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Far Infrared Spectra of Amine Complexes of Zinc-Phthalocyanine

Takashi KOBAYASHI, Natsu UYEDA, and Eiji SUITO*

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Far infrared spectra of charge transfer complexes formed by zinc-phthalocyanine with various amines have been examined in the crystalline state in the region 400～30 cm^{-1} and the new adsorption bands were observed in the region 120～220 cm^{-1}. It has been shown that these new bands are due to zinc phthalocyanine-amine intermolecular bond and their frequencies are in linear relation with the decomposition temperatures of the complexes. The structures of the molecular complexes were also discussed.

INTRODUCTION

It was reported in the previous paper[1] that zinc-phthalocyanine forms stoichiometric molecular complexes with various n-donor molecules such as heterocyclic amines, normal amines and dimethyl sulfoxide, all giving rise to stable crystalline powders. The infrared absorption spectra of these complexes were observed in rock salt region in view of characterizing the bonding state for complex formation. The result showed remarkable shifts toward higher frequencies as far as those of adduct molecules were concerned. Such a tendency to blue-shift for n-donor molecules strongly indicated that the intermolecular bond forces are governed by the charge transfer mechanism. However, neither considerable changes in the absorption bands assigned for zinc phthalocyanine nor other particular bands which might be directly ascribed to the complex formation were detected in this region. The present investigation on the far infrared spectra of the complexes has been undertaken (1) to study the effect of complex formation on the spectra of zinc phthalocyanine, and also (2) to find out possible new bands due to the intermolecular bonding in the complexes. Although many species of adduct n-donor molecules were reported in the previous paper, the samples were limited here only to typical amines such as pyridine, 2-methyl-pyridine (α-picoline), 4-methyl-pyridine (γ-picoline), piperidine, aniline, methylamine, trimethylamine n-propylamine and n-hexylamine.

EXPERIMENTAL SECTION

1. Preparation of Samples

The zinc-phthalocyanine was synthesized according to Linstead[2] *et al.* The crude product was washed with acetone in a Soxhlet extractor for 24 hours and then purified by repeated sublimation in a silica tube with a nitrogen atmosphere flowing at a rate

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* 小林隆史, 植田 夏, 水渡英二: Laboratory of Crystal and Powder Chemistry, Institute for Chemical Research, Kyoto University, Uji, Kyoto.

of 50 cm^3/min. A portion of the resulting needle-like crystals was converted into a finely divided powder by the acid paste method and dispersed in various amines and aqueous solutions of gaseous amines. These suspensions were kept standing in stoppered glass tubes at 50°C for 48 hours to produce respective amine complexes of zinc phthalocyanine. After filtration the products were dried at about 50°C under reduced pressure.

2. Analysis Procedure

The far infrared absorption spectra of zinc-phthalocyanine as well as its amine complexes were recorded as Nujol mulls extended on polyethylene films. The instrument used here was a Hitachi FIS-3 Spectrometer which was operated at room temperature in a frequency region between 400 and 30 cm^{-1}.

The decomposition temperatures at which these complexes release adduct molecules to leave pure zinc-phthalocyanine in its β-crystal form were determined by differential thermal analysis as reported in detail in the previous presentation.

RESULTS AND DISCUSSION

1. The Effect of the Crystal Structure

The crystal structure of the sample must be taken into consideration for the interpretation of the far infrared spectra when the materials are crystalline states as in the present case. It is well known that most of the metal phthalocyanines, including zinc derivative, exist in at least two polymorphic forms, namely, the metastable α-form and the stable β-form. Since far infrared spectra sensitively depend upon the crystal structure, spectra of both forms of zinc-phthalocyanine were compared on the basis of difference of molecular stacking in two polymorphs. The β-form crystals of Cu, Ni, Co and many other divalent metal derivatives are, as determined by Robertson[3] and also by Brown,[4] isomorphic with one another all assuming the space group of $P2_1/a$ of the monoclinic system. When a projection is taken normal to the molecular plane, the metal ion located at the center of the phthalocyanine ring lies exactly over and under the bridge nitrogen atoms in the nearest neighbor molecules parallelly stacked as shown in Fig. 1(b). The central metal ion, therefore, is surrounded by ten nitrogen atoms, four of which are the coordinating nitrogens in the pyrrol rings and the other four of which are the bridge nitrogens connecting four isoindole rings to form the planar phthalocyanine ligand. The final two nitrogens are those in the nearest neighbor molecules on both sides. In other words, the metal ion is positioned at the center of a square bonded configuration located within a larger octahedral array of six nitrogen atoms. Although crystal data of the α-polymorph were proposed by Robinson and Klein,[5] a more feasible structure was suggested by Ashida *et al.*[6] on the basis of the conspicuous isomorphic behavior of α-polymorphs of various metal phthalocyanines including Pt-derivative whose crystal structure was formerly determined by Robertson and Woodward[7] and recently refined by Brown.[8]

The crystal belongs to the space group of C2/n of monoclinic system and the stacking manner of parallelly oriented two planar molecules is shown in Fig. 1(a) again as

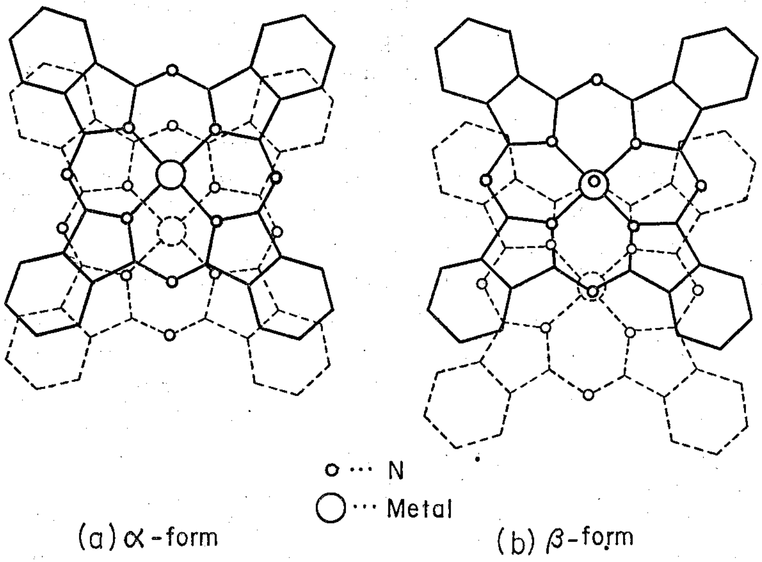

Fig. 1. Comparison of molecular stacking of metal-phthalocyanines in (a) α- and (b) β-modifications.

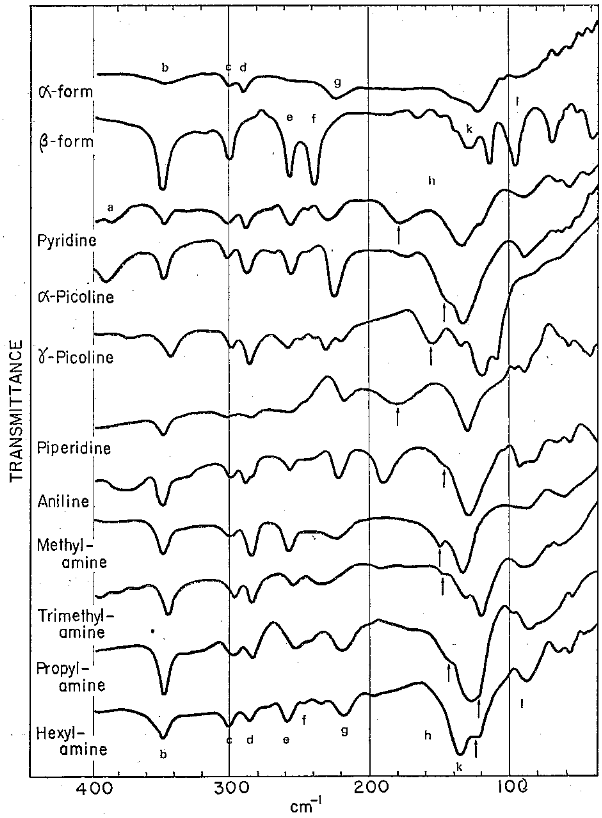

Fig. 2. Far infrared spectra of zinc-phthalocyanine and its amine complexes.

a projection taken normal to the molecular plane. The central metal ion is no more positioned right under or over the bridge nitrogen atoms of the nearest neighbor molecules, although the overlapping area is much greater than that of the β-polymorph. The crystal structure is not known yet as to the most of the amine complexes of zinc derivative excepting n-hexylamine complex. However, a comparative study[1] of X-ray powder diffraction patterns of complexes indicated the apparent difference in the crystal structures which are characteristic of the individual amines involved in them. When spectra are closely examined, the influence of such differences in molecular environment can be obviously recognized. The far infrared spectra of both polymorphs as well as those of the amine complexes are reproduced in Fig. 2, whereas the frequencies of the maximum absorptions are listed in Table I. According to the assignment reported in the previous paper[9] with respect to the dimorphs, the 354 cm^{-1} band for the β-form is an out-of-plane vibration of the pyrrol ring. Although this band also appears in the spectra of α-form, the intensity is greatly diminished when compared with that of β-form. The 300 cm^{-1} band (c) of β-form, assigned as a macrocylic ring deformation, is split into two bands at 303 cm^{-1} and 292 cm^{-1} in the case of the α-form. The most remarkable difference in the spectra can be seen in the behavior of the 258 cm^{-1} bands (e) for the β-form, which disappeared in the spectra of α-form. A remarkable band shift is also found with the one at 242 cm^{-1} for β-form, which appeared at 224 cm^{-1} in the case of the α-form.

These differences in the spectra are apparently ascribed to the dimorphism where

Table I. Far Infrared Spectra of Various Amine Complexes of Zinc-Phthalocyanine

	Zn-phthalocyanine		Amine complex									
	α-form	β-form	pyridine	α-picoline	γ-picoline	piperidine	aniline	methylamine	trimethylamine	propylamine	hexylamine	
a				389			375					a
b	350	354	349	347	345	349	349	350	347	349	350	b
c	303	300	303	303	302	302	301	300	299	300	303	c
d	292	—	288	286	286	285	288	286	286	286	288	d
d′							282					d′
e	—	258	258	258	259	257	259	259	256	254	260	e
f	—	242	244	244	250	242	242	—	—	248	250	f
f′					240						237	f′
g	224	—	228	226	232	218	224	225	230	224	221	g
g′		163			220							g′
h			*180*	*145*	*157*	*180*	*150*	*150*	*146*	*118*	*125*	h
i′	125	128			138							i′
i		114	133	136	121	130	131	135	122	130	138	i
l′	92	95	89	89	108	96	94			98		l′
l		70			84	88	84	87	90	86	88	l

b: Out-of-plane def. pyrrol rings. c: Pc-ring def. d, d′: Complex dependent. e: β-Type inplane pyrrol ring def. f, f′: In-plane Pc-ring def. g, g′: α-Type complex dependent. h: Complex bonding. i, i′: Complex dependent. l, l′: Zn-ligand vibration. Pc: Phthalocyanine ligand.

the stacking manner of the parallelly oriented planar molecules mainly causes the essential difference between the two crystal structures. The normal distance between two successive molecules is almost the same 3.5 Å for both crystal forms. This value is also common to the intermolecular distance for crystals of many other polycyclic aromatic compounds as well as for graphite crystal. This fact strongly indicates that the stacking distance is closely related to the interaction of π-electronic orbitals of adjacent planar molecules which consist of highly conjugated macrocylic rings. As already pointed out, the extent of over-lapping of molecular planes for the α-form is greater than that for the β-form. It seems reasonable to consider that the dimorphism would cause a certain variation of the distribution of π-electron density in the individual molecules of the two polymorphs, which in turn, affect their vibrational configurations.

The disappearance of 292 cm^{-1} band in the case of the β-polymorph seems to be closely related to the formation of the octahedral array of the six bridge nitrogens which surround the central zinc ion. Since the metal ion and the bridge nitrogen of the neighboring molecule assume the closest distance between these two molecules, a certain interaction can exist to make 292 cm^{-1} band forbidden. Such an octahedral configuration is not considered to be incidental but has a necessary contribution to grant the β-form the most stable crystal structure of all the polymorphs. As to the α-form crystal, such an octahedral array does not exist, so that the 292 or 224 cm^{-1} band appears as the infrared active mode.

As listed in Table I, the absorption peaks can be classified in 7 to 8 groups. Generally, the absorption bands of amine complexes include those of both α- and β-forms to some extent. However, it may be interesting to note that peaks which are characteristic of β-form are rather diminished while those for the α-form are enhanced in some cases. For instance, the absorption bands (e) at 254$\sim$260 cm^{-1}, which are assigned as in-plane pyrrol ring vibration in the previous paper decrease in the intensity, coming close to that of α-form for which no remarkable absorptions are observed at that frequency. Similar effects are also found with those groups of bands as f at around 242 cm^{-1} and 1 at around 85 cm^{-1}.

On the contrary, some others, not observed in the spectra of the β-form, are considerably enhanced to resemble in appearance to that for the α-form. Such an effect is evident for those bands as d and g which appear at about 288 cm^{-1} and 220 cm^{-1}, respectively. It is also observed that even those bands as c at 300 cm^{-1}, which are common to both α- and β-forms, also decrease their intensities, coming rather close to that of the α-form which is weaker than the β-form. All these observations indicate that the spectra of amine complexes tend to assume close resembrance to those of the α-form.

As pointed out in the previous paper on the basis of the blue shifts in the absorption bands which are characteristic of the adduct amine molecules, the nitrogen atoms are considered to participate in the coordination as can be expected from their strong electron donating property due to the non-bonding lone-pairs. Thus, the molecular configuration would appear as illustrated in Fig. 3 as an example. Such a configuration has been proposed by Elvidge[10)] on the basis of spectroscopic studies with respect to Cr-phthalocyanine and also by Vogt *et al.*[11)] as a result of X-ray analysis with a pyridine complex of Mn-phthalocyanine. Recent result of X-ray analysis[12)] on a single

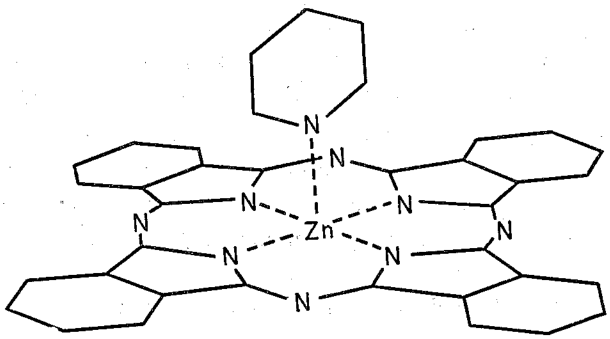

Fig. 3. An example of assumed structure of amine complex of zinc-phthalocyanine.

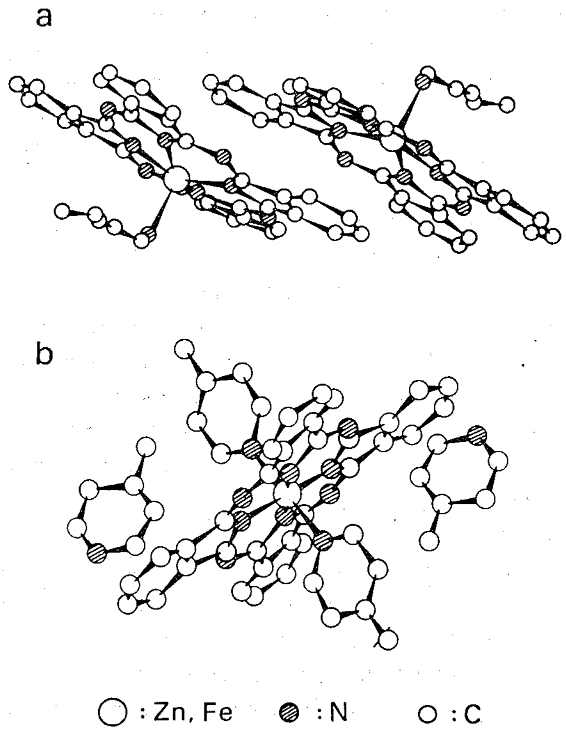

Fig. 4. Structure and stacking of amine complexes of metal phthalocyanines
(a) Zinc-phthalocyanine and n-hexylamine
(b) Iron-phthalocyanine and 4-methylpyridine.

crystal of zinc-phthalocyanine complex with n-hexylamine also clearly evidenced the postulation concerning the zinc-amine nitrogen bonding. A similar configuration was also established by X-ray diffraction analysis with respect to γ-picoline complex of iron-phthalocyanine.[13)]

It should be pointed out that the formation of complex leads to a remarkable change in structure where the parallel stack of planar molecules into columns can not be formed any more. In the case of 1 : 1 complex which forms a square pyramidal configuration, a possibility exists that two phthalocyanine molecules face to each other as shown in Fig. 4a, which is a schematic reproduction of n-hexylamine complex. As to 1 : 2 complex, having a configuration with two adduct molecules attached to both faces, even such a parallel facing can not be anticipated at all.

Thus, on complex formation, the octahedral nitrogen array in a stacked column of phthalocyanine molecules totally disappears quite contrary to the β-form. The effect of the disappearance may be most evident from the feature of those bands as d and g, which are all characteristic of α-form only being enhanced much more. Contrarily, the decrease in the intensity of other bands such as e and f is also considered to have certain relationship to new structures free from the nitrogen-octahedron.

2. The Effect of the Complex Formation

When zinc-phthalocyanine forms complexes with amines, two types of influences can be expected on the far infrared spectra in addition to that of crystallographic environment. One is the variation of the characteristic spectra of the original constituents, resulting in the frequency shift or intensity change, and the other is the appearance of new bands which are directly associated with the intermolecular bonding for the complex formation.

The 354 cm^{-1} band (b), assigned as an out-of-plane deformation of pyrrol ring, shifted to lower frequencies on complex formation. The amount of such red shift is in good accord with the ionization potential of each amine, that is, the ability of donating electrons. The electron donating ability of pyridine molecule, in general, increases with the methylation at various position in the order γ-picoline$>$$\beta$-picoline$>$ pyridine. As apparent from Table I, the frequency shift of the 354 cm^{-1} band is larger for γ-picoline than for pyridine. Although the relative order of shift is reversed as to α- and γ-picoline, this fact may be interpreted in terms of steric effect of methylated position on the bonding for the complex formation. A similar steric effect was also observed with the formation of methyl aniline complex as reported in the previous paper.1) The effect of methylation can be more evidently observed in other examples. With trimethylamine complex, the frequency shift appears much larger than that of methylamine complex, showing the stronger electron donating ability due to the three methyl groups.

The 258 cm^{-1} band of the β-form (e) assigned as an in-plane vibration of pyrrol ring showed a tendency to shift to the higher frequency region, though the amount was very small. Such an increase in the frequency of the in-plane vibration of pyrrol ring indicates the increase in the bond order between the isoindole nitrogen and two adjacent carbons.

As discussed in the previous paper,1) coordinated divalent zinc atom, which is forced to fit in the square planar configuration of phthalocyanine ring, still tends to assume tetrahedral structure so that the zinc-nitrogen bonding in the phthalocyanine is weaker than any other divalent metal derivatives as deduced from the data of their far infrared spectra. On complex formation, however, the coordination number changes. Then, it is no more necessary for the zinc ion to assume the instable tetrahedral bond structure.

The 3d electronic configuration of divalent zinc atom is 3d^{10} and usually becomes

$3d^{10}4s^{2}4p^{6}$ by the use of sp^3 hybrid orbitals when it coordinates to four ligands, most naturally assuming tetrahedral configuration. On the other hand, the zinc atom has no choice other than fitting itself into a square planar configuration due to the rigid phthalocyanine ring where the electron configuration should be $3d^{10}4s^{2}4p^{4}4d^{2}$ with a sp^2d hybridization. This latter configuration is essentially less stable than sp^3 tetragonal configuration as far as zinc atom is concerned. In the case of complex formation with amines, the zinc atom in phthalocyanine can assume at least five coordinated square pyramidal structure by the use of sp^3d hybrid orbitals which seems more stable than sp^2d orbitals for square planar coordination of zinc.

The most striking feature which is different either from the α- or the β-form in intensity and frequency can be found around 90 to 120 cm^{-1}. These bands are closely related to that of β-form at 98 cm^{-1} which is assigned as metal-ligand vibration and to those at 114 and 128 cm^{-1}.

The total appearance in this range is essentially similar to that of the α-form rather than the β-form as discussed in the foregoing section. However, the positions of major peaks are shifted to higher frequencies in the range of 114 to 128 cm^{-1} with considerably increased intensities. These remarkable frequency shifts to higher frequency range and the enhancement in intensities of the band due to the metal-ligand vibration can be interpreted in terms of the stabilization effect of the bonds between zinc ion and phthalocyanine ligand which assume the electronic configuration on as sp^3d hybrid orbitals as referred to in the case of the 258 cm^{-1} band of the in-plane vibration of pyrrol ring.

Although it has been pointed out that the absorption band at 242 cm^{-1} is crystal structure sensitive, the characteristic feature of this band is that they remain as doublet peaks for some of the complexes, being unlike the one for the α-forms. In addition to the influence of the crystal structure, this effect may be interpreted in terms of the molecular symmetry, as the far infrared spectra of H_2-phthalocyanine9) which has D_{2h} molecular symmetry also show a set of conspicuous doublet peaks at 238 and 230 cm^{-1}. It is reasonable to deduce that the addition of amine molecules on complex formation changes the molecular symmetry as a whole down to much lower groups than the original D_{4h} symmetry group of the plain zinc-phthalocyanine, particularly when a square pyramidal configuration is assumed.

3. The Vibrational Frequency and Decomposition Temperature

The absorption bands so far discussed are mostly those associated with zinc-phthalocyanine molecule and the effects of complex formation rendered rather indirect information about the nature of the intermolecular bonding. However, there appeared some new bands in the spectra as indicated by arrows in Fig. 2. Since these new bands were characteristic only of the amine complexes, they are considered to be caused by the intermolecular bonding between phthalocyanine and adduct amine. Although the intensities are rather small, the frequency of the maximum absorption greatly varies in a wide range from 125 to 180 cm^{-1}. It is empirically known that the absorption frequency is in linear relationship with the bond strength, namely the absorption for a strong band appears at high frequency region or *vice versa*.

It was found in the present case that the frequency of those bands of amine complex

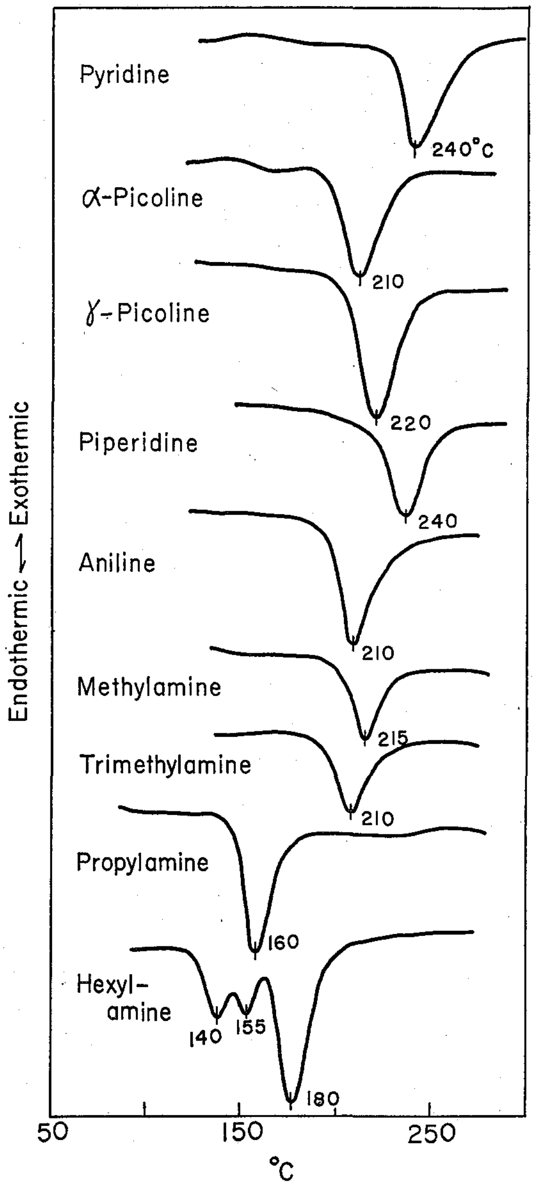

Fig. 5. Differential thermal curves of zinc-phthalocyanine complexes.

has a close relationship to the decomposition temperature T_D at which the complex releases the adduct molecules to leave pure Zn-phthalocyanine of the β-form. The decomposition temperature T_D was obtained from the differential thermal curve of the amine complex as shown in Fig. 5. As to the hexylamine complex for which three endothermic peaks appears, the highest decomposition temperature was taken as T_D, because the crystal includes various n-hexylamine molecules of different states, some of which are connected to zinc ion to show the higher decomposition temperature than the other unconnected ones. When the frequency of the absorption band assigned to the

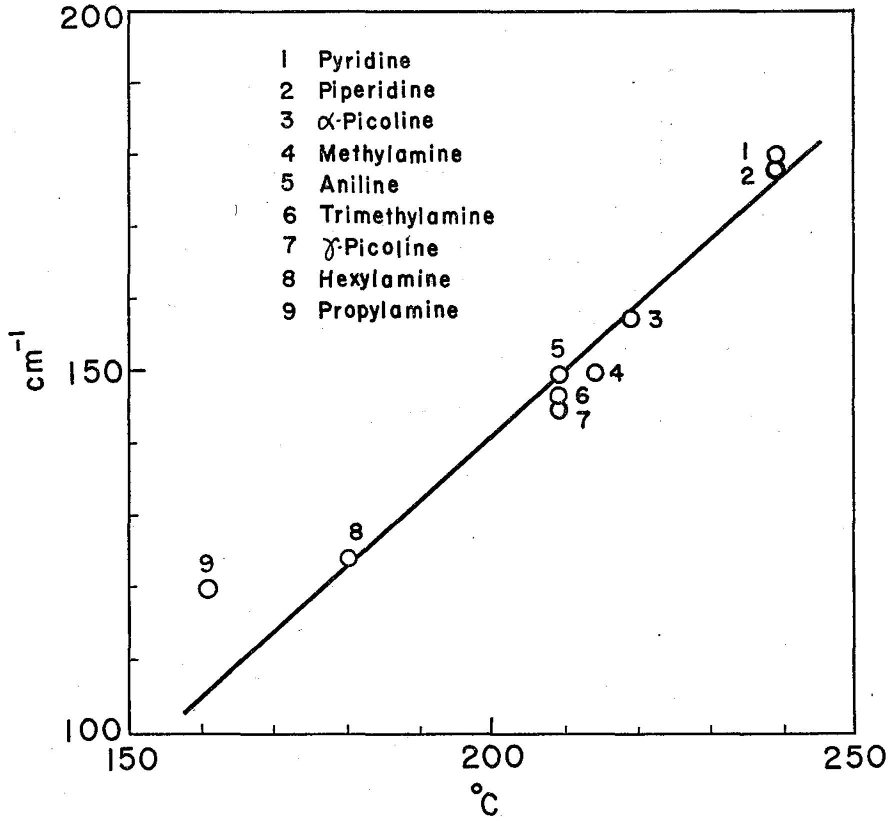

Fig. 6. Relationship between the decomposition temperature and absorption band for intermolecular bond of amine complex of zinc-phthalocyanine.

intermolecular bonding is plotted against the decomposition temperature which can be taken as the measure of bond strength, a comparatively well defined linear relationship is observed as shown in Fig. 6. As to propylamine complex, the strongest peak near 120 cm^{-1} appears rather broad. This effect is considered to be due to unresolved doublet peaks, one of which was taken as the peak due to the direct bonding. Thus, these new bands which appear in the range of 125 and 180 cm^{-1} is considered to be associated with the direct bonding between the adduct nitrogen of amine group and the central zinc ion.

It seems worthwhile to remember that the lower the ionization potential of amines, the stronger the electron donating ability which is expected to increase the intermolecular bond force for the complex formation. However, the electron donating ability is not always in the right order as far as the above series of complexes are concerned. This behavior is particularly remarkable with pyridine and picolines.

In the case of transition metal complex, the possibility of back donation must be taken into consideration. In fact, similar examples of such a reversed bond order was also reported in many cases, for instance, by Goldstein *et al.*[14] for heterocyclic base complexes of copper halides. Although no detailed information has been given in the present case, it seems plausible that the amount of back donation may be different, having a close relation to the stabilization effect due to the variation in the coordination number from square planar to square pyramidal or octahedral configuration.

REFERENCES

(1) T. Kobayashi, N. Uyeda, and E. Suito, *J. Phys. Chem.*, **72**, 2446 (1968).
(2) P. A. Barratt, C. E. Dent, and R. P. Linstead, *J. Chem. Soc.*, **1936**, 1719.
(3) J. M. Robertson, *ibid.*, **1936**, 1195, J. M. Robertson and I. Woodward, *ibid.*, **1937**, 219, J. M. Robertson, *ibid.*, **1935**, 615.
(4) C. J. Brown, *ibid.*, **1968**, 2488.
(5) M. T. Robinson and G. E. Klein, *J. Amer. Chem. Soc.*, **74**, 6294 (1952).
(6) M. Ashida, N. Uyeda, and E. Suito, *Bull. Chem. Soc. Japan*, **39**, 2616 (1966).
(7) J. M. Robertson and I. Woodward, *J. Chem. Soc.*, **1940**, 36.
(8) C. J. Brown, *ibid.*, **1968**, 2494.
(9) T. Kobayashi, *Spectrochim. Acta*, **26A**, 1313 (1970).
(10) J. A. Elvidge and A. B. P. Lever, *J. Chem. Soc.*, **1961**, 1257.
(11) L. H. Vogt, Jr., A. Zalkin, and D. H. Templeton, *Inorg. Chem.*, **6**, 1725 (1967).
(12) T. Kobayashi, T. Ashida, N. Uyeda, M. Kakudo, and E. Suito, *Bull. Chem. Soc. Japan*, **44**, 2059 (1971).
(13) T. Kobayashi, F. Kurokawa, T. Ashida, N. Uyeda, and E. Suito, *Chem. Comm.*, **1971**, 1631.
(14) M. Goldstein, E. F. Mooney, A. Anderson, and H. Gebbie, *Spectrochim. Acta*, **21**, 105 (1966).