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論文

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# 主論文

The far infrared spectra of  
phthalocyanine and its metal derivatives.

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## Abstract

The far infrared spectra ( $400\sim 30\text{ cm}^{-1}$ ) of phthalocyanine and its metal derivatives were systematically studied and the assignments were proposed for the individual absorption bands observed with particular attention to the absorptions characteristic to each metal phthalocyanine as well as the metal-ligand vibrations. The electronic configuration of the central metal ion was discussed on the basis of these metal-dependent bands in which the zinc derivative showed a special aspect in the spectra.

## Introduction

In the course of the study concerning polymorphic phase transformation of various kinds of phthalocyanine derivatives in organic suspension media<sup>1)</sup>, it was found<sup>2)</sup> that zinc-phthalocyanine, when dispersed in n-donor solvents whose electron donating abilities were mainly due to the non-bonding lone pairs, produced stable crystals of molecular complexes where zinc-phthalocyanine and the solvent molecules were bound stoichiometrically. In the previous paper<sup>3)</sup>, the infrared spectra of the phthalocyanine derivatives were studied in the region of  $400\sim 4000\text{ cm}^{-1}$  to obtain the available data for the study on the bond nature of the molecular complexes composed of zinc-phthalocyanine and n-donor solvents.

The far infrared spectra were also called for in order to investigate the structure and the nature of bonding between the zinc-phthalocyanine and n-donor solvent molecule, because it was expected that the frequencies of metal ligand vibration, macrocyclic vibration in phthalocyanine, lattice vibration and the intermolecular vibrations might be observed in this region. Unfortunately, however, there have been very few data about the spectra of phthalocyanine in this region because of the complexity of the molecule. The far infrared spectra of various metal phthalocyanines were, therefore, investigated and the assignments were also proposed in the present paper.

#### Experimental

The metal phthalocyanines used were Fe-, Co-, Ni-, Cu-, Zn-, Pd- and Pt-phthalocyanines which were capable of purification by sublimation without decomposition. They were prepared by the reaction of phthalonitrile with metal dusts or metal chlorides and purified by repeated sublimation at 550°C under a reduced pressure of nitrogen gas flow.

The metal-free phthalocyanine was obtained by decomposition of the dilithium phthalocyanine by dispersing in acid or water and then sublimated repeatedly.

The spectra of the specimens which were prepared as Nujol mulls were recorded with a Hitachi Model FIS-3 double

beam spectrometer.

### Vibrational Frequencies and Assignments.

The infrared spectra of the phthalocyanine and its metal derivatives roughly resemble one another as shown in Fig. 1. The absorption frequencies are listed in Table 1 where each series of corresponding band was designated as (a), (b), (c), (d), (e), (f), (g), (h), (i), (j), and (k) respectively. The last column of Table 1 shows the vibrational assignments proposed on the basis of comparative analysis.

#### 1) Metal independent bands

The molecular symmetry of  $H_2$ -phthalocyanine is  $D_{2h}$  whereas the divalent metal derivatives have  $D_{4h}$  symmetry as shown in Fig. 2. The infrared active modes of vibration in  $D_{4h}$  symmetry are only two, namely  $A_{2u}$  and  $E_u$ . The  $E_u$  mode of vibrations splits into two infrared active modes,  $B_{2u}$  and  $B_{3u}$ , for molecules of  $D_{2h}$  symmetry. This relationship is well detected with respect to the spectra in Fig. 1.

The absorption bands (d) for metal-phthalocyanines which appeared at about  $233\text{ cm}^{-1}$  were observed to split into the doublet at  $238$  and  $230\text{ cm}^{-1}$  for  $H_2$ -phthalocyanine. Similar effects were also observed with metal dependent absorption bands (b) around  $300\text{ cm}^{-1}$  for metal derivatives and at higher frequency region as listed in Table 2 where

previous data are also referred to for comparison. These bands were caused by  $E_u$  mode of vibrations since the corresponding band for  $H_2$ -phthalocyanine split into the doublet. On the basis of such splitting behaviour, the  $230\text{ cm}^{-1}$  and  $238\text{ cm}^{-1}$  bands for  $H_2$ -phthalocyanine and the related series (d) for other metal-phthalocyanines were assigned to in-plane vibrations of macrocyclic ring respectively. Other two sets of bands (f) and (g) were observed around  $140\text{ cm}^{-1}$  and  $125\text{ cm}^{-1}$  respectively with  $H_2$ -, Fe-, Co-, Ni- and Cu-phthalocyanines. These bands shifted only very little with the variation of metal excepting Zn-phthalocyanine which showed the absorptions at  $132\text{ cm}^{-1}$  and  $116\text{ cm}^{-1}$ . They were considered as metal independent vibrations together with the one observed at about  $235\text{ cm}^{-1}$  which, designated as (d), also showed a similar tendency not to change too much with the variation in the species of metal ion. The former two metal independent vibrations designated as (f) and (g) at  $140$  and  $125\text{ cm}^{-1}$  were assigned to  $A_{2u}$  out-of-plane deformation because no splitting occurred for  $H_2$ -phthalocyanine with  $D_{2h}$  symmetry. The metal independent absorption bands in this region may be considered as those by the vibrations of phthalocyanine macrocyclic ring.

## 2) Metal dependent bands

There existed three remarkable metal dependent bands

in each spectrum of metal phthalocyanines in the far infrared region. Two of them were also observed in H<sub>2</sub>-phthalocyanine. One is at 342 cm<sup>-1</sup> and the other at 259 cm<sup>-1</sup> and 269 cm<sup>-1</sup> as a doublet. On the basis of the same criterion concerning the splitting behaviour, the 342 cm<sup>-1</sup> series (a) were assigned to out-of-plane vibrations associated with the isoindole ring which was closely connected to the metal ion. The frequencies of these metal dependent bands shifted in the order

H<sub>2</sub> < Cu < Zn < Pd < Fe < Co < Ni < Pt --- for band (a)

and Zn < H<sub>2</sub> < Cu < Fe < Pd < Co = Ni < Pt --- for band (b).

As far as the first transition metals are concerned, the orders appear as follows:

Cu < Zn < Fe < Co < Ni --- for band (a)

and Zn < Cu < Fe < Co = Ni --- for band (b).

Especially for the latter band, the frequency shift for zinc-derivative is anomalously large and together with copper phthalocyanine, the frequency of the band shows a conspicuous inversion assuming even lower value than that of out-of-plane vibration of macrocyclic ring which appeared around 300 cm<sup>-1</sup> (band (c)). This fact will be discussed later with other metal dependent bands in view of the configuration of electron orbitals of metal ion in the phthalocyanine molecule. These two sets of bands are considered to be due to the isoindole ring judging from the strong metal-dependent behaviour.



### 3) Metal-ligand vibration

The third metal dependent bands (e) which appeared with high intensities in the region  $150\text{ cm}^{-1} \sim 200\text{ cm}^{-1}$  for Fe-, Co-, Ni- and Cu-phthalocyanines and at  $100 \sim 150\text{ cm}^{-1}$  for Zn-, Pd- and Pt-phthalocyanines were assigned to the metal-ligand vibrations because these strong bands were not observed in the spectrum of metal-free phthalocyanine. The frequencies of the metal-ligand vibrations in the derivatives shifted to higher frequency region in the order

$$\text{Zn} < \text{Pd} < \text{Pt} < \text{Cu} < \text{Fe} < \text{Co} < \text{Ni} \text{ --- for band (e).}$$

The tendency appeared the same as that for the band (b) if Pd and Pt are excluded. Such an order is considered to be closely associated with the metal-ligand bonding strength as will be discussed later.

### 4) Other bands

In the region of  $100\text{ cm}^{-1} \sim 30\text{ cm}^{-1}$ , broad medium intensity bands (h) were observed in all the phthalocyanines except for the zinc derivative around  $90\text{ cm}^{-1}$ . Moreover, a few additional bands existed in this region for every phthalocyanine and the anomalies of zinc and copper were also observed on these bands. The divalent metal phthalocyanine crystals belonging to  $P2_1/a$  are theoretically expected to have three infrared active lattice vibrations. It was reported by Shimanouchi<sup>4)</sup> that naphthalene whose crystal

belongs to the same space group showed absorptions due to lattice vibrations at 98, 66 and 53  $\text{cm}^{-1}$ . Metal phthalocyanines whose molecule is much greater than naphthalene, the absorption bands due to the lattice vibration is expanded to appear at a region much lower than 100  $\text{cm}^{-1}$ . Therefore, some of those bands observed in this region may be assigned to the absorptions due to the lattice vibration, although more detailed examination is considered necessary to reach a better understanding.

#### Discussion

1) The absorption frequencies of the characteristic bands and the electronic configuration in the orbitals of the metal ions.

The stabilities of divalent metal complexes have some relationships to the electronic configurations of the metal ions. According to Irving-Williams<sup>5)</sup>, the second ionization potentials of divalent metals have an important effect on stability constant of the divalent metal complexes. The order of the second ionization potential of divalent metals is



Boucher<sup>6)</sup> reported that, in the case of divalent metal derivatives of the porphyrins, the order of the infrared frequency shifts followed the order of stability of the

metalloporphyrins which had been determined by Phillips<sup>7)</sup> on the basis of replacement reactions, dissociation reaction, and various electronic spectral data. It may be well understood that the data for the first transition metal derivatives of phthalocyanine are in good agreement with the Irving-Williams stability order for complexes of nitrogen-containing ligands excepting Zn and Cu, when the absorption frequencies of metal-ligand vibrations are plotted against the second ionization potential of each metal as shown in Fig. 3.

The deviations of Zn- and Cu-phthalocyanines from this rule for the first transition metal series were interpreted in terms of the electronic structure of central metal ions coordinated with the macrocyclic ring of phthalocyanine molecule. The rule of Irving-Williams stability order is applicable to a series of metal complexes where  $dsp^2$  square-planar hybrid orbitals were used. When the differences of the energy levels between the  $dsp^2$  hybrid orbitals and  $sp^3$  ones of metal ions are negligibly small, this rule can also be applied to the series of complexes where either  $sp^3$  or  $dsp^2$  configuration is used. In the phthalocyanine macrocyclic ring, the divalent metal ions are forced to take square-planar four coordinated structures, which are energetically stable for the  $Fe^{++}$ ,  $Co^{++}$ ,  $Ni^{++}$ ,  $Pt^{++}$  and  $Pd^{++}$ , by the use of  $dsp^2$  hybrid orbitals as shown in Fig. 4. On the contrary, the most stable form for four coordinated

Zn-complexes is the tetrahedral one by using the  $sp^3$  hybrid orbitals because all of the 3d orbitals are occupied by ten electrons of zinc atom itself. For example, the 8-hydroxyquinoline as well as diethyldithiocarbamate<sup>8)</sup> forms four coordinated tetrahedral complex with zinc, whereas the former chelating reagent forms square-planar one with copper or nickel ion as is apparent from the results of the crystal structure analysis of these complexes established by Palenik<sup>9,10)</sup> by X-ray diffraction method.

In order to fit in a square planar configuration, the zinc ion must use  $4s4p^24d$  hybrid orbitals which are less stable than  $4s4p^3$  orbitals for the same ion. For copper ion, the 3d orbitals are occupied by nine electrons and the electronic configurations of outer orbitals in four coordinated complexes are  $4s4p^3$  tetragonal form or  $4s4p^24d$  square configuration like zinc ion. The  $3d4s4p^2$  hybrid orbitals of the copper with one 3d electron elevated to 4p orbital as shown in Fig. 4 (Cu-(a)) are equally stable to the  $4s4p^3$  or  $4s4p^24d$  orbitals. In square-planar configuration, both of the complexes with  $dsp^2$  or  $sp^2d$  hybrid orbitals have been observed to exist and for copper phthalocyanine the  $dsp^2$  configuration is considered to be possible in view of the magnetic moment<sup>11)</sup>. These orbital configurations of divalent metals have an important effect upon the vibrational frequencies of metal-nitrogen bond and other metal dependent absorp-

tion bands as well.

Particularly, the outer orbital complex, which assumes the forced  $sp^2d$  hybrid orbitals, may cause the lowering of the absorption frequency of metal-ligand vibration and also other anomalies in the spectra. In the series of far infrared spectra of the first transition metal phthalocyanines, the zinc-derivative showed conspicuous anomaly as noted above. These anomalous aspects of the spectrum of zinc-phthalocyanine in the absorption bands at  $258\text{ cm}^{-1}$ ,  $242\text{ cm}^{-1}$ ,  $132\text{ cm}^{-1}$ ,  $116\text{ cm}^{-1}$  and  $98\text{ cm}^{-1}$  are well explained on the basis of these consideration.

The copper derivative was also a little exceptional. For example, the frequencies of two metal dependent absorption bands in the first transition series increased in the order of  $\text{Fe} < \text{Co} < \text{Ni}$  but decreased at Cu more than  $25\text{ cm}^{-1}$ . Moreover the band due to the metal-ligand vibration showed the same tendency. This tendency may arise from the unpaired electron existing in the outermost  $4p_z$ -orbital of Cu ion which acted as repulsive forces against the four nitrogens in phthalocyanine ring and weakened the individual bonds between them and metal ion. It is very interesting to note that in the periodic table copper atom is positioned between nickel and zinc and that in the systematic study of far infrared spectra of the metal phthalocyanines, the spectrum of copper derivative also showed intermediate aspect of the

spectra of nickel- and zinc-phthalocyanines.

These absorption frequencies concerning metal-ligand vibration must be, as might be expected, in some relation to other physical and chemical natures regarding the metal-nitrogen bonds. Unfortunately, however, few systematic data have been reported about these bonds on metal phthalocyanine. The bond lengths between the nitrogen and metal ion in various metal porphyrins reported by Gouterman<sup>12)</sup> were adopted since the molecular patterns of the porphyrins are quite the same as those of the metal phthalocyanines as far as the central configuration is concerned. When the reciprocals of the bond lengths are plotted against the absorption frequencies for metal phthalocyanines obtained in this work, a linear relationship was obtained excepting iron as shown in Fig. 5. This fact strongly indicates that the magnitude of the absorption frequency depends on the bond length between metal and ligand nitrogen.

## 2) The effects of crystal structures on the spectra.

It is well known that  $H_2$ -, Fe-, Co-, Ni-, Cu- and Zn-phthalocyanine assume at least two polymorphic forms, the stable  $\beta$ -form and the unstable  $\alpha$ -form, and also that they have isomorphic crystal structure with one another for the individual crystal modifications. The  $\beta$ -phthalocyanine is one of the polymorphs prepared by sublimation which is known

to produce highly pure materials for such metal phthalocyanines as used here. The crystal structure of the  $\beta$ -form is monoclinic belonging to the space group  $P2_1/a$  with two molecules per unit cell. Their unit cell dimensions which were reported by Robertson<sup>13)</sup> and refined by Brown<sup>14)</sup> are listed in Table 3. No  $\beta$ -form structures have been known for Pt- and Pd-phthalocyanine and they usually have a crystal structure which corresponds to the  $\alpha$ -polymorph of other metal phthalocyanine when purified by sublimation.

As all the samples used in the present investigation were purified by sublimation, their crystal structures were also obtained to examine the spectral changes caused by the difference of crystal structures in the far infrared region.

The metal phthalocyanines except for Pt- and Pd-derivatives have three metal dependent bands (a), (b) and (c) respectively and the intensities of the bands are all strong. On the contrary, the Pt- and Pd-derivatives show only one strong band respectively at  $380\text{ cm}^{-1}$  and  $366\text{ cm}^{-1}$  which were assigned to out-of-plane vibrations where the pyrrol rings are more closely involved. Another metal dependent  $E_u$  bands (b) near  $320\text{ cm}^{-1}$  became weaker than the absorption band of  $A_{2u}$  mode near  $300\text{ cm}^{-1}$ . Besides, the intensity of the  $E_u$  bands (d) around  $240\text{ cm}^{-1}$  are very weak with Pt- and Pd-derivatives. The facts that the metal dependent out-of-plane vibration caused the strong absorption and the inten-

sities of the in-plane vibration became weak suggest that these spectral differences of Pt- and Pd-derivatives from other metal phthalocyanines were caused by the difference of the molecular stacking in crystals as shown in Fig. 6. There are eight nitrogen atoms in a phthalocyanine molecule, four atoms are located at a distance about 1.80 Å around the central metal ion and other four at about 3.38 Å. In the  $\beta$ -form crystal, each one of the nearest neighbour molecule along the b-axis contributes a nitrogen at the same distance of 3.38 Å as four nitrogen in the molecule. Therefore, the central metal atom may be described as lying at the center of a square planar configuration which were situated in a larger octahedral array of six nitrogen atoms as shown in Fig. 6(b). On the other hand, in the  $\alpha$ -polymorphs including Pt-phthalocyanine and possibly Pd-derivative, no nitrogen atoms of neighbouring molecules are situated right over and under the central atom. The distance between two neighbouring molecules in this case is 3.41 Å. Inasmuch as the lattice vibrations or other crystal-structure-dependent absorptions are expected to appear in the far infrared region, it is necessary to use the samples with the same crystal structure in order to perform a comparative study concerning the far infrared spectra of various metal phthalocyanines systematically. As already stated, the intensities of absorption bands for Pt- and Pd-derivatives with the  $\alpha$ -modification are found weaker than



those for the  $\beta$ -modification of the derivatives of other metals. This tendency is more conspicuous for the absorption bands such as (b), (c), (d), (e) and (g) which are mostly associated with the deformation of the macrocyclic ring of phthalocyanine molecule.

However, it seems necessary to compare the difference of the spectra due to the crystal structure with respect to the polymorphs of the same metal derivative to discuss the effects of crystal structures on the spectra as will be reported in the near future. When the effects of crystal structure on the vibration and lattice energy are well understood it may be possible to clarify the reason why the polymorphism of various phthalocyanines exists.

It must also be pointed out that the far infrared spectra of phthalocyanine derivatives are very useful and convenient method for non-destructive analysis to distinguish the kind of metal in phthalocyanine derivatives, when compared with other technique such as X-ray powder diffraction because the crystal structures of some metal phthalocyanines are so close to each other in order to discriminate them only by the measurement of lattice parameters.

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- Table 1 The absorption frequencies of phthalocyanine and its various metal derivatives.
- Table 2 The absorption bands by  $E_u$  mode of vibrations.
- Table 3 The crystal data of various phthalocyanines.  
\* The Pd-phthalocyanine showed the isomorphous crystal structure with Pt-derivative but the unit cell constants were not obtained.
- Fig. 1 Far infrared spectra of phthalocyanine and its various metal derivatives.
- Fig. 2 Molecules of metal-free ( $H_2$ )-phthalocyanine and metal derivative.
- Fig. 3 Relation between second ionization potentials of metal and the absorption frequencies of metal-nitrogen vibration.
- Fig. 4 Diagrammatic presentation of the electronic configurations of the outer orbitals of divalent metals. The black points show the electrons donated by ligand nitrogens.
- Fig. 5 Relation between the reciprocals of metal-nitrogen bond distances in metal porphyrins and the absorption frequencies of metal-ligand vibrations in metal phthalocyanines.
- Fig. 6 Molecular stacking of phthalocyanine derivatives in two crystal modifications.

Table 1 The absorption frequencies of phthalocyanine and its various metal derivatives.

H <sub>2</sub> -	Fe-	Co-	Ni-	Cu-	Zn-	Pd-	Pt-		band
342	367	375	377	352	354	366	380	metal dependent. isoindole ring	(a)
282	301	303	302	302	303	301	308	macrocyclic ring deform. (maybe bridge nitrogen)	(c)
269	309	319	319	285	258	316	320	metal dependent. isoindole ring.	(b)
259	268	268							
238	234	233	232	233	242	238	240	macrocyclic ring deform.	(d)
230	161	174	185	153	98	119	144	metal-ligand	(e)
	155	156	153		167	167	152		
						161			
140	140	146	141	140	132	135	126	macrocyclic ring deform.	(f)
127	125	127	126	123	116	112	117	macrocyclic ring deform.	(g)
90	90	89	92	92	80	92	89		(h)
				85		88			
				79					
65	69	60	64	70	66	67	67	} lattice?	(i)
57	58	57	56	60	58	58	58		(j)
49	49	49		50		48			(k)
45	45	45	44				42		
40	41	41	40			39			

Table 2 The absorption bands by  $E_u$  mode of vibrations.

$H_2-$	Fe-	Co-	Ni-	Cu-	Zn-	Pd-	Pt-
230							
238	234	233	232	233	242	238	240
259							
269	309	319	319	285	258	316	320
489							
498	518	519	521	509	502	516	514
552							
559	574	574	578	575	575	581	578
617							
625	642	642	645	640	637	648	645

Table 3 The crystal data of various phthalocyanines.

Phthalocyanine	a (A)	b (A)	c (A)	$\beta$	Space Group
$C_{32}H_{18}N_8$	19.9	4.72	14.8	$122^{\circ}12'$	$P2_1/a$
$C_{32}H_{16}N_8Fe$	20.2	4.75	15.1	$121^{\circ}42'$	$P2_1/a$
Co	20.2	4.77	15.0	$121^{\circ}3'$	$P2_1/a$
Ni	19.9	4.71	14.9	$121^{\circ}54'$	$P2_1/a$
Cu	19.4	4.79	14.6	$120^{\circ}56'$	$P2_1/a$
Zn	19.2	4.87	14.52	$120^{\circ}2'$	$P2_1/a$
Pd	*				
Pt	26.29	3.82	23.9	$94^{\circ}6'$	$C2/n$

\* The Pd-phthalocyanine showed the isomorphous crystal structure with Pt-derivative but the unit cell constants were not obtained.

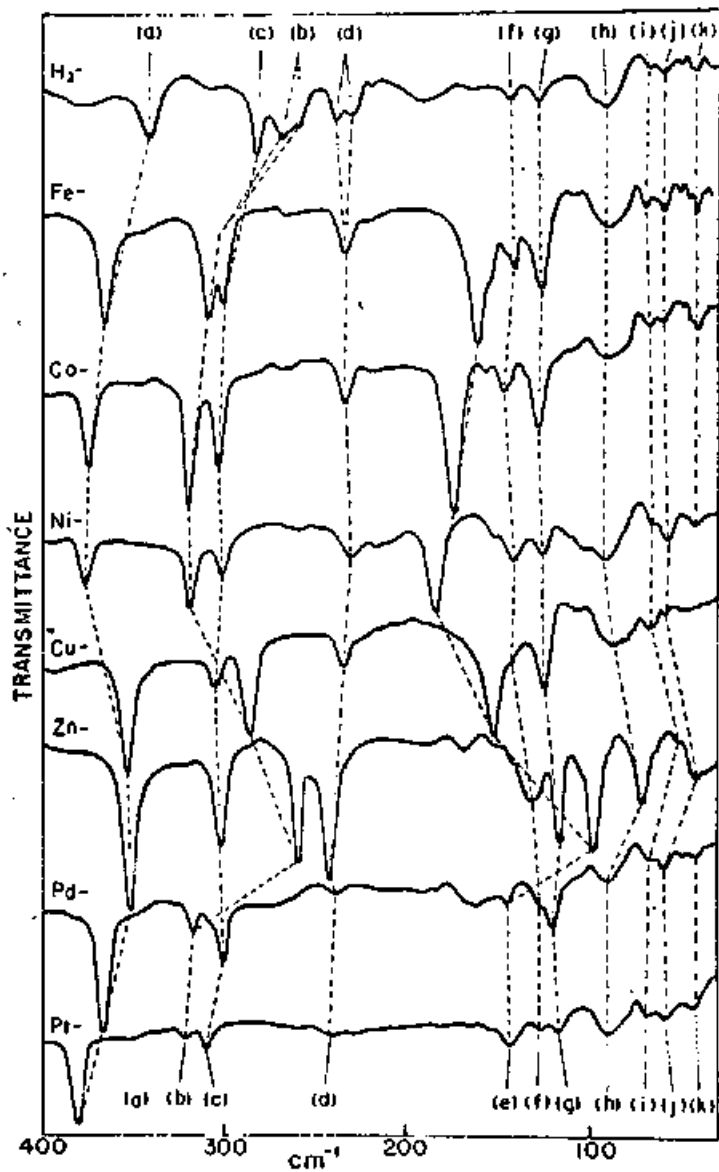
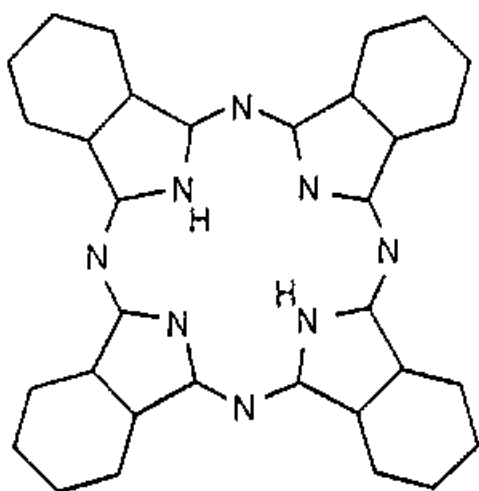


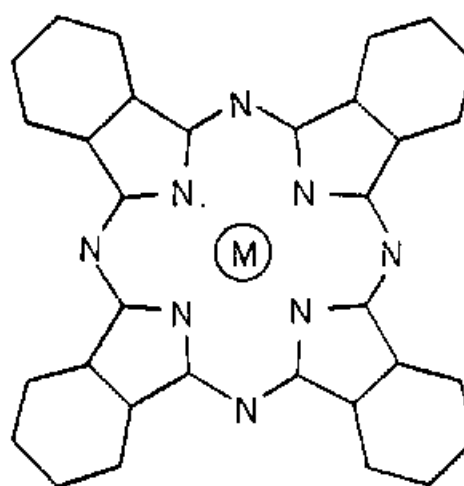
Fig. 1

Far infrared spectra of phthalocyanine and its various metal derivatives.





(a)



M... Fe<sup>+</sup>, Co<sup>+</sup>, Ni<sup>+</sup>, Cu<sup>+</sup>, Zn<sup>+</sup>, Pd<sup>+</sup>, Pt<sup>+</sup>

(b)

Fig. 2 Molecules of metal-free (H<sub>2</sub>)-phthalocyanine and metal derivative.

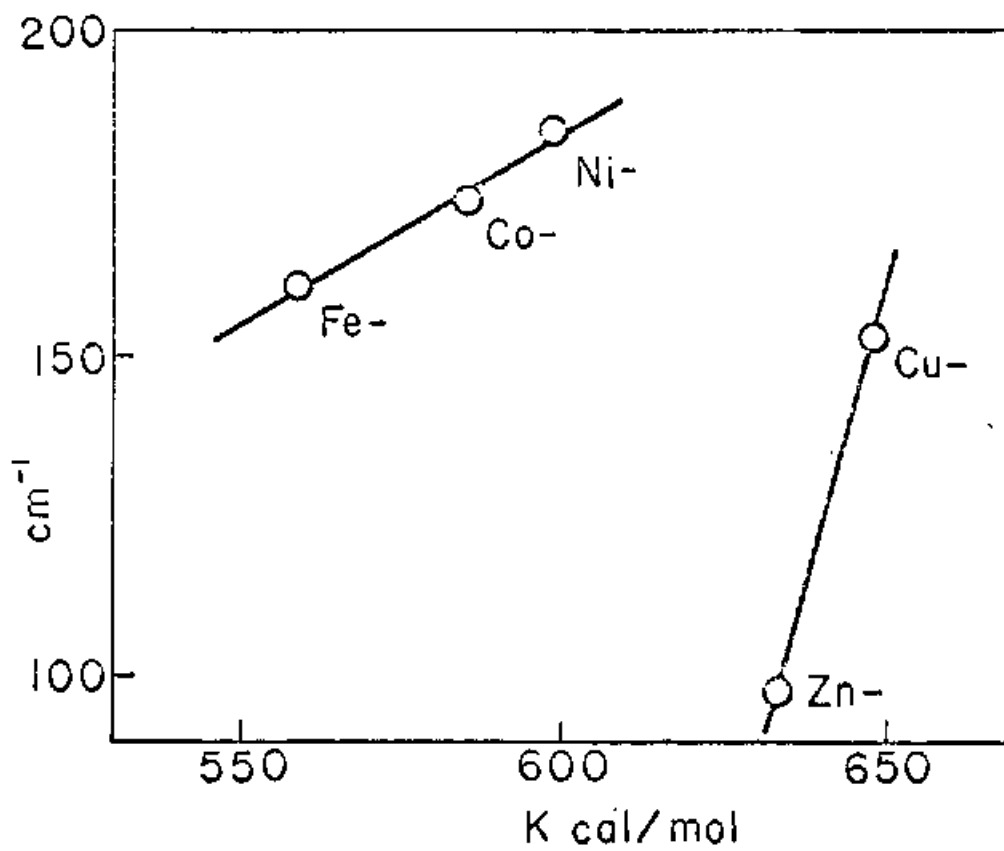
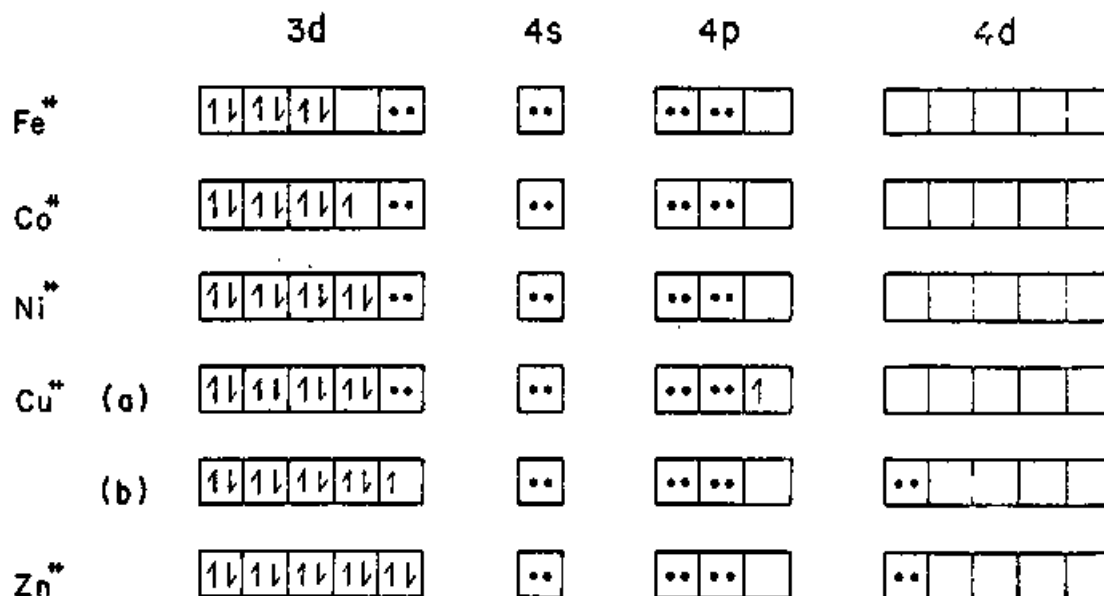


Fig. 3 Relation between second ionization potentials of metal and the absorption frequencies of metal-nitrogen vibration.



**Fig. 4** Diagrammatic presentation of the electronic configurations of the outer orbitals of divalent metals. The black points show the electrons donated by ligand nitrogens.

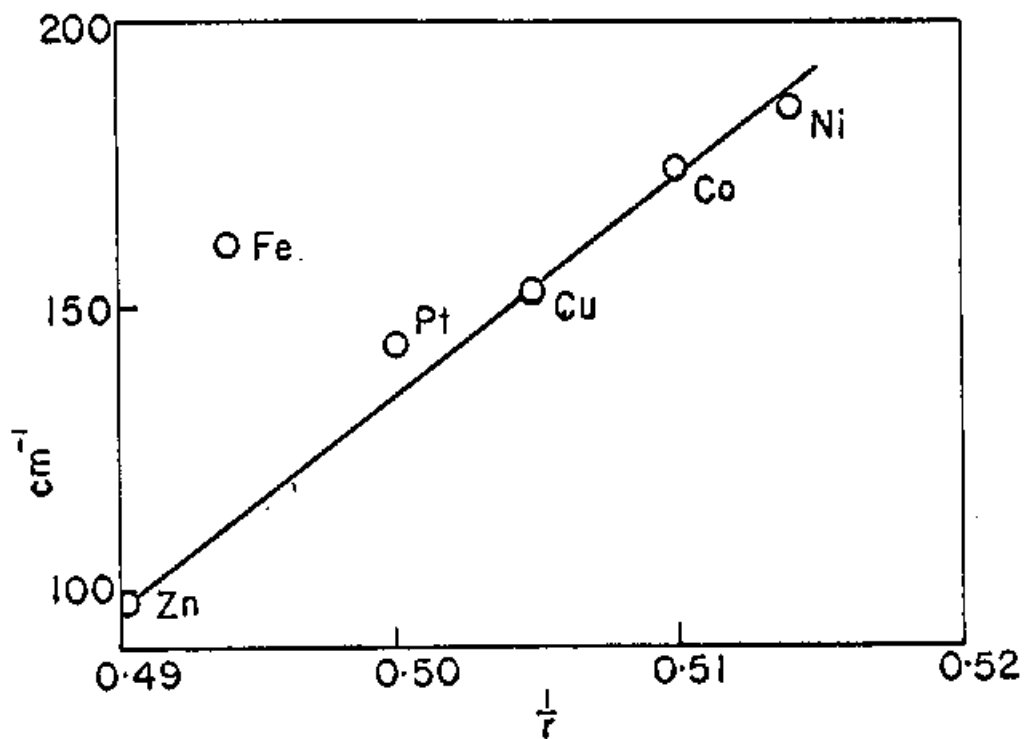
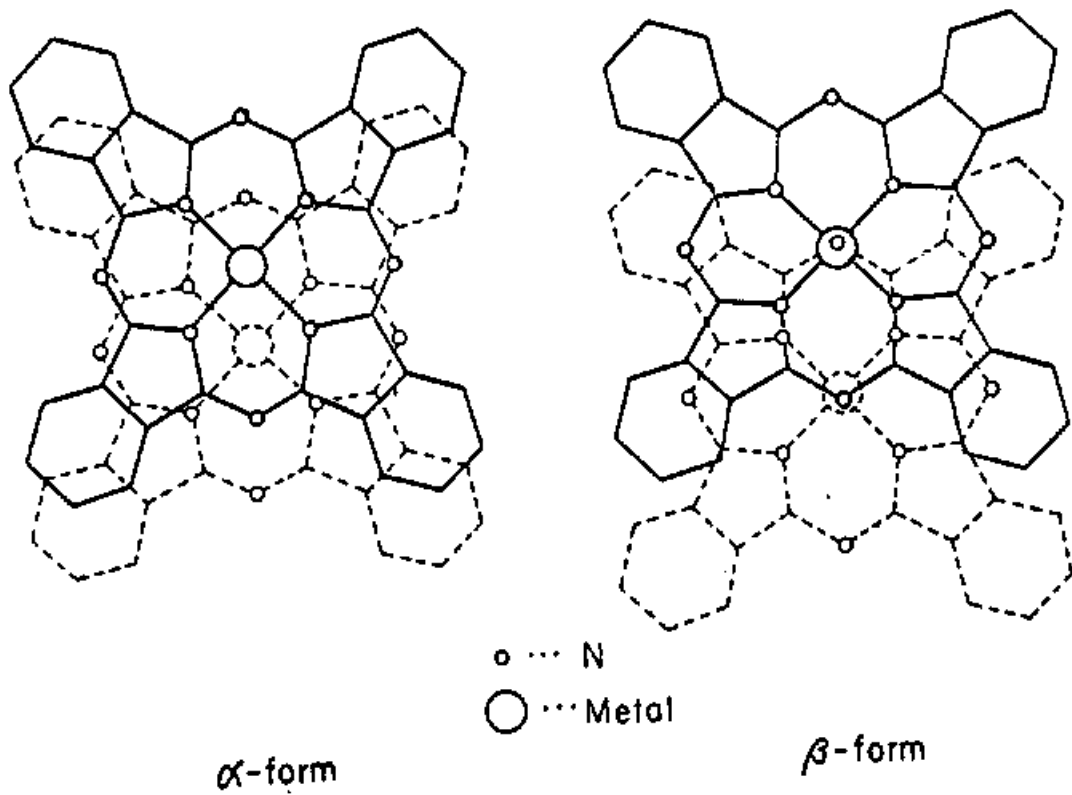


Fig. 5 Relation between the reciprocals of metal-nitrogen bond distances in metal porphyrins and the absorption frequencies of metal-ligand vibrations in metal phthalocyanines.



**Fig. 6** Molecular stacking of phthalocyanine derivatives in two crystal modifications.