

## Formation and Properties of Various Amine Complexes of Iron-Phthalocyanine

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The formation of additive complexes was studied in regard to iron-phthalocyanine (FePc) dispersed in various amines. The compositions were determined by means of weight-loss measurement and from the thermal behavior of the additive complexes as observed by DTA and X-ray powder diffraction. The decomposition temperature ranges from 100 to 300°C, above which the crystallites are converted into the  $\beta$ -form of pure FePc. Infrared absorption spectra indicated that amine molecules are coordinated to the central metal of FePc, while some extra molecules are freely included in the space of crystal lattice. From kinetic study of visible light absorption spectra, it was found that new absorption appears when the second molecule of the two is combined to the Fe atom of Pc-ring, indicating that a charge transfer mechanism is involved in the complex formation.

### INTRODUCTION

The behavior of transition metal derivatives of porphyrin calls for biological significance when it forms additive complexes with various n-donor molecules which have the ability of co-ordinating to the central metal ion. In the previous paper,<sup>1)</sup> we reported on the formation and properties of similar complexes of zinc-derivative of tetrabenztetraazaporphyrin (zinc-phthalocyanine) suspended in various n-donor dispersion media. Infrared spectra<sup>1,2)</sup> were examined to presume the binding state of adduct molecules and the exact molecular structure was determined by X-ray diffraction analysis with a normal amine complex.<sup>3)</sup>

In the present paper, we extended similar study to iron derivative which was found to produce stoichiometric complexes as in the previous case.

### EXPERIMENTAL SECTION

#### 1. Preparation of Samples

The iron phthalocyanine (FePc) was synthesized<sup>4)</sup> by heating a stoichiometric mixture of pure iron and sublimation-purified phthalonitrile at 270–350°C for about 5 hours and with constant stirring. The crude FePc was purified by washing for 24 hours with pure acetone in a Soxhlet extractor and then by repeated sublimation in a silica-tube with a nitrogen atmosphere flowing at 50 cm<sup>3</sup>/min. The resulting needle-like crystals were converted into a finely divided powder by the acid-paste method.

The organic suspension media are mainly various amines as listed below:

1: methylamine, 2: dimethylamine, 3: trimethylamine, 4: ethylamine, 5: *n*-plopyl-

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amine, 6: *n*-butylamine, 7: *n*-hexylamine, 8: pyridine, 9:  $\gamma$ -picoline, and 10: aniline.

About 1 g of FePc powder was dispersed in 10 ml of each solvent of the above group and was left in stoppered glass tubes for 48 hours at 50°C. The precipitated powder was separated from individual media by filtration and was dried at 50–70°C under reduced pressure. The separated solvents or suspension media, which were colored in greenish-blue, were also stored for further examinations.

## 2. Analytical Procedures

**a. X-ray Powder Diffraction.** The crystal forms of the dried precipitates were identified by X-ray powder diffraction with Mn-filtered FeK $\alpha$  radiation from a source operated at 30 kV. The scanning speed was 1°/min and the time constant was set at 2.5 sec for automatic recording of the intensities of reflected X-rays. The dimensions of dispersion and receiving slits were fixed to be 2.0 and 0.5 mm, respectively, for the goniometer radius of 175 mm. The X-ray diffraction analysis was also applied to specimens which were subjected to differential thermal analysis.

**b. Differential Thermal Analysis (DTA).** As for DTA, specimen of 200 mg of each powder was heated to about 300°C at a rate of 10°C/min for temperature elevation. A Pt-Pt10%Rh thermocouple was used to detect the temperature difference between the sample and  $\alpha$ -alumina powder used for the reference. Since one to four peaks of endothermic reaction appeared in most of the DTA curves, the weight loss due to the heat treatment was examined for all these specimens in order to determine the compositions of additive complexes.

The crystallographic change caused by the heat treatment was detected by another X-ray diffraction measurement of the specimens which were taken from the furnace right after the DTA scanning produced a peak. The temperature of the furnace was controlled with an accuracy of  $\pm 0.5^\circ\text{C}$ .

**c. Infrared Absorption Spectroscopy.** The infrared absorption spectra of the specimen obtained in  $\gamma$ -picoline, *n*-propylamine, and aniline as well as their decomposition intermediates were recorded with a Perkin-Elmer Model 521 grating spectrometer. The accuracy in frequencies was  $\pm 0.5\text{ cm}^{-1}$ , as calibrated with polystyrene film. The specimens for  $\gamma$ -picoline and *n*-propylamine were prepared with nujol while that obtained in aniline was measured with KBr pellet.

**d. Visible-Light Absorption Spectroscopy.** The powder of FePc was vacuum-evaporated from a fused silica crucible onto quartz plates to form thin films of 500 to 3000 Å thick. These films were exposed to vapor of those amines as listed above. After the film color turned to green, the absorption spectra were measured in a range of wavelength between 350 and 750 nm. On the other hand, FePc was dissolved in  $\alpha$ -chloronaphthalene of special grade to have a concentration of  $10^{-5}$  mole/l. Another  $\alpha$ -chloronaphthalene solution of pyridine which had been distilled for dehydration ( $10^{-3}$  mole/l) was prepared, 5 portion of which was mixed with 1 portion of former solution of FePc. The change of absorption spectra was recorded to follow the additive complex formation in solution. The apparatus used was Shimadzu Multipurpose Spectrometer (MPS-50 L).

## RESULTS AND DISCUSSION

The composition of each precipitate was determined by the combined use of differential

thermal analysis and gravimetry. Figure 1 is to show the differential thermal curves in which the endothermic reactions are demonstrated as downward deflections. Apparently, the DTA curves generally showed at least one distinct deflection peak and, in other cases, two to four distinct peaks are observed, all ranging between 100 and 290°C as listed in Table I. It was confirmed by X-ray powder diffraction that the final products beyond the highest peak are to be the  $\beta$ -form of pure FePc for all specimens. The compositions of specimens before the individual thermal peaks are estimated by the comparison of the predicted weight losses with the actual values observed by the gravimetry. All calculations made were on the assumption that the weight losses are due to the solvated molecules of the dispersion media in which the individual precipitates were produced. Since no other components are involved in the system and since the final products of heating are always pure FePc, the assumption seems to be reasonable and in other words, the new crystal phases are all solvated complexes. It is interesting to note that the adduct molecules are always released in pairs and sometimes stepwisely as far as the dispersion media used in the present case are concerned. Table I includes only two decomposition temperatures even for those specimens which exhibited more DTA peaks as *n*-hexylamine and aniline complexes.

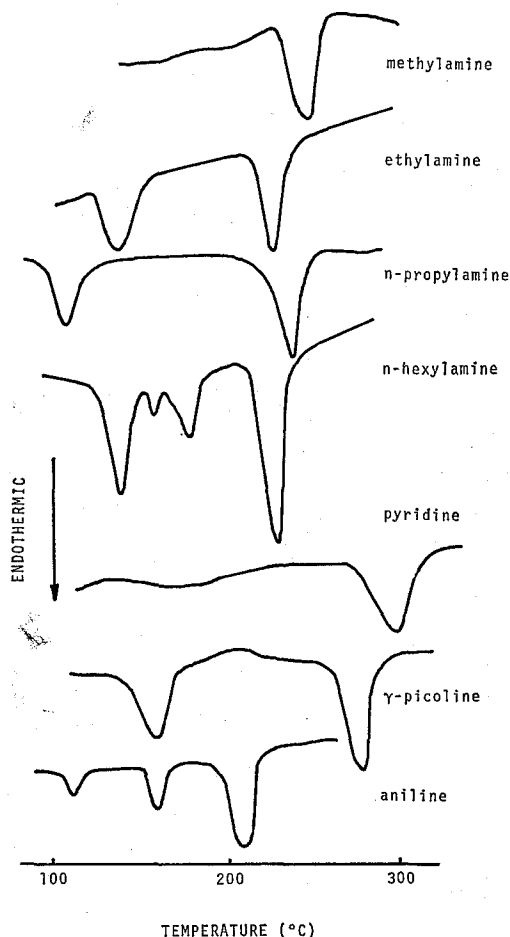


Fig. 1. DTA curves of various amine complexes of Fe-phthalocyanine.

Amine Complex of Iron-Phthalocyanine

Table I. Composition and Decomposition Temperature of Various Amine Complexes of Fe-Phthalocyanine

Complex forming amine	Boiling point of amine(°C)	Compo- sition	Decom.* temp. (°C)	Weight loss (%)		Compo- sition	Decom.* temp. (°C)	Weight loss (%)	
				obs.	calc.			obs.	calc.
methylamine	-6.3					1:2	240	10.0	9.8
ethylamine	16.6	1:4	130	15.0	13.6	1:2	220	12.7	13.7
<i>n</i> -propylamine	47.8	1:4	100	15.7	14.7	1:2	230	17.1	17.2
<i>n</i> -hexylamine	128	1:4	130	22.3	20.8	1:2	220	24.6	26.2
pyridine	115					1:2	290	25.5	21.8
$\gamma$ -picoline	143	1:4	150	20.6	19.8	1:2	270	25.5	24.7
aniline	185	1:6					200	51.3	49.5

\* Decomposition temperature, defined as an extrapolation at zero rate temperature elevation for DTA.

Table II. Interplanar Spacings of Various Amine Complexes of Fe-Phthalocyanine (FePc), Calculated from X-ray Powder Diffraction only (Group A) and Additional Data on Single Crystal Diffraction (Group B)

Group A:

<i><math>\alpha</math></i> -FePc		<i><math>\beta</math></i> -FePc		FePc (methylamine) <sub>2</sub>		FePc (dimethylamine) <sub>2</sub>		FePc (Ethylamine) <sub>2</sub>	
<i>d</i> (Å)	I/I <sub>0</sub>	<i>d</i> (Å)	I/I <sub>0</sub>	<i>d</i> (Å)	I/I <sub>0</sub>	<i>d</i> (Å)	I/I <sub>0</sub>	<i>d</i> (Å)	I/I <sub>0</sub>
12.7	vs	12.8	vs	12.4	vs	12.1	m	16.6	w
11.8	vs	9.67	vs	8.10	s	11.6	w	12.3	w
8.68	s	8.42	m	6.75	s	10.9	w	9.42	vs
5.95	w	7.12	m	6.33	m	9.58	vs	9.07	s
5.63	m	6.33	m	5.25	s	9.30	vs	8.71	m
5.42	m	5.75	w	5.14	s	8.68	s	6.87	m
4.04	w	4.90	s	4.47	w	8.17	w	6.47	m
3.65	s	4.80	s	4.23	s	7.32	m	6.15	w
3.51	s	4.15	w	4.14	w	6.97	w	5.93	s
3.30	s	3.88	w	4.02	w	6.55	m	5.57	m
3.18	s	3.75	s	3.80	m	6.41	s	4.66	s
		3.40	s	3.71	w	6.18	w	4.44	s
		3.18	m	3.47	s	5.78	m	4.39	s
		2.93	s	3.09	m	5.43	w	4.18	m
		2.84	w	2.97	w	4.75	m	3.89	m
				2.92	m	4.61	s	3.84	m
						4.46	m	3.77	s
						3.87	m	3.54	s
						3.77	m	3.43	s
						3.64	s	3.24	m
						3.44	m	3.20	m
						3.30	m	3.12	w
						2.95	s	3.08	m

Table II. (Cont.)

FePc (ethylamine) <sub>4</sub>		FePc ( <i>n</i> -propylamine) <sub>2</sub>		FePc ( <i>n</i> -hexylamine) <sub>2</sub>		FePc (pyridine) <sub>2</sub>		FePc ( $\gamma$ -picoline) <sub>2</sub>	
<i>d</i> (Å)	I/I <sub>0</sub>	<i>d</i> (Å)	I/I <sub>0</sub>	<i>d</i> (Å)	I/I <sub>0</sub>	<i>d</i> (Å)	I/I <sub>0</sub>	<i>d</i> (Å)	I/I <sub>0</sub>
9.08	vs	13.5	w	16.8	vs	14.3	w	11.1	vs
8.43	vs	9.27	vs	14.6	m	10.1	vs	10.3	w
7.78	w	8.82	vs	12.7	m	9.00	m	9.18	s
7.73	s	7.52	s	9.75	m	8.17	m	7.69	s
6.75	s	6.37	m	9.58	s	7.94	w	7.32	w
6.36	w	5.72	w	9.42	s	7.30	m	7.04	w
5.60	w	4.86	w	8.48	vs	6.70	m	6.22	w
5.44	m	4.47	vs	7.27	s	5.27	w	6.02	w
4.68	vs	4.42	m	7.00	m	5.07	s	5.36	m
4.47	m	2.70	s	5.96	m	5.02	s	5.24	m
4.26	m			5.72	m	4.66	m	4.96	s
4.15	s			4.73	w	4.62	w	4.71	m
3.36	s			4.47	s	4.35	m	4.30	m
2.79	m			4.32	m	4.28	w	4.24	s
2.67	w			4.26	s	4.19	w	4.00	w
2.58	m			3.99	s	3.89	s	3.91	m
				3.73	m	3.65	w	3.73	w
				3.57	w	3.44	s	3.61	s
				3.41	m	3.31	m	3.54	w
				2.84	s	3.12	w	3.48	m
						3.05	s	3.33	m
								3.10	s

Neither weightlosses nor variations in X-ray diffraction patterns were observed before and after these extra peaks such as at 155°C and 180°C for *n*-hexylamine. It is considered that the released amine molecules are partly occluded in the pores among the powder particles and partly adsorbed on particle surfaces. The former may evaporate at 155°C, a little higher than the boiling point of the solvent, whereas the latter is desorbed at much higher temperature as 180°C. The desorption temperature was actually confirmed in the previous work<sup>1)</sup> in regard to a similar system of Cu-phthalocyanine (CuPc) wetted with *n*-hexylamine.

It is obvious from the data in Table I, that the precipitates of FePc formed in various amines are all solvated complexes with stoichiometric compositions. As to *n*-propylamine complex, the ratio of 1 : 4 does not seem to result in a good accordance of calculated and observed values of weight loss upon heating. However, this composition is assigned for the stoichiometry because X-ray diffraction analysis revealed that the present complex is isomorphic with a cobalt phthalocyanine (CoPc) complex with the same amine, for which the composition of 1 : 4 stands with a good accuracy. The stepwise decomposition of each complex, having a pair of amine molecules released at definite temperature, means that the original complexes include different species of adduct molecules which have different manner of solvation.

The X-ray powder diffraction patterns are reproduced in Fig. 2, and the interplanar spacings of all the specimens are listed in Table II. In addition to the data for pure FePc

Amine Complex of Iron-Phthalocyanine

Table II. (Cont.)

Group B:

FePc( $\gamma$ -picoline) <sub>4</sub>				FePc(aniline) <sub>6</sub>			
(hkl)	$d_{\text{obs.}}$	$d_{\text{calc.}}$	I/I <sub>0</sub>	(hkl)	$d_{\text{obs.}}$	$d_{\text{calc.}}$	I/I <sub>0</sub>
(200)	12.6	12.60	vs	(001)	12.1	12.25	w
(210)	10.3	10.30	m	(110)	10.4	10.46	vs
(020)	9.04	9.04	vs	(011)	8.82	8.89	m
(111)	8.42	8.40	vs	(11 $\bar{1}$ )	8.30	8.38	m
(220)	7.32	7.30	m	(20 $\bar{1}$ )	7.72	7.89	m
(211)		7.30		(111)	7.52	7.59	m
(400)	6.29	6.30	s	(020)	6.40	6.45	m
(311)	6.12	6.10	m	(120)	6.02	6.07	m
(230)	5.39	5.38	m	(220)	5.19	5.23	s
(002)	5.14	5.15	s	(112)	5.05	5.07	w
(411)		5.14		(221)	4.62	4.65	m
(131)	5.04	5.05	m	(320)	4.35	4.37	s
(102)		5.05		(130)	4.18	4.18	m
(112)	4.86	4.85	s	(003)	4.03	4.08	m
(231)	4.77	4.78	m	(113)	3.93	3.94	m
(202)		4.76		(230)	3.85	3.88	w
(421)	4.59	4.60	s	(31 $\bar{2}$ )	3.75	3.77	m
(040)	4.47	4.47	w	(330)	3.46	3.48	vs
(022)		4.46		(32 $\bar{2}$ )	3.36	3.37	w
(331)	4.39	4.40	vs	(331)	3.26	3.27	s
(122)		4.39					
(041)	4.12	4.10	m				
(431)	3.98	3.99	vs				
(402)		3.98					
(232)	3.72	3.72	w				
(422)	3.69	3.65	m				
(440)		3.65					
(212)	3.43	3.44	s				
(441)		3.44					
(213)	3.26	3.26	m				
(242)		3.26					
(123)	3.18	3.18	s				
(313)	3.13	3.13	w				
(060)	2.97	2.98	m				
(133)	2.93	2.95	m				
(423)	2.85	2.86	w				
(333)	2.80	2.80	s				

Table II. (Group B, cont.)

FePc( <i>n</i> -propylamine) <sub>4</sub>				FePc( <i>n</i> -hexylamine) <sub>4</sub>			
(hkl)	<i>d</i> <sub>obs.</sub>	<i>d</i> <sub>calc.</sub>	I/I <sub>0</sub>	(hkl)	<i>d</i> <sub>obs.</sub>	<i>d</i> <sub>calc.</sub>	I/I <sub>0</sub>
(001)	9.55	9.61	vs	(200)	13.9	13.97	s
(110)	9.27	9.32	s	(210)	11.2	11.27	w
(200)	8.60	8.33	m	(001)	10.2	10.10	vs
(11 $\bar{1}$ )	7.72	7.75	vs	(120)	8.96	9.02	s
(011)	7.30	7.31	w	(310)	8.43	8.37	m
(21 $\bar{1}$ )	6.85	6.78	m	(211)	7.22	7.19	w
(111)	5.95	5.97	m	(400)	6.96	6.99	w
(020)	5.55	5.62	w	(320)	6.63	6.67	m
(201)	5.19	5.22	w	(311)	6.09	6.13	w
(12 $\bar{1}$ )	4.97	4.98	w	(40 $\bar{1}$ )		6.06	
(310)		4.98		(230)	5.83	5.78	w
(002)	4.80	4.81	s	(420)	5.63	5.62	w
(012)	4.49	4.42	m	(321)	5.36	5.35	m
(400)	4.17	4.17	m	(13 $\bar{1}$ )		5.35	
(22 $\bar{2}$ )	3.84	3.86	vs	(330)	5.29	5.24	m
(32 $\bar{1}$ )	3.71	3.70	m	(131)	5.17	5.21	s
(321)	3.62	3.61	m	(002)	5.03	5.00	w
(312)	3.50	3.53	m	(340)	4.24	4.24	m
(031)		3.49		(521)	4.18	4.18	s
(31 $\bar{2}$ )	3.42	3.39	m	(620)		4.18	
(222)	3.27	3.24	w	(601)	4.06	4.07	w
(032)	3.02	2.99	s	(032)	3.93	3.94	w
(014)	2.93	2.77	m	(42 $\bar{2}$ )		3.94	
				(412)	3.80	3.79	vs
				(71 $\bar{1}$ )		3.79	
				(441)	3.73	3.74	vs
				(621)		3.74	
				(771)	3.51	3.51	m
				(800)	3.48	3.49	w
				(10 $\bar{3}$ )	3.37	3.37	m
				(81 $\bar{1}$ )		3.37	

of the  $\alpha$ - and  $\beta$ -forms, the figure and table include those for the fresh precipitates as well as for the intermediate products of thermal decomposition. The diffraction features are all different as the composition is varied even for the same solvated molecular species. The interplanar spacings for pure  $\alpha$ - and  $\beta$ -forms, ranging between 13 and 9 Å generally corresponding to the separation of molecular columns of stacked planar molecules which have themselves the diagonal dimension of about 13 Å. As apparent from the list in Table II, the largest separation, or interplanar spacing, also ranges between 9 and 16 Å, reflecting that the molecular packing in the crystals is still governed by the arrangement of planar phthalocyanine molecules. In view of the presence of different species of solvated molecules, the dimension of unit cell was compared for those complexes subjected to X-ray single crystal diffraction. The crystal data are listed in Table III, together with the unit cell

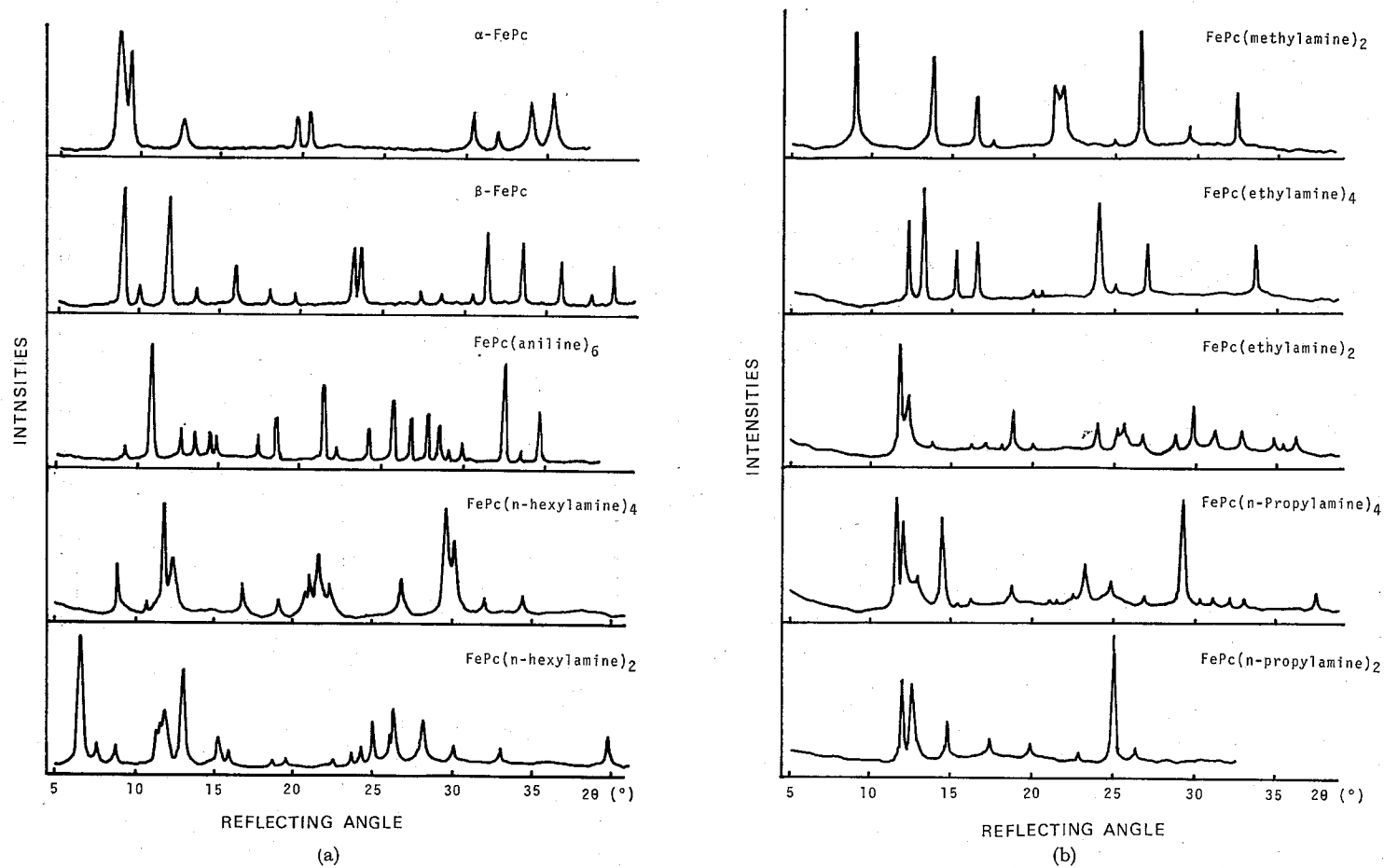


Fig. 2. X-ray powder diffraction patterns of various amine complexes of Fe-phthalocyanine (FePc).



Table III. Crystal Data for Several Amine Complexes of Fe-Phthalocyanine (FePc)

Crystal	FePc( $\gamma$ pic) <sub>4</sub>	FePc(propylam) <sub>4</sub>	FePc(hexylam) <sub>4</sub>	FePc(anil) <sub>6</sub>
System	Orthorhombic	Monoclinic	Monoclinic	Monoclinic
M.W.	938	804	969	1126
S.G.	Pbca	P2 <sub>1</sub> /a	P2 <sub>1</sub> /a	P2 <sub>1</sub> /a
a(A)	25.19	18.73	28.12	18.11
b(A)	17.86	11.25	29.10	12.90
c(A)	10.30	10.80	10.09	12.42
(°)	—	117.2	106.5	99.5
V(A <sup>3</sup> )	4634	2024	5385	2862
D(obs.)	1.339	1.331	1.189	1.306
D(calc.)	1.336	1.319	1.199	1.306
Z	4	2	4	2

M. W.: Molecular weight, S. G.: Space group, pic: picoline, propylam: propylamine, hexylam: hexylamine, anil: aniline, V: unit cell volume and D: density

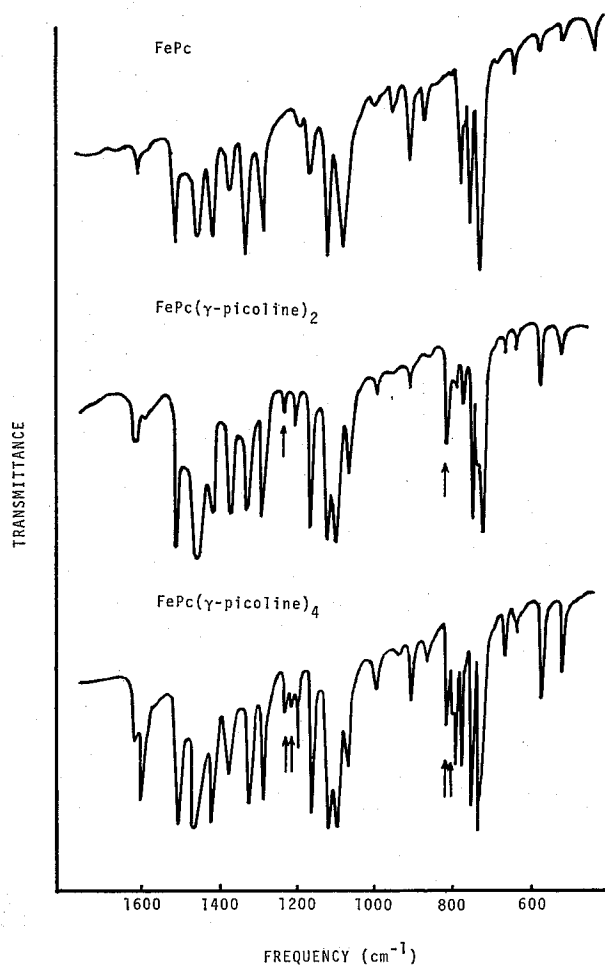


Fig. 3. Infrared absorption spectra of Fe-phthalocyanine (FePc) and its  $\gamma$ -picoline ( $\gamma$ -pic) complexes.

volume and the density of complex crystals. Apparently, the density, ranging between 1.19 and 1.34, is much smaller than those of the pure  $\alpha$ - and  $\beta$ -forms which are 1.59 and 1.52, respectively. The volumes of unit cell exceed 2000 Å<sup>3</sup> for every two phthalocyanine molecules, which are again larger than those of plain crystals, indicating that fairly wide spaces are included in the crystal lattice.

The infrared spectra, as reproduced in Fig. 3, were examined in order to obtain information about the nature of different species of adduct molecules. Here the results with the complexes of  $\gamma$ -picoline are demonstrated for the example, since the adduct molecules exhibited a very definite spectral behavior depending upon their compositions. In Fig. 3 the infrared spectra of plain FePc of the  $\beta$ -form<sup>5)</sup> is reproduced for comparison. Although the spectra of complexes resemble those of the plain compound, a few absorption peaks due to the adduct  $\gamma$ -picoline molecules are clearly observed without overlapping the peaks of FePc as indicated by arrows. It has to be noted that each absorption peak of the adduct molecule in the complex which has four  $\gamma$ -picoline molecules appear as doublet. The wave numbers in cm<sup>-1</sup> are listed in Table IV, where similar data for aniline complex are also included. When compared with corresponding absorption bands of pure  $\gamma$ -picoline, considerable blue shifts are observed for the singlet of FePc(pic)<sub>2</sub> and one of each doublet of FePc(pic)<sub>4</sub>, where pic stands for  $\gamma$ -picoline. Goodgame *et al.*<sup>6)</sup> reported that similar blue shifts occur to  $\gamma$ -picoline which is co-ordinated to ions of the first transition metal in halogenized complexes. Partial blue shifts were reported by Haque *et al.*<sup>8)</sup> also for  $\gamma$ -picoline molecules which are combined with halogens and inter-halogen compounds which are all regarded as strong electron acceptors. It is apparent from the above observations that two groups of  $\gamma$ -picoline exist in the complex of FePc( $\gamma$ -pic)<sub>4</sub>, one of which is strongly combined to FePc and the other is considered to exist rather freely in a wide space of the complex crystal. The existence of these amine molecules of two different groups is apparently the origin of the stepwise process of thermal decomposition.

As assigned by Green *et al.*,<sup>7)</sup> the absorption bands of  $\gamma$ -picoline at 800 and 1224 cm<sup>-1</sup> are  $\gamma$ (CH) and  $\beta$ (CH), respectively. In the case of  $\gamma$ -picoline complex of ZnPc, these two absorption bands also exhibited similar amount of blue shifts, which are considered to be due to the variation of  $\pi$ -electron density distribution caused by the co-ordination of  $\gamma$ -picoline to the central metal of ZnPc. The X-ray diffraction analysis for the FePc complex showed that two  $\gamma$ -picoline molecules are bonded with their nitrogen atoms facing to Fe atom perpendicularly from both sides of macromolecular ring of phthalocyanine. It was also confirmed that the other two  $\gamma$ -picolines are located in a space among the complex molecules. Judging from the distance from the surrounding molecules, the free  $\gamma$ -picoline molecules are not likely to be influenced by any strong interaction.

Table IV. Infrared Absorption Bands for  $\gamma$ -Picoline ( $\gamma$ -pic) and Aniline (anil) Complexes of Fe-Phthalocyanine (FePc)

Complexes	Wave number of absorption peak in cm <sup>-1</sup>			
FePc( $\gamma$ -pic) <sub>4</sub>		1237	1225	815 803
FePc( $\gamma$ -pic) <sub>2</sub>		1236		814
$\gamma$ -picoline		1220		801
FePc(anil) <sub>6</sub>	3410	3315	3260	
aniline	3434	3397		

On the other hand, aniline in  $\text{FePc}(\text{anil})_6$  shows more conspicuous behavior. As apparent from Table IV, absorption bands appear at 3410, 3315, and 3260  $\text{cm}^{-1}$ . According to Lady and Whestel,<sup>9</sup> free aniline gives rise to NH-stretching vibrations at 3484(a) and 3379(s) $\text{cm}^{-1}$ . It was also reported by Hill and Curran<sup>10</sup> that absorption bands of aniline appear at 3236, 3210, and 3121  $\text{cm}^{-1}$  when it is co-ordinated to Ni, Mg, Cu, and Zn ions, exhibiting red shifts to lower frequencies by 149 through 187  $\text{cm}^{-1}$ . Taking these data into account, it is presumed that the shifting to lower frequencies is caused by the lowering of NH-bond order due to the co-ordination of nitrogen to the central metal ion of FePc.

Figure 4 shows visible light absorption spectra of vacuum-deposited thin film of FePc and that exposed to pyridine vapor as well as those of  $\alpha$ -chloronaphthalene solutions of FePc with and without addition of excess amount of pyridine. The position of absorption peaks are listed in Table V for these spectra. The strong absorption between 600 and 700 nm, which cause these complexes to exhibit blue color, are due to  $\pi$ -electronic transitions. Obviously, these transitions are sensitively influenced by the different molecular environments, solution or solid film. It should be noted, however, that a new absorption appears at 410 nm whenever FePc forms complex regardless of the state of the product.

Every amine complex examined here has a similar new absorption characteristic of the adduct molecules. When the transition energy of each absorption is plotted against the ionization potential<sup>11</sup>) of the corresponding amine, a fairly good linear relationship is observed as shown in Fig. 5, indicating that the absorptions around 420 nm are due to charge transfer forces between FePc and amine molecules. Since the combination is based on the perpendicular co-ordination of lone pair of amine nitrogen, the charge transfer takes place through this bonding. Dale<sup>12</sup>) reported similar absorption bands of FePc complexes formed in dimethyl-sulfoxide solution saturated with various amines. Although no definite linear relationships between the wave number and the ionic potential were observed, perhaps being due to the presence of complex-forming solvent DMSO, the absorption bands were empirically interpreted in terms of the charge transfer force. The obvious

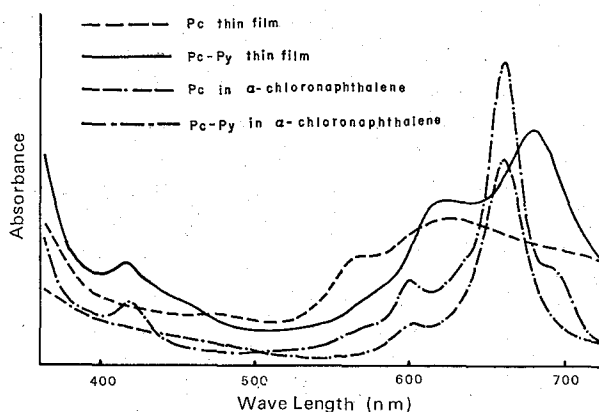


Fig. 4. Visible light absorption spectra of Fe-phthalocyanine (FePc) and its pyridine complexes formed in  $\alpha$ -chloronaphthalene and in vacuum deposited films. 1: FePc (thin film), 2: FePc-pyridine (thin film), 3: FePc in  $\alpha$ -chloronaphthalene, and 4: FePc-pyridine in  $\alpha$ -chloronaphthalene.

Amine Complex of Iron-Phthalocyanine

Table V. Visible Light Absorption for Various Amine Complexes of Fe-Phthalocyanine (FePc) in Thin Solid Film and in  $\alpha$ -Chloronaphthalene Solution

Complex	Wavelength of absorption peak (nm)					Ionization potential (eV)
A. Thin film						
FePc			570	625		
methylamine	386	435	576	623	684	8.79
dimethylamine		428	570	615	650	8.24
trimethylamine		425	570	615	650	7.82
ethylamine	385	430	573	616	653	8.86
<i>n</i> -propylamine	383	430	573	620	655	8.78
<i>n</i> -butylamine		431	570	620	656	8.71
pyridine		414	573	628		9.26
$\gamma$ -picoline		419	570	613	651	9.56
B. $\alpha$ -chloronaphthalene solution						
FePc			600		662	
FePc(pyridine)			600		662	694
FePc(pyridine) <sub>2</sub>		415	600	635 <sup>s</sup>	662	

s: shoulder

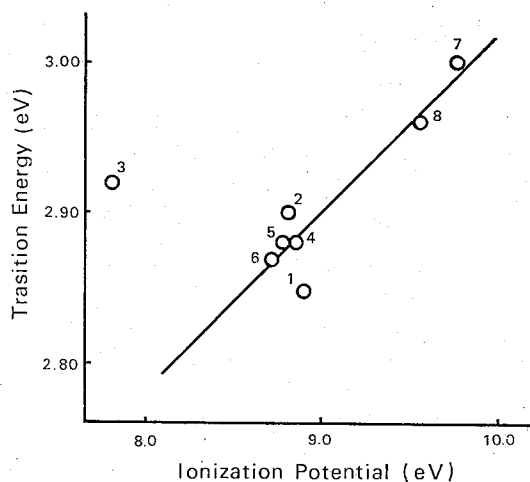


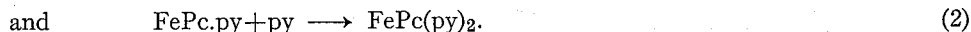
Fig. 5. The relationship between the ionization potential of the adduct molecule of amine and the transition energy of charge transfer spectra of Fe-phthalocyanine complexes with the amine. 1: methylamine, 2: dimethylamine, 3: trimethylamine, 4: ethylamine, 5: *n*-propylamine, 6: *n*-butylamine, 7: pyridine, and 8:  $\gamma$ -picoline.

deviation from the line for methyl-, dimethyl- and trimethylamines may be due to the influence of methyl group which would cause a considerable steric hindrance for the stable co-ordination.

Figure 6 demonstrates the variation of absorption spectra with time, which was observed in  $\alpha$ -chloronaphthalene solution of FePc mixed with excess amount of pyridine. Apparently, the solution changes color in two successive stages: (1) On addition of

pyridine, FePc solution instantly changes into purple blue, and (2) slowly into blue green. In this latter stage, the charge transfer band begins to appear at 420 nm and gains intensity.

The absorption band is superimposed on the tail of another strong absorption appearing at shorter wave length. The equilibrium moves to the side of complete formation of complex with the addition of an excess amount of pyridine, giving  $0.19 \times 10^5$  for the extinction coefficient. From the peak height on the background, the rate of production of the molecular complex can be determined. When the logarithm of  $C$ , the concentration of the product of the first stage, is plotted against the time  $t$ , a linear relationship was obtained, indicating that the process follows the first order reaction. It was found that the spectra of the final product coincides with an  $\alpha$ -chloronaphthalene solution of FePc(py)<sub>2</sub>. It was then inferred that the two stages of complex formation can be assigned as follows:



The reaction of the first stage takes place very quickly whereas the second stage proceeds rather slowly. After the formation of the complex is completed, two co-ordinated pyridine molecules are likely to behave equally without showing any distinction between them. It was found difficult to isolate the mono-pyridine complex of FePc, in contrast to the case of similar amine complexes of ZnPc which were found to form many square pyramidal five-coordinated structures.

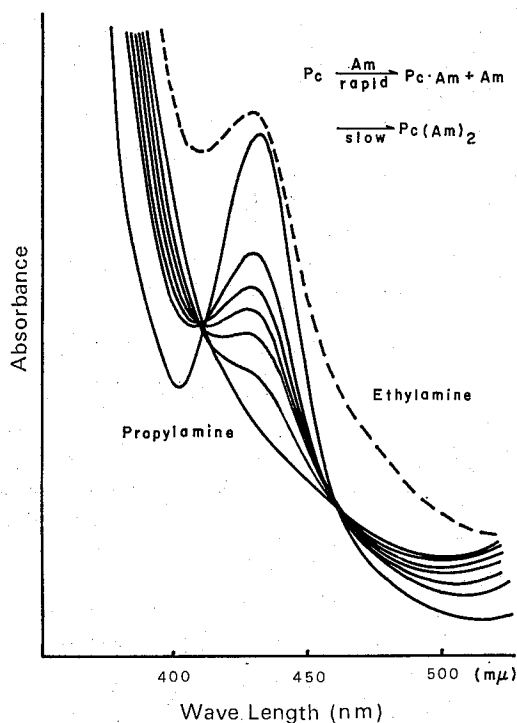


Fig. 6. Time dependence of visible light absorption spectra for the formation of pyridine (py) complex of Fe-phthalocyanine (FePc) in  $\alpha$ -chloronaphthalene.

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