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Structure and Some Properties of (Alkoxo)(subphthalocyaninato)boron(III)

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A few (alkoxo)(subphthalocyaninato)boron(III) complexes, [BX(subpc)] (X = OMe, OEt, OBu^t, and OPh), were prepared and characterized. The molecular structure of [B(OEt)(subpc)] was determined by an X-ray structure analysis; the boron atom is situated 0.642 Å upward from the triangle plane of three isoindoline nitrogen atoms. The geometry of the boron atom is distorted tetrahedral, and the complex shows a wine-glass shape. The mass spectra showed that a part of the hydrogen atoms of the subphthalocyanine ring are displaced by the halogen atoms of boron trihalide or solvents. The complexes showed strong absorption bands at around 560 (Q band) and 300 nm (B band) in chloroform, respectively. The complexes decomposed in solution under irradiation with visible light. The first oxidative or reductive half-wave potential of [B(OEt)(subpc)] was observed at 1.06 V (vs. SCE) or −1.11 V, respectively.

Recently, metallophthalocyanines have evoked much interest due to their electroconductivity, photoconductivity, electrochromic property, and catalytic activity.[1] As analogues of phthalocyanine which consists of four isoindoline units, the so-called superphthalocyanine (five isoindoline units) and subphthalocyanine (three isoindoline units), [BX(subpc)] (X = F, Cl) have also been reported.[2,3] The superphthalocyanine complex of uranyl with a 22 π-electron system shows a Q band at 915 nm, and easily changes to phthalocyaninatocopper(II) with a 18 π-electron system (670 nm) by a reaction with copper chloride.[2] On the other hand, [BX(subpc)] with a 14 π-electron system shows a Q band around 570 nm, and also changes to phthalocyanine by a reaction with 1,3-isoindolinediimine.[4,6] Recently, a plane-binuclear subphthalocyanine complex of boron(III) and (tri-*t*-butylsubphthalocyaninato)(phenyl)boron(III) were also prepared.[7,8]

The ring-expansion reaction of subphthalocyanines is an attractive method for preparationing an unsymmetrical phthalocyanine derivative with substituents at a particular position on the ring.[5] It has been further reported that the subphthalocyanine derivatives presented very large second-order molecular polarizabilities, and were expected to serve as novel tragets for second-order nonlinear optical applications; these second-order polarizabilities were mostly associated with the octupolar contribution, and were comparable to those found in the most efficient linear compounds, such as polyenes.[9]

In this study, a few alkoxy derivatives of [BX(subpc)] (X= methoxy, ethoxy, *t*-butoxy, or phenoxy) were prepared, and the structure of [B(OEt)(subpc)] was determined by an X-ray crystal-structure analysis to further elucidate interesting properties, such as the electronic spectra, electrochemistry, and second-order optical nonlinearities, as well as the ring expansion of subphthalocyanines.

Experimental

Reagents. All of the reagents were of analytical grade or of the highest grade available, and were used without further purification.

Preparation of Subphthalocyanine Complexes. [BBr(subpc)]. The complex was prepared by a modified method described in the literature.[3] A 1-chloronaphthalene solution (10 cm^3) of 3.6 g (14 mmol) boron tribromide was added to a 1-chloronaphthalene solution (30 cm^3) of 3.7 g (29 mmol) phthalonitrile, and the reaction mixture was heated at ca. 160 °C for 1 h. It was then poured into 400 cm^3 of benzene, and an insoluble material was filtered off. After concentration of the filtrate to adequate amounts, it was poured on a silica-gel column. Using chloroform as an eluent, a reddish-purple solution was eluted out. By adding adequate amounts of hexane to the concentrated eluent, reddish-purple powders of [BBr(subpc)] were obtained. Yield 8%. Found: C, 61.02; H, 2.97; N, 17.21%. Calcd for $C_{24}H_{12}N_6BBr$: C, 60.67; H, 2.65; N, 17.69%. UV-vis ($CHCl_3$)λ (log ε) = 255^{sh} (4.48), 271 (4.54), 303 (4.60), 508^{sh} (4.34), 543^{sh} (4.60), 567 (4.86) nm. ^{1}H NMR ($CDCl_3$) δ = 7.33—7.42 (m, 6H, aromatic), 8.58—8.67 (m, 6H, aromatic).

[B(OMe)(subpc)]. After heating the reaction mixture as mentioned for 1 h at ca. 160 °C, 20 cm^3 of methanol was added to the solution, and heated at ca. 90 °C for an additional 30 min. Then, after evaporating the methanol, the resulting solution was poured into 400 cm^3 of benzene. The decomposed products were then filtered off, and the filtrate was purified by a silica-gel column using chloroform as an eluent. Metallic luster crystals were obtained by slowly condensing the mixture solvent of diethyl ether and petroleum ether (2 : 1, v/v) of [B(OMe)(subpc)] at room temperature. Yield 5%. Found: C, 70.19; H, 3.62; N, 19.47%. Calcd for $C_{25}H_{15}N_6BO$: C, 70.45; H, 3.55; N, 19.72%. UV-vis ($CHCl_3$) λ ($\log\varepsilon$) = 256^{sh} (4.34), 270 (4.48), 303 (4.57), 507^{sh} (4.30), 542^{sh} (4.60), 561 (4.87). ^1HNMR ($CDCl_3$) $\delta = 1.50$ (s, 3H, CH_3), 7.85—7.96 (m, 6H, aromatic), 8.80—8.91 (m, 6H, aromatic).

[B(OEt)(subpc)]. Using ethanol instead of methanol, [B(OEt)(subpc)] was prepared in a similar way as that described for the preparation of [B(OMe)(subpc)]. Golden luster crystals were obtained from diethyl ether. Yield 15%. Found: C, 70.63; H, 4.07; N, 18.70%. Calcd for $C_{26}H_{17}N_6BO$: C, 70.93; H, 3.89; N, 19.09%. UV-vis ($CHCl_3$) λ ($\log\varepsilon$)=256 (4.30), 270 (4.43), 302 (4.54), 506^{sh} (4.34), 541^{sh} (4.57), 561 (4.85). ^1HNMR ($CDCl_3$) $\delta = 0.19$ (t, 3H, CH_3, $J = 14$ Hz), 1.53 (q, 2H, CH_2, $J = 21$ Hz), 7.81—7.92 (m, 6H, aromatic). 8.82—8.90 (m, 6H, aromatic).

[B(OBu^t)(subpc)]. Using *t*-butyl alcohol as the solvent, [B(OBu^t)(subpc)] was prepared; the golden microcrystals were obtained from diethyl ether. Yield 7%. Found: C, 71.44; H, 4.58; N, 17.56%. Calcd for $C_{28}H_{21}N_6BO$: C, 71.81; H, 4.52; N, 17.95%. UV-vis ($CHCl_3$) λ ($\log\varepsilon$)=255 (4.43), 271 (4.54), 303 (4.65), 507^{sh} (4.40), 542^{sh} (4.65), 562 (4.93). ^1HNMR ($CDCl_3$) $\delta = 0.04$ (s, 9H, CH_3), 7.84—7.91 (m, 6H, aromatic), 8.81—8.89 (m, 6H, aromatic).

[B(OPh)(subpc)]. The complex was prepared using phenol as the solvent; reddish-purple powders were obtained from acetone Yield 18%. Found: C, 73.78; H, 3.57; N, 17.14%. Calcd for $C_{30}H_{17}N_6BO$: C, 73.79; H,3.51; N, 17.21%. UV-vis ($CHCl_3$) λ ($\log\varepsilon$) = 255 (4.51), 267 (4.57), 305 (4.60), 506^{sh} (4.40), 542^{sh} (4.70), 562 (4.91). ^1HNMR ($CDCl_3$) $\delta = 5.39$(d, 2H, phenoxy, $J = 11$ Hz), 6.75 (t, 2H, phenoxy, $J = 15$ Hz), 6.61 (t, 1H, phenoxy, $J = 16$ Hz), 7.85—7.94 (m, 6H, aromatic), 8.81—8.90 (m, 6H, aromatic).

Measurements. The electronic spectra in solution and the infrared spectra (KBr pellets) were measured on Shimadzu UV-3100 and Hitachi 260-50 spectrophotometers, respectively. The ^1HNMR spectra were recorded using a JEOL-GX 270 spectrometer at 270 MHz. The chemical shifts were determined in ppm using TMS as the internal standard. The mass spectra were recorded with a JEOL-01SG-2 double-focusing mass spectrometer. Cyclic voltammetric measurements were performed in a dichloromethane solution containing tetrabutylammonium perchlorate (0.1 mol dm^{-3}) on a Hokuto Denko HA-501 potentiostat with a Hokuto Denko HF-201 function generator. A glassy carbon disk, a platinum coil, and a standard calomel electrode (SEC) were used as a working electrode, a counter electrode, and a reference electrode, respectively. For a steady-state irradiation of the complexes, a sample solution in a glass cell with a 1-cm light path length was irradiated with a 100-W halogen lamp at 25 °C. Light having a wavelength shorter than 420 nm was cut off by using a Toshiba L-42 glass filter.

X-Ray Crystal Structure Analysis. The unit-cell parameters and intensities were measured on a Rigaku AFC-5R diffractometer with graphite-monochromated Cu*Kα* radiation ($\lambda = 1.5418$ Å) at 23(1) °C. The intensity data were collected by the ω–2θ scan technique, and were corrected for Lorentz-polarization effects, but not for absorption.

Crystal Data: $C_{26}H_{17}N_6BO$, F. W. = 440.27, monoclinic, space group $P2_1/n$, $a = 16.577(2)$, $b = 14.483(2)$, $c = 9.051(2)$ Å, $\beta = 102.39(1)°$, $V = 2122.4(5)$ Å^3, $Z = 4$, $D_m = 1.387(1)$ g cm^{-3} (by potassium citrate aqueous solution), $D_c = 1.378$ g cm^{-3}, μ(Cu*Kα*) = 6.65 cm^{-1}, crystal dimensions 0.39 × 0.38 × 0.30 nm. Of the 3383 reflections measured in the range $4 \le 2\theta \le 125°$, 2904 with $I \ge 3\sigma(I)$ were assumed to be observed. The structure was solved by direct methods (SIR88[10)]) and refined by a block-diagonal least-squares method (LSBL[11)]) using a unit weight. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were found at their calculated positions in a difference Fourier map, and fixed at their positions. The final discrepancy factor (R) is 0.057 for 1471 reflections with $|F_o| \ge 3\sigma|F_o|$.

The atomic coordinates and thermal parameters of non-hydrogen atoms are listed in Table 1. The anisotropic thermal parameters of non-hydrogen atoms, the atomic coordinates and thermal parameters of hydrogen atoms, and F_o–F_c tables have been deposited as Document No. 69050 at the Office of the Editor of Bull. Chem. Soc. Jpn.

Results and Discussion

Although the [BX(subpc)] complexes (X=alkoxy) showed reddish purple in both solution and the powder, a metallic luster in the crystallic from. The alkoxy derivatives are stable in air for over several months, and soluble in common organic solvents; e.g. the solubility of the complexes is ca. 1×10^{-3} mol dm^{-3} in chloroform. While the purification of [BBr(subpc)] with column chromatography was difficult due to its strong adsorption on silica gel, probably due to its

Table 1. Atomic Coordinates and Isotropic Thermal Parameters of Non-Hydrogen Atoms with Estimated Standard Deviations in Parentheses

Atom	x	y	z	$B_{eq}/\text{Å}^2$ [a)]
N1	0.2337(2)	0.6054(2)	0.7901(3)	3.58(2)
C2	0.2349(2)	0.6519(2)	0.9232(4)	3.71(3)
C3	0.2505(2)	0.5820(2)	1.0416(4)	3.73(3)
C4	0.2610(2)	0.5889(3)	1.1975(3)	4.33(4)
C5	0.2707(2)	0.5079(3)	1.2820(4)	4.83(4)
C6	0.2671(2)	0.4208(3)	1.2097(5)	5.01(4)
C7	0.2549(2)	0.4133(3)	1.0537(4)	4.43(4)
C8	0.2476(2)	0.4945(3)	0.9697(4)	3.84(3)
C9	0.2307(2)	0.5118(2)	0.8067(4)	3.76(3)
N10	0.1998(2)	0.4544(2)	0.6912(3)	3.95(3)
N11	0.1582(2)	0.5878(2)	0.5405(3)	3.64(3)
C12	0.1602(2)	0.4948(3)	0.5606(4)	3.85(3)
C13	0.1008(2)	0.4577(3)	0.4331(4)	4.01(3)
C14	0.0810(2)	0.3680(3)	0.3828(4)	4.52(4)
C15	0.0202(2)	0.3569(3)	0.2524(4)	4.97(4)
C16	−0.0226(2)	0.4321(3)	0.1736(4)	5.15(4)
C17	−0.0048(2)	0.5224(3)	0.2256(4)	4.69(4)
C18	0.0582(2)	0.5349(3)	0.3528(4)	3.92(3)
C19	0.0932(2)	0.6182(3)	0.4342(4)	3.86(3)
N20	0.0640(2)	0.7045(2)	0.4328(3)	4.06(3)
N21	0.1645(2)	0.7325(2)	0.6592(3)	3.68(2)
C22	0.0961(2)	0.7580(2)	0.5523(4)	3.80(3)
C23	0.0596(2)	0.8350(2)	0.6166(4)	3.76(3)
C24	−0.0109(2)	0.8869(3)	0.5615(4)	4.36(4)
C25	−0.0340(2)	0.9523(3)	0.6573(4)	4.70(4)
C26	0.0121(2)	0.9653(3)	0.8047(5)	4.86(4)
C27	0.0814(2)	0.9118(3)	0.8626(4)	4.30(3)
C28	0.1053(2)	0.8472(2)	0.7671(4)	3.74(3)
C29	0.1678(2)	0.7759(2)	0.7953(4)	3.78(3)
N30	0.2080(2)	0.7386(2)	0.9271(3)	3.73(3)
B31	0.2176(2)	0.6523(3)	0.6379(4)	3.70(4)
O32	0.2863(1)	0.6700(2)	0.5720(3)	4.34(3)
C33	0.3601(2)	0.7067(3)	0.6597(5)	5.09(4)
C34	0.4196(3)	0.7238(3)	0.5614(5)	6.12(5)

a) $B_{eq} = (4/3)\sum_i \sum_j B_{ij}\boldsymbol{a}_i\cdot\boldsymbol{a}_j$.

change to a hydroxy derivative, the alkoxy derivatives were easily purified on a silica-gel column.

Mass Spectra. In the mass spectrum of [B(OEt)(subpc)], a parent peak (M^+/e) was observed at 440 with several weak peaks at 474, 520, 554, and 577, corresponding to such species as $(M+Cl)^+$, $(M+Br)^+$, $(M+Cl+Br)^+$, and $(M+2Br)^+$ (where M shows [B(OEt)(subpc)] (Fig. 1). This shows that a part of the hydrogen atoms on the benzene rings of subphthalocyanine were substituted by halogen atoms, as had been previously reported for concerining the formation of metallophthalocyanine complexes from phthalonitrile and metal halide.[12] The bromine atom might be supplied from boron tribromide. Although the chlorine atom is also assumed to result from the 1-chloronaphthalene used as the solvent, the chlorine-substituted derivative was also obtained upon heating phthalonitrile and boron tribromide in 1-bromonaphthalene. For the present, the source of the chlorine atom is unknown. The degree of halogen-atom substituted might be less than one percent, based on the results of elemental analyses.

Molecular Structure. The final atomic coordinates and equivalent isotropic temperature factors of [B(OEt)(subpc)] are given in Table 1. Important bond lengths and angles for the complex are listed in Table 2. An ORTEP drawing of the complex is shown in Fig. 2 together with the numbering scheme.

The crystallographic inversion centers are located on the plane of N11, B31, O32, N30, and C34. The boron atom is situated 0.642(5) Å upward from the triangle plane containing the three N1, N11, and N21 atoms. The geometry of the boron atom is distorted tetrahedral, and molecule shows a wine-glass shape. While two planes of the benzene ring (C3–C8) and the pyrrole ring (N1, C2, C3, C8, and C9) are almost coplanar (0.38°), those of the benzene ring (C13–C18) and the pyrrole ring (N11, C12, C13, C18, and C19) are slightly bent (3.37°). Furthermore, two planes of the benzene ring (C23–C28) and the pyrrole ring (N21, C22, C23, C28, and C29) are slightly bent (2.94°). The B–O bond is not perpendicular to the triangle plane, but is slightly tilted to the pyrrole ring (N21, C22, C23, C28, and C29). Thus, the dihedral angle (N21–B31–O32) is smaller (ca. 7°) compared with the remaining two N–B–O angles. A residual electron density (four times stronger than that of the back ground) was observed at 1.49 Å from the C6 atom. This density may result from the halogen atom, which was also identified by the mass spectra. By a partial displacement of the hydrogen atom with the halogen atom, the observed molecular weight seems to be slightly larger than the calculated value.

Table 2. Selected Bond Lengths (Å), Angles (deg), and Distances (Å) for [B(OEt)(subpc)]

Bond lenghts			
B31–N1	1.507(5)	B31–O32	1.418(5)
B31–N11	1.499(5)	O32–C33	1.412(5)
B31–N21	1.499(5)		
Bond angles			
N1 –B31 –N11	102.8(3)	N11 –B31 –O32	110.5(4)
N1 –B31 –N21	103.6(3)	N21 –B31 –O32	117.5(3)
N1 –B31 –O32	117.7(3)	B31 –O32 –C33	120.6(3)
N11 –B31 –N21	103.3(3)	O32 –C33 –C34	109.5(4)
Distance from the triangle plane (N1, N11, N21)			
B31	0.642(5)	C9	−0.432(6)
N10	−0.533(6)	C12	−0.372(6)
N20	−0.523(6)	C19	−0.372(6)
N30	−0.609(6)	C22	−0.437(6)
C2	−0.469(6)	C29	−0.461(6)

Since the B–N bond length (1.500 Å) of [B(OEt)(subpc)] is logger than that (1.467 Å) of [BCl(subpc)],[13] the distance of the boron and the triangle plane of the three nitrogen atoms is longer for [B(OEt)(subpc)] (0.642 Å) than for [BCl(subpc)] (0.588 Å). The subphthalocyanine rings of these complexes are considerably bent compared with the phthalocyanine ring of [AlCl(pc)].[14]

Electronic and Infrared Spectra. While metallophthalocyanine complexes showed intense absorption bands

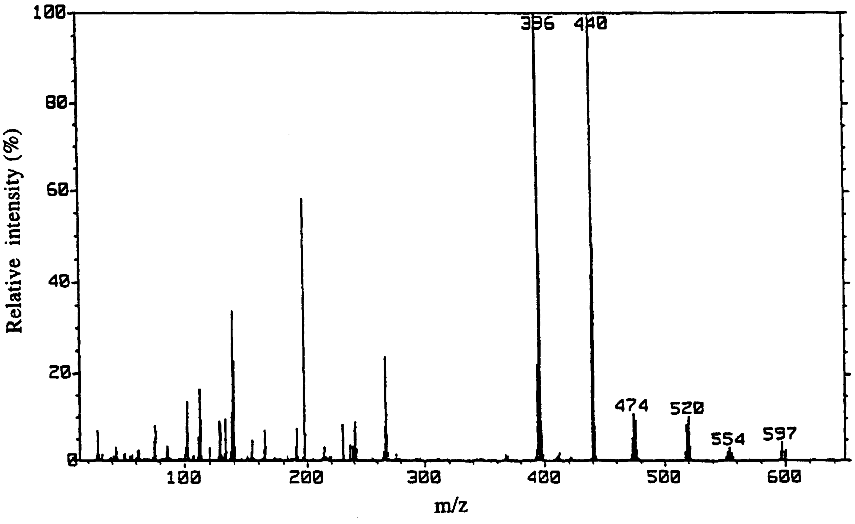

Fig. 1. The mass spectrum of [B(OEt)(subpc)].

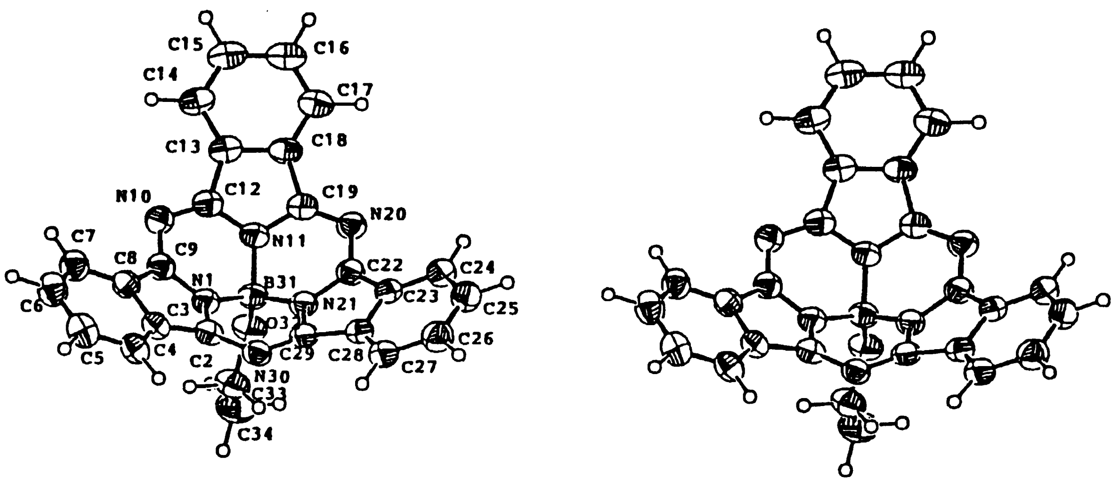

Fig. 2. A ORTEP drawing of the [B(OEt)(subpc)] complex with the atom-numbering scheme.

at 650—700 nm (Q band) and ca. 350 nm (B band), the [BX(subpc)] complexes (X = F, Cl, Br) showed absorption bands around 560 nm (Q band) and 300 nm (B band); [B(OEt)(subpc)] showed the Q band at 562, 561, 558, or 558 nm in benzene, chloroform, acetone, or methanol. The Q band of [AlX(pc)] shifted to a shorter wavelength (ca. 20—30 nm) upon changing the axial halogen ligands to the alkoxy groups.[15] However, the change in the halogen ligands of [BX(subpc)] scarcely shifted the Q band, because the subphthalocyanine ring bends more than does the phthalocyanine ring, and, thus, the kinds of axial ligands of [BX(subpc)] scarcely affect the electron density of the ring.

All of the complexes decomposed after 80-min irradiation with visible light in dichloromethane; the order of the decomposition rate was OPh < OMe < OEt < Br. The polar solvents easily decomposed the complex under irradiation: benzene < chloroform≈dichloromethane≪DMF < DMSO.

In the infrared spectra, new bands were observed between 1330 and 1350 cm^{-1} in the alkoxy derivatives, which were tentatively assigned to the stretching vibration of the B–O bonding.[16]

^{1}H NMR Spectra. While the proton signal of the axial methoxy ligand of (methoxo)(tetra-*t*-butylphthalocyaninato)aluminium(III) appeared at a high magnetic field (−0.92 ppm) compared with that of free methanol (3.41 ppm),[17] that for [B(OMe)(subpc)] appeared at 1.50 ppm (Table 3). This might have resulted from the facts that the subphthalocyanine ring strongly bends and the protons of the axial methoxy ligand are far from the ring, as well as the small ring current of subphthalocyanine (14π-electron system) compared with that of phthalocyanine (16π-electron system). The proton signals of the benzene ring of subphthalocyanine also appeared at a high magnetic field (7.9 and 8.8 ppm) compared with those of phthalocyanine (8.4 and 9.5 ppm) due to the small ring current of subphthalocyanine.

Cyclic Voltammetry. The first oxidative or reductive half-wave potential of the subphthalocyanine ring in [B(OEt)(subpc)] was observed at 1.06 V (vs. SCE) or −1.11 V, respectively. A new anode peak appeared at −0.4 V by sweeping over −1.8 V, probably due to a decomposition of the complex on the second reductive half-wave potential

Table 3. ^{1}H NMR Spectral Data of Subphthalocyanine Complexes and Some Alcohols (ppm in $\mathrm{CDCl_3}$)

	Axial ligands			Aromatic	
	$\mathrm{CH_3}$	$\mathrm{CH_2}$	OPh		
[BBr(subpc)]				7.33 — 7.42	8.58 — 8.67
[B(OMe)(subpc)]	1.50 (s)			7.85 — 7.96	8.80 — 8.91
[B(OEt)(subpc)]	0.19 (t)	1.53(q)		7.81 — 7.92	8.82 — 8.90
[B(OBu^t)(subpc)]	0.04 (s)			7.84 — 7.91	8.81 — 8.89
[B(OPh)(subpc)]			5.39 (d) 6.61 (t) 6.75 (t)	7.85 — 7.94	8.81 — 8.90
MeOH	3.41				
EtOH	1.20	3.67			
t-BuOH	1.27				
PhOH			6.81 6.91 7.21		

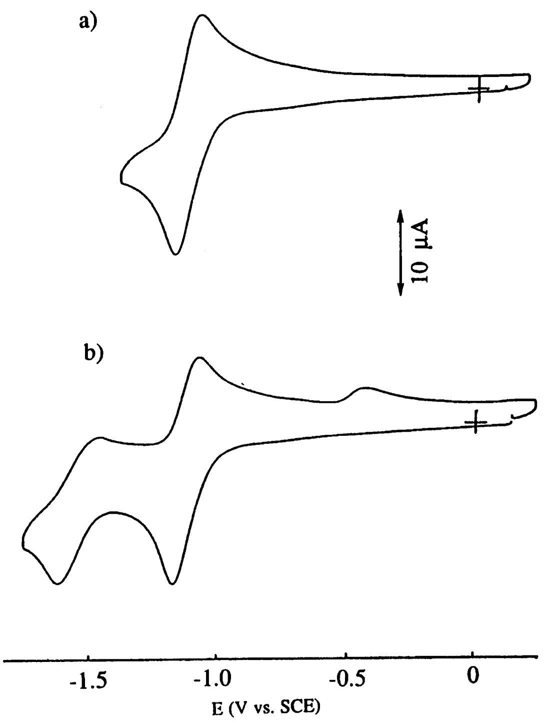

Fig. 3. Cyclic voltammograms of [(B(OEt)(subpc)] at scan rate of the 100 mV s^{-1} in dichloromethane: [complex] = 5.0×10^{-4} mol dm^{-3}; scan ranges, a) 0.2—−1.4 V, b) 0.2—−1.8 V.

Table 4. Half-Wave Potentials for Subphthalocyanine and Phthalocyanine Complexes in Dichloromethane (V vs. SCE)

Complexes	C^+/C	C/C^-
[BBr(subpc)]	1.03[a)]	−1.06[b)]
[B(OMe)(subpc)]	1.05[a)]	−1.10
[B(OEt)(subpc)]	1.06	−1.11
[B(OBu^t)subpc)]	1.03	−1.11
[B(OPh)(subpc)]	1.09[a)]	−1.05
[AlCl(pc)][c)]	1.15	−0.42

a) Epa, b) Epc, C) in DMF.

(Fig. 3). The axial ligands of [BX(subpc)] scarcely affected the half-wave potentials, probably due to the same reason as that described for the ^{1}H NMR spectra (Table 4).

While the first oxidative potential of [BBr(subpc)] and [AlCl(pc)] both appeared at ca. 1.1 V, those first reductive potentials of [BBr(subpc)] and [AlCl(pc)] appeared at −1.1 and −0.5 V, respectively. That is, [AlCl(pc)] is more easily reduced compared with [BBr(subpc)]. Using the approximation that the first oxidative or reductive half-wave potential corresponds to a HOMO or LUMO energy level, the difference in the first oxidative and reductive half-wave potentials might be related to the absorption band of the π–π* transition (Q band),[18)] which agrees with the fact that the Q band (570 nm) of [BBr(subpc)] is shifted to a shorter wavelength compared with that (670 nm) of [AlCl(pc)].

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