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Preparation of New Phthalocyanine Complexes of Yttrium(III) and Some Lanthanoid(III) Ions

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Phthalocyanine complexes of yttrium(III) and lanthanoid(III) ions, Pc_3Ln_2 (Pc = phthalocyanine anion, Ln = lanthanoid(III) cation) were prepared and characterized. A Q band undergoes a blue shift with a decrease in ionic radius of the lanthanoid(III) ions, while an X band undergoes a red shift.

Since the preparation of phthalocyanine complexes of lanthanoid(III) was reported by Kirin et al.,1) many interesting characteristics have been reported on the complexes.2) For instance, bis(phthalocyaninato)lutetium(III) exhibits an electrochromism,3) and its application for an electrochromic display has been extensively investigated.4) Study of electroconductivity and application for gas sensors of bis(phthalocyaninato)lanthanoid(III) complexes, PcLnPcH were also reported.5,6) Recently, a photo-induced oxidation of the complexes has been reported, which will give a clue to photochemistry of the complexes.7) The structure of bis(phthalocyaninato)neodymium(III) was revealed out to be of a sandwich type from an X-ray diffraction analysis.8) Recently, Cian et al. also reported the X-ray structures of the lutetium(III) complexes with mono- and diphthalocyanine.9) It is valuable to prepare stacked phthalocyanine complexes of lanthanoid(III) which might have remarkable characteristics of electroconductivity, electrochromism and photo-catalyst. In this paper, new phthalocyanine complexes of lanthanoid ions, Pc_3Ln_2 (Ln = Y(III), Nd(III), Gd(III), Er(III), and Lu(III)) are prepared and characterized.

A mixture of o-phthalonitrile (3.0 g, 2.4 mmol) and yttrium(III) acetate hexahydrate (0.6 g, 3.0 mmol) was heated up to ca. 230 °C, and then the melted mixture was kept at that temperature for ca. 8 h. The obtained crude product was then poured into 300 dm^3 of chlorobenzene, and the Pc_3Y_2 complex was extracted into the solvent. The complex was further purified by means of a column chromatography on active alumina.[10] Other complexes were also prepared in a similar method described above. Preparation of the Pc_3Y_2 complex was spectrophotometrically followed (Fig. 1); an absorption band for a monophthalocyanine complex first appeared at 665 nm (1), subsequently followed by the appearance of the band characteristic of the radical sandwich-type complex at 460 nm (2). After the heating was continued for several hours, the band at 665 nm was shifted to 633 nm, which indicates the formation of the Pc_3Y_2 complex (3-4).

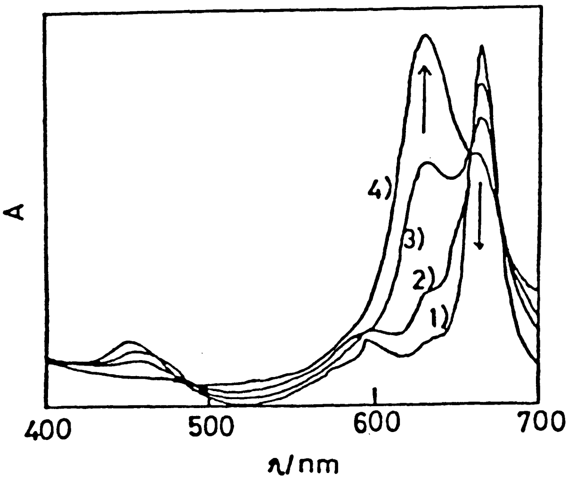

Fig. 1. Spectral changes during the complex formation. 1) 2.5 h, 2) 3.5 h, 3) 7 h, and 4) 8 h after melting of the mixture.

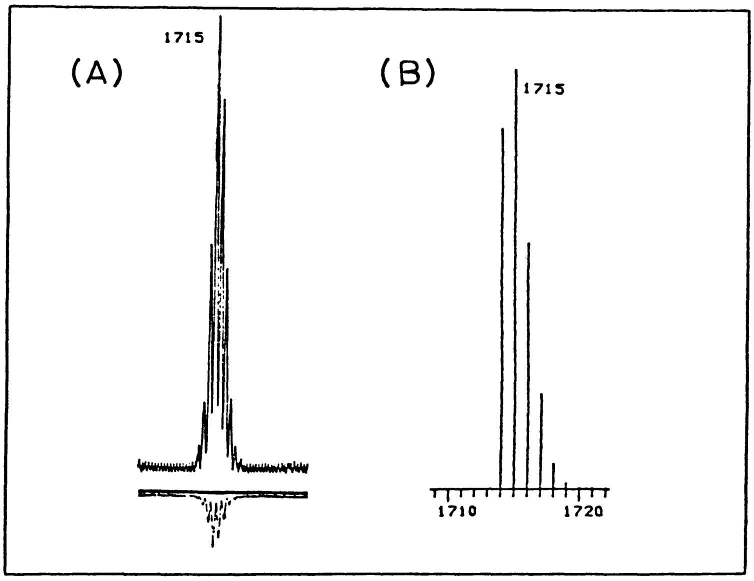

Fig. 2. Mass spectra of the Pc_3Y_2 complex.
(A) observed, (B) calculated natural isotopic abundances.

In a mass spectrum of the Pc_3Y_2 complex, an univalent ion species shows a multiplet from m/z 1711 to m/z 1719 in accordance with isotopic abundance probabilities, which confirms the formula of $C_{96}H_{48}N_{24}Y_2$.

The electronic spectra of $PcYCH_3COO$, PcYPcH, radical PcYPc, and Pc_3Y_2 complexes are shown in Fig. 3. The spectrum of Pc_3Y_2 is similar to that of PcYPcH; a Q band appears at 633 nm with accompanying a weak band (tentatively named as an X band) at 705 nm. The Q band is shifted to the shorter wavelength with a decrease in the ionic radius in consistent with those of the PcLnPcH complexes (Fig. 4).[11] This might be implied by the reason that the distance of macrocycles in the complex is shortened with the decrease in the ionic radius, resulting in the increase in π - π interactions. On the other hand, the X band is shifted to the longer wavelength with the decrease in the ionic radius. It is also reported that the PcLnPcH complex shows the X band, but the radical $\dot{\mathrm{P}}$cLnPc complex does not.[12] The reason why the X bands appear in these complexes is unknown at present.

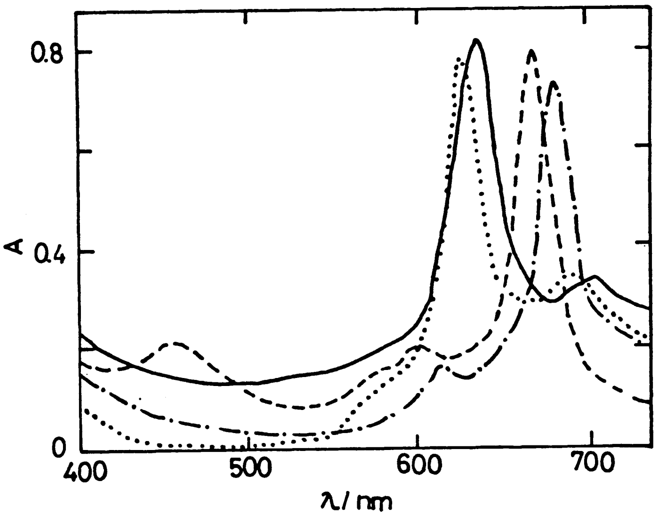

Fig. 3. Electronic spectra of the complexes in chlorobenzene. —·—) $PcYCH_3COO$, ····) PcYPcH, – – –) $\dot{\mathrm{P}}$cYPc, and ——) PC_3Y_2; [complex] = ca. 1 x 10^{-5} mol dm^{-3}.

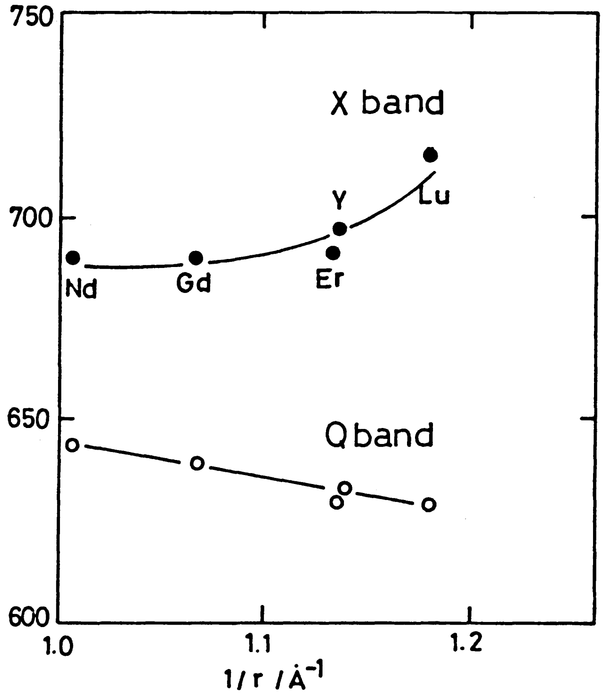

Fig. 4. Plots of absorption maximum of the Q and X bands against the reciprocal of the ionic radius of the lanthanoid(III) ions.

As a possible structural formula of the complex, a tridecker type might be proposed (Fig. 5). X-Ray crystallographic studies for these complexes are now in progress.

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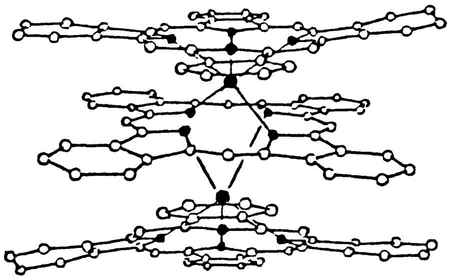

Fig. 5. The proposed structure.

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10) The complex was confirmed by means of an elemental analysis and IR spectra. Found: C, 67.34; H, 2.84; N, 17.70%. Calcd for $C_{96}H_{48}N_{24}Y_2 \cdot 2THF$: C, 67.17; H, 3.44; N, 18.08%. In the IR spectra of the complex, the band of a free phthalocyanine at 1008 cm^{-1} disappeared, and new two bands appeared around 1050 cm^{-1}, in consistent with those of usual metallophthalocyanine complexes.

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