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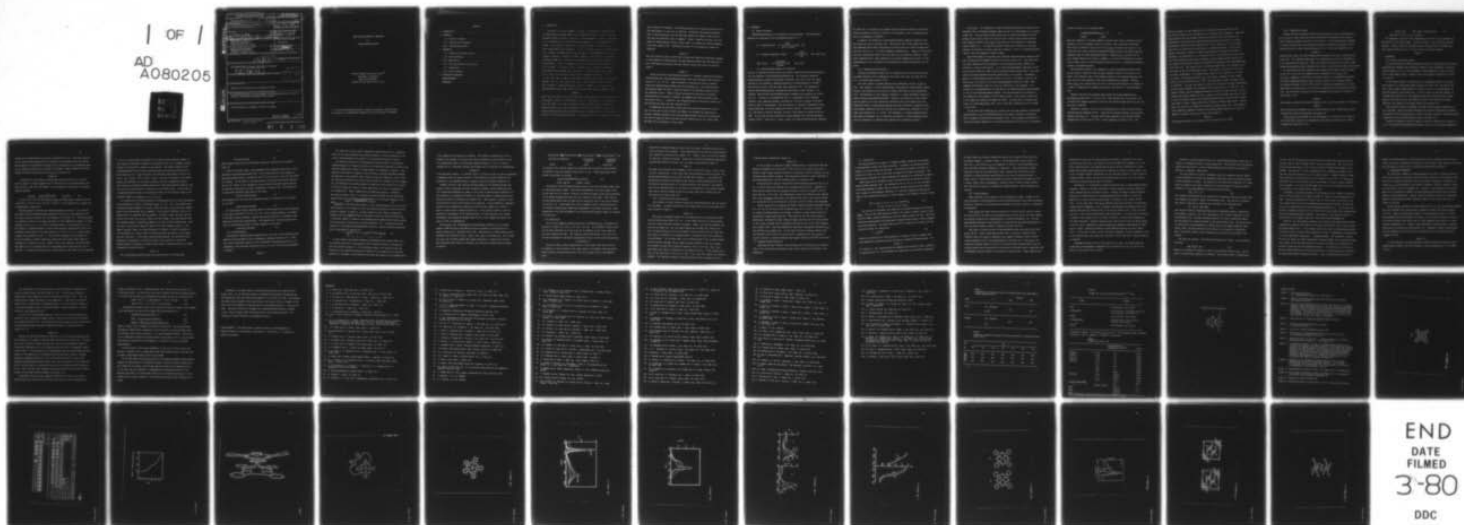
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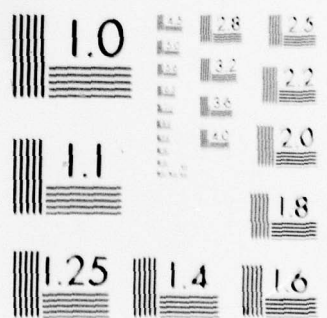
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SOME NEW DEVELOPMENTS IN CHEMISTRY

OF

METALLOPHTHALOCYANINES

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CONTENTS

A. INTRODUCTION	1
B. SYNTHESIS	
(i) General synthesis	3
(ii) Sandwich-type complexes	4
(iii) Supherphthalocyanine	8
C. PROPERTIES	
(i) Visible and infrared spectra	9
(ii) Electrochromism	12
(iii) NMR spectra	15
(iv) X-ray photoelectron spectroscopy	16
(v) Conductivity	18
(vi) Electrochemistry	19
D. COORDINATION CHEMISTRY	23
ACKNOWLEDGEMENT	26
REFERENCES	27

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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 dicyanide by heating in pyridine at 100°C. However, they obtained a blue compound containing copper [2]. Later this blue compound was identified as copper(II)-phthalocyanine. Thus, 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 *pasphtha* (rock oil) and *cyanide* (dark blue). Later Robertson *et al.* elucidated the structures of phthalocyanine and nickel(II), copper(II), and platinum(II) phthalocyanines using single crystal X-ray diffraction analysis (Figure 1).

(Figure 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 [4,5]. Many bioinorganic interests have centered on these compounds because metallophthalocyanines have much the same general structure as the naturally occurring metalloproteins. Of significance are the studies on the copper-

sible addition of dioxygen to iron(II)phthalocyanine in an aqueous solution [10-13]. More improvements 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, Moser, and Thomas with metals complexed since their reports [8,9]. References are given to the synthesis of these new compounds.

(Figure 2)

Since the review of Lever, and the book of Moser and Thomas 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 Figure 3.

(Figure 3)

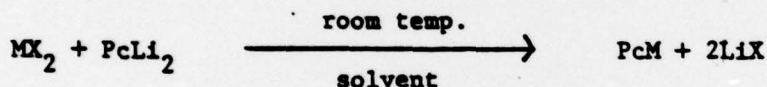
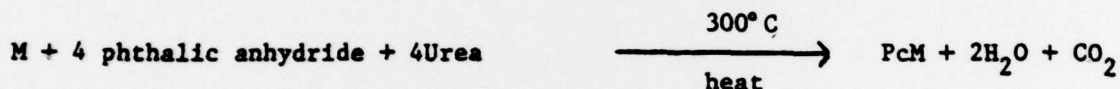
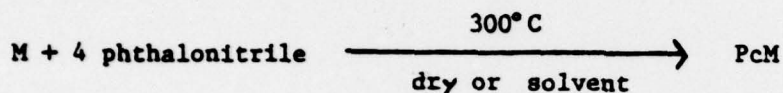
During this period, metallophthalocyanines of f elements (sandwich-type metallophthalocyanines and uranylsuperphthalocyanine) have been synthesized and characterized [16, 17, 29, 30, 31]. Some new methods of studying the nature of phthalocyanine and metallophthalocyanines have been reported; e.g., X-ray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

(1) General synthesis

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



Pc = phthalocyanine dianion, M = metal(II)

The use of catalysts with metal salts and phthalic anhydride has proved successfully 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 by 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 Robertson 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 [52-55].

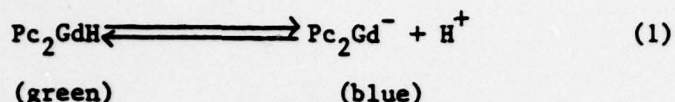
The first complex of unusual geometry was synthesized by Barrett et al. in 1936. This complex, a tin(IV) phthalocyanine containing two phthalocyanine ligands (Pc_2Sn), was prepared by the reaction of $PcSnCl_2$ with $PcNa_2$ in chloronaphthalene [53]. The absorption of this complex is shifted to a longer 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 a 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 679nm, 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 as shown in the following scheme:



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.* and Misumi and Kasuga who concluded that their green complex was monophthalocyanine because the visible spectrum resembles those of normal monophthalocyanines. Mackey *et al.* 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). 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, electrochromism) [59].

Moskelev and Kirin also prepared water soluble sulfonated ammonium salts, $\text{NH}_4[(\text{SO}_3\text{NH}_4)_4\text{Pc}_2\text{M}]$ with $\text{M} = \text{Y}, \text{Gd}, \text{Lu}$ [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 ($\text{An} = \text{Th}, \text{Pa}, \text{U}$) 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 diphtalocyanine 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 diphtalocyanine 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 macrocycles 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 (Figure 4).

(Figure 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 (Figure 5) [65]. Perkin and Whelen also syn-

(Figure 5)

thesized 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].

An uranyl phthalocyanine complex was also prepared from uranyl salts and phthalonitrile but no structure was suggested until experiments by Lux et al. [67].

Lux et al. suggested a structure of the uranyl complex of cyclopentakis(2-iminoisoindolenin)(superphthalocyanine, SPCh₂, Figure 6) based on the following evidence: the compound sublimes at 400 to 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 [29]. The electronic spectrum can be well explained by the electron-gas model of Kuhn (Table 1) [68].

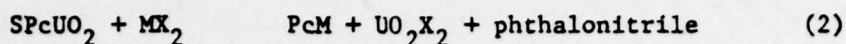
(Figure 6)

This ligand is probably the first 20-annulene with a π -electron system to be realized.

(Table 1)

This structure was determined from an X-ray diffraction study by Marks et al. which confirmed the structure proposed by Lux et al. [30].

Marks et al. also reported that the replacement of the uranyl ion in SpcUO₂ by other metal ions produces the corresponding four-subunit transition metal complex in high yield (equation 2) [31].



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

The mechanistic features of the transmetalation reaction were investigated in most detail for the CuCl_2 system. As shown in Figure 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 infrared.

(Figure 7)

C. PROPERTIES

(i) Visible and infrared spectra

It has been known that infrared absorption spectra of phthalocyanine and metallo-phthalocyanine 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 to 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 to 900 nm region change sharply as a result of the α to β transformation 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 E_a 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].

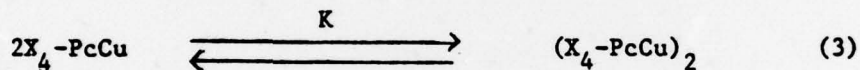
The electronic spectra of monomeric and dimeric phthalocyanine complexes are also different. Hush and Woolsey interpreted the spectral differences of monomeric and dimeric silicon phthalocyanine in terms of excitation coupling of neutral-excitation transitions of the two phthalocyanine rings of the dimer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

Abkowitz and Monahan studied the degree of molecular association of copper-4,4', 4'', 4'''-tetraoctadecylsulfonamidophthalocyanine ($\text{X}_4\text{-PcCu}$, X =octadecylsulfonamide) in

benzene and tetrahydrofuran by electronic and ESR spectra [72]. Electronic spectra in the visible region demonstrates 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].

(Figure 8)

A comparison of the resolved solution dimer spectrum with that of the solid shown in Figure 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.



In the 10^{-6} to 10^{-3} (M) concentration range, the dimerization constants (K) are $(1.58 \pm 0.09) \times 10^4 \text{ (M}^{-1}\text{)}$ and $(1.41 \pm 0.50) \times 10^2 \text{ (M}^{-1}\text{)}$ 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 84) 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 further amounts of DMF (90% v/v), the spectrum

in the $g \approx 2$ region shows the presence of a highly resolved spectrum, similar to that observed by Rollman and Iwamoto in dimethylsulfoxide, due to monomeric species though a very weak $\Delta H=2$ transition is still present. The study of dimeric-tetra-sulfophthalocyanine and its metal derivatives shows the equilibrium constants for dimer formation [74]. From this study, the stability of the dimers is found to be $\text{Cu(II)} > \text{H}_2 > \text{Fe(II)} > \text{VO}^{3+} \sim \text{Zn(II)} > \text{Co(II)}$. 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. $5\text{\AA}$ [73].

The infrared and far infrared 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 infrared active for complexes with D_{4h} symmetry, is known to split into two other infrared 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.

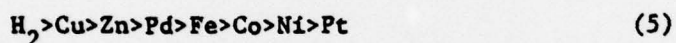
(Table 2)

The corresponding absorption peaks are always shifted in the same order.

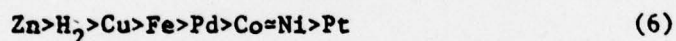


This strongly indicates that the absorption bands are affected by the complexed metal ion.

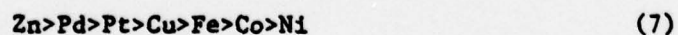
In the far infrared region, three remarkable metal dependent bands exist in each spectrum of metallophthalocyanines [76]. Two of these bands are also obtained in metal-free phthalocyanine, one being at 342 cm^{-1} and the other at 259 cm^{-1} and 289 cm^{-1} as a doublet. On the basis of the same criterion 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:



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



The third group of metal dependent bands (7) which appears with high intensities in the region $150\text{--}200 \text{ cm}^{-1}$ 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:



(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 1.0V may be distinguished in Figure 9.

(Figure 9)

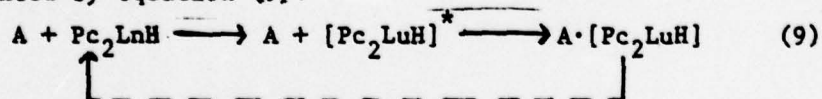
The transition from one type of spectrum to another gives rise to isosbestic points on the optical density plots giving evidence of a direct conversion of one form of diphthalocyanine into another as the electrode potential is varied.

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 Figure 9. Comparison of the spectra in Figures 9a and 9b reveals a profound similarity between the spectrum of the protonated form, Pc_2LuH , in solution (Figure 9b, curve 2) and the absorption spectrum of the film on the electrode at a potential of 0.0V (Figure 9a), and similarity also exists between the spectrum of the ionized form, $[\text{Pc}_2\text{Lu}]^-$, in solution (Figure 9b, curve 1) and the spectrum of the film at a potential of -0.8V (Figure 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:

$$[\text{Pc}_2\text{Lu}]^- + \text{H}^+ \rightleftharpoons [\text{Pc}_2\text{LuH}] \quad (8)$$

Comparison of the absorption spectrum of the diphthalocyanine film at an electrode potential of 1.0V (Figure 9a) with the absorption spectrum of the film of the molecular complex, $[\text{Pc}_2\text{LuH}] \cdot \text{I}_2$, on glass (Figure 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 equation (9):



In this equation the asterick 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

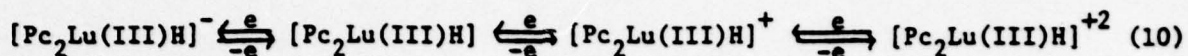
of the complex as the potential is reduced. The validity of equation (9) is confirmed by the presence of a loop in the curves relating the optical density at the 673 nm absorption band to the electrode potential (Figure 10, curve 1), which is probably due to a difference between the pathways for the formation and decomposition

(Figure 10)

of the molecular complex. In contrast, curve 2 in Figure 10 does not show a hysteresis, in agreement with the complex identity of the forward and reverse pathways in the ionization of the dipthalocyanine at negative electrode potentials (Reaction 8).

Moskalev and Kirin also observed electrochromism for the dipthalocyanine 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 dipthalocyanine complexes was studied by Nicholson and Galiardi [78]. They prepared a display in which $\text{Pc}_2\text{Lu(III)H}$ 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 alphanumeric.

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:



one-electron reduction

one-electron
oxidationtwo-electron
oxidation

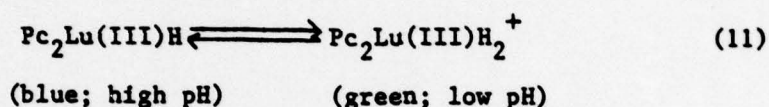
violet

blue

green

yellow-red

In equation (10), the blue species is $\text{Pc}_2\text{Lu(III)H}$ and the green is $[\text{Pc}_2\text{Lu(III)H}]^+$, as opposed to the other groups's results [16, 17, 48]. Corker et al. also interpreted the pH effect as follows:



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 equation (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.

(iii) NMR spectra

In the proton magnetic resonance spectrum of $\text{PcGa(OSi(C}_2\text{H}_5)_3)_2$, multiplets are centered at $\delta(\text{ppm})$ 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.

(Illustration 1)

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.

These metal complexes having the ring current and vacant coordination sites 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 *et al.* reported NMR studies of lithium, zinc, and uranium phthalocyanines (Table 3).

(Table 3)

The high field multiplets were assigned to the β ring protons (*e.g.*, 7.94 for PcZn , 7.09 for $(\beta\text{-CH}_3)_4\text{PcZn}$). 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 described 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 Figure 11.

(Figure 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) (Figure 11a). The 1s binding energies of the aza nitrogens in both structures are so closed that they cannot be observed as two separate peaks (a limitation due to the resolution of spectrometer). On the other hand, the 1s binding energy of the nitrogen bonding with the central hydrogen atom is higher than the energies of the aza nitrogens. Two nitrogen 1s peaks with a relative intensity ratio of 0.33 [$2\text{N}_1 : (2\text{N}_2 + 4\text{N}_3)$] (see figure 11a) should be observed for the bonded structure. In the bridged structure, on the other hand, a ratio of 1.0 [$4\text{N}_1 : (2\text{N}_2 + 2\text{N}_3)$] (see figure 11b) should be observed. The observed nitrogen 1s spectrum indicates that the bonded structure

of phthalocyanine predominates (Figure 12).

(Figure 12)

In the nitrogen 1s 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]. 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.

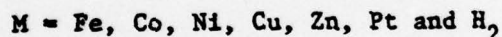
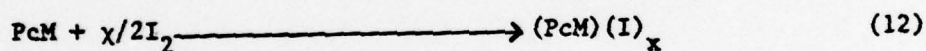
Tsutsui *et al.* also investigated the ESCA of diphtalocyanine-lanthanides Pc_2LnH ($Ln = La, Ce, Pr, Nd, \text{ and } Gd$) and -actinides Pc_2An ($An = Th \text{ and } U$) [34,35,84]. As in copper(II) phthalocyanine, the nitrogen 1s spectra of these sandwich-type complexes show a single sharp peak [84]. 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 accidentally 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 et al. 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 (equation 12). The exact composition obtained depends on the conditions and hence is a direct measure of the degree of partial oxidation.



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 fit to equation (13), where E_a is the activation energy for conductivity.

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

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

(Table 4)

all values of χ , the conductivities are dramatically increased by iodine oxidation. In particular for $\chi < 3$, 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 $(\text{PcCu})(\text{I})_{1.71}$ and $(\text{PcPt})(\text{I})_{0.93}$ are comparable to those of $(\text{quinoline})(\text{TCNQ})_2$ 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 electron paramagnetic resonance study of PcNiI provides evidence that the partial oxidation is predominately 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 et al. 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 et al. [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 et al. also synthesized oxidized species of first row transition metal phthalocyanines, and the isolated species were characterized by electronic and infrared spectra, magnetism, ESR and Mössbauer spectral methods, and oxidative titrations [100]. These compounds were

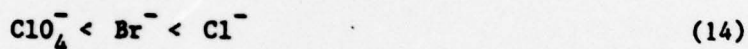
prepared by the reaction of oxidizing agents with $PcM(II)$ complexes (M is a first row transition metal e.g., when thionyl chloride was mixed with chromium, iron, and cobalt phthalocyanines, the oxidized species were produced ($Cl_2M(III)Pc(-1)$). Manganese phthalocyanine when oxidized may be expected 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 existence 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 subsequent reductions and oxidation 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 eg- π^* ligand orbital or vacant d orbitals of central metal depending on its redox potentials. Carefully analyzing data, they reported that the central metals of Mn, Fe, and Co complexes are reduced among these complexes accompanying 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 occur 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 on an iron(II)phthalocyanine complex was reported in a nonaqueous solvent by Lever *et al.* [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 equation (14) with Fe(II)Pc(-2) being most easily oxidized in a tetraethylammonium or lithium chloride solution.



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:



where Me_2SO and DMA are dimethylsulfoxide and N,N'-dimethylacetamide, respectively. The tendency in equation (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 be oxidized.

The reduction reaction - the Fe(II)Pc(-2)/Fe(I)Pc(-2) couple - is also affected by solvent:



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 dz^2 energy level of iron is unstabilized. Thus, the iron(I) state (an electron added to one of the dz^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 *et al.* mentioned, one of the biological roles of cytochrome, in which a protein component can be changed, is to alter the environment of an iron atom to significantly change the potential of the Fe(III)/Fe(II) couple [89].

Futhermore, in porphyrin systems a four-coordinate iron(I) complex is available, while a five-coordinate iron 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 tetraphthnylporphine 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 the surface bound metallophthalocyanine complexes was compared with those of the 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 derivatives 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 come of interest because of their varied chemical and physical properties being reflected in the biological significance of porphyrinic materials (such as chlorophyll, hemoglobin, cytochrome, and vitamin B₁₂) 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 infrared 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 an X-ray diffraction study (Figure 13) [116].

(Figure 13)

In this structure a pyridine molecule is situated between two benzene rings of 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. 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 et al. reported that iron(II) tetrasulfophthalocyanine reversibly complexes dioxygen in an aqueous solution (Figure 14) [11].

(Figure 14)

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 Bush 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 the dioxygenated iron(II)tetrasulfophthalocyanine depends on the stability of the sandwich-type structure which contains dioxygen between two complexes (Figure 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 definite 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].

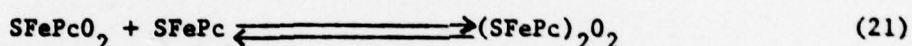
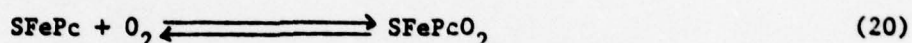
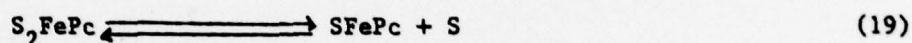
Furthermore, Ercolani et al. examined kinetically the reaction of iron(II) phthalocyanine with dioxygen in concentrated (96%) sulfuric acid by measuring the

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 equation (17), while the second step is irreversible and obeys the rate law of equation (18).

$$R(\text{mol l}^{-1}\text{s}^{-1}) = 12.1[\text{O}_2][\text{PcFe}]/(1 + 3.92 \times 10^{-2}[\text{O}_2]) \quad (17)$$

$$R(\text{mol l}^{-1}\text{s}^{-1}) = (3.2 \times 10^{-5} + 6.1[\text{O}_2])[\text{PcFe}] \quad (18)$$

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



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, equation (15)), it seems more likely that dioxygen uptake is favored only in weakly coordinating solvents such as H_2O and DMF.

On the other hand, Lever *et al.* isolated an dioxygenated manganese phthalocyanine complex and characterized it by elemental analysis, infrared (isotopic substitution with oxygen-18), electronic, ESR and mass spectral methods and by magnetism [125]. It was found that 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.

Futhermore, the oxygen adduct of chromium phthalocyanine was reported by Nill et al. [126]. As the oxidation product of chromium phthalocyanine, Ercolani et al. and Elvidge and Lever had reported the formula of Cr(III)PcOH [127,128]. From infrared and Raman spectra, magnetic data, mass spectra, and isotopic effect of oxygen, on the other hand, this compound is characterized as an oxo(phthalocyaninato) chromium (IV) dimer. During the reaction of dioxygen with chromium(II)phthalocyanine, dioxygen is split, and the oxygen atoms form double bonds to one chromium atom each. The chromium is thereby oxidized to the oxidation state IV.

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REFERENCES

1. A. Braun and J. Tcherniac, *Ber.*, 40 (1907) 2709.
2. H. de Diesbach and E. von der Weid, *Helv. Chim. Acta*, 10 (1927) 886.
3. C. E. Dent, R. P. Linstead and A. R. Lowe, *J. Chem. Soc.*, (1934) 1033.
4. R. P. Linstead and J. M. Robertson, *J. Chem. Soc.*, (1936) 1195.
5. J. M. Robertson and I. Woodward, *J. Chem. Soc.*, (1937) 219.
6. J. M. Robertson, *J. Chem. Soc.*, (1935) 615.
7. J. M. Robertson and I. Woodward, *J. Chem. Soc.*, (1940) 36.
8. A. B. P. Lever, *Advances in Inorganic Chemistry and Radiochemistry*, 7 (1965) 27.
9. a) F. H. Moser and A. L. Thomas, *Phthalocyanines*, ACS Monograph 157, Reinhold Publishing Corporation, New York, 1963. (b) B. D. Berezin, *Coordination Compounds of Porphyrins and Phthalocyanine (Russ.)*, Nauka, Moscow, USSR, 1978.
10. J. H. Weber and D. H. Busch, *Inorg. Chem.*, 4 (1965) 469.
11. D. Vonderschmitt, K. Bernauer and S. Fallab, *Helv. Chim. Acta*, 48 (1965) 951.
12. G. McLendon and A. E. Martell, *Inorg. Chem.*, 16 (1977) 1812.
13. I. Collomati and C. Ercolani, *Inorg. Nucl. Chem. Lett.*, 12 (1976) 799.
14. I. S. Kirin and P. N. Moskalev, *Zh. Neorg. Khim.*, 16 (1971) 3179.
15. P. N. Moskalev and I. S. Kirin, *Zh. Neorg. Khim.*, 15 (1970) 13.
16. I. S. Kirin, P. N. Moskalev and Yu. A. Moskalev, *Russ. J. Inorg. Chem.*, 10 (1965) 1065.
17. S. Misumi and K. Kasuga, *Nippon Kagaku Zasshi*, (Japanese) 92 (1971) 335.
18. Yu. A. Buslaev, A. A. Kuznetsova and L. F. Goryanov, *Akad. Nauk SSSR, Neorg. Mater.*, 3 (1967) 1701.
19. V. F. Borodkin, M. I. Alyanov, F. P. Cnegireva, V. G. Shishkin and A. P. Snegireva, *U.S.S.R. Pat.* 478016.
20. H. Przywarska-Boniecka, *Roczniki Chem.*, 40 (1966) 1627.
21. G. Pfrepper, *Z. Chem.*, 10 (1970) 76.
22. K. Yoshihara, G. K. Wolf and F. Baumgaertner, *Radiochim. Acta*, 21 (1974) 96.

23. M. Keen and B.W. Malerki, J. Inorg, Nucl. Chem., 27 (1965) 1311.
24. F. Lux, D. Dempf and D. Graw, Angew Chem., 80 (1968) 792; Angew, Chem. (Int. Ed. Engle.), 7 (1968) 819.
25. F. Lux, D. Brown, D. Dempf, R.D. Fischer and W. Hagenberg, Angew, Chem., 81 (1969) 913.
26. F. Lux, F. Ammentorp-Schmidt, D. Dempf, D. Gran and W. Hagenberg, Radiochim. Acta., 14 (1970) 57.
27. W. Hagenberg, Dissertation (Technische Universitat Munchen, 1973).
28. P.N. Moskalev and G.N. Shapkin, Radiokhimiya, 19 (1977) 356.
29. F. Lux, Proceedings of the Tenth Rare Earth Research Conference, Carefree, Arizona, May 1973, Vol. II, p. 871.
30. V.W. Day, T.J. Marks and W.A. Wachter, J. Am. Chem. Soc., 97 (1975) 4519.
31. T.J. Marks and D.R. Stojakovic, J. Am. Chem. Soc., 100 (1978) 1695.
32. Y. Niwa, H. Kobayashi and T. Tsuchiya, J. Chem. Phys., 60 (1974) 799.
33. Y. Niwa, H. Kobayashi and T. Tsuchiya, Inorg. Chem. 13 (1974) 2891.
34. K. Tatsumi, K. Kasuga and M. Tsutsui, J. Am. Chem. Soc., 101 (1979) 484.
35. R. Dubois, J.C. Carver and M. Tsutsui, J. Coord. Chem., 6 (1976) 123.
36. T. Sekiguchi and Y. Bansho, Shikizai Kyokaishi (Japanese), 37 (1964) 191.
37. F.H. Moser, Kirk-Othmer Eneycl. Chem. Technol. 2nd Ed., 15 (1968) 488.
38. S.P. Potnis and A.B. Daruwala, Paintindia, 19 (1969) 21.
39. E.R. Inman, Rv. Progr. Coloration Relat, Top., 2 (1971) 62.
40. K. Heinle, Farbe Sack, 73 (1967) 735.
41. Y. Bansho, Yuki Gosei Kagaku Koykai Shi (Japanese), 30 (1972) 514.
42. H.J. Hovel, Solar Cells, Vol. II in the series Semiconductors and Semimetals, Academic, New York, 1975.
43. F. Gutman and L.E. Lyons, Organic Semiconductors, Wiley, New York, 1967.
44. G. Barnhart, U.S. Pat. 2602800.
45. J.D. Compton, U.S. Pat. 2668171.

46. V.F. Borodkin and K.V. Usacheva, Izvest. Vysshikh Ucheb. Zavedeni, Khim, i Khim. Tekhnol., (1958) 142.
47. N. Fukada, Nippon Kagaku Zasshi, 75 (1954) 1141.
48. S.A. Borisenkova, A.S. Erokhin, V.A. Novikov and A.P. Rudenko, J. Org. Chem. USSR. 11 (1975) 1998.
49. S.A. Borisenkova, L.M. Il'ina, E.V. Seonova and A.P. Rudenko, Zh. Organ. Khim., 9 (1973) 1827.
50. V.F. Borodkin, Yu. G. Erykalov and K.V. Usacheva, Zh. Prikl. Khim., 29 (1956) 1606.
51. V.I. Klyuev. M.I. Al'yonov and L.S. Shiryaev, Izv. Vuzov, Ser. Khim. i Khim. Tekhnol., 12 (1969) 1106.
52. R.P. Linstead, J. Chem., Soc., (1934) 1016.
53. P.A. Barrett, C.E. Dent and R.P. Linstead, J. Chem., Soc., (1936) 1719.
54. P.A. Barrett, D.A. Frye and R.P. Linstead, J. Chem., Soc., (1938) 1157.
55. J.M. Robertson, J. Chem., Soc., (1936) 195.
56. W.E. Bennett, D.E. Broberg and N.C. Baenziger, Inorg. Chem. 12 (1973) 930.
57. I.S. Kirin, P.N. Moskalev and M.J. Ivannikova, Russ. J. Inorg. Chem., 12 (1967) 497.
58. A.G. MacKay, J.F. Boas and G.J. Troup, Aust. J. Chem., 27 (1974) 955.
59. G.A. Corker, B. Grant and N.J. Clecak, J. Elektrochem. Soc., 126 (1979) 1339.
60. P.N. Moskalev and I.S. Kirin, Russ. J. Inorg. Chem., 16 (1971) 57.
61. P.N. Moskalev and I.S. Kirin, Russ. J. Inorg. Chem., 15 (1970) 7.
62. A. Gieren and W. Hoppe, J. Chem. Soc., Chem. Commun. (1971) 413.
63. K. Kasuga, M. Tsutsui, R.C. Pettersen, G. Pepe, N. van Opdenbosh and E.F. Meyer, Jr., J. Am. Chem. Soc., (submitted).
64. F. Baumann and B. Binert, German Pat. 83939; U.S. Pat. 2768867; British Pat. 687655.
65. G. Barnhalt and B.F. Skiles, U.S. Pat. 2772284; British Pat. 745359.
66. M.A. Perkins and M.S. Whelen, U.S. Pat. 2782207.
67. M.K. Friedel, B.F. Hoskins, R.L. Martin and S.A. Moason, J. Chem. Soc. Chem. Commun., (1970) 400.

68. H. Kuhn, Fortschr. Chem. Org. Naturstoffe (Wein), 17 (1959) 404. Insert for L the length of the 20 membered ring.
69. A.A. Ebert and H.B. Gotilieb, J. Am. Chem. Soc., 74 (1952) 2806.
70. A.E. Lucia and F.D. Verderame, J. Chem. Phys., 48 (1968) 2674.
71. N.S. Hush and I.S. Woolsey, Mol. Phys., 21 (1971) 465.
72. M. Abkowitz and A.R. Monahan, J. Chem. Phys., 58 (1973) 2281.
73. P.D.W. Boyd and T.D. Smith, J. Chem. Soc., (1972) 839.
74. H. Sigel, P. Waldmeier and B. Prijs, Inorg. Nuclear Chem. Letters, 7 (1971) 161.
75. T. Kobayashi, F. Kurokawa, N. Uyeda and E. Saito, Spectrochim. Acta A, 26 (1970) 1305.
76. T. Kobayashi, Spectrochim. Acta A, 26 (1970) 1313.
77. P.N. Moskalev and I.S. Kirin, Russ. J. Phys. Chem. 46 (1972) 1019.
78. M.M. Nicholson and R.V. Galiardi, Gov. Rep. Announce. Index (U.S.), 77 (1977) 112.
79. J.N. Esposito, L.E. Sutton and M.E. Kenney, Inorg. Chem. 6 (1967) 1116.
80. J.A. Eldridge, A.B.P. Lever and M.P. Sammes, Advan. Inorg. Chem. Radiochem., 7 (1965) 82.
81. J.E. Maskasky and M.E. Kenny, J. Am. Chem. Soc., 95 (1973) 1443.
82. W. D. Horrocks, Jr. and E.G. Hove, J. Am. Chem. Soc., 100 (1978) 4386.
83. J. Berkowitz, J. Chem. Phys., 70 (1979) 2819.
84. K. Tatsumi and M. Tsutsui (unpublished results).
85. A. Gleizes, T.J. Marks and J.A. Ibers, J. Am. Chem. Soc., 97 (1975) 3545.
86. J.L. Peterson, C.J. Scramm, B.M. Hoffman and T.J. Marks, J. Am. Chem. Soc., 99 (1977) 286.
87. C.J. Schramm, D.R. Stojakovic, B.M. Hoffman and T.J. Marks, Science, 200 (1978) 47.
88. A.B.P. Lever and J.P. Wilshire, Can. J. Chem., 54 (1976) 2514.
89. A.B.P. Lever and J.P. Wilshire, Inorg. Chem., 17 (1978) 1145.
90. R. Taube, H. Munke and J. Peterson, Z. Anorg. Allg. Chem., 390 (1972) 257.

91. R. Taube and H. Dreves, *Angew. Chem.*, 7 (1967) 313.
92. E. Fluck and R. Taube, *Develop. Appl. Spectrosc.*, 8 (1970) 244.
93. S. Naito and K. Tamaru, *Z. Phys. Chem.*, 94 (1975) 150.
94. M. Ichikawa, M. Soma, T. Onishi and K. Tamaru, *Bull. Chem. Soc. Jpn.*, 41 (1968) 1739.
95. S. Mizuo, M. Ichikawa, M. Soma, T. Onishi and K. Tamaru, *J. Phys. Chem.*, 73 (1969) 1174.
96. S. Mizuo, M. Ichikawa, M. Soma, T. Onishi and K. Tamaru, *J. Phys. Chem.*, 73 (1969) 1174.
97. M. Ishikawa, M. Sudo, M. Soma, T. Onishi and K. Tamaru, *J. Am. Chem. Soc.*, 91 (1969) 1538.
98. K. Watanabe, T. Kando, M. Soma, T. Onishi and K. Tamaru, *Proc. Roy. Soc. A*, 333 (1973) 511.
99. H. Edain, *U.S. Pat.* 3984478.
100. J.F. Myers, G.W.R. Canham and A.B.P. Lever, *Inorg. Chem.*, 14 (1975) 461.
101. L.D. Rollmann and R.T. Iwamoto, *J. Am. Chem. Soc.*, 90 (1968) 1455.
102. D.W. Clack, N.S. Hush and I.S. Woolsey, *Inorganica Chimica Acta*, 19 (1976) 129.
103. A. Wolberg and J. Mansassen, *J. Am. Chem. Soc.*, 92 (1970) 2982.
104. L.A. Constant and D.G. Davis, *Anal. Chem.*, 47 (1975) 2253.
105. K.M. Kadish and L.A. Bottomley, *J. Am. Chem. Soc.*, 99 (1977) 2380.
106. D. Lexa, M. Monenteaux and J. Mispelter, *Biochim. Biophys. Acta*, 338 (1974) 151.
107. V.R. Shepard, Jr. and N.R. Armstrong, *J. Phys. Chem.*, 83 (1979) 1268.
108. G.S. Marks, "Heme and Chlorophyll," Van Nostrand, Princeton, N.J., 1969, p. 140.
109. J.E. Falk, "Porphyrins and Metalloporphyrins," Elsevier, New York, 1964.
110. G.A. Taylor and M. Tsutsui, *J. Chem. Ed.*, 52 (1975) 715.
111. C. Ercolani and C. Neri, *J. Chem. Soc. A*, (1967) 1710.
112. C. Ercolani, C. Neri and G. Sartori, *J. Chem. Soc. A*, (1968) 2123.

113. I. Mochida, K. Takeyashi, H. Fujitsu and K. Takeshita, *J. Mol. Catal.*, 3 (1977) 417.
114. D.V. Stynes and B.R. James, *J. Am. Chem. Soc.*, 96 (1974) 2733.
115. S. Omiya, Dissertation (Texas A&M University, 1978).
116. S. Omiya, M. Tsutsui, D.L. Cullen, E.F. Meyer, Jr. and I. Bernal, *Inorg. Chem.*, (submitted).
117. J.J. Weiss, *Nature*, 202 (1964) 83; 203 (1964) 183.
118. L. Pauling, *Nature*, 203 (1964) 182.
119. M. Zerner, M. Gouterman and H. Kobayashi, *Theor. Chim. Acta.*, 6 (1966) 363.
120. A. Rossi-Fanelli and E. Antonini, *Arch. Biochem. Biophys.*, 72 (1957) 243.
121. J.P. Collman, R.R. Gagne, T.R. Halbert, J.C. Marchon and C.A. Reed, *J. Am. Chem. Soc.*, 95 (1973) 7868.
122. N. Farrell, D.H. Dolphin and B.R. James, *J. Am. Chem. Soc.*, 100 (1978) 324.
123. C. Ercolani, F. Monacelli and G. Rossi, *Inorg. Chem.*, 18 (1979) 712.
124. J. Almog, J.E. Bladwin and J. Huff, *J. Am. Chem. Soc.*, 97 (1975) 227; C.J. Weschler, D.L. Anderson and F. Basolo, *J. Am. Chem. Soc.*, 97 (1975) 6707; E. Tsuchida, K. Honda and H. Sata, *Inorg. Chem.*, 15 (1976) 352, and the references cited therein.
125. A.B.P. Lever, J.P. Wilshire and S.K. Quan, *J. Am. Chem. Soc.*, 101 (1979) 3668.
126. K.H. Nill, F. Wasgestian and A. Pfeil, *Inorg. Chem.*, 18 (1979) 564.
127. J.A. Elridge and A.B.P. Lever, *J. Chem. Soc.*, (1961) 1257.
128. C. Ercolani, C. Neri and P. Porta, *Inorg. Chim. Acta*, (1967) 415.

TABLE 1

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

Cmpd	L	$\lambda_{\max}(\text{nm})$	
		calc	exp
Pc_2U	16 - annulene		
	21.6Å [•]	645	643
SPcUO_2	20 - annulene		
	27Å [•]	910	915

TABLE 2

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

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

TABLE 3

¹H NMR data for PcM and SPcM derivatives*, ** [31]

Compd	¹ H NMR
PcZn	9.50 (8 H,m), 7.94 (8 H,m)
(β -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)
(β -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 C₆D₆ at 30°C. *** 2% Me₂SO-d₆ added to enhance solubility, Key: s = singlet; d = doublet, m = multiplet.

TABLE 4

Conductivity data* [30]

		Room Temperature Conductivity ($\Omega^{-1}\text{cm}^{-1}$)	E _a (ev)
(PcCu)I _x	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	4x10 ⁻³	0.127
	2.74	2x10 ⁻³	0.070
	3.85	1x10 ⁻⁴	0.254
(Quinolinium)(TCNQ) ₂		4.0	0.03
"	(single crystal)	100	~0
PcNi		1x10 ⁻¹¹	1.6
PcCo		2x10 ⁻¹⁰	1.6
PcFe		2x10 ⁻¹⁰	

* All measurements employed compressed pellets except as noted.

A Legend for an Illustration

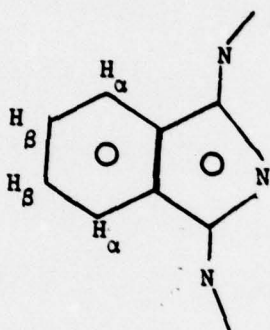
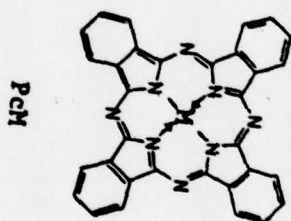
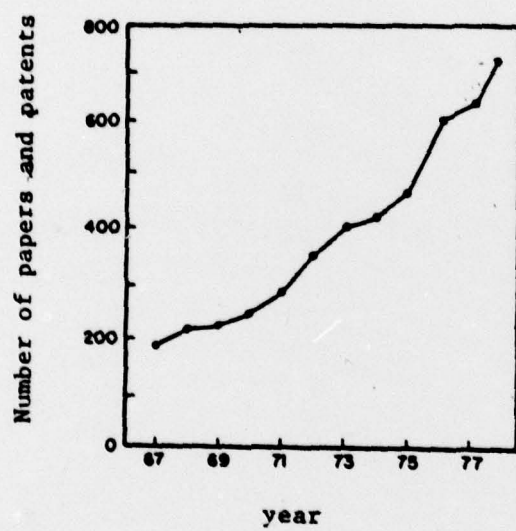


FIGURE CAPTIONS

- Figure 1. Metallophthalocyanine.
Pc = phthalocyanine dianion, M = metal(II) ion.
- Figure 2. Number of papers and patents published during the past decade.
From Chemical Abstracts.
- Figure 3. Metals for which phthalocyanine complexes have been made: O, metallophthalocyanines mentioned by Lever [8], @, more recent metallophthalocyanines. Some of lanthanide and actinide phthalocyanines have been mentioned by Lever, but the characterization of these compounds was not complete. References for the new metals are as follows: Sc[14], Y[15], Ln[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].
- Figure 4. Elevation view of bisphthalocyaninatoneodymium(III) [63].
- Figure 5. Proposed metallophthalocyanine precursors.
M = Ni(II) and Cu(II).
- Figure 6. Structure of uranylsuperphthalocyanine [30].
- Figure 7. The reaction of uranylsuperphthalocyanine with CuCl_2 in 300/1 = 1-chloronaphthalene/DMF at 75°C [31].
- Figure 8. Absorption spectra of $\text{X}_4\text{-PcCu}$: -, monomer molecular in benzene; ---, dimer molecule in benzene, ---, solid phase [73].
- Figure 9. a) Absorption spectra of a film of lutetium-diphthalocyanine on the electrode at different electrode potentials in 0.1M 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 $[\text{Pc}_2\text{Lu}]^-$ at pH 11.5; 2) protonated form Pc_2LuH at pH 4; 3) absorption spectrum of a film of the molecular complex $[\text{Pc}_2\text{LuH}]\text{I}_2$ on glass [77].
- Figure 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].
- Figure 11. The molecular structures of PcH_2 : (a) bonded PcH_2 ; (b) bridged PcH_2 .
- Figure 12. The nitrogen 1s spectrum for PcH_2 using MgK α x-ray. The spectrum is deconvoluted into overlapping Gaussians [32].
- Figure 13. Structure of PcOs(II)(CO)Py [98].
- Figure 14. Proposed structure of dioxygenated iron(II) tetrasulfophthalocyanine.



Phthalocyanine



Tautaul Fig. 3

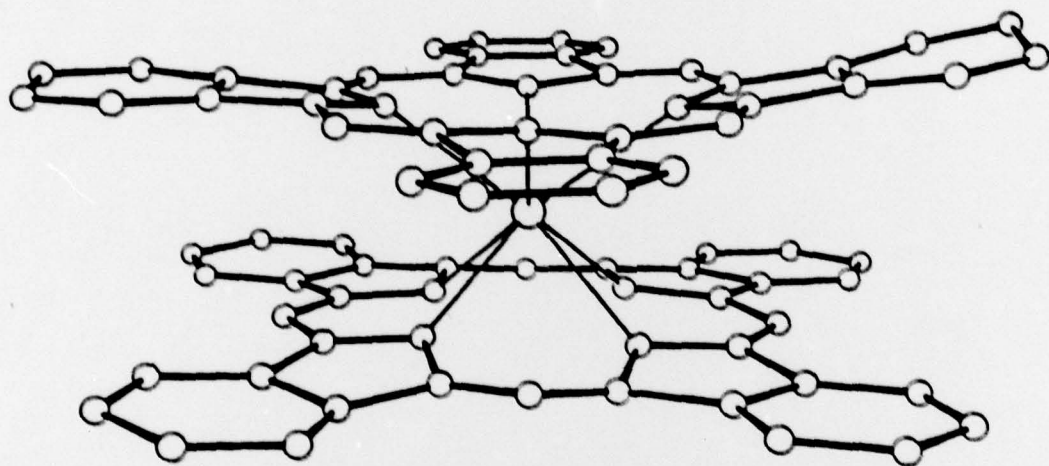
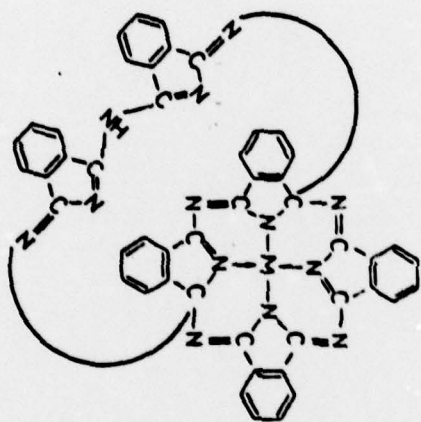
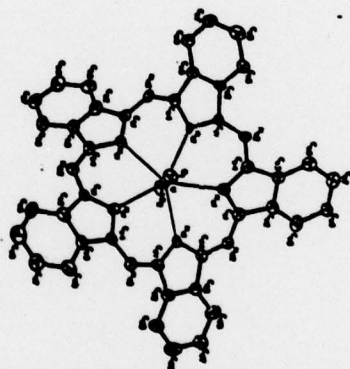


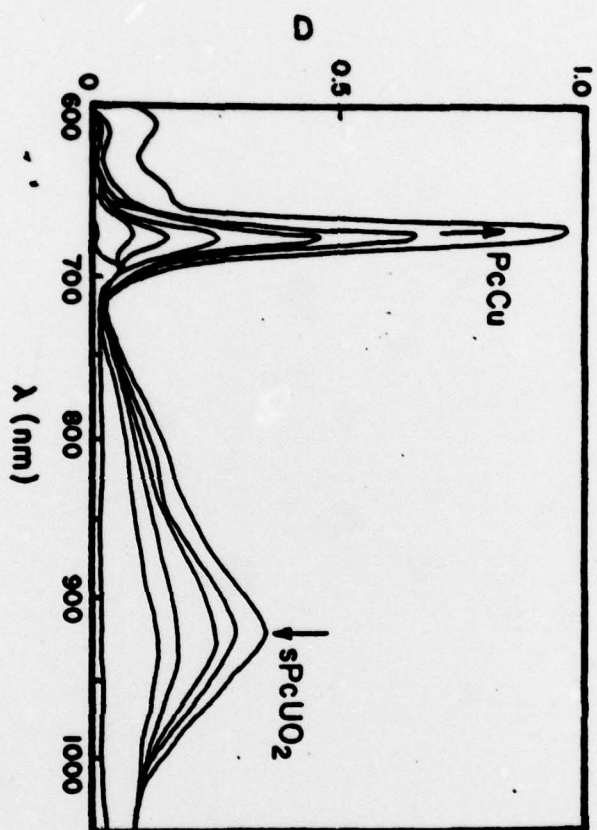
Fig. 4

M. Tautou 24. 5

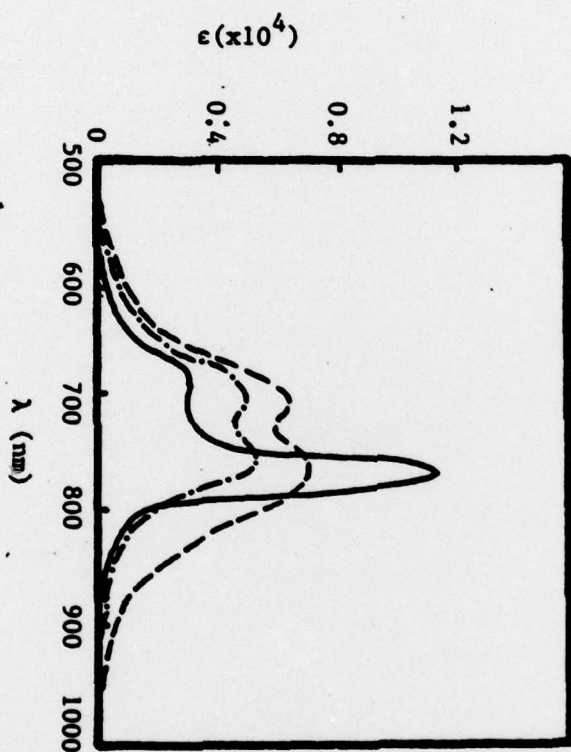




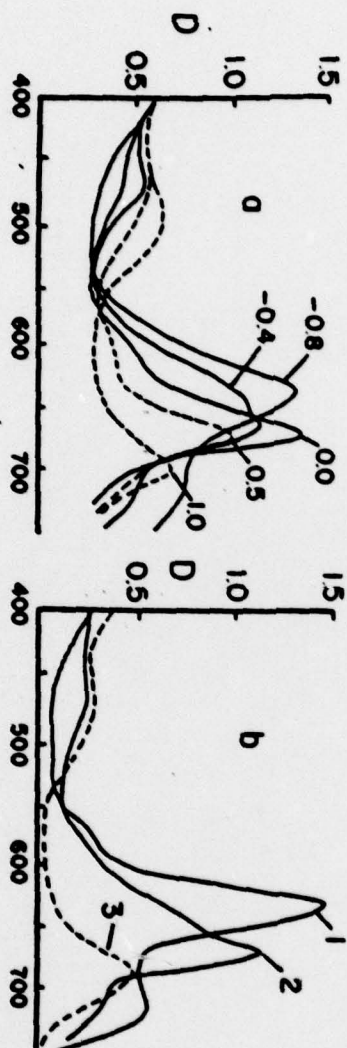
m. Tautau Fig. 6



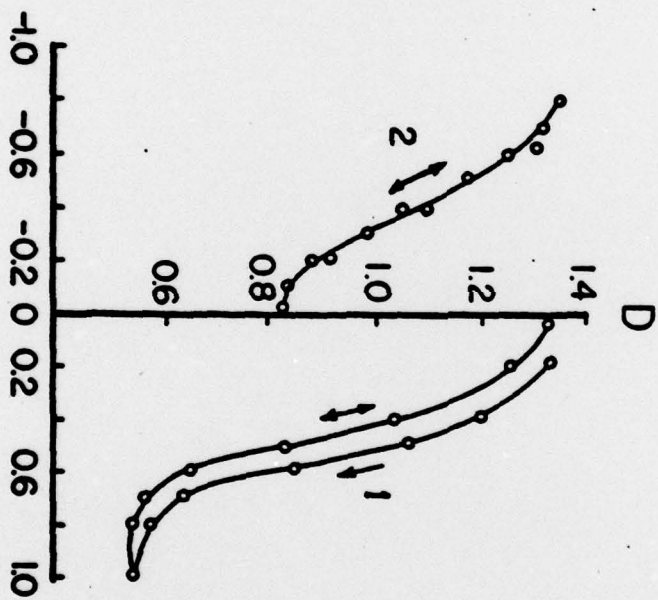
m. Teutoul. 2y. 7



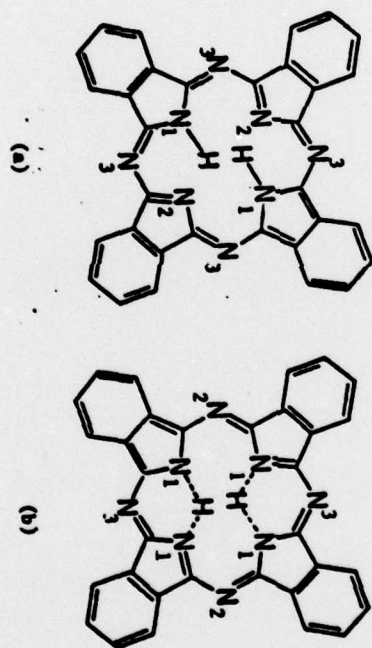
И. И. Ионов



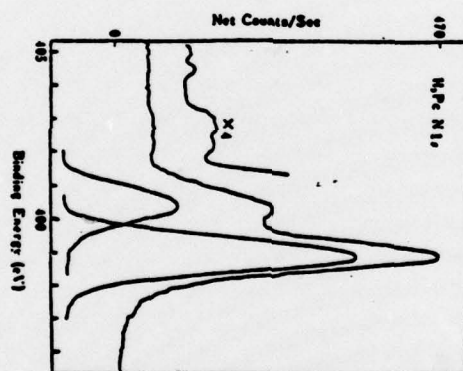
Mr. Tautou, Fig. 9



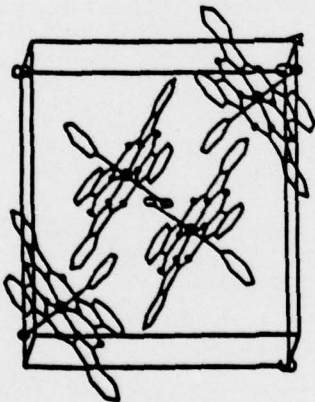
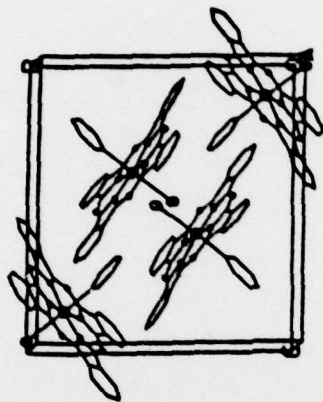
M. Tautou, Fig. 10



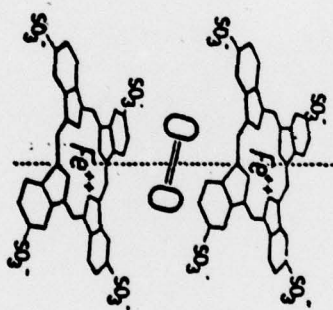
see Textbook, p. 11



Mr. Tuckers, Dy. 12



W. Teutsch, 8y. 15



See Teutaul, Fig. 16