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Effect of Substituents on the Oxidation Potential of Phthalocyanines and Electrocrystallization

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A series of tetra- or octasubstituted phthalocyaninatocobalt derivatives were prepared and their oxidation behaviors were examined in relation to the nature of substituents. The oxidation potentials of phthalocyanines, especially those of rings were affected by the nature of both substituents and axial ligands. These oxidation potentials were in a linear relation with the Hammett's constants for substituents or axial ligands. The electrocrystallization proceeded when an oxidation potential higher than that for the phthalocyanine ring was given to the solution. This potential shift was therefore revealed to be an important factor to control the electrocrystallization of these phthalocyanines.

Phthalocyanines are being widely used as dyes, catalysts, photocatalysts, major component for solar energy conversion systems, conductive materials, and so on. The redox processes of metallophthalocyanines have been well analyzed in detail,[1] because it is quite important to design geared redox cycles as well as models for biologically active metalloporphyrins. On the other hand, we have reported the preparation of inherently conductive crystals of metallophthalocyanine by way of the electrocrystallization technique.[2] The applied potential was revealed to have a considerable effect on the efficiency of the crystal growth.[2c] These experimental results triggered us to examine the relation between the structure and the oxidation potential of phthalocyanines to get the best conditions for the electrocrystallization. The redox reaction of phthalocyanine occurs both at the central metal ion and on the phthalocyanine ring. The redox processes of some unsubstituted phthalocyanines have clearly been identified by cyclic voltammetry, coulometry, UV/Visible spectroscopy, and ESR spectroscopy.[3,4] Indeed, two successive oxidations and four successive reductions of the ring have been reported.[3] Effects of solvent, chemical environment or axial ligand on the redox potentials of metallophthalocyanines have also been reported.[4] Substituents to the phthalocyanine ring are also expected to be effective for the shift of oxidation potential, but only a few examples have hitherto been reported, such as tetrasulfonated compounds.[1a,3]

The effects of substituents on the oxidation potential of the ring of phthalocyaninatocobalt derivatives were examined in this paper for the purpose of obtaining useful data with regard to electrocrystallization.

Experimental

Materials. Substituted phthalocyaninatocobalt(II) derivatives prepared in this study are summarized in Table 1.

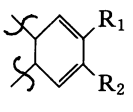
Phthalocyaninatocobalt(II).[5] Phthalonitrile (29.0 g: 0.23 mol) and cobalt(II) acetate (12.0 g: 0.07 mol) were dissolved in 1000 ml of dehydrated methanol. 1,8-Diazabicyclo[5.4.0]-undec-7-ene (DBU) (38 ml) was added dropwise into the methanol solution under stirring at room temperature, then the solution was refluxed for 24 h. After cooling, the red-purple colored precipitate was filtered. The crude product was boiled in 10%-HCl then in 10%-NaOH aqueous solution, washed with water until the aqueous solution reached neutral. The washed precipitate was dried in vacuo. Ten grams of phthalocyaninatocobalt(II) was obtained with 30% yield. Calcd for $C_{32}H_{16}N_8Co$: C, 67.3; H, 2.8; N, 19.6; Co, 10.3%. Found: C, 68.1; H, 2.7; N, 20.0; Co, 9.1%.

Tetranitrophthalocyaninatocobalt(II).[6] **(a) 4-Nitrophthalonitrile:** A total of 30.0 g (0.16 mol) of 4-nitrophthalic anhydride and 84.0 g (1.40 mol) of urea was suspended in 500 ml of 1,2,4-trichlorobenzene, heated at 150 °C for 72 h under stirring. The precipitate was filtered and then washed with aqueous ammonia, yielding 16.6 g of 4-nitrophthalamide with 49.6% yield.

4-Nitrophthalamide (16.0 g: 0.08 mol) was suspended in 200 ml of dehydrated *N,N*-dimethylformamide. Trichloromethyl chloroformate (30 ml) was added dropwise to the solution under vigorous mixing at 5 °C, and kept under moderate stirring for 72 h. The solution was poured into 1000 ml of ice water, and then the phase-separated precipitate was filtered. A crude product was purified as light yellow needle with 73% yield by sublimation at 150 °C under

Table 1. Substituted Phthalocyanines

Compound		
Abb.	R_1	R_2[a]
$(CN)_8PcCo$	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

a) 

10^{-2} Torr (1 Torr=133.322 Pa). Mp 140 °C. IR (cm^{-1}) 2240 (C≡N).

(b) Tetranitrophthalocyaninatocobalt(II): A total of 8.6 g (0.04 mol) of 4-nitrophthalonitrile and 2.1 g (0.01 mol) of cobalt(II) acetate was dissolved in 300 ml of freshly distilled nitrobenzene and stirred at 150 °C for 24 h. The precipitate was filtered and washed with methanol. The crude product was washed with 10%-HCl then with 10%-NaOH as described above. Yield 20%. Calcd for $C_{32}H_{12}N_{12}O_8Co$: C, 51.1; H, 1.6; N, 22.4; Co, 7.8%. Found: C, 50.0; H,1.9; N, 21.6; Co, 8.1%. IR (cm^{-1}): 1530, 1340 (NO_2).

Tetraaminophthalocyaninatocobalt(II).[7] Tetranitrophthalocyaninatocobalt(II) (2.0 g: 2.7×10^{-4} mol) was mixed with sodium hydrogensulfide (1.5 g: 2.7×10^{-2} mol) in 100 ml of *N,N*-dimethylformamide at 100 °C for 5 h. After cooling, 6 M-NaOH (1M=1 mol dm^{-3}) was slowly added until the pH reached 10 to precipitate the product. A dark-blue product was filtered and washed with distilled water until the solution was completely neutralized. Yield 65%. Calcd for $C_{32}H_{20}N_{12}Co$: C, 60.9; H, 3.2; N, 26.6; Co, 9.3%. Found: C, 61.9; H, 3.0; N, 25.8; Co, 9.3%. IR (cm^{-1}): 3400, 3200, 1600(NH_2).

Tetracarboxyphthalocyaninatocobalt(II).[8] Trimellitic anhydride (20.0 g: 0.10 mol), urea (48.0 g: 0.80 mol), cobalt(II) acetate (6.9 g: 0.45 mol) and ammonium molybdate (0.20 g: 1.7×10^{-1} mol) were suspended in 300 ml of freshly distilled nitrobenzene, then the suspension was heated at 150 °C with stirring for 24 h. After cooling, the precipitate was filtered and washed with dehydrated methanol. Crude tetracarbamoylphthalocyaninatocobalt(II) (10.0 g) was obtained as a blue-purple precipitate. Then it was treated with 2 M-KOH aqueous solution under reflux. After the gas evolution ceased, 200 ml of pure water was further added, then filtered again. The filtrate was acidified to pH 2 with 6 M-HCl aqueous solution to precipitate the product. The precipitate thus obtained was washed with distilled water for several times. The product was dissolved in 500 ml of KOH aqueous solution (pH 10). The filtrate was again acidified to pH 2. This purification procedure was repeated three times. A red-purple product was obtained with 35% yield. Calcd for $C_{36}H_{16}N_8O_8Co$: C, 57.8; H, 2.1; N, 15.0; Co, 7.9%. Found: C, 56.0; H, 2.3; N, 14.6; Co, 8.3%. IR (cm^{-1}), 1720 (COOH).

Octacyanophthalocyaninatocobalt(II).[9] Tetracyanobenzene (6.0 g: 0.31 mol) and cobalt(II) acetate (0.74 g: 4.8×10^{-3} mol) were dissolved in 500 ml of *N,N*-dimethylformamide and heated at 150 °C for 2 h. The solution was slowly dropped into 2000 ml of diethyl ether under stirring, then the obtained precipitate was filtered and washed with dehydrated methanol. Yield 50%. Calcd for $C_{40}H_8N_{16}Co$: C, 62.3; H, 1.0; N, 29.1; Co, 7.6%. Found: C, 61.9; H, 1.2; N, 28.9; Co, 8.0%. IR (cm^{-1}): 2225 (C≡N).

Octacarboxyphthalocyaninatocobalt(II).[9] Octacyanophthalocyaninatocobalt(II) (0.5 g: 6.5×10^{-4} mol) was treated with KOH in ethylene glycol-water mixture (15/2 by vol) at 160 °C for 24 h. The reaction mixture was diluted with 100 ml of water and then filtered. The filtrate was acidified to pH 2 to precipitate the product. The blue product was filtered and purified by the same procedure as that for tetracarboxy derivative. Yield 50%. Calcd for $C_{36}H_{16}N_8O_{16}Co$: C, 49.4; H, 1.8: N, 12.8; 0, 29.3; Co, 6.7%. Found: C, 49.2; H, 1.7; N, 13.0; O, 29.2; Co, 6.7%. IR (cm^{-1}) 1700 (COOH).

Octamethylphthalocyaninatocobalt(II).[10] **(a) 1,2-Dibromo-4,5-dimethylbenzene:**[11] A few mg of iron powder and iodide were added to a cooled (5 °C) *o*-xylene (220 g: 2.06 mol). When the characteristic color for iodine disappeared, 660 g (4.1 mol) of bromine was added dropwise. When a half amount of bromine was added, 200 ml of dichloromethane was added to dilute the reaction medium. A residual amount of bromine was added slowly and the solution was maintained at 5 °C for 72 h. Dichloromethane (200 ml) was added and the excess bromine was neutralized with sodium bisulfite. An organic extract was washed with distilled water and dried over $MgSO_4$, evaporated to complete dryness. Recrystallization from hexane yielded white crystals with 40% yield. Mp 87.5—88 °C. ^1H NMR (CCl_4) δ=2.1 (s, 6H, $-CH_3$), 7.15 (s, 2H, arom).

(b) 1,2-Dicyano-4,5-dimethylbenzene: 1,2-Dibromo-4,5-dimethylbenzene (90.0 g: 0.34 mol) was heated under reflux for 5 h with CuCN (86.0 g: 0.96 mol) in 950 ml of *N,N*-dimethylformamide. After cooling, the reaction mixture was poured slowly into 1000 ml of aqueous ammonia and stirred for 12 h with air bubbling agitation. The blue solution was filtered and washed with distilled water until the filtrate was neutralized. The product was extracted with ether by Soxhlet extractor. Recrystallization from methanol yielded 24 g of white crystals. Yield 45%. Mp 117—117.5 °C. ^1H NMR ($CDCl_3$)δ=2.3 (s, 6H, $-CH_3$), 7.5 (s, 2H, arom).

(c) Octamethylphthalocyaninatocobalt(II): 1.2-Dicyano-4,5-dimethylbenzene (8.0 g: 0.05 mol) and cobalt(II) acetate (2.70 g: 0.02 mol) were heated under reflux for 24 h in 400 ml of ethylene glycol. After cooling, the blue-purple product was filtered and purified by treating with 1M-NaOH aqueous solution and then with 1M-HCl aqueous solution. Yield 30%. Calcd for $C_{40}H_{32}N_8Co$: C, 70.3; H, 4.7; N, 16.4; Co, 8.6%. Found: C, 70,3 ; H, 4.8 ; N, 15.9 ; Co, 9.0%.

Octamethoxyphthalocyaninatocobalt(II).[6] **(a) 1,2-Dibromo-4,5-dimethoxybenzene:** Veratrole (75.0 g: 0.54 mol) was dissolved in carbon tetrachloride (220 ml), then bromine (29 ml: 1.1 mol) was added dropwise into the solution at 0—5 °C. The mixed solution was stirred for 48 h. The reaction mixture was washed with 10%-NaOH aqueous solution and then with distilled water. The solvent was evaporated, and the obtained white product was recrystallized from chloroform. Yield 71%. Colorless plate crystals. Mp 81.5—82 °C. ^1H NMR (d_6-acetone)δ=3.9 (s, 6H, OCH_3), 7.0 (s, 2H, arom).

(b) 1,2-Dicyano-4,5-dimethoxybenzene: The reaction conditions were very close to those for 1,2-dicyano-4,5-dimethylbenzene. A mixture of 1,2-dibromo-4,5-dimethoxybenzene (15.8 g: 0.05 mol) and CuCN (13.4 g: 0.15 mol) was heated under reflux for 5 h in 200 ml of *N,N*-dimethylformamide. The follow-up procedure was the same as that for 1,2-dicyano-4,5-dimethylbenzene described above. Recrystallization from methanol yielded 6.0 g of white needles. Yield 64%. Mp 180—180.5 °C. ^1H NMR ($CDCl_3$) δ=3.9 (s, 6H, OCH_3), 7.1 (s, 2H, arom).

(c) Octamethoxyphthalocyaninatocobalt(II): 1,2-Dicyano-4,5-dimethoxybenzene (2.60 g: 1.5×10^{-2} mol) and cobalt(II) acetate (0.80 g: 4.5×10^{-3} mol) were mixed in 100 ml of ethylene glycol and refluxed for 24 h. The reaction mixture was cooled and filtered, then washed with methanol. The purification procedure with 1M-NaOH and 1M-HCl aqueous solution was the same as described above. Calcd for $C_{40}H_{32}N_8O_8Co$: C, 59.2; H, 3.9; N, 13.8; O, 15.8; Co, 7.3%. Found: C, 58.6; H, 4.0; N, 13.4; 0, 16.0; Co, 8.0%.

Potassium (dicyanophthalocyaninato)cobaltate(III).[12] As tetra- or octasubstituted (dicyanophthalocyaninato)cobaltate(III) derivatives were synthesized and purified with the same procedure, a representative method is mentioned here.

Procedure (a): Phthalocyaninatocobalt(II) (2.1 g: 3.7×10^{-3} mol) was suspended in 70 ml of nitrobenzene with thionyl chloride (14 ml: 0.2 mol) and heated at 60 °C for 6 h. After cooling, the mixture was filtered and washed with dehydrated methanol. Dichlorophthalocyaninatocobalt(III) obtained as a brown precipitate,[13] was dried in vacuo. Yield 76%. Calcd for $C_{32}H_{16}N_8Cl_2$: C, 59.8; H, 2.5; N, 17.5; Co, 9.2; Cl, 11.1%. Found: C, 58.7; H, 2.6; N, 17.1; Co, 10.3; Cl, 11.3%.

Dichlorophthalocyaninatocobalt(III) (3.80 g: 6.0×10^{-3} mol) and KCN (5.85 g: 9.0×10^{-3} mol) were mixed in 200 ml of ethanol and was heated under reflux for 72 h. The blue-purple product was filtered and washed with cold water. The product was placed in a thimble of Soxhlet extractor and extracted with dehydrated acetone for 72 h. The extract was evaporated and the product was recrystallized from dehydrated acetone to yield purple crystals with 78% of yield.

Procedure (b): Phthalocyaninatocobalt(II) (3.4 g: 6×10^{-3} mol) was mixed with KCN (7.5 g: 0.12 mol) in 350 ml of ethanol and heated for 72 h. After cooling, the product was filtered and washed with cold water. The purification procedure was the same as that for procedure (a). Yield 50%. Calcd for $C_{34}H_{16}N_{10}CoK$: C, 61.6; H, 2.4; N, 21.1; Co, 8.9; K, 5.9%. Found: C, 61.8; H, 3.0; N,20.5; Co, 8.7; K, 5.9%. IR (cm^{-1}) 2130 (C≡N).

Potassium (dithiocyanatophthalocyaninato)cobaltate(III). Dichlorophthalocyaninatocobalt(III) (1.65 g: 2.6×10^{-3} mol) was suspended in 200 ml of dehydrated ethanol with KSCN (0.75 g: 7.7×10^{-3} mol) for 6 h. After cooling, the blue-purple product was filtered and washed with cold water. The product was purified with the same procedure as that for potassium (dicyanophthalocyaninato)cobaltate(III). Yield 82%. Calcd for $C_{34}H_{16}N_{10}S_2K$: C, 56.2; H 2.2; N, 19.3; S, 8.8; Co, 8.1; K, 5.4%. Found: C, 56.4; H, 2.1; N, 19.4; S, 8.3; K, 5.6%. IR (cm^{-1}) 2100 (C≡N).

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

Spectroscopies. IR spectra were obtained with Hitachi 260-30. ESR spectra were obtained with JES-FE-3X, Nippon Denshi Co. Ltd. UV/Visible spectra were obtained with Varian Cary 17D. Details of the spectroscopic measurements were mentioned in previous papers.[2]

Results and Discussion

I) Oxidation Behaviors of Substituted Phthalocyanine Derivatives. The oxidation potentials of metallophthalocyanines have been reported by Lexa et al.,[14] and Wolberg et al.[15] They measured the oxidation potentials of metallophthalocyanines in *N,N*-dimethylformamide or 1-chloronaphthalene by cyclic voltammetry. The oxidation potential of the phthalocyanine ring was about 1.0 V vs. SCE. The oxidation potential of 0.9 V vs. Ag-AgCl in acetonitrile was obtained in our measurements, this result seemed reasonable comparing with the data in Table 2. The oxidation or reduction of the phthalocyanine ring directly reflects the electrostatic interaction between the ring and metal.[3] For OTi(IV), OV(IV), Ni(II), Cu(II), or Zn(II) complexes, the central metal ions do not show its oxidation until the phthalocyanine ring was oxidized. On the other hand, Fe(II) and Co(II) derivatives showed the ring oxidation at oxidation potentials after the oxidation of central metal ions and the reduction was also followed by the reduction of metal.[1a,14-17] In the potential range from 0 to +2.0 V (vs. Ag-AgCl) the oxidation between Co(II)/Co(III) occurred, but the oxidation processes for the phthalocyanine ring and metal were clearly distinguished with each other.

Only a few redox processes for octasubstituted phthalocyanine have hitherto been reported. Redox processes for octa-*t*-butyl-[18] and octacyanophthalocyaninatozinc(II)[19] have been reported, and the latter showed reversible four step one-electron redox reac-

Table 2. Metallophthalocyanine Electrochemistry

Complex	P^+/P (V vs. Ag-AgCl)	Solvent	Ref.
H_2Pc	1.143	CLN	15
	0.668	DMF	1k
	0.77	MeCN	This work
MgPc	0.743	DMF	22
	0.693	DMF	1f, 3
	0.653	DMF	14, 17b
AlPcCl	1.193	DMAc	22
	0.983	DMF	14, 17b
	0.958	DMF	16
	0.953	DMF	1k
$SiPc(OR)_2$[a]	1.44	CHC	1 l
FePc	0.78	MeCN	This work
	0.234[b]	CLN	15
	0.703	DMF	1h
CoPc	0.90	MeCN	This work
	0.843	DMAc	22
	0.814	CLN	15
	0.683	DCB	3, 26
NiPc	0.69	MeCN	This work
	1.093	CLN	15
CuPc	0.68	MeCN	This work
	1.023	CLN	15
ZnPc	0.65	MeCN	This work
	0.723	CLN	1g, 15
	0.823	DMF	22
GaPcCl	0.908	DMF	1f, 3
CdPc	0.583	DMF	1f, 3, 14, 17
InPcCl	0.873	DMF	1f
	0.883	DMF	1k
BaPc	0.498	DMF	3
HgPc	0.293	DMF	1f, 3
PbPc	0.713	DMF	1f, g, k

a) R: $Si(n\text{-}C_6H_{13})_3$, b) Fe(II) ↔ Fe(III), solvent CLN: 1-chloronaphthalene, DMF: *N,N*-dimethylformamide, MeCN: acetonitrile, DMAc: *N,N*-dimethylacetamide, CHC: dichloromethane, DCB: dichlorobenzene.

Table 3. Oxidation Potentials of Octasubstituted Phthalocyaninatocobalt(II)

Compound	P^+/P[a] (V vs. Ag-AgCl)	Hammett's constant[b]
$(CN)_8PcCo$	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.
b) For benzene derivatives from Ref. 20.

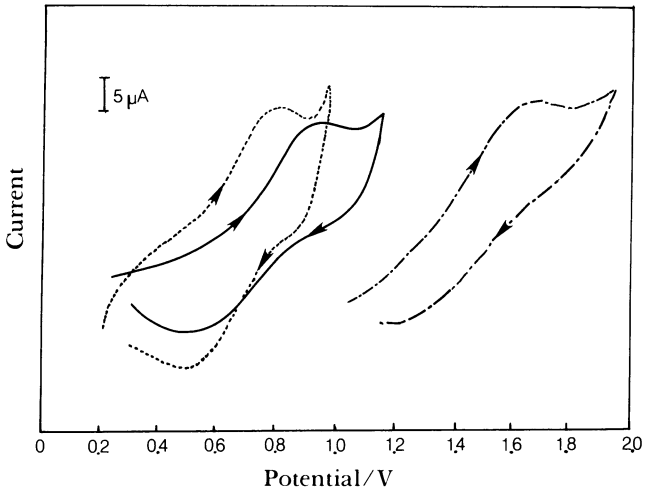


Fig. 1. Cyclic voltammograms for octasubstituted phthalocyanine in acetonitrile solution. 10 mM TEAC, scan rate: 50 mv s^{-1}.
Phthalocyaninatocobalt(II): (——), octamethylphthalocyaninatocobalt(II): (----), octacarboxyphthalocyaninatocobalt(II): (-·-·-). The electrode potential was measured vs. Ag-AgCl.

tions. The oxidation potentials of the phthalocyanine ring we measured are summarized in Table 3, and some of the cyclic voltammograms are shown in Fig. 1. 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 negatively by 0.13 V as shown in Table 3. The oxidation potential of octasubstituted derivatives was in the order of the following substituents;

$$-CN > -COOH > -H > -OCH_3 > -CH_3. \quad (1)$$

A good linear relation between the oxidation potential and the Hammett's constant for benzene derivatives[20] is observed as shown in Fig. 2. This suggests that the Hammett's constant for benzene derivatives 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

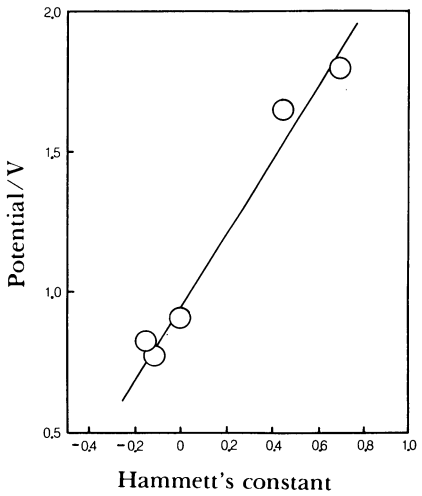


Fig. 2. Relation between the oxidation potential and the Hammett's constant of substituent for octasubstituted phthalocyaninatocobalt(II).

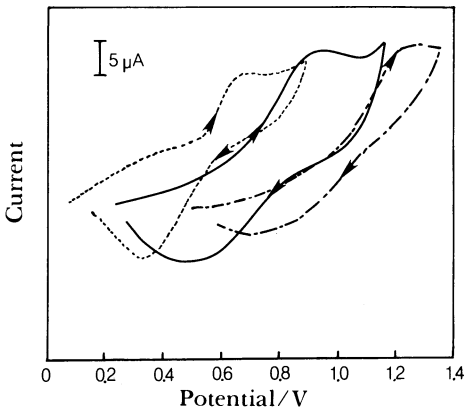


Fig. 3. Cyclic voltammograms for tetrasubstituted phthalocyanine in acetonitrile solution. 10 mM TEAC, scan rate: 50 mV s^{-1}.
Phthalocyaninatocobalt(II): (——), tetramethoxyphthalocyaninatocobalt(II): (----), tetracarboxyphthalocyaninatocobalt(II): (-·-·-). The electrode potential was measured vs. Ag-AgCl.

Hammett's constant (K) as shown in Eq. 2.

$$E_{ox} = 1.30\,K + 0.96 \quad (2)$$

This relationship should be useful not only for the estimation of a suitable potential for electrocrystallization as described later but also for the regulation of oxidation potential of phthalocyanines for the design of some catalytic systems.

For tetrasubstituted derivatives, the substituents also affect the oxidation potential just as the octasubstituted derivatives do. Though the redox processes of tetrasubstituted phthalocyanines such as tetra-*t*-butyl-, tetrasulfo-, and tetrakis(dodecanesulfonylamino)phthalocyanine have also been reported,[1a,3,21] the effects of substituent on the oxidation have not been summarized yet. The oxidation potentials of tetrasubstituted phthalocyaninatocobalt(II) derivatives were measured with cyclic voltammetry (Fig. 3), and are

Table 4. Oxidation Potentials of Tetrasubstituted Phthalocyaninatocobalt(II)

Compound	P^+/P[a] (V vs. Ag-AgCl)	Hammett's constant[b]
$(NO_2)_4PcCo$	1.30	0.81
$(COOH)_4PcCo$	1.24	0.44
PcCo	0.90	0
$(CH_3O)_4PcCo$	0.73	−0.12
$(NH_2)_4PcCo$	0.72	−0.30

a) In acetonitrile solution, 10 mM TEAC, 25 °C.
b) For benzene derivatives from Ref. 20.

Table 5. Tetrasubstituted Phthalocyanine Electrochemistry

Compound	P^+/P (V vs. Ag-AgCl)	Solvent	Ref.
$TsPcH_2$	0.943	DMSO	1a
TsPcCr	0.764	DMF	1f
TsPcCo	1.134	DMSO	1a
	0.443	DMF	3
TsPcNi	1.024	DMSO	1a
	0.993	DMF	3, 21a
TsPcCu	1.154	DMSO	1a
	0.993	DMF	3
TdPcFe	0.643	DMF	3
$(COOH)_4PcFe$	1.26	MeCN	This work
$(COOH)_4PcCo$	1.24	MeCN	This work
$(COOH)_4PcCu$	1.22	MeCN	This work
$TbPcH_2$	0.668	CHC	3
TbPcTiO	0.893	DMF	3
TbPcVO	0.983	DMF	3
TbPcCr	0.748	DMF	3
TbPcCo	0.683	DMF	22

Solvent DMSO: dimethyl sulfoxide, DMF: *N,N*-dimethylformamide, MeCN: acetonitrile, CHC: dichloromethane Ts: tetrasulfo-, Td: tetrakis(dodecylsulfonyl)-, Tb: tetra-*t*-butyl-.

summarized in Table 4. The solvents are weak donors, but the solvent coordination does not perturb strongly the oxidation as summarized in Table 5. Tetranitro and tetracarboxy derivatives showed 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. It was found as well that tetramethoxy and tetraamino derivatives which showed their oxidation peak at +0.73 V and +0.72 V, respectively, which is smaller than it for unsubstituted one. The oxidation potential for tetrasubstituted compound was shifted by their substituents as the following order;

$$-NO_2 > -COOH > -H > -OCH_3 > -NH_2. \quad (3)$$

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 shown in Fig. 4. It is a similar relationship to that for octasubstituted ones as shown in Fig. 2. This also delivers the following equation:

$$E_{ox} = 0.59\,K + 0.88 \quad (4)$$

The potentials of tetra-*t*-butyl- and tetrasulfophthalocyaninatocobalt(II) which have been measured in dichlorobenzene and *N,N*-dimethylformamide, respectively,[3,22] are also shown in Table 5. These data also lied on this relation as shown in Fig. 4. As mentioned above, the oxidation potentials of substituted metallophthalocyanine have not been investigated substantially. For the potentials of substituted derivatives examined here, a good linear relationship between the oxidation potential and the Hammett's constant of substituent was firstly found for both tetra- and octasubstituted complexes. In our experimental data a potential shift as much as about 1.0 V is noted, though it has been reported that the redox potential shift was generally seen within 100 mV by substituent such as chloro, methyl, *t*-butyl, sulfo, and carboxyl group.[3]

The oxidation potentials of potassium dicyano derivatives were also analyzed by cyclic voltammetry. The results are summarized in Table 6. The relation between the oxidation potential and the Hammett's constant of substituent which was found for octa- and tetrasubstituted derivatives was also available for these compounds. A similar linear relationship should be observed as long as the compounds had the same axial ligands.

Table 6. Oxidation Potentials of $K^+[R_nPcCoX_2]^-$ in Acetonitrile Solution[a]

Compound	P^+/P (V vs. Ag-AgCl)
$K^+[PcCo(CN)_2]^-$	1.10
$K^+[(CH_3O)_8PcCo(CN)_2]^-$	0.65
$K^+[(CH_3)_8PcCo(CN)_2]^-$	0.63
$K^+[(NH_2)_4PcCo(CN)_2]^-$	0.59
$K^+[PcCo(SCN)_2]^-$	0.98

a) No supporting electrolyte was added.

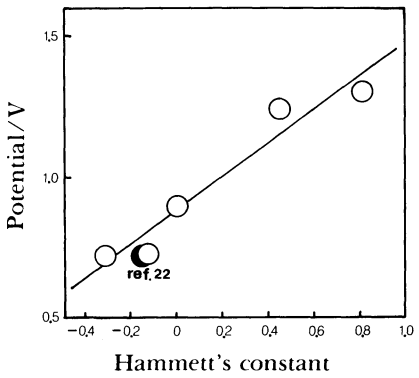


Fig. 4. Relation between the oxidation potential and the Hammett's constant of substituent for tetrasubstituted phthalocyaninatocobalt(II).

II) Effect of Axial Ligand on the Oxidation Behavior Effects of axial ligand on the oxidation potentials of metallophthalocyanine have been reported widely by Lever et al.,[1e,3,23] and Dolphin et al.,[24] through the analyses in several coordinating solvents. The effects of coordinating solvents on the oxidations are recognized for the strength of σ-donor ability of solvent, which means the occurrence of π-back donation. The stronger the σ-donor ability of solvent, the lower the potential shifts. The oxidations at the central metal ion are considered to be affected similarly, for example when strong σ-donor solvents bind to the Co(II) or Fe(II) complex, electrons in dz^2 orbital of metal are destabilized and the oxidation of metal (d^6-d^7) should occur more easily. The potential shift and the strength of σ-donor ability of solvent are the following.

$$\text{DMAc} = \text{DMF} > \text{DMSO} > \text{pyridine (redox potential)} \quad (5)$$

$$\text{DMAc} = \text{DMF} < \text{DMSO} < \text{pyridine } (\sigma\text{-donor ability}) \quad (6)$$

For these solvent systems, relation between the Gutmann Donicity Number[25] of solvent and the oxidation potential is depicted as linear.[26] For the reduction of Co(II)/Co(I) system, the same tendency was observed.[26] But contrary to these results, the potential is more positive with the strength of σ-donor ability for Fe(III)/Fe(II) system. This seemed to be the reason that the π-back donation in d^6 state (Fe(II)) was stronger than that in d^5 state (Fe(III)) by higher charge density in metal ion.[26]

Similar effects are expected for the phthalocyanine complexes which have the same two axial ligands, such as CN^- or SCN^-. With CN^- which is an electron-withdrawing group bound to metallophthalocyanine, the oxidation potential of the ring shifted to more positive side than that for uncoordinated complex. Furthermore, the CN^- coordinated derivative gave more positive oxidation potential than the SCN^- coordinated one as shown in Fig. 5. This is because CN^- withdraws electrons more strongly than SCN^-. For these phthalocyanine compounds, only one axial ligand can be replaced, for example to pyridine. It has been found that the stronger σ-donor axial ligand shifts the CN band to lower frequency in the IR spectrum.[12,27] This is one of the proofs that σ-donor ability of axial ligand affects the oxidations.

III) Effect of Central Metal Ion on the Oxidation Potentials of Substituted Metallophthalocyanines. We prepared tetracarboxyphthalocyaninatoiron(II) and that of copper(II). Their oxidation potentials of the phthalocyanine ring were +1.26 and +1.22 V vs. Ag-AgCl, respectively. Fe, Co, or Cu was introduced into tetracarboxy derivatives as central metal ion, the sequence of the oxidation potential (Fe> Co> Cu) was the same as that for unsubstituted metallophthalocyanines. This suggests that though an interaction between the central metal ion and the phthalocyanine ring did affect the oxidation potential, its magnitude was much less than that of the effect of substitution on rings. The relation between the metal and the oxidation potential of the ring might be explained as follows. The increase in the number of d-electrons of transition metal shifted the oxidation potential to a lower side, suggesting a strong coordination of nitrogen atoms in the ring to metal ion. When the $3dx^2$-y^2 orbital was empty as for Fe(II) and Co(II) complexes, this coordination bond should accommodate the oxidation of the ring. On the other hand, when the $3dx^2$-y^2 orbital was filled as for Cu(II) complex, charges on the metal made it easier to ionize the ring, i.e., oxidize.[15] This could be the main reason for the unusual oxidation potential of phthalocyaninatocopper(II).

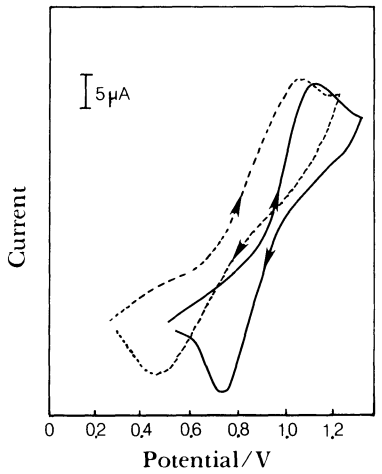


Fig. 5. Cyclic voltammograms for $K^+[PcCo(X)_2]^-$ in acetonitrile solution. Scan rate: 50 mV s^{-1}. X= CN: (——), X=SCN: (----). The electrode potential was measured vs. Ag-AgCl.

IV) Control of Electrocrystallization with Applied Potential. Electrocrystallization was carried out for potassium (substituted dicyanophthalocyaninato)cobaltate(III) in acetonitrile. A cell construction has already been shown elsewhere.[2b] It was found that electrocrystallization occurred when the solution was stored under the oxidative moiety of the phthalocyanine ring in the case of cyanophthalocyaninatocobalt(III).[2] The relation between the yield of crystals and applied potential for substituted phthalocyanine was shown in Fig. 6. Not all phthalocyanine derivatives could be crystallized in electric field because of the presence of structural isomers for tetrasubstituted derivatives. Even though, those were crystallized when the solution was stored under the oxidative moiety of the ring. It was clear that the drastic decrease in the solubility of phthalocyanines through the oxidation of phthalocyanine rings was the essential factor for the electrocrystallization. The difference in the crystal yield as shown in Fig. 6 is therefore attributed to the difference in the solubility of oxidized compounds. Though cyanophthalocyaninatocobalt(III) obtained

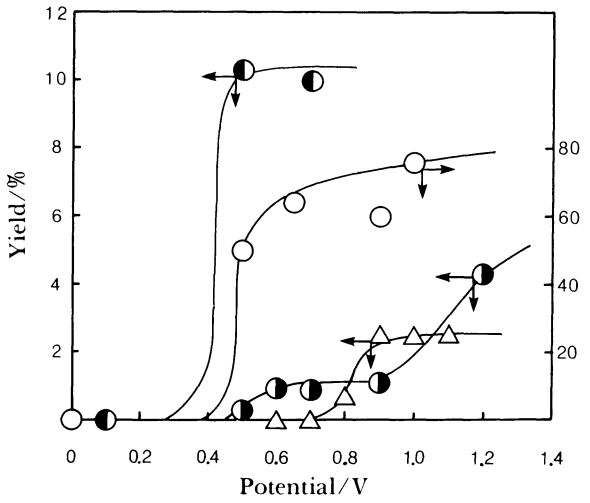


Fig. 6. Relation between the yield of crystals and the applied potential for electrocrystallization of substituted phthalocyanines.
○: Cyanophthalocyaninatocobalt(III), ◑: octamethyl-substituted derivative, ◐: octamethoxy-substituted derivative, △: thiocyanatophthalocyaninatocobalt(III).

through electrocrystallization was insoluble in organic solvents, introducing substituents to phthalocyanine ring probably made the solubility higher. For this reason, the crystals were partially soluble in the solution which made the yield low. The lower yield for the system having thiocyanato group as axial ligand could also be explained in terms of this. There are four structural isomers in the case of tetrasubstituted derivatives. They are generally more soluble than octasubstituted ones owing to the decrease of symmetry (except the increased 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 seemed therefore to be as follows.

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

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

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 the 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 crystals. However, stable phthalocyaninatocobalt(III) radical complexes such as Pc^{1-} $Co^{3+}Cl_2$ and $Pc^{1-}Co^{3+}Br_2$ were reported,[14] and no Pc^{1-} $Co^{3+}(CN)_2$ was obtained when $K^+[PcCo(CN)_2]^-$ was prepared from $Pc^{1-}Co^{3+}Cl_2$. This suggests strongly that $[Pc^{1-}Co^{3+}(CN)_2]$ should be unstable. Though $(CN)_2$ have not been detected yet, the mechanism described above is considered reasonable. The molecular arrangements and conductivities of crystals will be reported elsewhere.

Conclusion

A series of tetra- or octasubstituted phthalocyaninatocobalt(II) were synthesized, and the effect of substituent group on the oxidation was examined in terms of the Hammett's constant. A linear relationship between the oxidation potential of the ring and the Hammett's constant of substituent was confirmed for all cases of tetra-, octasubstituted derivatives and even for derivatives with different axial ligands. Electrocrystallization of phthalocyanine derivatives was initiated by the oxidation of the phthalocyanine ring, that was suggested from the effect of applied potential on the crystal yield for a series of substituted phthalocyanines.

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