Copper Phthalocyanine과 그 Azo 置換錯鹽들의 對稱과 Spectra

趙 南 淑* · 金 基 煥* · 韓 治 善**

延世大學校 化學科

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Symmetry and Spectra of Complexes of Azo-Substituted Copper Phthalocyanine

Nam-Sook Cho*, Ki-Hwan Kim* and Chi-Sun Hahn**

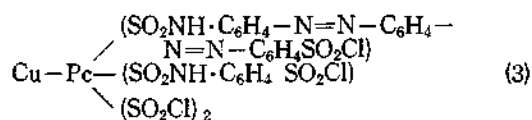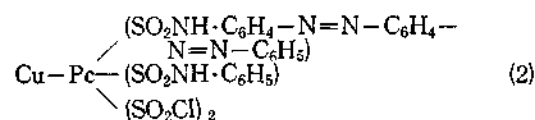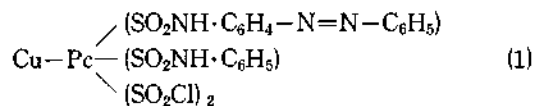*Department of Chemistry, Yonsei University*

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要 約 Copper phthalocyanine 과 그것에 azo基가 도입된 몇가지 錯鹽들의 UV 吸收 spectra 를 對稱論, ligand field theory 그리고 分子軌道論的見地에서 考察하였으며 또한 이들 錯鹽의 構造를 論하였다.

Abstract The UV absorption spectra of the copper phthalocyanine and its azo derivatives in pyridine have been examined on the basis of symmetry operation, ligand field theory and molecular orbital consideration. The above treatment was also employed to determine the structure of the synthesized complexes.

Introduction

The chemical formula of the copper phthalocyanine-azo (Cu-Pc-Azo) complexes synthesized in this study are as follows:

$$Cu-Pc \begin{cases} (SO_2NH \cdot C_6H_4 - N=N-C_6H_5) \\ (SO_2NH \cdot C_6H_5) \\ (SO_2Cl)_2 \end{cases} \quad (1)$$

$$Cu-Pc \begin{cases} (SO_2NH \cdot C_6H_4 - N=N-C_6H_4 - \\ \quad N=N-C_6H_5) \\ (SO_2NH \cdot C_6H_5) \\ (SO_2Cl)_2 \end{cases} \quad (2)$$

$$Cu-Pc \begin{cases} (SO_2NH \cdot C_6H_4 - N=N-C_6H_4 - \\ \quad N=N-C_6H_4SO_2Cl) \\ (SO_2NH \cdot C_6H_4 \ SO_2Cl) \\ (SO_2Cl)_2 \end{cases} \quad (3)$$

Both the absorption and intensity maxima in the UV spectra of copper phthalocyanine (Cu—Pc)[1] and the above complexes remarkably differ from those of absorption bands due merely to π and lone pair electrons usually seen in the ultraviolet and visible regions. This difference seems to be caused by the existence of a transition element having d orbital electrons which participate in the absorption transition of the complexes. As shown in *Figure* 1, the Cu—Pc, the parent molecule of these complexes, has a copper atom with positive character in the center of the complex, surrounded by four ide-
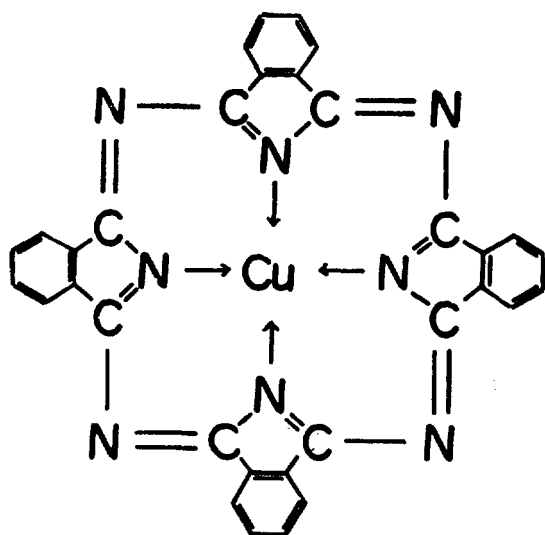
Figure 1. The structure of copper phthalocyanine.

ntical phthaloimino groups whose nitrogen atoms form dipoles with the copper atom.[1]

Thus, these four phthaloimino groups become ligands, and since the central atom has d electrons it should be apparent, judging from the structure of the complex and the orientation of the dipoles, that they form a typical square planar ligand field, even though not linked by strong electrostatic bonding. Therefore, a study of the UV absorption spectra of Cu-Pc by symmetry operation and ligand field theory (LFT) seems to be called for, and the same treatment would seem appropriate for the Cu-Pc-Azo complexes. Furthermore, the structure, that is the position of substituted groups in the complexes, is to be considered as well.

Experimental

Preparation of Compounds. Copper phthalocyanine tetrasulfonyl chloride (I).—Into 29. 3 g (0.25 M) of chlorosulfuric acid (Wako reagent grade) 5.8 g (0.01 M) of Cu-Pc obtained by Wyler's method[2] were gradually added. The reaction ran at 130°C for 3hr. Upon completion

of the reaction, the mixture was cooled to room temperature in an ice-bath and then treated with 6 g (0.05 M) of thionyl chloride (Wako reagent grade) at 110° for 1.5 hr. Both reactions evolved large volumes of hydrogen chloride gas. At the end of the reaction, the temperature of the mixture was dropped to below 5° by adding a good amount of ice and treating the vessel in an ice-bath. Blue crystals were collected by suction, washed with ice-cold water until the filtrate shown neutral and dried in vacuo, yield 6.5 g (96 %), mp>250°.

Copper phthalocyanine bis-sulfanilamide-bis-sulfonyl chloride. $Cu-Pc (SO_2NH-C_6H_5)_2 (SO_2Cl)_2$ (II) The chlorosulfonyl group in compound (I) and the amino group in aniline were condensed together by Hinsberg's reaction. Into 1.9 g (0.02 M) of aniline were added 9.7 g (0.01 M) of $Cu-Pc (SO_2Cl)_4$ in small quantities. Upon vigorous stirring, the color of the mixture turned to dark green. A small amount of saturated aq. NaOH solution was added and the reaction allowed to run overnight with stirring. Upon addition of an excess amount of 20 % HCl solution, blue crystals formed. The crystals were collected by suction and washed with cold water several times, dried in vacuo, yield 8.3 g (92 %). The crude product was purified by dissolving in 5 % NaOH and precipitation with HCl, then washed with ice-water, mp>250°.

Complex No. 1, Condensation of Cu-Pc· (SO₂ NHC₆H₅)₂· (SO₂Cl)₂ with benzene diazonium chloride. The benzene diazonium chloride used here was synthesized by diazotization. Then in to 50 ml of 10 % aq. NaOH solution were added 10.2 g (0.01 M) of purified (I) in small portions. The hydrogen ion concentration of the solution was kept at pH=9 to 10 and the color of the solution appeared blue. A con-

tainer of the solution was placed in an ice-bath and a good amount of ice added to the solution into which was added benzene diazonium chloride previously prepared slowly with good stirring so as to keep the temperature of the solution below 5°. At the same time, a saturated aq. NaOH solution was added from time to time in order to keep the pH of the solution between 9 and 10. The reaction was run for 7 hr. Upon completion of the reaction, the color of the mixture turned to a dark green when acidified to pH 3 to 4 with concentrated HCl. The crystals were collected by suction and washed with cold water to remove the excess acid and unreacted benzene diazonium chloride, dried in vacuo, yield 9.3 g (83 %), mp>250°. Anal. calcd. for $C_{50}H_{28}CuN_{12}O_8S_4Cl_2$: N, 10.78 S, 14.13; Found: N, 11.01; S, 13.98.

Complex No. 2, Condensation of Cu-Pc· $(SO_2 NHC_6H_5)_2$· $(SO_2Cl)_2$ with p-aminoazobenzene. This complex was prepared by condensing compound (Ⅱ) with p-azobenzenediazonium chloride (Ⅲ). Compound (Ⅲ) was obtained by diazotization of p-aminoazobenzene which was synthesized from aniline.[4] Into 50 ml of 10 % aq. NaOH solution were dissolved 10.2 g (0.01 M) of pruified compound (Ⅱ) with good stirring. The color of the solution changed to blue at a pH around 9 to 10. Keeping the temperature below 5° by adding ice and cooling the vessel in an ice-bath, previously prepared p-az obenzene diazonium chloride (Ⅲ) was slowly added to the above solution at such a rate that the reaction temperature stayed below 5°. Saturated aq. NaOH solution was added to the mixture so as to keep the pH of the reaction mixture at around 9 to 10. The reaction took place for 7 hr. As the reaction proceeded, the color of the mixture changed to greenish blue and then dark green in turn. Upon completion of the reaction, the product was acidified to

pH=3~4 with concentrated HCl solution. Dark greenish crystals were colleced on Büchner funnel by suction, washed to remove acid and unreacted diazonium salt, dried in vacuo, yield 10.9 g (81 %), mp>250°. Anal. calcd. for $C_{62}H_{36}CuN_{14}O_8S_4Cl_2$: N, 15.83: S, 9.84. Found: N, 15.22; S, 9.02.

Complex No. 3, Chlorosulfonation of complex No. 2. Into 30 g (0.25 M) of chlorosulfuric acid were gradually added 13.6 g (0.01 M) of complex No. 2. The reaction mixture was warmed up gently and kept at 110° for 2 hr. Upon completion of the reaction, the mixture was cooled to room temperature as quickly as possible by plunging the vessel into an ice-bath and then 6 g of thionyl chloride were added. The reaction was run again at 110° for 1 hr. The mixture was poured slowly onto ice lowering the temperature to below 5°. Dark greenish crystals were collected by suction, washed with ice water, dried in vacuo, yield 14.1 g (91 %), mp>250°. Anal. calcd. for $C_{62}H_{34}CuN_{14}O_{12}S_5Cl_4$: N, 13.22: S, 12.88. Found; N, 12.99; S, 12.07.

Preparation of Solutions and Measurements of Spectra. Preliminary tests show that the optimum concentration of solutions for UV measurements was $2.0 \times 10^{-5} M$. Thus, this concentration was used throughout in this work. Pyridine (Wako reagent grade) was used as the solvent and the pH of the solutions were adjusted with HCl and NH_4Cl buffer (both Ishizu reagent grade). Measurements of pH were carried out with a Hitachi Horiba H-5 pH meter. UV spectra were measured with a Beckman model DU-2 spectrophotometer employing 1 cm quartz cells. Pyridine was also used as a reference solution.

Results and Discussion

As it has already been pointed out in the

introduction that the Cu-Pc formed a ligand field, if the copper atom, a transition metal in the Cu-Pc, were isolated, five d orbitals might degenerate due to the centro-symmetric force. However, since the Cu-Pc has an extremely higher degree of symmetry belonging to the D_{4h} group[5,6] and also an electrostatic field, even though very weak, due to the ligand field produced by the phthaloimino groups in the molecule coinciding with the centro-symmetric field of the central copper atom, these five d orbitals would not remain in the degenerate state as in the case of an isolated transition element. In general, a transition metal belonging to a D_{4h} point group has four ligands. Thus, most of the electrons on these orbitals are presumably repelled by the negative character of the ligands, and the degeneracy tends to split substantially. It is known by qualitative treatments that the energy of d orbitals in the case of a D_{4h} point group such as Cu-Pc splits as in *Figure* 2[5c]

Although there could be a number of possible transitions between these split energy levels, since these are $g{\rightarrow}g^*$ transitions and the molecule has such a high degree of symmetry with its identity element, I, most of these transitions are forbidden by the selection rule. If some of these trantisions were assumed to occur, avoiding the forbidden selection rule in some way, they would, in general, appear only
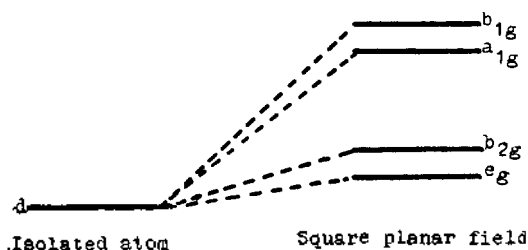

.Isolated atom   Square planar field

Figure 2. Ligand field splitting of the five degenerate 3d orbitals in a square planar molecule.

weakly in the visible region. In sharp contrast with this, however, as shown in *Figuse* 3, an extraordinarily intense absorption band appears at $\lambda_{max}=678\,m\mu$ which is hardly assignable as a transition band due only to the split energy levels of d electrons.

Therefore, it seems more profitable to speculate on the interaction between p and d electrons in the central transition element and delocalizable electrons in the ligands. From the fact that sulfonyl group has been substituted on the Cu-Pc ring in this work, it is quite reasonable to consider that the Cu-Pc ring has aromatic character. This implies that the copper element is surrounded by aromatic units. Thus, the interaction between p and d electrons in the transition element and π electrons in the ligands should take place equally well, and the transition between orbital species due to the interaction of π electrons in the aromatic ligands with p and d electrons in the central copper atom rather than the repulsion of d electrons due to the negative character of the ligands would adequately explain the UV absorption spectra of the Cu-Pc and its azo substituted complexes. Rather than stop with this consideration of the spectra of the Cu-Pc with only pure LFT, it would be seem reasonable to treat it also with MO theory. The labil electrons in a system consisting of a transition atom having d electrons and aromatic ligands, such as the Cu-Pc in this study, seem most likely to transfer toward the copper atom from the ligands due to the positive central atom; and consequentry, the main intense band at $678\,m\mu$ can be a charge transfer transition band. The hybrid orbital formed by the central copper atom is supposed to be dsp^2, and in a D_{4h} point group, d, s and p orbitals belong to b_{1g}, a_{1g} and e_u species, respectively. The most likely transition among the various possible

excitations, which would conserve orbital symmetry in a D_{4h} point group and avoid the forbidden selection rule, is the $e_u \rightarrow b^*_{1g}$ excitation. In other words, it can be said that the bond between the central copper atom and the nitrogen atom which is the basic center of each ligand is not a pure σ bond, but rather to a large extent π bond. Experimental evidence supporting the above proposal is based not only on the fact that such extraordinarily intense main band can hardly be explained by pure ligand field transition, but also on the following results which strongly support the above interpretation. First of all, as shown in *Figure* 3 and 4, the Cu-Pc itself, as well as all other substituted complexes (1), (2) and (3), has a

very intense peak at 350→355 mμ.

This strong band at 350−355 mμ might, at a glance, be referred to a transition band due to the excitation of π electrons in the aromatic azo groups of the Cu-Pc-Azo complexes. However, the experimental fact that the transition band at 350−355 mμ also appears even in Cu-Pc itself which has no such aromatic azo groups is strong evidence that the transition band at 350−355 mμ is not due to azo groups in this case, and it rather clearly indicates the existence of the interaction between π electrons in the ligands and p and d electrons in the central copper atom. Secondly, the maximum intensity at λ_{max}=670−680 mμ of the Cu−Pc and the complexex (1) to (3) varies remarkably with
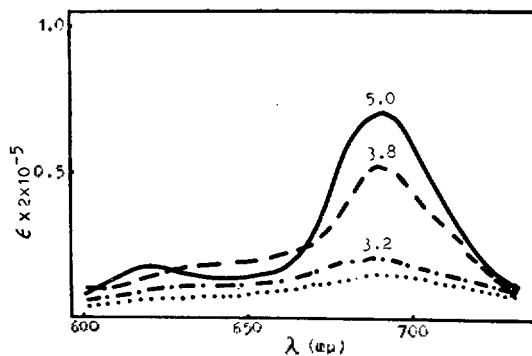

Figure 3. The absorption spectra of Cu-Pc in pyridine at pH=1 and 12.

Figure 5. The hypochromic effect of the absorption spectra of the Cu-Pc varying with pH.

Figure 4. The absorption spectra of the substituted complexes No. (1), (2) and (3) at pH=12.
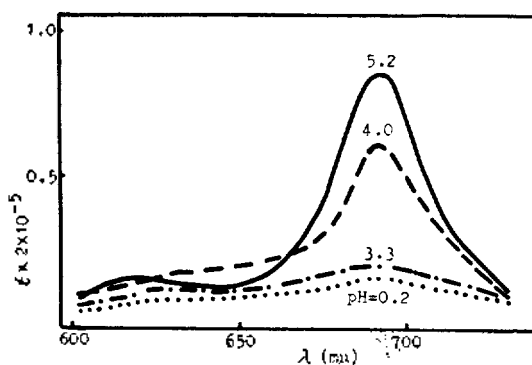

Figure 6. The hypochromic effect of the absorption spectra of the complex No. 1 varying with pH.

the change of pH of the solution.

That is, it can be seen readily in *Figure* 5 to 8 that the intensity of the main band obviously decreases with decreasing pH in the sol-
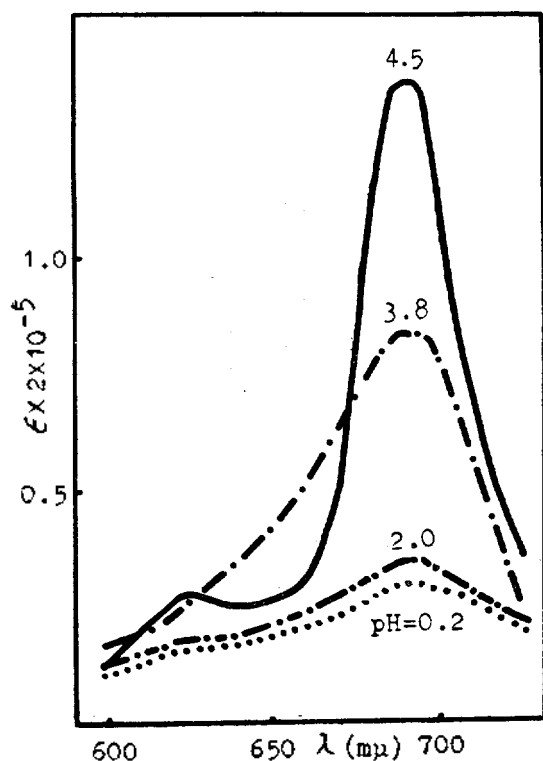

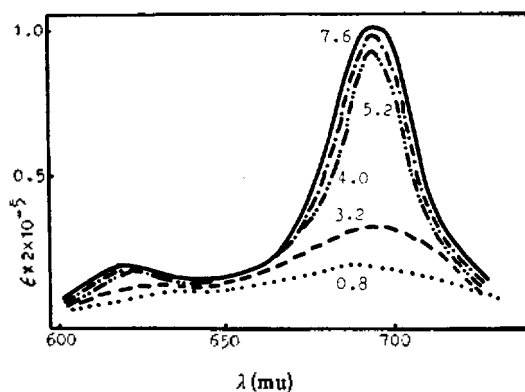*Figure* 7. The hypochromic effect of the absorption spectra of the complex No. 2 varying with pH.

Figure 8. The hypochromic effect of the abosorption spectra of the complex No. 3 varying with pH.

ution in all cases, although there is no blue or red shift with the change of hydrogen ion concentration. This implies that there is a decrease in the probability of the charge-transition. In other words, the interaction between π electrons in the ligands and p and d electrons in the central atom is restricted by protons, and consequently, the probability of excitation for the charge-transfer transition is decreased. However, it seems difficult to interpret the spectra of the Cu-Pc and its complexes (1) to (3) by charge-transfer transition alone because another band appears at $\lambda_{max} = 625\,m\mu$ with a shoulder near $678\,m\mu$ which is not as intense as the main band, and furthermore, there is no distinguishable variation in its intensity with change of pH in the solutions. In general, absorption bands in the visible region due to ligand field transitions submerge under charge-transfer transition bands, and the weak band at $625\,m\mu$ is not likely to be due only to a charge-transfer transition. This band, thus, might reasonably be ascribed to a strong ligand field transition having σ character owing to the splitting of d electrons in the $d_{x^2-y^2}$ orbital of the central atom by the ligands.

Finally, it remains to examine the structure of the complexes (1) to (3). It is readily seen that the substituents in a phthaloimino group would be located at similar sites, either 3 or
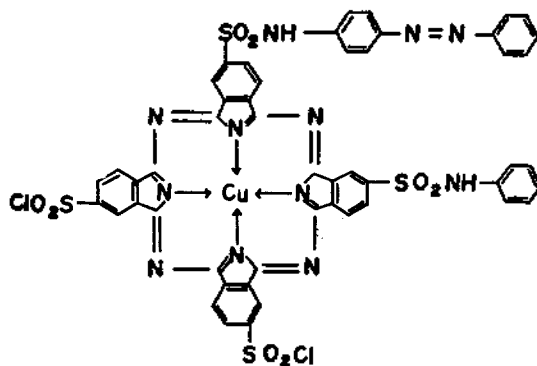

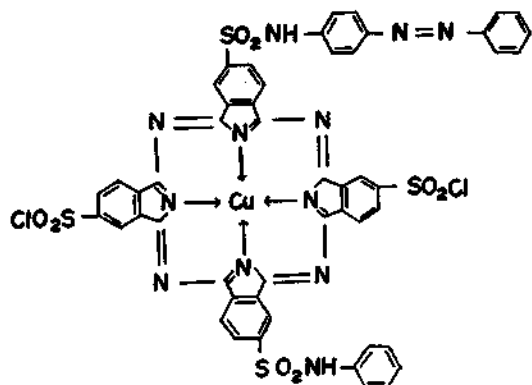*Figure* 9. A plausible structure of the complex No. 1

Figure 10. The proposed structure of the complex No. 1.

4-position, in a benzene ring. However, there could be two different places for the two thionyl groups in the molecule. One is where the two thionyl groups are substituted in two adjacent benzene rings as in *Figure* 9 and the other is when the two groups are oriented far apart as in *Figure* 10.

Even though the latter can possess neither a precise I element nor C_2^s element as a whole, it is quite conceivable that the latter structure has a much higher degree of symmetry than the former. And also the latter is more favorable to π electron transfers from the ligands into the central atom without much distortion of the symmetry of the square planar hybrid orbital, $d_{x^2-y^2}$. The choice of the structure in *Figure* 10 is also firmly supported by the experimental fact that λ_{max} and ε_{max} in the spectra of the complexes (1) to (3) are not significa-

ntly different from that of the parent molecule, Cu-Pc, which has an extremely high degree of symmetry as described in the foregoing discussion.

Acknowledgement

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