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Preparation and Electrochemical Properties of the Green Ytterbium(III) and Lutetium(III) Sandwich Complexes of Octabutoxy-Substituted Phthalocyanine

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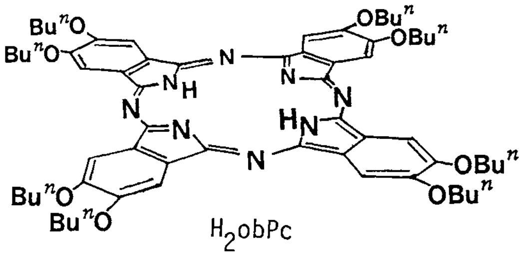
The Yb(III) and Lu(III) sandwich complexes of 2,3,9,10,16,17,23,24-octabutoxyphthalocyanine (H_2obPc) were prepared and characterized. Those electrochemical properties in CH_2Cl_2 were studied by means of cyclic voltammetry and absorption spectra in 320 – 1600 nm region monitored during controlled-potential electrolysis.

The green forms of lanthanoid(III) diphthalocyanine complexes (green $Ln(Pc)_2$, Ln=lanthanoid) have been extensively investigated since the electrochromism of the lutetium complex was reported in 1972.$^{1)}$ Those detailed features, e.g., spectroscopic and electrochemical properties,$^{2)}$ coordination formula ($[Ln^{3+}(Pc^{2-})(Pc^{\cdot -})]^0$, $Pc^{\cdot -}$=phthalocyanine monoanion radical),$^{3,4)}$ sandwich structures,$^{5)}$ have been revealed in the 1980's. Recently, the experimental and theoretical studies on the electronic spectra of the green $Ln(Pc)_2$ including near-infrared (NIR) region have been undertaken, and have provided significant information on the electronic structures and the chemically oxidized and reduced species of these complexes.$^{6,7)}$ Though the examination of electrochemical behaviors of the absorption spectra including NIR region is desired to investigate the details of redox reactions of the green $Ln(Pc)_2$, such examination has not been reported yet. In this study we have prepared and characterized the titled complexes (Yb complex=1, Lu complex=2) using H_2obPc, since the complexes of such substituted Pc are highly soluble in alkyl halides compared to those of the non-substituted Pc, and thus they are expected to be favorable



H_2obPc

for measurements of properties in solution, and to be easily purified without employing the train sublimation method.[8)] The electrochemical behaviors of 1 and 2 in CH_2Cl_2 have been examined by cyclic voltammetry and UV–VIS–NIR absorption spectra monitored during controlled-potential electrolysis.

The 1-octanol suspension (3 cm^3) of Yb- or $Lu(CH_3COO)_3\cdot 4H_2O$ (0.20 mmol) and H_2obPc[9)] (0.13 mmol) was refluxed (5 h). Then the solid obtained by adding methanol (30 cm^3) was dissolved in $CHCl_3$, and chromatographed over silica gel column (Wakogel C-200, eluent $CHCl_3$). By the addition of the deep green main fraction of the eluate (reduced in volume to ca. 5 cm^3) to methanol (100 cm^3), 1 and 2 were obtained as the dark green fine crystals. Anal. ($C_{128}H_{160}N_{16}O_{16}$Yb or Lu) C, H, N. The molar electric conductivities of the CH_2Cl_2 and nitrobenzene solutions of 1 and 2 (1×10^{-4} M (= mol dm^{-3}), at 298 K) are almost zero, which suggests that the molecules of 1 and 2 are uncharged in the solutions. The magnetic properties of 2 (an intense signal observed on the X-band ESR spectra in solid (g=2.000, ΔH_{pp}=0.2 mT) and in CH_2Cl_2 (g=2.002, ΔH_{pp}=0.5 mT) at 295 K; the effective magnetic moment=1.98 B.M. at 291 K) resemble those of the green $Lu(Pc)_2$.[3)] These facts confirm the presence of one unpaired electron per one molecule, and hence the molecule of 2 contains the monoanion radical of the ligand, $obPc^{\cdot -}$. From the magnetic measurements for 1, the presence of the unpaired electron could not be ascertained.[10)] The UV–VIS–NIR absorption spectra of 1 and 2 in CH_2Cl_2 (described in the next page) are similar to each other, and to those of the corresponding green $Ln(Pc)_2$.[2,6,7)] By the above observations, 1 and 2 can be represented as the formula, $[Ln^{3+}(obPc^{2-})(obPc^{\cdot -})]^0$ (Ln=Yb, Lu).[4)]

The cyclic voltammograms (CVs) of the CH_2Cl_2 solutions of 1 and 2 containing 0.1 M $Bu^n_4NClO_4$ (TBAP) were measured to determine the applied potentials for controlled-potential electrolysis. The CVs of 1 and 2 show one redox couple in the oxidation side (Ox), and two redox couples in the reduction side (Red1, Red2). Those wave shapes (peak splittings: $60<\Delta E_p<80$ mV; peak height ratios are almost unity) suggest the existence of one-electron redox processes with good reversibility. The half-wave potentials, $E^{Ox}_{1/2}$, $E^{Red1}_{1/2}$, and $E^{Red2}_{1/2}$ /V *vs.* SCE, of the 1×10^{-4} M solutions are evaluated to be +0.26, -0.15, and -1.27 for 1, and +0.25, -0.19, and -1.29 for 2.[11)] These CV parameters show little concentration dependence over the explored range of 1×10^{-5} — 2×10^{-4} M. The applied potentials for the oxidation, first reduction, and second reduction of the electrolysis were: 1 +0.51, -0.40, and -1.37; 2 +0.50, -0.44, and -1.39 V *vs.* SCE.[12)] The solution of both complexes change in color from green to yellow in oxidation, and to blue in reduction. The absorption spectra of 1 and 2 show similar changes in the course of the electrolysis. The reduced blue solutions by the first and second reductions showed the same spectra. Each colored solution shows a good obedience to the Beer's law over the explored range of 1×10^{-5} — 2×10^{-4}

M. The absorption spectra of 1 monitored during the electrolysis are shown in Fig. 1. The absorption maxima of major bands of the 1×10^{-5} M solutions of 1 and 2 are given in Table 1. According to the report by Markovitsi et al.,$^{6)}$ the absorption spectra of the initial green species for 1 and 2 can be interpreted as the superposition of those of obPc^{2-} and obPc$^{\bullet -}$. In the case of 1, for instance, the 666 nm band is the Q band of obPc^{2-}; the 478 and 910 nm bands are characteristic of obPc$^{\bullet -}$ (radical bands); the bands observed around 1404 nm are attributable to a obPc^{2-} → obPc$^{\bullet -}$ charge-transfer (CT) transition.$^{6)}$ The absorption observed in 320 – 400 nm region is the superposition of the B bands of obPc^{2-} and obPc$^{\bullet -}$ (temporarily termed the 368 nm bands). During the oxidation of 1, the following spectral change is observed: The Q, CT, and 368 nm bands disappear; the radical bands increase in intensity and shift to 500 and 937 nm; the two new bands appear at 386 and 704 nm. Such change is ascribed to the ligand-centered oxidation of obPc^{2-}. The coulometric measurements performed during the oxidation of 1 and 2 offer the confirmative results of the one-electron oxidation. Hence, the oxidized yellow species of 1 and 2 are represented as $[Ln^{3+}(obPc^{\bullet -})_2]^+$. The spectral change during the first reduction of 1 is: the disappearance of the Q, radical, and CT bands; the appearance of the two new bands at 628 and

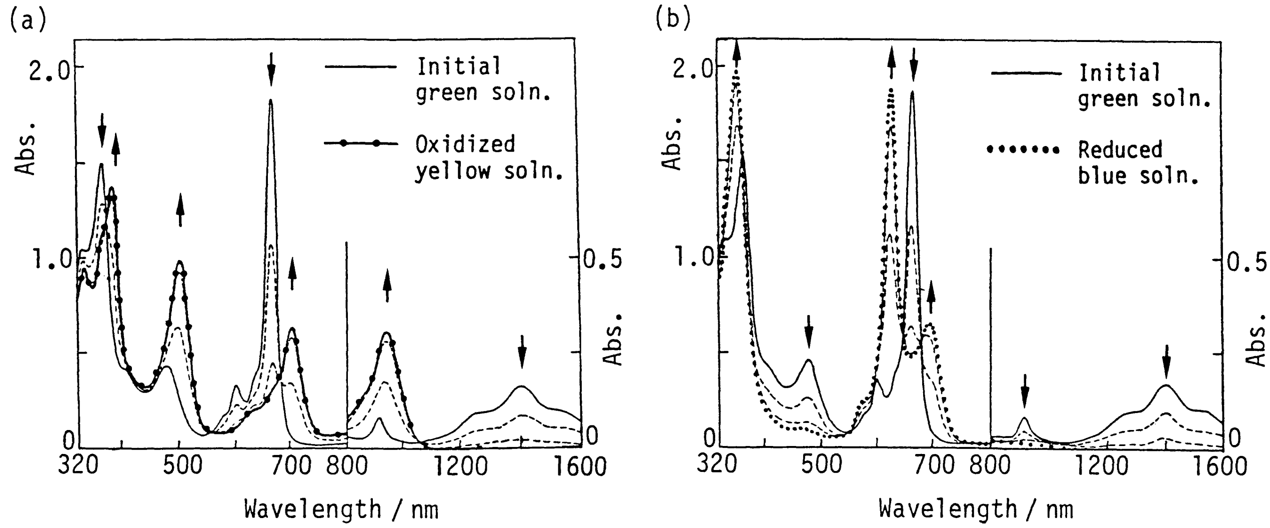


Fig. 1. Absorption spectra of the 1×10^{-5} M solution of 1 monitored during (a) the oxidation and (b) the first reduction.

Table 1. Absorption maxima of major bands of the 1×10^{-5} M initial, oxidized, and reduced (by the first reduction) solutions of 1 and 2

Complex	Solution	Absorption maxima / nm (log ε)				
1	Initial green	368(5.15)	478(4.60)	666(5.25)	910(3.88)	1404(4.20)
	Oxidized yellow	386(5.11)	500(4.95)	704(4.77)	937(4.45)	
	Reduced blue	359(5.28)	628(5.26)	696(4.80)		
2	Initial green	368(5.14)	478(4.60)	666(5.24)	914(3.85)	1400(4.20)
	Oxidized yellow	385(5.14)	498(4.99)	702(4.81)	934(4.48)	
	Reduced blue	359(5.30)	626(5.26)	698(4.81)		

696 nm; the seeming blue shift (to 359 nm) with the increase in intensity of the 368 nm bands.13) The absorption spectra of the reduced blue species of 1 and 2 are almost the same as those of $\mathrm{Bu^{\mathit{n}}_4N^+\,[Ln^{3+}(obPc^{2-})_2]^-}$ (Ln=Yb, Lu),14) whose complex anions are expected to possess the same electronic structures as the one-electron reduced forms of 1 and 2. From the facts mentioned above and the CV data, it is inferable that the blue species of 1 and 2 are the ligand-centered one-electron reduced forms represented as $\mathrm{[Ln^{3+}(obPc^{2-})_2]^-}$. No any spectral change has been detected during the second reduction of the blue solutions generated by the first reduction. The absorption spectra of the yellow and blue solutions of 1 and 2 roughly resemble those of the chemically oxidized and reduced solutions of the green $\mathrm{Ln(Pc)_2}$.6) Preliminary ESR measurements for the electrolyzed solutions showed the decrease of the signal intensity of 2 for oxidation and reduction, but no signal was observed for 1.

References

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4) Ishikawa et al. have recently suggested the hole (unpaired electron) delocalization in the molecule of the green lutetium complex (represented as $\mathrm{[Ln^{3+}(Pc)_2{}^{3-}]^{\cdot 0}}$). See the Ref. 7.
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9) This ligand was obtained by the addition of excess methanol and a few drops of concd HCl to the reaction mixture of 1,2-dibutoxy-4,5-dicyanobenzene (bcbz) and lithium metal (molar ratio≃1:2.5) in 1-pentanol (1.5 $\mathrm{cm^3}$/1 mmol of bcbz) refluxed for 30 min. Its purification and isolation were carried out by the same procedures as those of 1 and 2 described in the text.
10) Effective magnetic moment of 1 is 4.71 B.M. at 297 K. No ESR signal was observed in solid and solution at room and liquid nitrogen temperatures.
11) The data of CVs described were obtained by the following conditions: electrodes=glassy carbon disk, Pt coil, and SCE; sweep range=+1.5 – −1.8 V *vs.* SCE; sweep rate=100 mV $\mathrm{s^{-1}}$; T(solution)=288±2 K.
12) The three electrode cell (Pyrex glass; Pt mesh electrodes and SCE; light pathlength=10 mm) used in this experiment was made by reference to the literature: N. Kobayashi and Y. Nishiyama, *J. Phys. Chem.*, 89, 1167(1985).
13) The completion of reduction could not be detected by the coulometric measurements, since the reduced species were not stable in the solutions.
14) These dark blue complexes were prepared by the reduction of 1 and 2 using hydrazine monohydrate together with excess TBAP in DMF. Abs. max./nm (log ε) of the 1×10^{-5} M $\mathrm{CH_2Cl_2}$ solution are: 359(5.29), 627(5.25), and 696(4.78) for Ln=Yb; 359(5.27), 626(5.22), and 696(4.78) for Ln=Lu.

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