition metal), e.g. when thionyl chloride was mixed with chromium, iron and cobalt phthalocyanines, the oxidized species ($Cl_2M^{III}Pc^{-1}$) were produced. Manganese phthalocyanine when oxidized may be expected to produce a radical product, but a five coordinate complex ($ClMn^{III}Pc^{2-}$) was obtained instead of a radical species. Vanadium, nickel, copper and metal-free phthalocyanines did not react with thionyl chloride and oxidized species were not obtained.

Furthermore, it is important to measure redox potentials of metallophthalocyanine complexes. Because of the poor solubility of these compounds, solution chemistry of these compounds has not proceeded so easily. Rollman and Iwamoto studied reduction potentials of sulfoderivatives of metallophthalocyanines in DMF, but could only measure two or three reduction steps because of the presence of the counter ion Na^+ [101]. On the other hand, Clack et al. measured reduction potentials of some metallophthalocyanines (manganese to zinc, aluminum and magnesium) by generating their reduction product, and oxidising them back to the neutral complex [102]. They could measure four or five reduction potentials using this method. It is known that an electron is added to $e_g - \pi^*$ ligand orbital or vacant *d* orbitals of central metal depending on its redox potentials. They reported that the central metals of the Mn, Fe and Co complexes are reduced together with the reduction of ligand. Oxidation potentials of metallophthalocyanines were also studied [103]. In the case of Fe(II), Co(II) and Ni(II) complexes, the first oxidation occurs at the central metal atom, where as in the case of Cu(II) and Zn(II), ligand oxidation is observed.

Subsequent oxidation occurs at the ligand in all cases. The ligand oxidation potentials are approximately independent of the metal ion for Fe, Co and Ni, but drop to a lower value for Cu and Zn.

Recently, an electrochemical study of iron(II) phthalocyanine was reported in non-aqueous solvents by Lever and Wilshire [89]. They reported that the oxidized product was $Fe^{III}Pc^{2-}$, and the reduced products were

$Fe^{I}Pc^{2-}$ and radical $Fe^{I}Pc^{3-}$ complexes, respectively.

From the results of a cyclic voltammetry study, the oxidation reaction shows a critical dependence on solvent and supporting electrolyte, and the reduction process is also dependent on solvent. The potential of the Fe^{III}-$Pc^{2-}/Fe^{II}Pc^{2-}$ couple shifts according to the order in eqn. (14) with Fe^{II}-Pc^{2-} being most easily oxidized in a tetraethylammonium or lithium chloride solution.

$$ClO_4^- < Br^- < Cl^- \qquad (14)$$

This tendency was explained by the concept that a supporting electrolyte having large electronegativity prefers a higher iron oxidation state. The iron(II) is oxidized more easily in DMF than in pyridine (Py) according to the following trend

$$Py < Me_2SO < DMA \simeq DMF \qquad (15)$$

where Me_2SO and DMA are dimethylsulfoxide and N,N'-dimethylacetamide, respectively. The tendency in eqn. (15) can be explained by the π-acceptor capability of the phthalocyanine ring. Strongly donating solvents act as axial ligands and enhance the back-donation of charge from metal to the phthalocyanine ring. The ferrous state is stabilized by the back-donation of charge, while in the higher oxidation state (ferric state) the back-donation does not seem to be so important (π mechanism). Thus, the iron(II) species is more stabilized in pyridine and is difficult to oxidize.

The reduction reaction, the $Fe^{II}Pc^{2-}/Fe^{I}Pc^{2-}$ couple, is also affected by solvent

$$DMA < Me_2SO < Py \qquad (16)$$

However, the tendency is contrary to that of the oxidation reaction, e.g. the potential is shifted most negatively in pyridine. This solvent effect is explained by the fact that the ferrous state is stabilized by increased donor properties of the solvent, that is, the d_{z^2} energy level of iron is destabilized. Thus, the iron(I) state (an electron added to one of the d_{z^2} orbitals) becomes more unstable (σ mechanism). The relation of π and σ mechanisms with the changing environment of the iron may tune the potentials of the iron redox couples. A similar tendency, though less pronounced, has been observed in iron porphyrins [104,105]. As Lever and Wilshire mentioned, one of the biological roles of cytochromes, in which a protein component can be changed, is to alter the environment of an iron atom to change significantly the potential of the Fe^{III}/Fe^{II} couple [89].

Furthermore, in porphyrin systems a four-coordinate iron(I) complex is available, while a five-coordinate iron(I) complex (low-spin d^7) exists in the phthalocyanine systems. This may be explained by the fact that the fifth ligand is attracted to the iron complex having the electron-withdrawing phthalocyanine ring more strongly than to the iron complex having the electron-donating porphyrin unit. This is also supported by comparing potentials for the Fe^{II}/Fe^{I} couple between iron phthalocyanine and iron tetraphenylporphine complexes. The potential of the porphyrin system is shifted 500 mV more negative than that of the phthalocyanine system [106].

Recently, the electrochemical behavior of surface bound metallophthalocyanine complexes was compared with those of solution and absorbed forms at SnO_2 in Me_2SO and aqueous media [107]. In this system, copper and cobalt tetrasulfophthalocyanines are bound to SnO_2 electrode surfaces modified by either (γ-aminopropyl) triethoxysilane or 3-(N-(2-aminoethyl)aminopropyl) trimethoxysilanes. The voltammetric results for both the copper and cobalt derivatised electrodes suggest that the phthalocyanines can be bound to the electrode surface in more than one fashion with subsequent variations in stability and electrochemical behavior. The stabilities of the bound cobalt and copper derivatives on SnO_2 electrodes may also facilitate their utilization in photoelectrochemical hydrogen production. Since no phthalocyanine solution is needed for photosensitization, multilayered stacks of the chemically modified electrodes on optically transparent substrates may provide higher light capture efficiencies than electrodes in contact with a concentrated phthalocyanine solution.

D. COORDINATION CHEMISTRY

The coordination chemistry of metalloporphyrins has become of interest because of their varied chemical and physical properties being reflected in the biological significance of porphyrinic materials (such as chlorophyll, hemoglobin, cytochromes and vitamin B_{12}) in photosynthesis, gas transport, enzymatic catalysis, metabolic regulation and control, electron transport, etc. [108—110]. This attention has also been given to the coordination chemistry of metallophthalocyanines which have structures similar to metalloporphyrins. However, there have been few studies on coordination aspects of metallophthalocyanine compounds because of their poor solubilities in almost all solvents.

Ercolani et al. synthesized nitrosyl derivatives of Cr-, Mn- and Fe-phthalocyanines and these compounds were characterized by elemental analysis and IR spectra [111—113]. Kinetic and equilibria studies of carbon monoxide binding to iron(II) phthalocyanine were also performed in toluene, but the carbonyl derivative could not be isolated because of the facile loss of carbon monoxide in the absence of a carbon monoxide atmosphere [114]. However, using ruthenium(II) phthalocyanine, a carbonyl derivative was isolated and characterized [115]. Osmium(II) carbonyl phthalocyanine was also prepared and its structure was determined by X-ray diffraction (Fig. 13) [116].

In this structure, a pyridine molecule is situated between two benzene rings of adjacent phthalocyanine ligands, and carbon monoxide is bound perpendicularly to the osmium(II) ion.

The reversibility of dioxygen bonding to iron(II) porphyrin complexes has received attention because they mimic heme [117—120]. Collman et al.

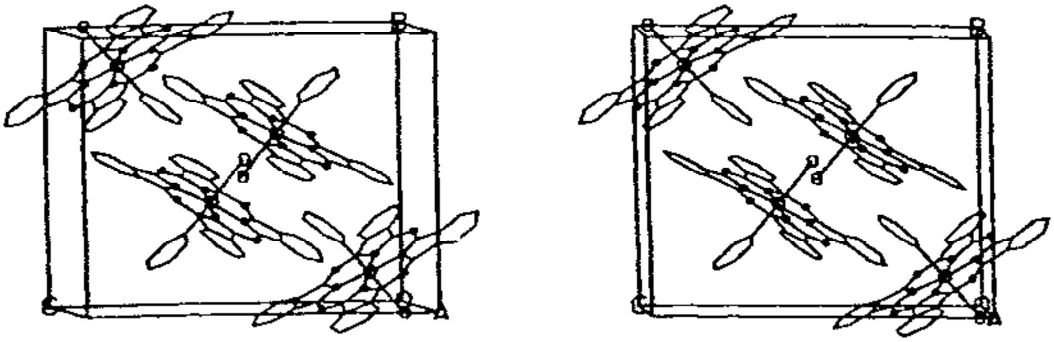


Fig. 13. Structure of PcOs(II)(CO)Py [98].

prepared a "picket-fence" type complex of an iron(II) porphyrin derivative [121]. This compound absorbs dioxygen reversibly at room temperature. James and his co-workers reported that a ruthenium(II) tetraphenylporphine or octaethylporphyrin complex is a reversible dioxygen carrier in dimethylformamide, dimethylacetamide, or pyrrole solvent at room temperature [122].

In the case of metallophthalocyanines, iron(II) tetrasulfophthalocyanine was reported to be a reversible dioxygen carrier in the solid state and to be oxidized in an aqueous solution [10]. On the other hand, Fallab and coworkers reported that iron(II) tetrasulfophthalocyanine reversibly complexes dioxygen in an aqueous solution (Fig. 14) [11].

McLendon and Martell reexamined the reaction of iron(II) tetrasulfophthalocyanine with dioxygen in an attempt to resolve these conflicting conclusions [12]. They supported the contention of Weber and Busch [10] that iron(II) tetrasulfophthalocyanine is irreversibly oxidized by air in an aqueous solution and that a dioxygenated complex is not formed. If the stability of

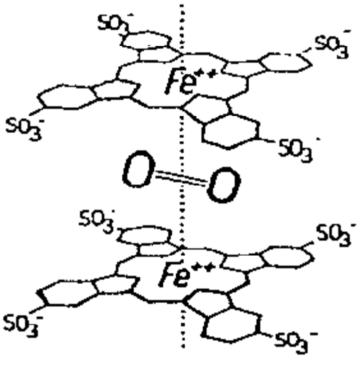


Fig. 14. Proposed structure of dioxygenated iron(II) tetrasulfophthalocyanine.

the dioxygenated iron(II) tetrasulfophthalocyanine depends on the stability of the sandwich-type structure which contains dioxygen between two complexes (Fig. 14), one of the stabilizing factors would be the hydrogen bonding between sulfonyl groups. Then, the concentration of the complex and pH of a solution seem to be important factors, yet no definitive evidence has been reported. About the same time, Collamati and Ercolani reported that iron(II) phthalocyanine can reversibly absorb dioxygen in 96% H_2SO_4 [13].

Furthermore, Ercolani et al. examined kinetically the reaction of iron(II) phthalocyanine with dioxygen in concentrated (96%) sulfuric acid by measuring the change in absorbancy [123]. Analyzing kinetic data, this reaction was found to be a two-step process. The first step is the fast reversible reaction following eqn. (17), while the second step is irreversible and obeys the rate law of eqn. (18).

$$R(\mathrm{mol\ l^{-1}\ s^{-1}}) = 12.1[\mathrm{O_2}][\mathrm{PcFe}]/(1 + 3.92 \times 10^{-2}[\mathrm{O_2}]) \quad (17)$$

$$R(\mathrm{mol\ l^{-1}\ s^{-1}}) = (3.2 \times 10^{-5} + 6.1[O_2])[\mathrm{PcFe}] \quad (18)$$

Considering the kinetic study of the reaction of iron(II) porphyrin with dioxygen, their experimental data show the following reaction mechanism [124]

$$\mathrm{S_2FePc \rightleftharpoons SFePc + S} \quad (19)$$

$$\mathrm{SFePc + O_2 \rightleftharpoons SFePcO_2} \quad (20)$$

$$\mathrm{SFePcO_2 + SFePc \rightleftharpoons (SFePc)_2O_2} \quad (21)$$

where S is HSO_4^- and the charges are omitted for simplicity. The pentacoordinate intermediate (SFePc) which is generated from the reaction of PcFe with HSO_4^- reacts with dioxygen and produces reversibly a 1 : 1 type dioxygenated complex. The reaction of the dioxygenated complex with another SFePc complex results in a 1 : 2 type species. This species is unstable and is decomposed to an iron(III) ion and an oxidized phthalocyanine.

From the result of the solvent dependence of the iron(II)/(III) couple (see Section C, eqn. (15)), it seems more likely that dioxygen uptake is favored only in weakly coordinating solvents such as H_2O and DMF. Recently Collamati [125] has reported the isolation of $(PcFe)_2O_2$.

Lever et al. isolated a dioxygenated manganese phthalocyanine complex and characterized it by elemental analysis, IR (isotopic substitution with oxygen-18), electronic, ESR and mass spectral methods and by magnetism [126]. This compound is a manganese(III) superoxide derivative. When imidazole was added to an aerated DMA solution of this superoxide derivative, a μ-oxy species which is easily reversed to the superoxide derivative under dioxygen was obtained.

As an oxidation product of oxygen with chromium(II) phthalocyanine, both Elvidge and Lever [128], and Ercolani et al. [129] reported Cr(III)-PcOH, confirmed by magnetic data and oxidative titration [129].

More recently Nill et al. [127] identified the oxidation product oxo(phthalocyaninato)chromium(IV) "dimer" using IR and Raman spectra, magnetic data, mass spectra and isotopic oxygen data. Further work is necessary to clarify the oxidation chemistry of chromium phthalocyanine.

ACKNOWLEDGEMENTS

The authors wish to thank the Office of Naval Research for financial support in the writing of this article. We thank Dr. R.L. Bobsein for helpful discussions.

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