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A Phthalocyanine Complex of Neodymium(III) Showing an Unusual Absorption Spectrum

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It is known that bis(phthalocyaninato)lanthanoid(III), HPcLnPc (Pc = phthalocyanine dianion: Ln = lanthanoid(III) cation), exhibits many characteristic properties such as electrochromism, electroconductivity, and photochemistry [1–3]. The structures of bis(phthalocyaninato)neodymium(III) and -lutetium(III) have also been reported; the metal ions occupy a central position between two parallel but staggered phthalocyanine ligands [4, 5]. Previously, we prepared a zirconium(IV) derivative of bis(phthalocyaninato)neodymium(III) which might be a model compound of a metal incorporation into the phthalocyanine ligand; a zirconium(IV) ion sits on one of the phthalocyanine ligands [6]. We communicate here a new phthalocyanine complex of neodymium(III) which shows an unusual absorption spectrum in the wavelength regions of 650 to 750 nm.

The new complex was prepared by refluxing KPcNdPc in tetrahydrofuran (THF) overnight, and was purified by means of column chromatography on silica gell; using chloroform as an eluent, the complex was eluted out. To exclude a radical $\dot{P}$cNdPc species, the chromatography was repeated twice. The complex was also prepared by refluxing HPcNdPc in THF, but the yield was low because of its poor solubility. Formation of the complex was further catalyzed by the addition of small amounts of zirconium(IV) oxychloride. At present, however, we have not succeeded in isolating the pure complex because of its lability and also of the difficulty of removing small amounts of contaminated radical species.

An electronic spectrum of the complex is shown with those of KPcNdPc and $PcNdCH_3COO$ in Fig. 1. In the spectrum of the complex, which is accompanied by a shoulder arising from the contaminated radical $\dot{P}$cNdPc species at 680 nm, two strong bands appeared around 700 nm whose intensities are almost identical. Two explanations might be possible: (1) the Q band undergoes a blue shift with the appearance of a new band; (2) the Q band splits into two components. In some phthalocayanine complexes of lanthanoid(III), *e.g.* HPcLnPc and Pc_3Ln_2, additional bands (X bands) appear at 680–730 nm, the positions of which depend upon the kinds of lanthanoid(III) ion [7, 8]. In the neodymium(III) complexes, the X bands appear at 680 nm as shoulders of the Q band. Thus, the band at 733 nm of the new complex is not the same as the X band.

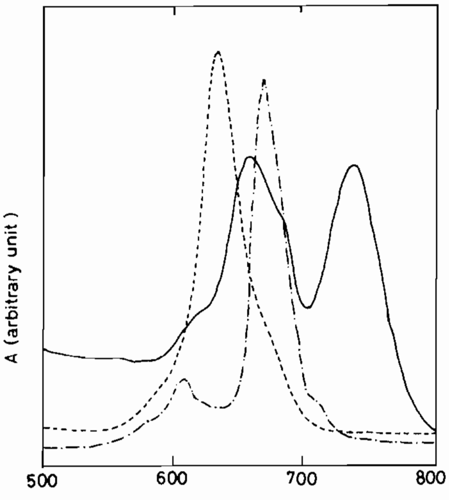

Fig. 1. Electronic spectra in chloroform: ——, the new complex; - - -, KPcNdPc; — · —, $PcNdCH_3COO$.

While metal phthalocyanine usually shows only one sharp Q band between 600 to 700 nm, a free-phthalocyanine shows two bands around 700 nm [9, 10]. This suggests that the symmetry of π-systems of the macrocycles might be decreased in the new complex; that is, the geometry of the complex is distorted from the symmetrical bis(phthalocyanin-

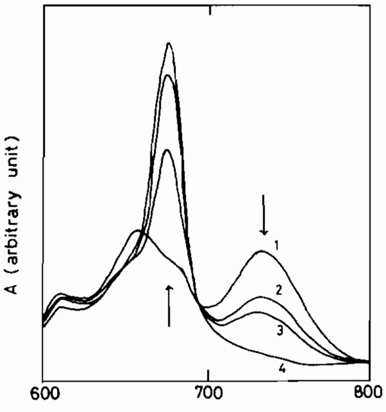

Fig. 2. Spectral changes by the addition of diethylamine: (1) the original spectrum, (2) 1 min, (3) 3 min, and (4) 15 min. after the addition of a few drops of 10% aqueous solution of diethylamine.

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ato)neodymium(III) complex. By the addition of adequate amounts of base such as diethylamine, the spectrum of the new complex was immediately changed to that of the monophthalocyanine complex (Fig. 2).

From the above results, the new complex might be an intermediate for the conversion of the diphthalocyanine complex to the monophthalocyanine. Further studies on this complex will be performed in this laboratory.

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