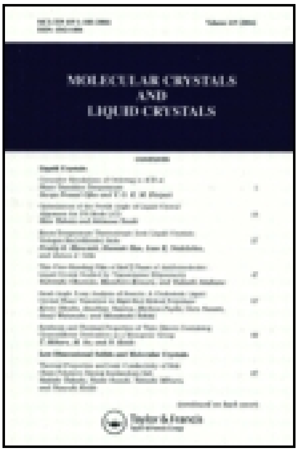

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Electrocrystallization of Metallophthalocyanines: Effects of Substituents on the Oxidation Potential and Crystallization

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Electrocrystallization of Metallophthalocyanines: Effects of Substituents on the Oxidation Potential and Crystallization

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A series of oxidation potentials of substituted metallophthalocyanines are examined with cyclic voltammetry. Relation between oxidation potential and the Hammett's constant of substituents is found to be linear for both octa- and tetrasubstituted derivatives. The oxidation potential shift is found to be calculated by electron-withdrawing or donating ability of substituents. Electrocrystallization of these compounds gives crystals which are composed of only cyanometallophthalocyanine. Crystals of substituted derivatives are analyzed to have different molecular arrangements from unsubstituted one because of steric effect of the substituents. Crystals of unsubstituted derivatives show highly inherent conductivity, but substituted ones show less conductivity due to the different molecular arrangements.

INTRODUCTION

We have firstly reported the preparation of inherently conductive crystals of metallophthalocyanine with a novel electrocrystallization technique.[1] This electrocrystallization technique is expected to be used for the preparation of a wide range of organic conductors. The electrocrystallization proceeded only when an oxidation potential, higher than that for the phthalocyanine rings, was given to the solution. The oxidation potential was shifted by the introduction of substituents to the phthalocyanine ring. This potential shift was therefore revealed to be an important factor to control the electrocrystallization of these phthalocyanines. These experimental results triggered us to examine the relation between structure and oxidation potential of phthalocyanines to get the best conditions for the electrocrystallization. The potentials of phthalocyanines, especially those of rings should be affected by the nature of the substituents, but only a few examples have hitherto been reported.

EXPERIMENTAL SECTION

Materials

Octa- and tetrasubstituted derivatives were prepared according to references.[2] Preparations of potassium dicyanophthalocyaninatocobalt(III) derivatives have been reported previously.[3]

Cyclic voltammetry

Cyclic voltammograms were obtained with Pt plate electrode which was coated with phthalocyaninatocobalt(II) derivatives in acetonitrile solution containing 0.1 molar tetraethylammonium chloride (TEAC). In case of potassium dicyanophthalocyaninatocobalt(III) derivatives, a Pt wire was used as working electrode in an acetonitrile solution of phthalocyanine. Cyclic voltammetry was carried out with Hokuto Denko HA-501G potentiostat and Hokuto Denko HB-105 function generator, at scan rate of 50 mV sec^{-1}.

Electrocrystallization

Electrocrystallization was carried out with the same potentiostat described above. Pt wires were used as electrode and any supporting electrolyte was not added. Detailed conditions and cell construction have been mentioned previously.[1,4]

X-ray diffraction

X-ray diffractions were obtained by Nicholet P3/ and X-ray powder diffractions by Philips PW-1700.

ESR spectroscopy

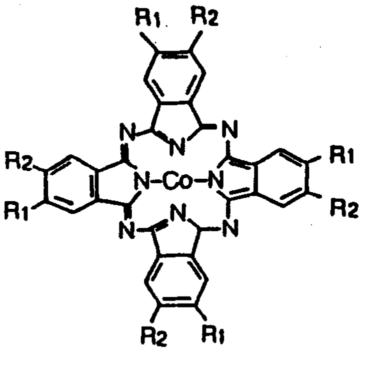
ESR spectra for a series of phthalocyaninatocobalt crystals were obtained by JES-FE-3X, Nippon Denshi Co. Ltd.

RESULTS AND DISCUSSION

I) The Oxidation Potential of Substituted Metallophthalocyanines and Electrocrystallization

Substituted phthalocyaninatocobalt(II) derivatives prepared in this study are summarized in Scheme 1. We measured cyclic voltammograms in the potential range from 0 to 2.0 V vs. Ag/AgCl. In this range, oxidation reaction of Co(II) to Co(III) occurred, but oxidation processes for the ring and metal were clearly distinguished with each other.[5]

The oxidation potentials of the phthalocyanine ring we measured are summarized in Table I. Electron-withdrawing groups, such as cyano and carboxyl groups were expected to reduce the negative charge on the phthalocyanine ring. On the contrary, electron-donating groups, such as methoxyl and methyl groups were expected to increase it. Octacyano derivative showed the oxidation peak of the ring at +1.80 V and octacarboxy derivative at +1.65 V, as expected. On the contrary, methoxyl groups shifted it in a negative side by 0.13



Compound		
Abb.	R_1	R_2
$(CN)_8PcCo$	CN	CN
$(HOOC)_8PcCo$	COOH	COOH
PcCo	H	H
$(H_3CO)_8PcCo$	OCH_3	OCH_3
$(H_3C)_8PcCo$	CH_3	CH_3
$(O_2N)_4PcCo$	NO_2	H
$(HOOC)_4PcCo$	COOH	H
$(H_3CO)_4PcCo$	OCH_3	H
$(H_2N)_4PcCo$	NH_2	H

Scheme 1

TABLE I

Oxidation potentials of octasubstituted phthalocyaninatocobalt(II)

Compound	P^+/P^a (V vs. Ag-AgCl)	Hammett's constant
$(CN)_8PcCo$	1.80	0.70
$(COOH)_8PcCo$	1.65	0.44
PcCo	0.90	0
$(CH_3O)_8PcCo$	0.77	−0.12
$(CH_3)_8PcCo$	0.83	−0.14

[a] In acetonitrile solution, 10 mM TEAC, 25°C.

V as shown in Table I. The oxidation potential of octasubstituted derivatives was analyzed to be in the order of the following substituents;

$$—CN > —COOH > —H > —OCH_3 > —CH_3 \qquad (1)$$

A good linear relation between the oxidation potential and the Hammett's constant for benzene derivatives is found as shown in Figure 1. This suggests that the Hammett's constant for benzene derivatives

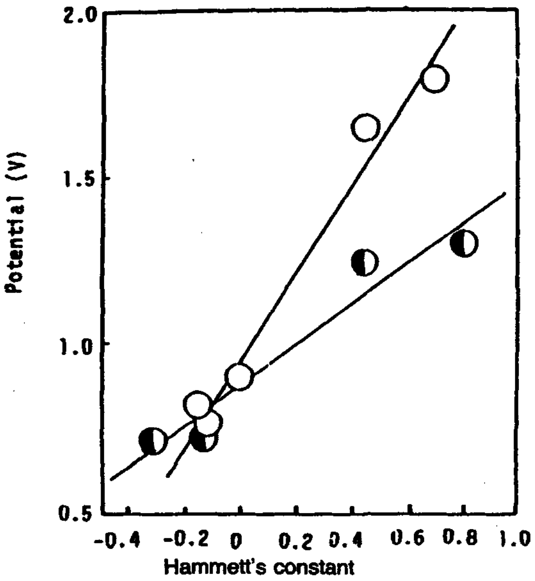


FIGURE 1 Relation between oxidation potential and the Hammett's constant of substituent for (○) octa-substituted and (◐) tetra-substituted.

is effective for the estimation of the oxidation potential of substituted phthalocyanine derivatives.

The oxidation potential (E_{ox}) was expressed as a function of the Hammett's constant (K) as shown in Equation (2).

$$E_{ox} = 1.30\,K + 0.96 \tag{2}$$

The measured oxidation potentials of tetrasubstituted phthalocyaninatocobalt(II) derivatives are summarized in Table II. Tetranitro and tetracarboxy derivatives showed more positive oxidation potentials than unsubstituted phthalocyaninatocobalt(II) as expected from the results for octasubstituted ones. For tetrasubstituted derivatives, nitro groups shifted its oxidation potential to more positive side by 0.40 V, and carboxyl groups by 0.34 V. Tetramethoxy and tetraamino derivatives showed their oxidation peaks at +0.73 V and +0.72 V, respectively. Those are smaller than that for unsubstituted one. The oxidation potential for tetrasubstituted compound was shifted by the substituents as the following order;

$$\text{—NO}_2 > \text{—COOH} > \text{—H} > \text{—OCH}_3 > \text{—NH}_2 \tag{3}$$

This sequence was also characterized by the Hammett's constant. The relation between the oxidation potential of tetrasubstituted phthalocyaninatocobalt(II) and the Hammett's constant for benzene derivatives is also shown in Figure 1. It is a similar relationship to that for octasubstituted ones. This also delivers the following equation;

$$E_{ox} = 0.59\,K + 0.88 \tag{4}$$

The slope for tetrasubstituted derivatives is almost a half of that for

TABLE II

Oxidation potentials of tetrasubstituted phthalocyaninatocobalt(II)

Compound	P^+/P^a (V vs. Ag-AgCl)	Hammett's constant
$(NO_2)_4$PcCo	1.30	0.81
$(COOH)_4$PcCo	1.24	0.44
PcCo	0.90	0
$(CH_3O)_4$PcCo	0.73	−0.12
$(NH_2)_4$PcCo	0.72	−0.30

[a] In acetonitrile solution, 10 mM TEAC, 25°C.

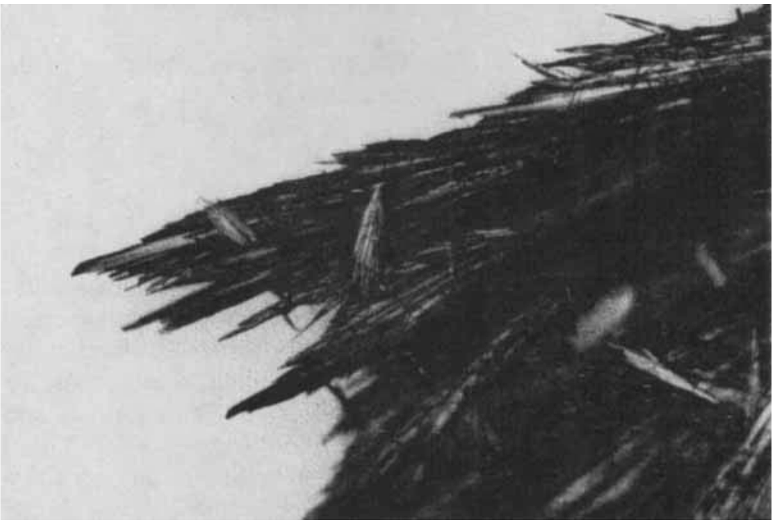


FIGURE 2 Micrograph of cyano(octamethylphthalocyaninato)cobalt(III). SEE COLOR PLATE I.

octatsubstituted ones. The reported oxidation potential of tetratertbuthylphthalocyaninatocobalt(II) also lied on this relation. As mentioned above, the oxidation potentials of substituted hmetallophthalocyanine have not been investigated substantially. For the potentials of substituted derivatives examined here, a good linear relationship between oxidation potential and the Hammett's constant of substituent was firstly found for both octa- and tetrasubstituted complexes. This relationship should be useful not only for the estimation of a suitable potential for electrocrystallization but also for regulation of oxidation potential of phthalocyanines with certain substituents for the design of some catalytic systems.

Electrocrystallization was carried out for potassium dicyanophthalocyaninatocobalt(III) derivatives in acetonitrile. A micrograph of typical crystals is shown in Figure 2. All obtained crystals were revealed to be composed of only one component, cyanophthalocyaninatometal(III) derivative.[3] The relation between the yield of crystals and applied potential for substituted phthalocyanines was shown in Figure 3. Not all phthalocyanine derivatives could be crystallized in electric field because of the presence of structural isomers for tetrasubstituted derivatives. However those were sometimes phase separated when the solution was stored under the oxidative moiety

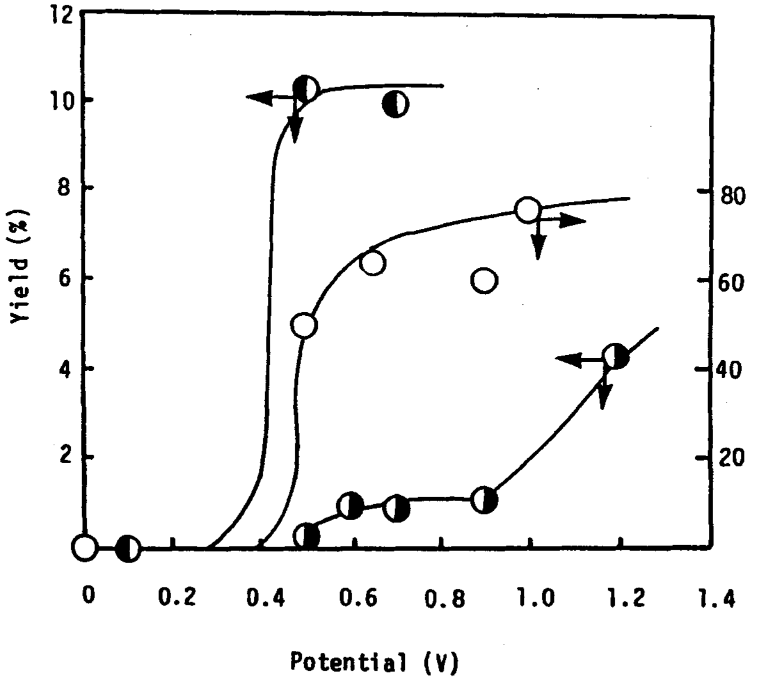


FIGURE 3 Relation between the yield of crystals and the applied potential for electrocrystallization of substituted phthalocyanines. ○: cyanophthalocyaninatocobalt(III), ◑: octamethyl-substituted derivative, ◐: octamethoxy-substituted derivative.

of the ring. It was clear that the drastic decrease in the solubility of phthalocyanines through the oxidation of phthalocyanine rings was essential factor for the electrocrystallization. The difference in the crystal yield as shown in Figure 3 is therefore attributed to the different solubility of the oxidized compounds. Though cyanophthalocyaninatocobalt(III) obtained through electrocrystallization was insoluble in organic solvents, introduction of substituents to phthalocyanine ring probably made the solubility higher. For this reason, the crystal is partially soluble in the solution which may remain the yield low. There are four structural isomers in the case of tetrasubstituted derivatives. They are generally more soluble than octasubstituted ones by the decrease of symmetry (except for the improved solubility by the nature of functional group). But it is clear that the existence of isomers is a negative factor for electrocrystallization. Octasubstituted derivatives gave better results on electrocrystallization. The mechanism of electrocrystallization seems to be depicted as follows.

anode $[Pc^{2-}Co^{3+}(CN)_2] \xrightarrow{-e} [Pc^{1-}Co^{3+}(CN)_2]$

$\longrightarrow Pc^{2-}Co^{3+}CN + CN$

cathode $K^{+} \xrightarrow{+e} K$

Scheme 2

At first, $[Pc^{2-}Co^{3+}(CN)_2]^-$ anion was oxidized at the anode surface to produce $[Pc^{1-}Co^{3+}(CN)_2]$. This complex seemed to be unstable, and it immediately changed to $Pc^{2-}Co^{3+}CN$ and CN radical changed to $(CN)_2$. On the other hand, metallic potassium deposited on the cathode. As crystal growth was observed only on the anode surface, this oxidation should occur on the crystal surface through the electron transfer reaction in the crystal. However, stable phthalocyaninatocobalt(III) radical complexes such as $Pc^{1-}Co^{3+}Cl_2$ and $Pc^{1-}Co^{3+}Br_2$ were reported,[6] no $Pc^{1-}Co^{3+}(CN)_2$ was obtained when $K^+[PcCo(CN)_2]^-$ was prepared from $Pc^{1-}Co^{3+}Cl_2$. This suggested strongly that $[Pc^{1-}Co^{3+}(CN)_2]$ should be unstable.

II. Molecular Arrangement and Conductivity of the Crystals

Crystals of unsubstituted cyanophthalocyaninatocobalt(III) were found to be stacked three-dimensionally which enable π-orbital overlap. As shown in Figure 4, one phthalocyanine plane is surrounded by ad-

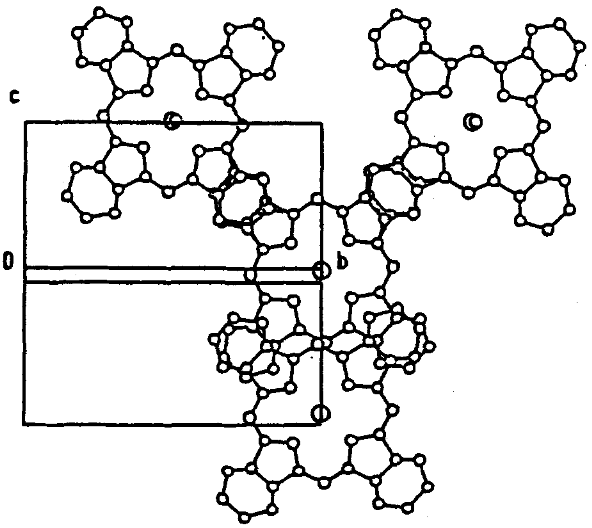


FIGURE 4 Schematic drawing of molecular packing of PcCoCN; projected onto the (301) plane.

jacent six ones. This new and unique packing strongly influenced its inherent conductivity.[1]

Substituents were also expected to affect the molecular arrangement. X-ray powder diffraction patterns of obtained crystals, cyanophthalocyaninatocobalt(III), -iron(III), and octamethyl-(cyanophthalocyaninato)cobalt(III) are shown in Figure 5. Diffraction pattern of cyanophthalocyaninatoiron(III) was the same as that of cyanophthalocyaninatocobalt(III). This suggested that iron derivative's arrangement might be similar in the crystal. But that of octamethyl substituted one was certainly different from those of unsubstituted one. By steric hindrance of methyl groups, phthalocyanine planes could not slip in the neighbor columns and three-dimensional structure was not formed. Other substituted derivatives showed different diffraction patterns from that of unsubstituted one. These results were also considered to be due to a serious steric hindrance as described above.

Conductivities were measured for a single crystal or pressed disk samples and summarized in Table III. Cyanophthalocyaninatocobalt(III) showed the conductivity of 57 S/cm without any doping.[1] This value was 11 orders higher than that of phthalocyaninatocobalt(II). This is mainly due to three-dimensional structure. Cyanophthalocyaninatoiron(III) showed the conductivity of 4×10^{-1} S cm^{-1}. This value was the same order to that for a pressed disk sample of cyanophthalocyaninatocobalt(III). Cyano(octamethylphthalocyaninato)cobalt(III) showed a low conductivity of 8×10^{-8} S cm^{-1}. It is confirmed that three-dimensional π-orbital overlap should be effective for the design of high conduction column.

To obtain the knowledge about carrier, ESR measurements were carried out. All crystals showed a sharp and strong signal corresponding to delocalized organic spin, e.g. for cyanophthalocyaninatocobalt(III) showed it at g-value of 2.003 with linewidth of 0.48 gauss. Spin concentration was extremely high, particularly cyanophthalocyaninatocobalt(III) had one spin per 1.2 molecule.[7] These high spin concentrations should be another reason for high conductivity. Thermoelectric power was about +40 μV K^{-1}, identifying holes as charge carrier.[7]

CONCLUSION

The electrocrystallization methodology is effective to prepare organic conductors in a wide range. This is also useful for the preparation of

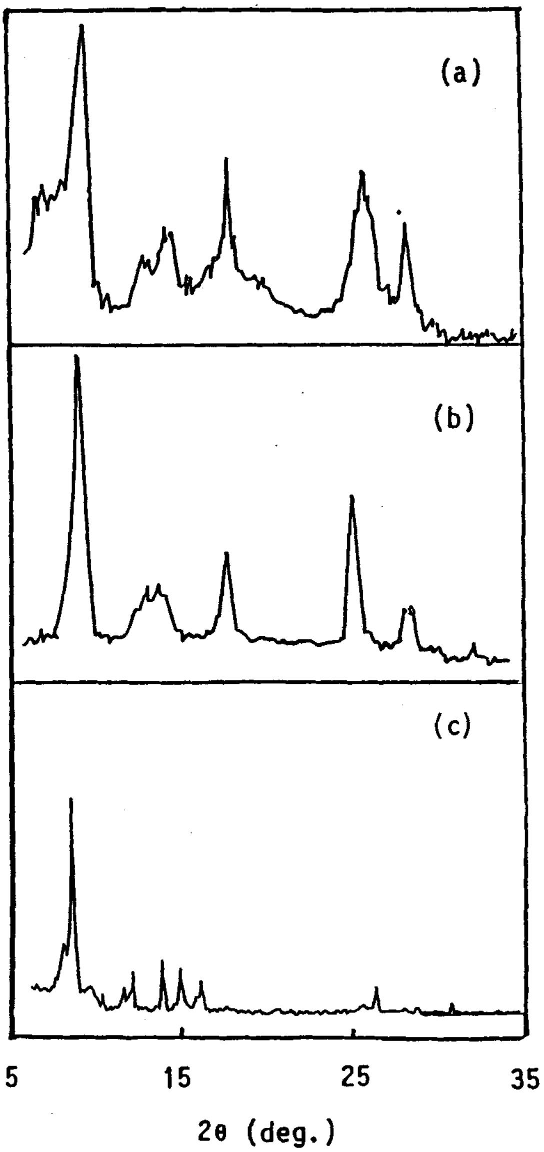


FIGURE 5 X-ray powder diffraction patterns of (a) PcFeCN, (b) PcCoCN, and (c) $(CH_3)_8PcCoCN$.

TABLE III

Conductivities of phthalocyanine derivatives

Compound	σ_{RT} (S cm^{-1})	Ea (eV)	sample form
PcCo	1.0×10^{-10}		pressed disk[a]
PcCoCN	5.7×10^{1}	0.04	single crystal[b]
	6.0×10^{-1}	0.02	pressed disk[a]
PcFeCN	4.0×10^{-1}	0.20	pressed disk[a]
$(CH_3)_8$PcCoCN	8.0×10^{-8}		pressed disk[c]

[a] measured by Van der Pauw four-probe method
[b] along the longer direction of the crystal growth measured by four-probe method
[c] measured by two-probe method

crystals of one-dimensional polyphthalocyanines as well as organic ferromagnets.

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