

The Radical Formation of Diphthalocyanine Complexes of Lanthanum(III), Neodymium(III) and Yttrium(III) with *p*-Benzoquinone

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Abstract

Three species of neodymium(III) phthalocyanine: PcNdPcH (λ max = 345 and 636 nm), radical PcNdPc (324, 470 and 676 nm) and PcNdCH₃COO (336 and 675 nm) were obtained from a crude neodymium(III) phthalocyanine mixture by column chromatography on silica gel. The diphthalocyanine complexes of lanthanum(III), neodymium(III) and yttrium(III) were oxidized to the radical with *p*-benzoquinone and the reaction rate was increased with the decrease of an ionic radius, e.g. the rate was increased with the decrease of the distance of two macrocycles in the complex.

Introduction

Since the first preparation of lanthanoid(III) diphthalocyanine, PcLnPcH (Pc = phthalocyanine dianion, Ln = lanthanoid(III) cation) was reported [1], more detailed investigations have been performed over the past two decades [2]. For instance, the structure of neodymium(III) diphthalocyanine was determined from an X-ray diffraction study. The complex has an exactly staggered orientation and the distance between the N₄ plane of the two macrocycles is 2.96 Å [3]. Application of the complexes for an electrochromic display has been further investigated [4]. Recently, those conductivities were also reported [5]. However, the situation of an acidic proton in the blue diphthalocyanine complexes (PcLnPcH) which should play an important role in those characteristics has been vague (e.g. once Corker *et al.* had formulated the green diphthalocyanine complex of lutetium(III) as (PcLuPc)⁺X⁻ [6] but it was recently identified to be the radical PcLuPc species [7]). In this paper, we report the further studies on the lanthanoid(III) phthalocyanine complexes and those radical formations with *p*-benzoquinone.

Results and Discussion

The crude products of neodymium(III) phthalocyanine were prepared by the reaction of neodymium(III) acetate and *o*-phthalonitrile (1:8 molar ratio) by a method described previously [1]. The crude products were dissolved in N,N-dimethylformamide (DMF) and were chromatographed on silica gel. The green solution was eluted by a solvent mixture of dichloromethane and 5% of methanol, followed by the blue eluent with dichloromethane and 10% of methanol. Finally, the greenish-blue solution was washed off with methanol (Fig. 1).

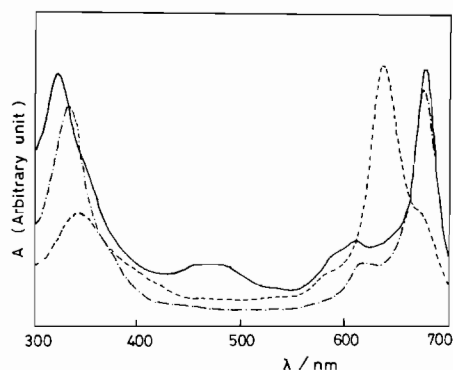


Fig. 1. Absorption spectra of the eluents: —, PcNdPc; ----, PcNdPcH; - · - ·, PcNdCH₃COO.

Spectra of the first and second eluates are consistent with those of the PcNdPc radical and PcNdPcH species, respectively [1, 7]. The results of elemental analyses confirmed that the both species were diphthalocyanine. Furthermore, the first eluate showed an intense ESR signal at $g = 2$ which was typical of a radical species of phthalocyanine [6–8], whereas the second did not. Although a spectrum of the third eluate of the monophthalocyanine is similar to that of the radical species in the 600 to 700 nm region, it has no absorption around 470 nm, characteristic of radical phthalocyanine [7, 8]. The crude products of yttrium(III) phthalocyanine were

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TABLE I. The Rate Constants of the Oxidation of the Lanthanoid(III) Diphthalocyanine Complexes with *p*-Benzoquinone

Run	k_{obs}^a (10^{-2} s^{-1})	Conditions
1	0.820 ± 0.043	PcNdPcH + BQ ^c ($2.00 \times 10^{-4} \text{ mol dm}^{-3}$)
2	1.18 ± 0.08	PcNdPcH + BQ ($2.50 \times 10^{-4} \text{ mol dm}^{-3}$)
3	1.25 ± 0.05	PcNdPcH + BQ ($3.00 \times 10^{-4} \text{ mol dm}^{-3}$)
4	1.42 ± 0.13	PcNdPcH + BQ ($3.50 \times 10^{-4} \text{ mol dm}^{-3}$)
	k^b ($10^2 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$)	
5	0.410 ± 0.021	PcNdPcH + BQ
6	2.86 ± 0.23	PcYPcH + BQ

^aThe first-order rate constants. ^bThe second-order rate constant. ^cBQ = *p*-benzoquinone.

separated in a similar way to that for the crude neodymium(III) complex. In the case of the lanthanum(III), although both PcLaPc and PcLaPcH species were obtained, the monophthalocyanine was not successfully eluted due to its decomposition during elution. The alumina column was also used for the separation of the crude products, as has been previously reported [1] but it was difficult to elute the three kinds of species separately.

Monophthalocyanine Complexes

The absorption spectra of the neodymium(III) and yttrium(III) monophthalocyanine complexes are almost the same with those of usual monophthalocyanine complexes of transition metals [9]. Infrared spectra of the complexes show a carbonyl stretching vibration around 1650 cm^{-1} , indicating the presence of the acetate ion in the complexes. Recently, it was reported that the lanthanoid(III)–monophthalocyanine complexes were prepared by exchange reaction of lithium phthalocyanine and β -diketone lanthanoid(III) complexes in methanol or acetone, and those radical species were also prepared in tetrahydrofuran [8]. The monophthalocyanine complexes obtained in this study showed no characteristic signal assignable to the free organic radical species in a benzene solution. From the results of the absorption spectra, this would indicate that the monophthalocyanine complexes are nonradical species.

Formations of Radical Species

The electrochromism of the lanthanoid(III)–diphthalocyanine complex is attributable to the generation of the various π -radical species which show different bright colors depending upon the applied potentials, e.g. the green PcLuPc radical was generated from the blue PcLuPcH in a DMF solution by electrolytic oxidation at a voltage equal or greater than -0.5 V [6].

The PcNdPc radical species was also prepared by chemical oxidation. With the addition of *p*-benzoquinone, the maximum absorption of PcNdPcH at

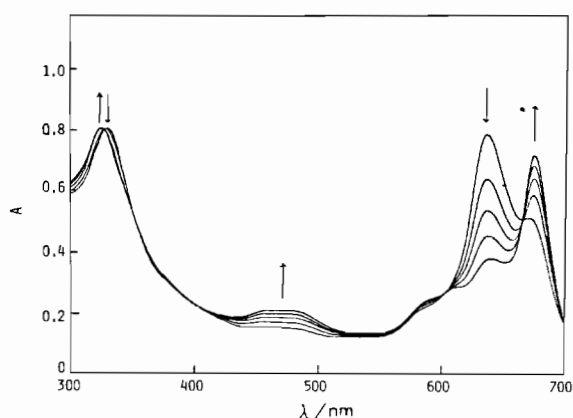


Fig. 2. Spectral changes during the oxidation of the PcNdPcH complex with *p*-benzoquinone in the solvent mixture of dichloromethane and 20% of methanol; $[\text{PcNdPcH}]_0 = 1.00 \times 10^{-5} \text{ mol dm}^{-3}$, $[\textit{p}\text{-benzoquinone}]_0 = 2.00 \times 10^{-4} \text{ mol dm}^{-3}$, $T = 20.0 \pm 0.1 \text{ }^\circ\text{C}$: (1) 30 s, (2) 1 min 30 s, (3) 5 min, (4) 20 min, (5) 1 h, after the reaction. The times given are for the scan start at 700 nm.

636 nm in the mixture solvent of dichloromethane and 20% of methanol, was shifted to 676 nm with the appearance of a new band around 470 nm, characteristic of the radical phthalocyanine ligand, where isosbestic points were found at 330, 357, 600 and 665 nm (Fig. 2). The PcNdPcH species was recovered by the addition of triethylamine or DMF to the solution.

A kinetic study on the radical formation was carried out to elucidate the reaction mechanism. The reaction rate was determined by an absorbance change at 636 nm by a pseudo first-order method. The plot of $-\ln(A_\infty - A_t)$ vs. time was linear for at least 80% completion, implying that the reaction order is first in the concentration of PcNdPcH. A_t and A_∞ represent the absorbances at time t and infinity, respectively. Furthermore, the pseudo first-order rate constant was proportional to the concentration of *p*-benzoquinone, showing the first-order with respect to the concentration of the oxidant (Table I).

The rate constant for the yttrium(III) complex is seven times that for the neodymium(III) complex. The oxidation rate of lanthanum(III) complex was so late that the rate constant could not be obtained. That is, the rate constant is increased with the decrease of an ionic radius of the lanthanoid(III) ion. It was reported that the bond length between the lanthanoid(III) ion and the nitrogen atoms in the macrocycles decreased with the decrease of the ionic radius [10]. The oxidation reaction must be facilitated with the two macrocycles approaching each other in the complex but the details are not known at present.

Experimental

Preparation of the Monophthalocyanine Complexes

The mixture of 3.0 g (15 mmol) neodymium(III) acetate·1.5 hydrate and 15 g (117 mmol) *o*-phthalonitrile was heated up to *ca.* 300 °C. The crude product was finely ground and was then dissolved in 100 cm³ of DMF solution. The solution was then poured into the silica gel column which had been expanded by ethanol. Using methanol as an eluent, the diphtalocyanine complex and decomposed materials were rapidly eluted, and subsequently the monophthalocyanine complex. After concentration of the eluate under a reduced pressure, the greenish-blue compound was precipitated and was dried *in vacuo* at 80–90 °C for 3 h. *Anal.* Found. C, 56.61; H, 2.86, N, 14.69. Calc. for PcNdCH₃COO·CH₃OH (Pc = C₃₂H₁₆N₈): C, 56.21; H, 3.11; N, 14.98%. The yttrium(III) monophthalocyanine complex was also prepared by a similar method. *Anal.* Found: C, 60.12; H, 3.21; N, 15.85. Calc. for PcYCH₃COO·CH₃OH: C, 60.70, H, 3.35; N, 16.17%. The diphtalocyanine complexes of lanthanum(III), neodymium(III) and yttrium(III) were prepared by the same method, reported previously, and were confirmed by elemental analyses and UV spectra.

Kinetic Measurements

Purification of *p*-benzoquinone was carried out with sublimation *in vacuo*, and the stock solution

was prepared just before the kinetic measurements. The solvents used for kinetic measurements were reagent grade and used without further purification. The reaction rate was measured by the absorbance change with time on a Hitachi 215 spectrophotometer. The temperature was kept at 20.0 ± 0.1 °C.

Other Measurements

The electronic spectra in solution and the infrared spectra using KBr pellets were measured on a Hitachi 215 spectrophotometer and a Hitachi 124 spectrophotometer, respectively. The ESR spectra (X-band) were measured with a JEOL-1X spectrophotometer.

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References

- 1 I. S. Kirin, P. N. Moskalev and Yu. A. Makashev, *Russ J Inorg Chem.*, **10**, 1065 (1965); S. Misumi and K. Kasuga, *Nippon Kagaku Zasshi*, **92**, 335 (1971).
- 2 K. Kasuga and M. Tsutsui, *Coord. Chem. Rev.*, **32**, 67 (1980).
- 3 K. Kasuga, M. Tsutsui, R. C. Petterson, K. Tatsumi, N. Von Opdenbosch, G. Pepe and E. F. Myer, Jr., *J. Am. Chem. Soc.*, **102**, 4836 (1980).
- 4 M. Nicholson and R. V. Gahard, *Gov. Rep. Announce. U.S.*, **77**, 112 (1977); M. Nicholson and T. P. Weismuller, *Gov. Rep. Announce. U.S.*, **83**, 6250 (1983).
- 5 L. W. ter Haar, W. E. Hatfield and M. Tsutsui, *Mol. Cryst Liq. Cryst.*, **107**, 181 (1984).
- 6 G. A. Corker, B. Grant and N. J. Clecak, *J. Electrochem Soc.*, 1339 (1979).
- 7 A. T. Chang and J. Marchon, *Inorg. Chim. Acta*, **53**, L241 (1981).
- 8 H. Sugimoto, T. Higashi and M. Mori, *Chem. Lett.*, 801 (1982); H. Sugimoto, T. Higashi, A. Maeda, M. Mori, H. Masuda and T. Taga, *J. Chem. Soc., Chem. Commun.*, 1234 (1983).
- 9 A. B. P. Lever, *Adv. Inorg. Chem. Radiochem.*, **7**, 27 (1965).
- 10 I. S. Kirin, P. N. Moskalev and Yu. A. Makashev, *Russ. J. Inorg. Chem.*, **12**, 369 (1967).